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physical sciences

Review of technological requirements for high-temperature materials R & D

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Joint Research Centre
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PREFACE

The preparation of a "European High-Temperature Materials White Book" was assigned to the Petten Establishment of the Joint Research Centre by decision of the Council of Ministers of the European Community on August 25th, 1975. The objective was the assessment of the requirements of European industry for advanced high-temperature materials and the R and D in hand in the member states and elsewhere, in order to provide criteria for the promotion of R and D in this field.

The Petten Establishment has compiled this White Book under the title "Review of the Technological Requirements for High-Temperature Materials R and D" from contributions by experts from the materials producing and using industries and research organizations. In order to make the view on the subject as broad and complete as possible, each section was originally dealt with by a principal author and then commented upon by a number of specialist reviewers with experience of the subject. Chapters 5 and 6 summarize the conclusions evaluated on the current R and D and future R and D requirements in Europe.

Although the material presented here covers the major part of the field, some aspects could not be fully, or not satisfactorily, dealt with. In the case of three of the White Book sections an author could not be contracted in time - only short summaries prepared by the editor are therefore included.

Future White Book revisions or supplements will permit completion, for in line with the advance of high-temperature materials technology it is intended to publish from time to time new information and appraisals of the changing research requirements. Emphasizing the value of stimulating feedback, it would be appreciated if any comments, suggestions and indications of prominent omissions or inaccuracies could be referred to the indicated address for correspondence.

Finally the co-operation of all those who provided information and suggestion is gratefully acknowledged. Thanks are due to all persons who have contributed time and effort to the realization of this survey and to writing, reviewing, editing, typing and publishing this report. Without the ready and willing help of all the people involved the White Book could not have been brought to its present condition.

Contents

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Coordination of Sections

B. Bathe	Appendix M
W. Betteridge *	2.1., 2.2., 2.3., 3.3. 5., 6., Appendices A-L
J. Bressers	3.8., 4.1.5., 4.1.6.
M. Cambini	3.9., 4.1.3., 4.1.4.
V. Guttmann	3.2., 3.4.
R.A.U. Huddle *	3.7.
G. Kemeny	3.10., 4.5.
R. Krefeld	4.2., 4.3.
E. Lang	3.6.
S.J. Lloyd	4.1.2., 4.4.

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3.2	C. Edeleanu,B.J. Estruch
3.3	J.H. Davidson
3.4	W. Betteridge,J.H. Davidson
3.5	The Editor
3.6	D.J. Burr
3.7	L.W. Graham,R.A.U. Huddle
3.8	J. Bressers
3.9	A.M. Anthony
3.10	G. Beghi
3.11	The Editor
4.1.1	The Editor
4.1.2	N.G. Persson
4.1.3	K.E. Volk
4.1.4	E. Williams
4.1.5	R. Eck,G.L. Miller
4.1.6	J.C. Chaston
4.2	J. Briggs
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C - L	Fulmer Research Institute Ltd.
M	B. Bathe

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R. Blackstone	3.9.
E. Bullock	4.4.
J.F.G. Condé	4.5.
P. Courvoisier	3.10.
K. Ehrlich	3.8.
P. Esslinger	3.6.
B.L. Eyre	3.8 .
R.J.E. Glenny	3.6 .
D.J. Godfrey	4.2 .
H.E. Gresham	3.6 .
E.D. Grosser	2.1, 2.3 .
R. Hancox	3.8 .
J. Harrison	3.4 .
H. Hausner	4.2 .
J. Henderson	3.6 .
G. Henrich	3.7 .
J. Heslop	4.1.3 .
I. Kirman	4.1.3 .
P. Kofstad	2.1.,2.2.,2.3
R. Krefeld	3.9.
H. Marchandise	3.6.
M. Mocellin	4.2.
H. Nickel	3.7.
H.G. Orbans	3.2.
R. Pichoir	4.5.
G. Reinacher	4.1.6.
B.M.U. Scherzer	3.8.
A.I. Smith	2.1.,2.2.,2.3. 4.1.3.,4.1.4.
A. Von den Steinen	4.1.3.
P. Strocchi	3.6.
R.P. Theisen	4.5.
T. Thomander	3.3.
S. Timoney	3.6.
P. Tipping	4.1.5.
K.E. Volk	2.1.,2.2.,2.3.
C.H. White	3.3.,3.4.
F.E. White	4.1.3.
D.P. Whittle	2.2.,2.3.
G. Wirth	3.6.
W. Van Witzenburg	3.8.
J. Zboril	3.6.

1. INTRODUCTION

The general standard of living within a society at any given time is dependent upon the sophistication of the available technology. Technical progress is usually measured in terms of increased efficiency or productivity. Processes involving high temperatures form an important part of modern industrial activity; however, it may be questioned whether, with further technical progress, the use of high-temperature processes and the trend towards higher temperatures is likely to increase or decrease. It has for example been suggested that high-temperature processes are inherently wasteful and that, in the long term, more efficient low-temperature alternatives will be developed. This may be true in a few cases but for a large number of processes, fundamental thermodynamics predicts that an increase in temperature leads to a higher overall efficiency, e.g. in the conversion of thermal energy to mechanical and subsequently to other forms of energy. Other processes which become more efficient as the temperature is increased are those in which the limiting factors involve microstructural or molecular kinetic processes; in such cases higher efficiency corresponds to a shorter reaction time and therefore higher productivity for the installed equipment.

A concise definition of "high temperature" is rather difficult: in considering the efficiency of energy conversion (power generation, engines for transport, etc.) and materials processing (chemical plant, glass and metal melting and shaping, etc.) temperatures above 600°C are usually important. High temperatures referred to in this White Book correspond to this temperature range.

The development of improved engineering materials is a difficult empirical activity. The acceptance of a material for a given application is in general a compromise between a large number of more or less stringent property requirements and cost factors. The large variety of high-temperature materials available is a reflection of the conditions encountered. Until the last century, the requirements of materials to operate at elevated temperatures were not very critical; low stress levels and moderate temperatures were involved and for many centuries these requirements were satisfied by ceramics derived from the firing of clays and other materials. Modern technology, however, makes much more stringent demands: materials are now required to be able to retain their strength and mechanical properties at higher and higher temperatures, and at the same time maintain adequate resistance to the environment in which they operate. Further progress will probably see a continued increase in the number of advanced materials to satisfy even more stringent and unusual requirements.

While wrought and cast iron possessed adequate properties in the early days of steam power when temperatures and stress levels were rather low, it later became apparent that in order to increase the thermal efficiency of steam-powered electricity-generating stations, materials with increased strength at elevated temperatures were required. This led to the development of special types of low-alloy and austenitic steels, with improved creep strength and high-temperature oxidation resistance: the properties of these materials were exploited.

The gas turbine had been developed by the early 1930's as a stationary power unit, and existing ferrous materials were then adequate for the critical components, turbine blades and vanes, since the unit operated at what must now be regarded as a very moderate temperature, and there was insufficient economic advantage to justify the development of specially improved materials. However, on the application of the gas turbine to the aircraft jet engine, it soon became apparent that existing ferrous alloys were inadequate, and attention was directed towards nickel-base and cobalt-base alloys. As a starting point, nickel-chromium heater element alloys, which possessed good oxidation resistance to 1100°C but only modest strength, and the cobalt-chromium dental casting alloys which had similar properties, were modified to improve their high-temperature strength capabilities. These studies led to the development of high-strength, precipitation-hardened nickel-base superalloys, and the somewhat lower strength, solid-solution-strengthened and carbide-strengthened cobalt-base superalloys. The nickel-base superalloys, in particular, have been improved over the last 30 years, with the emphasis on ever increasing high-temperature strength, but with a simultaneous decrease in the high-temperature corrosion-resistance as a result of a re-adjustment of alloy composition. Consequently, the need for protecting the higher strength alloys against excessive corrosive attack by the environment gave rise to the use of protective coatings.

In other applications including the chemical, metallurgical and petrochemical industries, it is easier to achieve a balance between high-temperature corrosion resistance and strength since strength requirements appear to be more moderate. Since the latter industries require materials in considerable quantities, the material cost factor is an important element in the selection criteria.

The refractory metals, including tungsten, molybdenum, etc. all possess attractive high-temperature strength, but are handicapped by their very poor oxidation resistance. Attempts to provide adequate protective coatings have been successful in a few cases but the high cost has generally confined their use to spacecraft applications. Chromium-base alloys demonstrate outstanding oxidation resistance, but are subject to nitrogen contamination. Alloys based on the precious metals, are of special but limited importance, and are too expensive to be practical for volume usage.

A further class of high-temperature materials in which current interest runs very high are ceramics. Ceramics have for a long time been used as heat-insulating materials; however the development of stronger thermal-shock resistant carbides, nitrides and oxynitrides enables us to consider their use for highly-stressed high temperature components. Their resistance to oxidation is excellent, but their inherent brittleness and lack of reproducible mechanical properties remain the major obstacles, making it a very challenging problem to utilize their high strength potential.

It is clear then, that the field of high-temperature materials embraces a wide range of metals, alloys and ceramics. Different combinations of corrosion resistance and strength are required in applications ranging from metallurgical, chemical and glass-producing industries, through stationary power generation, to transport by land, sea and air. Many questions remain unanswered and there is considerable scope for creative and inventive research to support and advance technological progress in many industries. Gas turbines are an example of a principle which had to wait for the development of suitable materials before it could become a viable technolgy. The commercialisation of some other technologies such as magneto-hydrodynamics, (M.H.D.), nuclear fusion, nuclear process heat, etc. are all similarly dependentupon the development of improved materials.

The purpose of this White Book is to review the field of high-temperature materials and their applications so as to indicate the essential requirements, the state of the technology at the present time, and to identify future trends and areas for development. The report first covers the important fundamental properties which define the current and likely future performance limits of high-temperature materials. The application areas are then briefly reviewed, followed by a description of materials by categories including alloys, ceramics, composites and coatings. Finally a review of world-wide current research activities enables recommendations to be drawn up for future research priorities.

2. FUNDAMENTAL CHARACTERISTICS

Modern high-temperature technology has at its disposal a wide range of materials, and their selection for a particular application depends on a variety of factors. Where metallic materials are involved mechanical, physical and chemical properties must be considered and while a metal or alloy may be selected largely on the basis of high-temperature strength, there is hardly an application in which the effect of the interaction of the metal with its environment can be ignored. A very wide range of properties may be relevant when materials are assessed, and a comprehensive list of these is given in Appendix Table B. However for any other material a much more restricted amount of data is usually available. In the following sections an indication is given of those characteristics which are of major significance in high-temperature technology.

2.1 RESISTANCE TO THE ENVIRONMENT

In this brief review the thermodynamic and kinetic factors involved in high-temperature oxidation and corrosion processes are summarised. Oxidation refers to attack by entirely gaseous components including not only oxygen but also nitrogen, sulphur, carbon, chlorine, etc. The term "corrosion" usually implies the presence of a liquid medium and a predominantly electrochemical mechanism of reaction; but, in high-temperature technology the term has come to be more loosely applied. "Hot corrosion" is a specific process which certainly appears to involve the presence of a liquid salt layer, but it is debatable whether it acts as an electrolyte in a process analogous to that in low-temperature corrosion.

2.1.1 Thermodynamics

The thermodynamics of reactions between metals and alloys and their high-temperature environments are best represented graphically as stability diagrams. The simplest case is a pure metal reacting with a pure oxidant when the standard free energy of formation of the product phase can be plotted as a function of temperature, see Fig. 2.1/1. Essentially, this is a stability diagram as the ordinate scale (ΔG^o) is also related to the dissociation pressure of the product phase: the product is stable above the line, and the metal below. Contours of constant oxidant pressure are straight lines radiating from the common point $\Delta G^o=0$, $T=0$, and their positions are shown on the periphery of Fig. 2.1/1. If the oxidant is not present as a single molecular species the calculation is more involved, since several reactions must be considered, together with reactions representing the equilibria between the different polymers of the gas phase. There are many compilations of standard free energy of formation data and stability diagrams for metal reactions with oxygen, sulphur, nitrogen and carbon (1-3).

These simple stability diagrams can also be used for gas mixtures, providing only <u>one</u> of the gaseous components reacts: for example H_2-H_2O or CO-CO_2 mixtures, where the ratio of gas

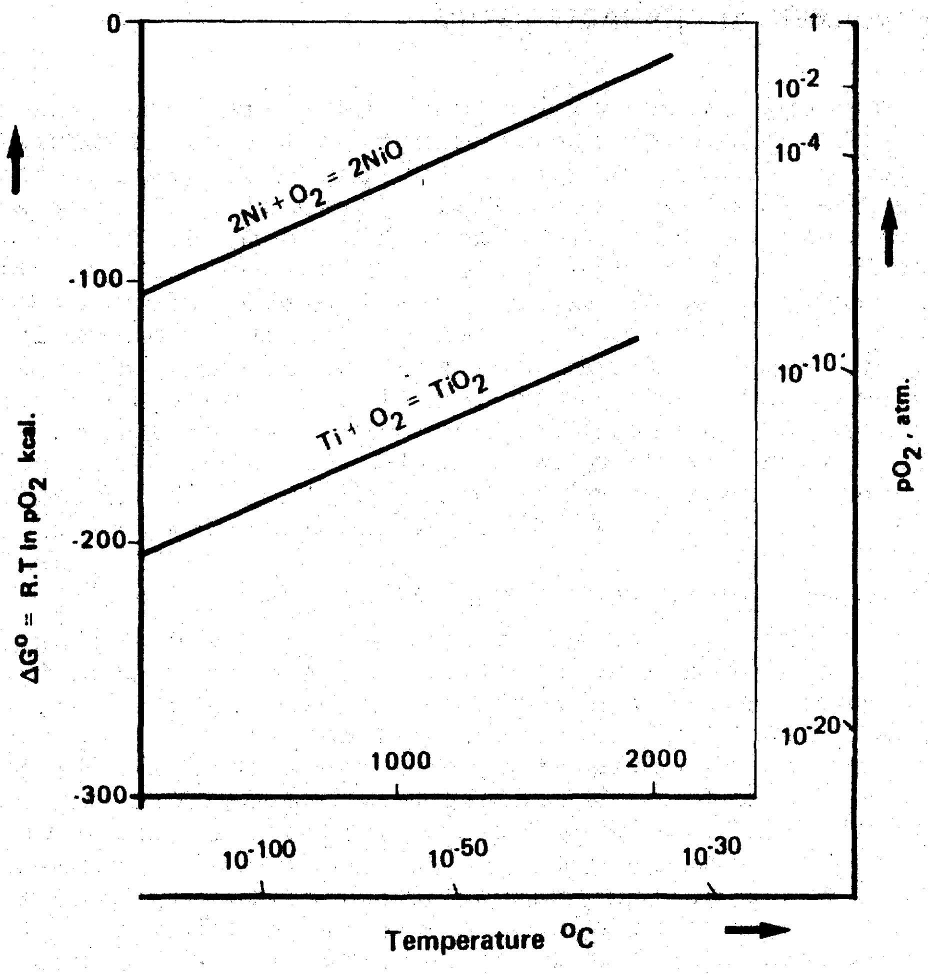

Figure 2.1/1. Free-energy diagram for oxidation of pure metals.

pressures is equivalent to an oxygen activity, and this can provide an alternative ordinate scale, also included in Fig. 2.1/1.

In atmospheres containing two oxidants, for example O_2+N_2, O_2+S_2 (or SO_2+SO_3), $CO+CO_2$, etc., providing the existence of all possible condensed phases is known, together with their standard free energies of formation, similar types of diagram can be produced: the regions of stability of the product phases are mapped onto isotherms with axes defining the thermodynamic activities of the two reactive gaseous components. Diagrams for metal-S-O, metal-C-O and metal-N-O systems are available in the literature (4-6). The introduction of temperature as a third coordinate easily provides a more complete three-dimensional representation of phase stability (7). The provision of multiple coordinates referred to different vapour species is again a possibility: this assumes that the gas phase maintains equilibrium among its constituent components - a justifiable assumption at high temperatures. A further condition usually assumed is that the condensed phases are at unit activity, and this is not always true. For example, if there is extensive solid solubility between two phases, it is clearly not correct to draw a sharp boundary between their stability regions.

The same principles can be applied in more complex gaseous atmospheres containing any number of possible reactants, providing all the possible reactions are taken into consideration, and any gaseous reactions are at equilibrium.

However, graphical representation is difficult with three components and impossible with more.

To analyse phase stabilities for binary and multicomponent alloys in gases containing one or more oxidants, superposition of the diagrams for the individual metals can serve as a good first approximation. However, with a knowledge of the activities of the alloy components and values of the free energies of formation of any ternary compounds, refinements can be added to the superimposed diagrams.

Many practical environments, particularly combustion gases, contain additional impurities, notably sodium, sulphur and vanadium compounds, arising from contaminants in the fuel or combustion air. These compounds are most effective in producing accelerated oxidation when they are present as liquid films on the surface of alloys. The nature of the deposit depends on the system considered, but Na_2SO_4, which is the main constituent of deposits in aero gas-turbine engines and as a consequence has received considerable attention, will serve as a convenient example to demonstrate the use of stability diagrams in interpreting the effects of salt/alloy and salt/oxide interactions on the corrosion rates of alloys. A similar approach is generally applicable to other fused salts (e.g. NaCl, Na_2CO_3, K_2SO_4, vanadium salts, etc.).

Na_2SO_4 can exist over a range of compositions, the compositions being defined by the oxygen and SO_3 activities (7); other variables such as sulphur activity or the activities of sulphide or oxide ions could equally well be used. The latter is a useful parameter in that it also defines the acidity of salts: salts with low oxide-ion activities are acidic. Both basic and acidic Na_2SO_4 can react with oxides formed in alloys and superposition of the oxide phase stability diagram on that for the appropriate section of the Na-O-S system provides a key to likely interactions. A number of these diagrams and their use in interpreting hot corrosion mechanisms are in the literature (7, 8) and have recently been summarized (9). As an example, Al_2O_3 is unstable at high oxygen-ion activities and forms the aluminate ion, AlO_2^-, whereas at low oxygen-ion activities the metal cation, Al^{3+}, is stable; for other common oxides, for example NiO, CoO or Cr_2O_3, the corresponding stable ions would be nickelate (NiO_2^-), cobaltate (CoO_2^-) and chromate (CrO_2^-) or the appropriate metal cation.

In more complex environments, multidimensional stability plots are required, although the principles are identical.

2.1.2 Kinetics

The composition of the reactive gas phase contacting the metal, or condensed salt layer, represents only one point on the stability diagram: upon the formation of a product phase contiguous with the metal, local equilibria may be set up internally which deviate greatly from the gas phase and thereby allow the formation of less stable compounds. The transport properties of all the phases are involved, and thus there is a strong interplay between the kinetic (diffusion) and thermodynamic aspects of high-temperature reactions.

One of the most effective means of representing these relationships with the corresponding oxide and subscale structures is by means of a 'diffusion path' on the appropriate stability diagram. (More commonly this would have ordinates related to concentration rather than activity). The diffusion path represents the locus of compositions through the surface scale and underlying alloy: in the case of diffusion-controlled growth the concentrations of all the components are parametric solutions to the diffusion equations (functions of the single variable $\lambda=x/\sqrt{t}$) and elimination of the λ yields a distance- and time-independent relationship between the compositions. The elements of multicomponent diffusion theory relating to high-temperature corrosion phenomena have been reviewed (10) and a useful summary of the relationship between observed diffusion structures and the corresponding phase diagram has been given (11).

Diffusion path analysis of this type can be used in two ways. Firstly as an aid to interpretation of the oxide structures produced under given circumstances and there are many examples of this in the literature (11). Secondly, it may be used in a predictive sense in that for a given system, providing the phase diagram is known and the transport properties of all the various phases have been determined, it is possible to calculate the diffusion path. This then would indicate important information regarding the sequence of phase produced in the scale, the types of oxides, the likely morphology of interfaces, and so on. Work along some of these lines is currently in its infancy (12).

Similar diffusion path analysis can be used to interpret the changes produced in molten salt deposits due to interaction with oxides or alloys. Again the composition of the as-deposited salt, which depends on the gaseous environment represents only one point on the stability diagram. However, activity gradients of the component species develop, and interpretation of their likely effect is facilitated by depicting this as a diffusion path. Several examples are in the literature (7, 8) However, limited thermodynamic data of fused salt systems and their relevant transport properties preclude any predictive use of this technique.

2.1.3 Further practical considerations

The thermodynamic and kinetic factors ultimately enable an alloy system to be selected on which a given oxide can form, and presumably in any application this is meant to be protective. It can break down and may not be re-formed. This is less predictable: however, it is particularly worrying since it means that the long term suitability of a material cannot be predicted from short term tests. It is not possible to present a general mechanism for breakaway, but usually some form of mechanical breakdown of the scale is involved.

In oxygen-containing atmospheres, it is reasonably clear that Cr_2O_3 and Al_2O_3 (and possibly SiO_2) are the best protective oxides and the composition ranges over which they can form, whilst now reasonably predictable using the methods outlined above, have been established and presented as oxide maps (not to be confused with oxide stability diagrams) showing the appropriate alloy composition ranges in Ni-Cr-Al and Co-Cr-Al systems for Cr_2O_3 and Al_2O_3 (13). These maps are not predictive in the sense that they are obtained from experiment rather than theory, but they do allow some extrapolation between the various measured compositions. The beneficial effects of rare-earth element additions to alloys forming Cr_2O_3 and Al_2O_3 scales, although known for a considerable time, are now being understood (14, 15). Additions of a dispersion of rare-earth oxides has a similar effect.

When reaction with other oxidants is considered, there is no single rationale by which the effects of compositional variations on the resistance of alloys can be predicted. The importance of some constituents, such as chromium, is recognized, but the levels required for effective performance in the different corrosion regimes, sulphidation, carburization, etc. are in dispute. The understanding of the roles played by these alloying constituents, essential to further significant progress in materials selection, has been developed to a reasonable level only for simple oxidation in oxygen or uncontaminated air.

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2.2 MECHANICAL PROPERTIES.

The essential difference between the mechanical properties required in a material for service at high temperatures and in one for service at normal temperatures is that the influence of time on the properties must be considered. The temperature at which this effect becomes apparent depends on the melting point of the material under consideration and also on the sensitivity of the method of measuring the strength, but, in general terms, high-temperature behaviour in pure metals may be considered to occur at temperatures above about 0.3 Tm, where Tm is the melting point in kelvins. Hence for lead (Tm 601K) "high-temperature" behaviour occurs at temperatures above 180K, i.e. even at subnormal temperatures; for aluminium (Tm 933K) high-temperature behaviour begins at 280K, i.e. at about normal temperature, while for iron (Tm 1808K) it begins at about 540K. The temperature limit for high-temperature behaviour of alloys is generally higher that that for pure metals, so that for practical engineering purposes relatively simple low-alloy steels have adequate strength at temperatures well above the limit for iron. Consequently, in the present context, consideration is restricted to temperatures above 600 °C (870K). In this temperature range the refractory metals with melting points above 2500°C (e.g. molybdenum, tungsten, niobium, tantalum) have inherent high-temperature strength, but by far the most important classes of material are specifically developed alloys based on iron, nickel or cobalt, which depending on service conditions, may be used in the temperature range 600-1100°C.

2.2.1 Short-time properties.

Although the time factor must be considered in all assessments of mechanical strength at elevated temperatures, the relevant properties can be separated into short-time and long-time groups. The techniques of measurement of short-time properties are necessarily different from those used for similar measurements at lower temperatures to allow for the time effect.

The tensile properties are normally determined under controlled strain-rate conditions in accordance with appropriate testing specifications (e.g. British Standard A4). A clearly defined yield point is not normally observed with high-temperature alloys, and the 0.2 per cent proof stress is usually determined, the strain-rate up to this point being commonly in the range 0.001-0.005/min. Beyond this point up to fracture an increased strain rate, e.g. 0.1/min. may be adopted. The elongation at fracture and the extent of uniform elongation are determined as indications of ductility and of structural instability, respectively; in some materials a well-marked minimum in elongation may be found at a certain temperature; this ductility trough may have important practical implications.

The elastic moduli of high-temperature materials are important in design both for the control of elastic strain under load as well as for the avoidance of resonant vibrations. They cannot be deduced reliably from normal hot tensile tests because of the difficulty of distinguishing between elastic, anelastic and plastic strains, and hence dynamic test methods are required. By appropriate selection of the vibration mode the tensile and rigidity moduli can be determined, from which Poisson's ratio can be calculated.

Torsional properties may be of interest in some high temperature applications and must be determined under controlled strain-rate conditions.

Hardness measured at normal temperature has little relationship to high-temperature properties but may be a simple and useful guide to the effectiveness of heat treatment procedures. Hot hardness may be relevant to some applications of high-temperature materials involving high surface loads, and could influence friction and wear behaviour; both static and dynamic test methods have been used. In either case a protective atmosphere is generally necessary to avoid surface oxidation, which would interfere with measurement of the impression, and in any case the results should be considered as comparative rather than absolute.

Impact properties at elevated temperatures may be important in practice and are particularly relevant in relation to materials which may not be completely structurally stable at the service temperature. The effect of long-term exposure to a high temperature can often be shown by a normal-temperature impact test, but since cooling rate from the elevated temperature may have an effect, testing at the elevated temperature is preferable. This is normally carried out by rapid transfer of the test specimen from a soaking furnace to the testing machine.

2.2.2 Creep.

The slow deformation of a material under the influence of an imposed constant stress is known as creep. A review of the physical basis of the creep of metals has been given by McLean (1). With the gradual increase of operating temperatures in the search for improved thermal efficiency, creep has become the limiting factor in the design of many engineering components, the need being either to restrict the creep deformation to a tolerable level or to avoid creep rupture; with some materials creep rupture may occur at relatively low strain levels (ca. 1 per cent) even though the elongation in a short-time tensile test after a preceding creep test may be much higher.

Most experimental studies of the creep of metals and alloys have been made using uniaxial tensile loading under isothermal constant-load conditions. The creep strain is recorded as a function of time and tests are commonly carried to total times equivalent to or approaching the expected life of an engineering component. Individual tests are made over a range of imposed stresses and at different temperatures, and are often continued until the test specimen fractures. The results are usually analysed and interpreted in a graphical manner by plotting for one temperature the stress against time to produce a given effect - see Fig. 2.2/1. Alternatively, stress may be plotted against temperature for specified times to produce a given effect - see Fig. 2.2/2.

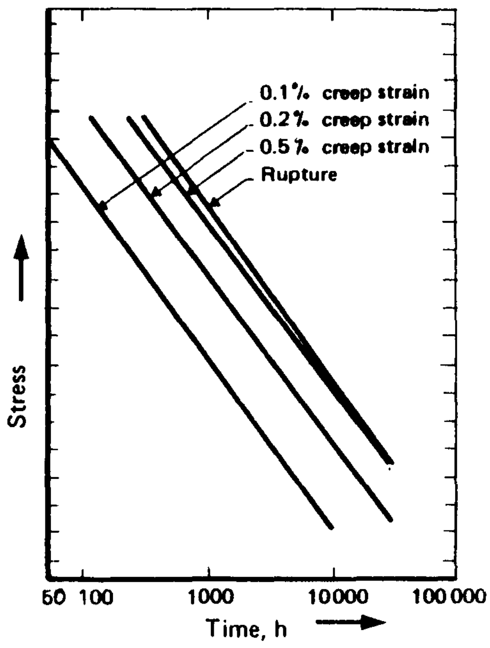

Fig. 2.2/1 Stress/log time curves for high-temperature alloy at 700°C.

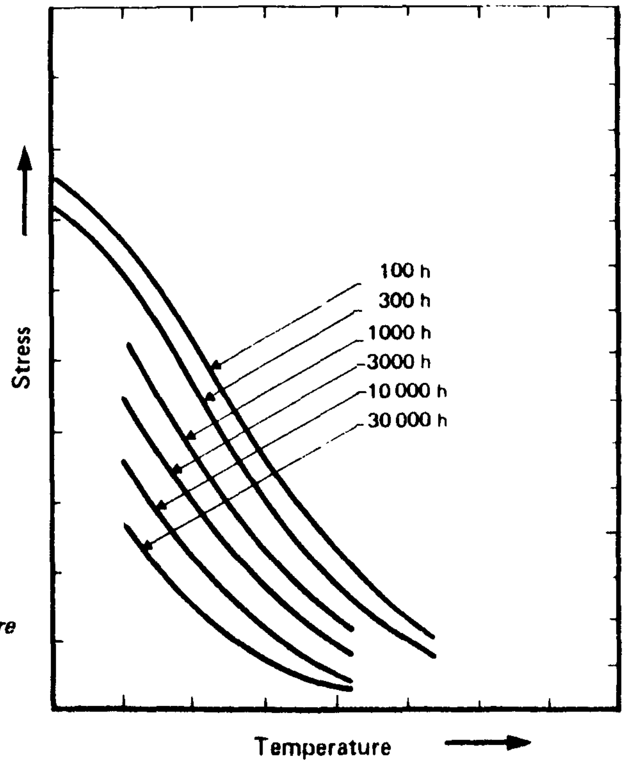

Fig. 2.2/2 Isochronous stress/temperature curves for stress-rupture of high temperature alloy.

Various attempts have been made to derive empirical relationships correlating stress, strain, temperature and time for a given material, in order to aid the interpolation and extrapolation of properties (2, 3, 4, 5). The best known of these is that due to Larson and Miller, but all should be used with caution, particularly in extrapolating beyond the range of temperature covered by actual experiment.

Very little creep testing has been carried out under complex stress systems, except in connection with the development of phenomenological theories for relating tensile creep data to multi-axial creep conditions (6). The application of uniaxial-stress creep data to engineering design is normally based on established design codes, e.g. ASME Boiler and Pressure Vessel Code. In such codes the design stress for a given temperature is determined by the lowest of a number of criteria including, for example, 67 per cent of the stress to cause rupture in 100,000 hours and the stress to produce 1 per cent total strain in 100,000 hours, as well as short-time criteria.

A common form of multi-axial creep test, of which the results may be directly applicable to design, is the tube-bursting test. In this a pressurized tube is exposed to the test temperature and the hoop stress required to produce failure in a given time is compared with the corresponding uniaxial rupture stress. The difference, often a reduction in nominal strength by a factor of 2-5, may be due to metallurgical structural differences, to surface effects, or to the use of an incorrect multi-axial rupture criterion.

In a number of applications of materials at elevated temperatures the parts are elastically deformed to a fixed strain, which is maintained constant during service; by a mechanism clearly related to creep the stress in the component gradually relaxes, so that on removal of the residual stress after a period of time, the elastic recovery is less than the initially applied strain. Many attempts have been made to calculate relaxation characteristics from uniaxial tensile creep data (7,8) and, although reasonable success has been achieved and recent multi-axial relaxation prediction methods are encouraging (9), there is no generally accepted procedure. Relaxation is important in the operation of bolts, constant-deflection springs, shrink-fit joints, etc.

2.2.3 Fatigue.

In many engineering applications of materials the effects of variation of imposed stress with time must be considered.

At normal temperatures the distinction between a static failure under the influence of a constant stress, and a fatigue failure under a varying stress is generally clearly defined, and the fatigue failure is generally related to the number and amplitude of the stress cycles. At elevated temperature, however, the distinction is much less clear. Under a constant stress a creep failure will occur after a certain period of time, while under a fluctuating stress, failure may occur similarly as the cumulative effect of creep damage or it may be due to fatigue damage, particularly if the cycles of imposed stress involve reversal of the stress direction.

In the former case the failure is related to the integrated stress-time pattern, while in the latter case failure is more closely related to the number of stress cycles, even though it is to some extent dependent on time. Since high-temperature fatigue testing can embrace a very wide range of stress patterns involving variation of mean stress, amplitude, frequency, etc., it is generally impossible to study a single material at all completely. Most fatigue testing, therefore, tends to be aimed at a specific application for which the test conditions are appropriately chosen, and the results are used in a comparative manner. In view also of the strong influence of surface condition, local stress concentrations, and internal stresses on the incidence of fatigue failures in service, the tendency is for fatigue testing to be carried out on actual or simulated engineering components rather than on idealised test bars.

2.2.4 Thermal Shock and Thermal Fatigue.

In some applications of high-temperature materials, e.g. gas-turbine nozzles, it is well established that failure is initiated by the formation of cracks due to rapid temperature changes. The steep temperature gradients in the material generated by rapid change in temperature of the surrounding medium, cause high stresses to be developed by differential expansion, and if the material has brittle fracture characteristics a single temperature cycle may be sufficient to reach the fracture stress; this causes a "thermal shock" failure, familiar as quenching cracks or grinding cracks in metal components. The damage caused by thermal stresses may, however, be cumulative, so that visible cracks are not developed until many cycles have been imposed; such a failure is termed "thermal fatigue".

Susceptibility to thermal shock or thermal fatigue is clearly related to a number of more basic physical and mechanical properties, including thermal expansion, thermal diffusivity, tensile strength, ductility, etc. and attempts have been made to establish a thermal fatigue index for the comparison of different materials (16). However, experimental comparison under simulated service conditions is generally the preferred technique and special equipment has been devised for such tests.

2.2.5 Creep-Fatigue Interaction.

Components operating at high temperatures are very often subjected to periods of steady operation interrupted by transient temperature and load variations. While the transient conditions have long been recognized as a possible source of failure due to fatigue, the periods of steady operation have only recently received attention. This is because at low temperatures fatigue damage is independent of the time elapsed between periods of rapid strain variation. However, in the creep range fatigue endurance is significantly reduced when hold periods are introduced between strain cycles, because of the accumulation of creep damage during hold periods. Thus, at creep temperatures, endurance is dependent both on the number of strain cycles and on the elapsed time between cycles.

Such effects are referred to as creep-fatigue interaction. All time-dependent effects like creep, relaxation, creep recovery, strain rate sensitivity etc. become important factors in designing for cyclic operation at high temperatures.

In general the interaction of creep and fatigue is detrimental, particularly when the dominant mechanisms of both are of the same type; for example, void generation in creep can reduce the fatigue life by nucleating fatigue cracks, thus by-passing the crack initiation phase of the fatigue process. Also a change of fracture mode from transgranular to intergranular may occur with an increasing relative amount of creep damage. There have been numerous attempts to correlate lifetime under superimposed creep and fatigue conditions. One hypothesis is that all the damage is due to creep, so that the tensile portion of the strain cycle contributes to the creep fracture in the same manner as the stress hold period (10). The modified fatigue approach (11) developed by Coffin and the universal slopes-method of Manson (12) extend the low-temperature fatigue relationships to temperatures in the creep range by introducing frequency- and hold-time-correction factors, respectively.

In the cumulative damage approach, creep and fatigue mechanisms are assumed to be mutually independent and fracture occurs when the sum of the creep and fatigue damage reaches a critical value. Fatigue damage is assessed by a cycle fraction, and creep damage by a time fraction. The ASTM-Code Case 1592 for the design of nuclear components at high temperatures recommends the application of a slightly modified linear damage rule (13).

A new method - termed "strain range partitioning" (14) - that has gained recognition in recent years, was introduced by Manson. It is based on the hypothesis that it is the capacity of the material to absorb anelastic strain, which governs high-temperature cyclic behaviour. The anelastic strain can be partitioned into plastic flow and creep. For each type of strain there is a different relationship between strain range and cycles to fracture. However, a disadvantage of the method is that certain temperature load cycles do not lend themselves readily to partitioning.

In contrast to the approaches described above, Coffin (15) concluded on the basis of results obtained in high vacuum that the degradation of fatigue endurance at high temperature is due to environmental factors rather than to creep. Further tests are needed to verify whether these findings are generally valid.

2.2.6 Friction and Wear.

Relative movement of parts in contact with one another at temperatures above 600°C is avoided if possible, since friction is generally high and hence rapid wear ensues. Lubrication is restricted to pre-placed solid lubricants, which are less efficient than liquid lubricants and do not have a cooling effect. Furthermore a tendency to contact welding exists, and seizure may take place, particularly when movement is intermittent. If mutual contact and relative movement cannot be avoided, a knowledge of the coefficient of friction and of the rate of wear is required, but these must be determined under conditions of temperature, loading and environment closely simulating the practical conditions under consideration. Both are very dependent on the presence of surface films or coatings of contaminants or corrosion products, and except in completely inert environments, are not characteristic of the basic material itself.

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2.3 PHYSICAL PROPERTIES

Although the physical properties of high-temperature materials are generally of less importance than their mechanical properties, a knowledge of these characteristics is often necessary for the selection of the optimum material for any application, and for the efficient design of a component. Relevant properties and an indication of their significance in high-temperature technology are listed below.

2.3.1 Melting Point

Except in very few cases, the solidus, i.e. the lowest temperature at which incipient melting commences, must be regarded as the upper limit for service of a material, even if it is effectively unstressed. This property may, for example, be the determining factor in the selection of a material for gas-turbine stator blades where occasional and local temperature abnormalities must be allowed for.

2.3.2 Density

This is primarily of importance in the high-speed rotating machinery e.g. gas-turbine rotors, in which the centrifugal stress is the main service stress. Materials for turbine blades are commonly compared in terms of the specific strength for a given criterion, i.e. absolute strength/density. The density also influences the natural frequency of vibration of components and hence may determine the incidence of fatigue failures due to resonance.

2.3.3 Thermal expansion

In any assembly of component parts of different materials, the thermal expansion of the materials will control the clearances between the components, or the stresses developed between them, as the temperature changes. The thermal expansion also controls the internal thermal stresses developed within a single component due to differences in temperature from point to point. It is necessary to determine the expansion coefficient over the maximum service temperature since differential thermal expansions and contractions may arise due to start-up and shut-down procedures, as well as to normal operating conditions.

2.3.4 Thermal conductivity

The thermal conductivity of high-temperature materials plays an important role in the determination of the temperature gradient, and hence the thermal stresses, developed within a single component. This is particularly so, for example, in the case of large rotors or discs of steam or gas turbines, and operating schedules need to be planned to allow for temperature equilibrium to be attained gradually to minimise thermal stresses. In the case of heat exchangers, however, the thermal conductivity of the material of construction is of less importance than the heat transfer coefficients between the fluid media and the solid tubes or sheets, and these latter are not a function of the bulk properties of the solid. Nevertheless knowledge of the thermal conductivity is necessary for the calculation of the heat flow. In the case of finned components for heat transfer purposes the correct design of fin section depends upon the conductivity of the material.

In many cases the thermal conductivity of high-temperature materials has been determined directly, but Powell (1) has shown that an empirical relationship, derived from the Wiedemann-Franz law, exists between the thermal conductivity and the more easily determined electrical resistivity.
For a number of austenitic steels and nickel-base high-temperature alloys the relation has the form

$$k = 2.2 \ . \ 10^{-4} \frac{T}{\rho} + 6.0$$

where k = thermal conductivity in W/mK
ρ = electrical resistivity in ohm.m
T = temperature in kelvins

2.3.5 Electrical resistivity

This property is of major significance in the case of electrical heating elements, but otherwise is of little importance in stress-carrying high-temperature alloys, except as a research tool for the study of precipitation and other structural changes. In the opposite sense the electrical conductivity is of practical importance in ceramic materials used as insulants in high-temperature electric furnaces, and is a useful research tool in the study of the ionic structure of such materials.

2.3.6 Specific heat

The specific heat or heat capacity of a high-temperature material may be of significance in cases of changing temperature, and, in particular, it enters into any attempt to derive a fundamental expression or index relating to thermal shock or thermal fatigue properties. Systematic measurements of specific heat over an appropriate range of temperature are, however, rarely available for high-temperature materials.

2.3.7 Emissivity

The emission or absorption of radiation may play a major role in determining the operating temperature of a component, particularly of thin sheet construction, such as combustion chambers, with a large ratio of surface area to volume of metal. Except in the case of parts operating in a non-corroding atmosphere, however, the emissivity is normally determined by the layer of corrosion product, e.g. oxide scale, and this usually means that the emissivity is close to 1.0.

Reference

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3. HIGH-TEMPERATURE PROCESSES AND APPLICATIONS

3.1 DEFINITION OF SCOPE

3.1.1 Material functions

Science traditionally classifies materials by their chemical composition. The term "high-temperature materials" therefore is, in scientific usage, mostly avoided. In fact it relates to a totally different system of classification, the application. To be defined, it requires the identification of the various areas of technology in which materials have their applications.

Generally speaking, one may define the "class" of high-temperature materials as including all materials which are able to accomplish a technical function at high temperature, and which are therefore, in practice or in concept, applied in high-temperature technology.

To be precise however, the range "high-temperature" needs definition. Moreover, even if in the proposed definition the term "technical function" has no basic limitation, the objective of the White Book is not wide enough to accept all technological items. So, at least for the present purpose, a restriction on the basis of some other criteria will be made.

Considering the technical functions of materials at high temperature, it is interesting to take note of a well-known development (mainly in metallurgy and combustion technology) which may be described as a "separation of functions" in the containment of hot media: the use of a combination of a metallic structure with a refractory or insulating lining. The required resistance to the high temperature environment and to the mechanical stress is divided up and allotted to two different specialized materials which are able to accomplish these functions separately:

- Resistance to corrosive attack by the high-temperature environment at low mechanical stress.
- Resistance to the mechanical stress at low temperature.

The "advanced" area of high-temperature materials technology begins where this separation of functions is no longer feasible, i.e. where both resistance functions have to be performed by the same material.

Thus high-temperature materials in the advanced meaning considered here are those which combine refractoriness and strength, independent of quantitative specifications. Accordingly this chapter of the White Book will only refer to applications which require materials having this capacity.

3.1.2 Applications of high temperature

Fig. 3.1/1 shows the operation temperatures of a number of relevant processes and systems. The temperatures of the actual components may differ appreciably from the values shown, depending of the functioning of the system and the temperature control applied, in particular the characteristics of cooling technology.

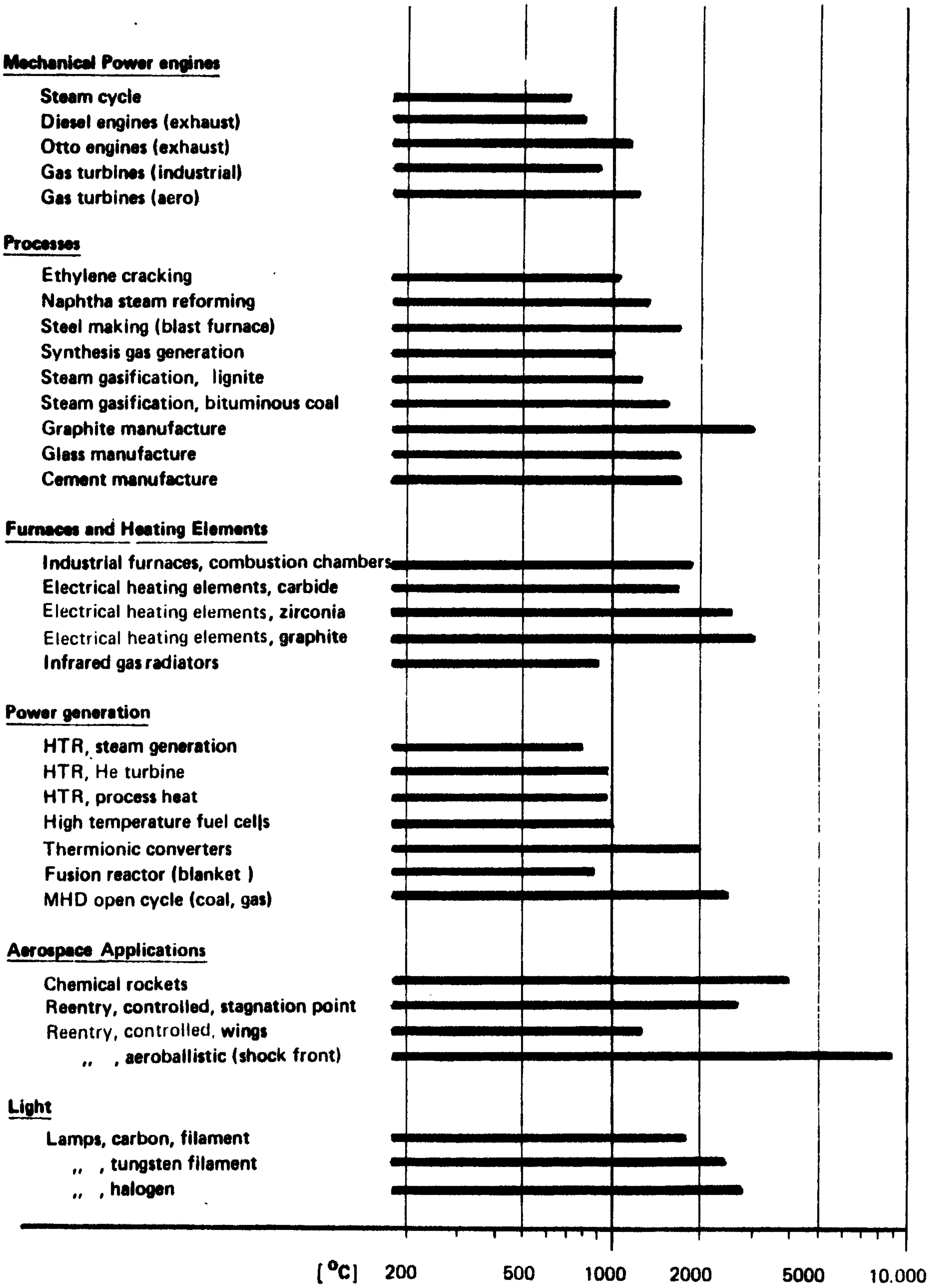

Fig. 3.1/1 *Actual maximum operation temperatures of high-temperature processes and systems.*

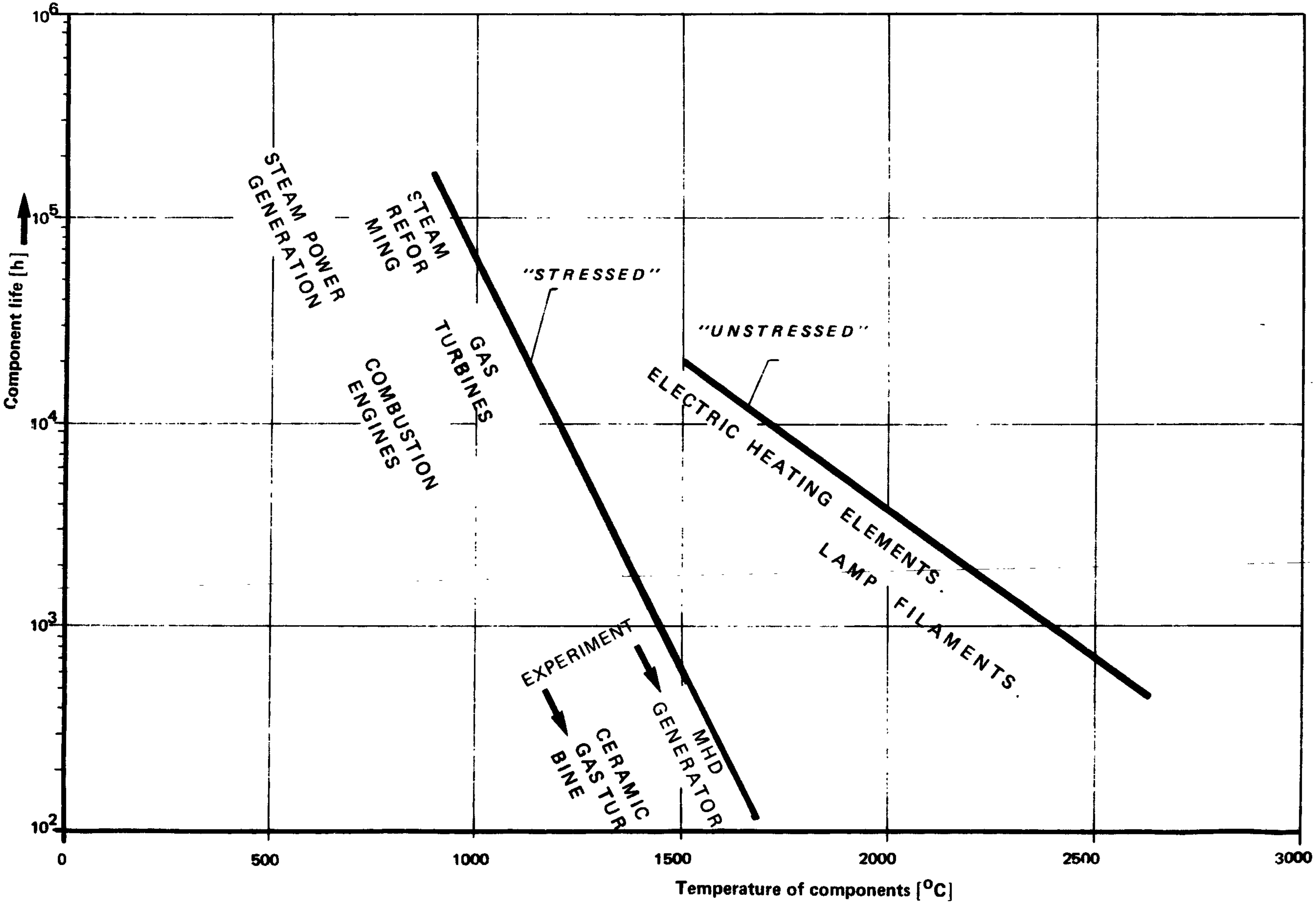

Fig. 3.1/2 Typical component life ranges of some actual high-temperature applications.

The main applications of high-temperature materials in the advanced sense described above are those for which a high thermal conductivity is a major requirement: in the first place all high-temperature heat-transfer systems. Further concerned are all applications in which either space, weight, cooling or specific strength requirements forbid the use of "function separation" (except coatings): in particular mechanical power engines. The application having the highest material temperature at long-time steady-state operation is the area of electric heating elements. In contrast to most other applications, heating element materials have a higher rather than lower temperature than their environment, and these temperatures can be so high that only stress-free and controlled-atmosphere operation is possible. Heating elements therefore represent an extreme case of an advanced high-temperature materials application, one of the two material functions being relaxed to maximize the other.

Temperatures higher than those of heating elements are involved in certain manufacturing processes (carbides, graphite), some types of flame, explosions (including nuclear), MHD generators, special glow lamps and, as shown by fig. 3.1/1 some aerospace systems.
To assess these systems in the light of the above approach, reference is made to a technological parameter which is uniquely able to quantify the performance of materials: the high-temperature service life of components. Apart from the general goals of engineering design common to all technologies, i.e. proper operation and economy, component life is a particularly sensitive parameter of high-temperature design and development, and can be considered as an important indicator of the technological state and the potential for further development of an application. Moreover it can be used to classify applications in terms of ranges which have technological relevance.

Figure 3.1/2 shows such ranges of component life for some high-temperature applications, and it appears that the technology of processes, engines and systems having unlimited operation period achieves minimum component lives of the order of several thousand hours. This class of application must be distinguished from applications having service lives of some 100 hours or less, down to even some minutes.

These "short-time" applications, which also include those having naturally limited and therefore short operation periods, have a number of characteristics which make them not comparable with applications having unlimited operation period. In general they apply unconventional techniques of temperature control like sweat cooling (rockets), dynamic heat absorption and ablation cooling (re-entry technology). Material functions other than mechanical strength and refractoriness then have higher relevance, so that R and D is going in a different direction. This also holds for glow lamps where the relationship between filament temperature, life, luminosity and economic parameters appears to be well under control, based on specific research on these aspects.

The short service life of experimental systems like MHD generators and ceramic gas-turbine components are not inherent, but reflect the current state of development of these applications. The prime goal of their development is indeed the extension of component life to an economically attractive length.

Apart from these experimental development areas, other short-time applications have characteristics and development goals very different from the general scope of the White Book, so that they are left out of consideration.

3.1.3 Temperature range

The life-temperature relationship of technologies shown in fig. 3.1/2 suggests that practical limits exist beyond which extension has not yet taken place. This appears to be true for applications in which components operate under mechanical stress, as well as for those without mechanical stress. Applications having, for example, more severe environmental conditions, thermal or mechanic load variations and shocks, or more severe reliability requirements and failure acceptance criteria, have much lower values than the apparently "best" applications shown in the figure. A transition area between the line marked "stressed" and the line marked "unstressed" must exist, but scarcity of data and the lack of a universal "load" parameter to replace the unquantified parameter "stress", make a more detailed evaluation too difficult.

Taking these aspects into account and neglecting precise quantitative analysis, one can consider the relation between the different applications shown in fig. 3.1/2 as realistic. It is certain that a large number of other applications could be added, in particular at the low-temperature end. It appears however that the critical development goal is to expand beyond the 1000°C/100000 hours range, since this is of practical technological importance, as demonstrated by the nuclear process-heat development. The technologies which are the closest to this area are steam reformers and gas turbines.

To draw a temperature range limitation not affecting the coherence between these areas, a line should be drawn between these technologies and steam power generation. The temperature range definition based upon applications should therefore refer to material temperatures higher than those at which components of the conventional steam cycle are operating.

On the basis of the limitation used here, therefore, the lower limit of the high-temperature range is at approximately 600°C. With respect to materials, this definition leads to the exclusion of low-alloy ferritic steels from high-temperature materials.

The evaluated criteria for the functions of materials, the service life of components and the temperature range have defined the boundaries for selection of the applications to which the subsequent sections of this chapter are related.

3.2 CHEMICAL TECHNOLOGY

3.2.1 Introduction

The chemical industry, which includes a wide range of the activities of the oil industry, has in service equipment operating at greatly different conditions. Its requirements overlap with those of the power industry, but the conditions under which chemical plants operate cover a much wider temperature range. Some of the reactions involved in the manufacture of chemicals are endothermic, and this requires the reactor vessel to perform the role of a heat exchanger as well. It is usual in such instances for the reactor to take the form of a piping system.

The design of such systems is covered by a number of national and international codes. Existing codes list materials and give design stresses for service conditions extending from the boiling point of nitrogen (-196°C) at one end to just above 800°C at the other. This is quite adequate for the requirements of the majority of chemical plants, but the last decades have seen the development of processes with increasingly higher operating temperatures requiring the use of alloys at service conditions beyond the scope of the existing codes. One such process is the steam reforming of hydrocarbons in the presence of a catalyst for the production of hydrogen or gas mixtures containing hydrogen and other gases, which are the starting point for the synthesis of ammonia, methanol and a number of other chemicals. Another process is the thermal cracking, i.e. without catalyst, of hydrocarbons for the production of ethylene and several useful by-products.

3.2.2 Catalytic Steam Reforming

In a reformer, a mixture of hydrocarbons and steam is introduced into a number of tubes containing the catalyst. Heat has to be supplied through the catalyst tube walls because the overall reaction is endothermic and also because it is necessary to raise the temperature of the reacting mixture to 800-900°C to obtain an economic yield.Typical operating pressures are up to 30 atm. and even higher.In order to achieve the rate of heat transfer required to heat the gases to these temperatures in a relatively short tube length,the tubes have to reach temperatures of 950°C or even higher.From the tubes,the reaction products, consisting mainly of hydrogen, carbon monoxide, carbon dioxide and excess steam are led to a secondary reformer or to a heat-recovery system and to other temperature reaction vessels.

A reformer consists of a number of vertical tubes containing the catalyst. The mixture of steam and naphtha or natural gas at a temperature of 400-500°C enters the tube through a small-bore pipe that forms an expansion loop. Because of its shape, this type of flexible connexion has become known as a 'pigtail' A typical catalyst tube is up to 12-15 m, with 100mm diameter and 20 mm wall thickness. This tube may either hang from the cold top end or be supported from the cold bottom end outside the furnace enclosure. The reformed gas leaves the catalyst tube at a temperature of 800-900°C through the outlet pigtail and is led into a header and transfer line which together may be nearly 100 m long, with a diameter of up to 400 mm and a wall thickness of 20 to 30 mm. Pigtails perform a double function: they provide the necessary flexibility to the connexion between tube and header, and in case of failure they can be 'nipped', thus allowing the isolation of the failed tube without having to shut down the plant. The alloys used for the early reformer furnaces had originally been developed for heat-treatment furnaces. Here the stresses to which the components were subjected were relatively low, and failures, if they occured, were unlikely to constitute a safety hazard or to lead to costly downtime. Alloys developed for aircraft engines were at times also considered but their cost was always found to be prohibitive.

In the second generation of reformers, designed in the late fifties and early sixties, the inlet header and the inlet pigtails, operating at a metal temperature in the range 450-600°C, were seamless tubes in carbon or low-alloy steel.The outlet pigtails which had to withstand temperatures above 800°C were almost invariably seamless tubes in Alloy 800 (20 per cent Cr, 32 per cent Ni, 0.10 per cent C max). The catalyst tubes and also the risers used in certain furnace designs were centrifugally-cast tubes in Alloy HK-40 (25 per cent Cr, 20 per cent Ni, 0.4 per cent C). The outlet header and the transfer line could be made in a heat-resistant alloy, which was usually the wrought Alloy 800 or the cast alloys HT or HU (18 per cent Cr, 37 per cent Ni, 0.4 per cent C),with external lagging, or in carbon steel with an internal refractory brick lagging, and an outside water jacket.

The alloys used for the first and second generation reformers are all basically high-chromium, high-nickel steels. Since then there has been a continuous trend for higher operating temperatures and pressures and a tendency to use stronger alloys. These stronger alloys have been obtained by increasing the percentage of chromium and nickel at the expense of the iron content,as well as by the addition of other alloying elements such as niobium,cobalt,tungsten,molybdenum,etc..Table 3.2/1 which does not pretend to be exhaustive,gives the names and nominal composition of some of these alloys,together with their methods of manufacture and applications. Some of these alloys are fairly recent developments and their properties and capabilities are not as well known as those of the more traditional alloys. The methods of manufacture of these alloys are closely tied up with their applications and composition. The high hot-strength of the plain chromium-nickel alloys has been achieved by increasing the carbon content of the original lower-carbon wrought alloys. This, however,has made them less ductile and very difficult, if not impossible, to hot work. One way of getting over this difficulty is casting the metal in the form of a tube of the required dimensions, instead of going through the long process of casting an ingot, rolling it into a billet, extruding a hollow, and then hot or cold drawing into a tube.Centrifugally-cast tubes with machined bores can be obtained nowadays completely free from porosity and other casting defects. Internal machining to remove the internal-bore microporosity of cast tubes also increases

Alloy	Compositions per cent				Method of Manufacture	Applications
	C	Cr	Ni	Other elements Balance Fe		
HK-40	0.4	25	20	-	Cast	Tubes
18/37 (HT/HU)	0.4	18	37	-	Cast	Headers
20/32/Nb	0.1	20	37	Nb	Cast	Headers
IN-519	0.3	24	24	Nb	Cast	Tubes
MORE-1	0.4	25	33	W	Cast	Tubes
36 X	0.4	25	35	Nb	Cast	Reformer Tubes
36 XS	0.4	25	35	Nb, W	Cast	Cracker Tubes
NA-22-H	0.5	26	48	W	Cast	Tubes, Structural Members
Supertherm	0.5	25	35	W, Co	Cast	Tubes, Structural Members
IN-643	0.5	25	47	W, Co, Mo, Nb, Ti, Zr	Cast	Tubes
UMCo 50	0.1	28	-	Co (50 /)	Cast	Tubes, Structural Members
UMCo 51	0.3	28	-	Co (50 /), Nb	Cast	Tubes, Structural Members
Alloy 800	0.1	20	32	Ti. Al	Wrought	Pigtails, Headers
Incoloy 802	0.3	20	32	Ti, Al	Wrought	Cracker Tubes
Incoloy 807	0.1	20	40	Ti, Al, Co, Mo, Nb	Wrought	Pigtails, Headers

Table 3.2/1 Nominal composition, method of manufacture and applications of the alloys used in petrochemical furnaces at temperatures above 815 °C.

carburisation resistance. In addition, in order to obtain optimum properties at high temperature, wrought alloys have either to be finished at temperatures above 1100-1150 °C or be given a heat treatment in the range 1150-1260 °C, depending on composition, treatments that are unnecessary for centrispun tubes. There are limits to the size in which centricast tubes can be produced, 50 mm bore being the smallest size that can be achieved at present. For this reason, whereas the majority of furnace tubes and a fair proportion of headers and transfer lines are cast, pigtails are invariably fabricated from wrought pipe.

3.2.3 Steam Cracking of Hydrocarbons for Olefine Production

In an olefine cracker a preheated mixture of steam and naphtha or other hydrocarbons is heated in tubes, where, in order to attain the optimum yield, the feedstock has to be heated in a fraction of a second to a temperature above 800 °C. The heat-transfer conditions are such, that in order to achieve this rate of temperature increase in the gas, the metal temperatures involved are up to 1050 °C. The operating absolute pressure is in the range 2 to 6 atm. Following this rapid heating the mixture is rapidly cooled in a heat exchanger where the heat removed from the cracker products is used to raise steam required in the process. The different components in the cracked gas are later separated by fractional distillation.

Among the unwanted by-products of the process there are heavy polymers and coke that tend to foul the inside surface of the quench boiler and of the tubes in the radiant section of the cracker furnace. This coke acts as unwanted thermal insulation on the heat-transfer surfaces,and in order to maintain the heat flux, the outside metal tube temperatures have to increase. Frequent decoking of the fouled surfaces is necessary, since otherwise the increased metal temperature would result in excessive metal wastage by carburisation and oxidation,and in creep failures.

Most olefine crackers differ from reformer furnaces in that rather than consisting of several individual tubes fed by pigtails from a header, whose product is in turn discharged into another header, they generally contain 2 or 4 flat coils, each consisting of several straight lengths joined by return U bends. The total length of the coil may be some 80 m, with tube diameters in the range 80-150 mm. Because of the lower operating pressures the tube wall need not be as thick as that of a reformer tube. Some modern designs however have several tubes in parallel, which are fed by a common inlet header and then discharge into a common outlet header. Because of the absence of catalyst, the tubes have a uniform section between the headers and therefore reduced-section pigtails do not exist.

The radiant-section coils of an olefine cracker were initially in HK-40 alloy, but alloys of the 25/35 chromium-nickel type with niobium,tungsten, etc. additions are being used nowadays. These improved alloys provide better resistance to both creep and carburisation-oxidation.

3.2.4 Common features ot High-Temperature Petrochemical Furnaces

Although in reformers and olefine crackers operating conditions are not the same, their requirements have a lot in common. In both cases operating metal temperatures are well above those for which existing codes list maximum allowable stresses. On the outside the tubes are in contact with flue gases of similar temperature and composition, and on the inside with mixtures of steam and hydrocarbons at high temperature with the possibility that carburisation-oxidation may take place.With regard to stresses, although crackers operate at lower pressures than reformers, they also operate at higher temperatures, so that creep-rupture strength is lower and therefore lower stresses are allowed. Finally, there is the fact that up to now the same, or very similar, alloys and manufacturing and fabricating methods have been used for the construction of both types of furnace. Although in very general terms it can be said that for existing designs, carburisation problems in crackers tend to be more a limiting factor than strength, and that the reverse is true for reformers, the nature of the problems is such that they can be considered together, and this is reflected in the fact that work for the development of new alloys with improved resistance to carburisation and higher creep-rupture strength, as well as the collection of the data that form the basis for the derivation of the maximum allowable stresses required for the design codes, is in the hands of the same alloy manufacturers and developers.

Although in the early days of steam reforming and olefine cracking component failures as a result of simple creep or carburisation-oxidation were common, such failures are nowadays rare. Such difficulties were mainly due to the fact that the strength data used in design in those early days were unreliable and this, coupled with the inexperience of plant operators, led to overheating and/or overloading and therefore to failures.

3.2.5 Mechanical Design of High-Temperature Petrochemical Furnaces

For temperatures above 815°C, the maximum allowable stress values for the alloys quoted in Table 3.2/1 are not given in any national codes. However, for some of these alloys extensive collections of creep-rupture data have been assembled by several public and private organisations. Although not complying fully with the ISO requirements such collections have been used to derive maximum allowable stresses by parametric methods and have been used for the design of many successful plants.

The design of furnace tubes, pigtails,headers, etc. is based on the fact that during service, at high temperature, the components of a chemical plant are subjected to stresses arising from:-

a) own weight
b) externally applied forces and moments
c) internal pressure
d) thermal gradients

By adopting a suitable geometry and using adequate compensating springs and counterweights, it is possible in the case of tubes and piping to reduce the stresses arising from a) and b) to acceptable values,

The effect of internal pressure is to give rise to tensile hoop and longitudinal stresses and to a compressive radial stress. For a reasonably thin-walled tube the hoop stress is approximately twice the longitudinal stress and since, as already mentioned, the stresses arising from weight and external forces can usually be kept relatively low, the maximum stress, i.e. the one that determines the required tube-wall thickness is the hoop stress due to internal pressure.

This hoop stress has to be kept below the maximum allowable stress for the tube material at the operating temperature. To allow for the unavoidable scatter in material properties and to introduce a safety margin, the values for the maximum allowable stresses given in the design codes are derived from the relevant mechanical property (which in the case of a furnace tube is the stress that will cause rupture by creep in the intended life of the plant)by multiplying it by an agreed factor. Design within the creep range has to be therefore, for a limited life,usually 10^5 hours (i.e. approximately 10 years), although in some instances components may have to be replaced after shorter times for other reasons, e.g. pigtails in reformers and tubes in crackers because of carburisation. The hoop stress is usually calculated by using the mean diameter formula. However, this simple criterion can lead to difficulties.

In tubes of appreciable wall thickness the hoop stress at different points along a radius depends on the distance of the point from the tube axis. However, bursting tests carried out with a variety of tube materials have indicated that the life of a thick-wall tube operating at a constant and uniform temperature is in good agreement with that predicted on the assumption that the hoop stress at all points has a value equal to that calculated using the mean diameter formula.

In the case of tubes in a fired heater there is an appreciable thermal gradient across the wall, and as a result very high thermal stresses are created. The value of these stresses in a typical furnace tube may reach values at least an order of magnitude higher than the hoop stress calculated by the mean diameter formula in absence of thermal gradient.As a result,the material creeps at a very high rate,and if it were not for the fact that in creeping the stress in the material quickly relaxes, the tube would fail in a very short time. As a result of relaxation the thermal stresses eventually reach a tolerable value. However, if after the thermal stresses have relaxed to a low level, the thermal gradient is removed or inverted, as happens for instance when the furnace cools down, a stress system of opposite sign appears in the tube and some new yield takes place in the material until these thermal stresses have relaxed to a low value. The process repeats itself with every heating/cooling cycle of the furnace. But every time that the stresses relax, this is at the expense of a certain amount of creep damage occuring in the component, and after a number of cycles the accumulated creep damage may exceed what the material can take and failure will occur.

Strictly speaking the correlation between creep at constant stress and temperature and cyclic creep, and between creep in uniaxial and in multiaxial stress systems, has not yet been accurately established. However, using certain approximations and simplifications it is possible to make predictions regarding the performance of a component subjected to cycling under a multiaxial stress system starting from data obtained from constant-stress and constant-temperature uniaxial creep tests done in a laboratory. Although the results of these calculations do not always agree quantitatively with actual performance they are often qualitatively acceptable in that they show the correct trends.

Several computer programmes based on the finite element analysis have been developed to carry out such calculations. The component is assumed to be divided into finite volumetric elements. Over an element of time, it is assumed that within each volumetric element, the stress, the temperature, and therefore the strain rate, remain constant. Using the functional relationship relating strain with stress, temperature and time, and provided that continuity is maintained at the boundaries of the finite elements, it is possible to calculate the values attained by the variables at the end of a time element. These new values are used to repeat the process over the second and successive time elements, and in this way it is possible to follow the deformation and accumulation of creep damage and to arrive at where, when and how failure will occur in the component.

Although tests under cycling conditions are at present being carried out to check the predictions made using such programmes, in most cases this refers to situations in which the specimens are subjected to uniaxial stress systems, and so far no results have been published related to the accuracy of the predictions resulting from tests on tubes subjected to thermal gradients. Besides, very few tests have been done with materials having mechanical properties of the type exhibited by the alloys used in petrochemical furnaces.
Apart from the problem of trying to predict life or performance of tubes, there is the separate problem of the performance and early failure of welds. Ideally it would be desirable to use welding materials and welding techniques leading to welded joints having properties identical to those of the parent metal. It is often assumed that this can be achieved by using consumables of the same composition as the parent metal. However,experience has shown that this is not the case. This is not surprising since it is well known that mechanical properties often depend on heat treatment as much as on composition. The heat treatment(i.e. the heating/cooling cycle) in the case of a welded joint is different from that of the bulk of the parent metal and furthermore different welding techniques involve different heating/cooling cycles. Moreover, the use of consumables of the same composition as the parent metal, is not always possible, either because the weld is between two different materials or because the parent-metal composition is not one that leads to the deposition of sound weld metal.

3.2.6 Future Requirements and Prospects

It is clear therefore that there is a need to improve our understanding of the behaviour and performance of the materials used in high-temperature chemical plants under real operating conditions, i.e. involving temperature gradients and cycling, as distinct from their behaviour under the simplified conditions prevailing in ordinary laboratory creep tests. It is important to find the correlation between these two types of behaviour in such a way that laboratory data can be applied with confidence to the solution of real plant and design problems.

In the case of the usual tube materials the tests should be aimed mainly at checking whether the assumed relationships between simple and complex creep are acceptable, by means of tests in rigs in which tube samples could be subjected to internal pressure under a temperature gradient, and where both temperature and pressure could be altered.
In the case of welding problems the study should include a careful study of the metallurgical factors involved in the production of welds and in their performance in service, an area in which very few hard facts are available at present. Special attention should be paid to elucidate the reasons why welds of identical composition obtained by different techniques differ so much in performance.This should be followed by the study of a model,using a programme similar to the one outlined above, but also taking into account factors such as the difference in creep properties,ductility,expansion coefficient etc, between weld and parent metal.

The effect of weld/parent-metal boundary geometry and of features analogous to stress-relieving grooves in fatigue situations, should also be considered. Finally, rig and/or plant tests should be carried out to check whether the theoretical predictions yielded by the model agree with the experimental results.

In both reformers and ethylene crackers, the yield, and in some cases the purity, of the products can be improved by operating at higher temperatures and/or pressures. There seems to be, therefore, an incentive for materials of improved properties. However it has to be borne in mind that improving the product yield does not necessarily mean improving the financial yield, if the former has to be achieved by using a plant of higher capital cost.Furthermore, the effect of improvement in materials can easily be nullified by the adverse effect that e.g. increased temperature may have on factors that may not be very obvious at present, such as the formation of an unknown undesirable by-product. These concepts are fundamental to the planning of any new material development work for the future, which without any doubt has to be tied up to both process development work and to the financial implications of any changes in materials. The fact that higher efficiency use of that energy locked up in the products is more desirable than marginal yield improvement has also to be considered.

3.3 ELECTRIC HEATING ELEMENTS

3.3.1 Outline of Process

Electricity provides a very clean, uniform and convenient means of heating, both for industrial furnaces and domestic appliances. Its use is limited principally by heater element life and maximum temperature capability, together with the fact that it is still generally a more expensive form of energy than fossil fuels, although with good furnace design it is possible to obtain higher efficiencies.

Mechanical strength requirements for a heater element are low; it must be able to support its own weight and must be sufficiently ductile to absorb thermal strains. However, this aspect becomes important if resistance to environmental degradation makes it possible to work at very high homologous temperatures.

The total heat input, W, required to maintain a furnace at a temperature T_f is determined by losses to the exterior. Except in cases of forced convection, this heat is lost from the heater elements almost exclusively by radiation, so that

$$W = \varepsilon\sigma S(T_e - T_f)^4$$

where ε is total emissivity, σ is Stefan's constant, S is the total radiating surface area and T_e is the temperature at the surface of the heater elements. The absolute maximum value of T_e is obviously the melting temperature, but for a reasonable life T_e is limited by environmental attack or mechanical deterioration. The latter considerations place minimum restrictions on the cross section and thickness of the elements. On the other hand, thickness should not be too great in order to limit the temperature gradient between the centre and the surface, and a large surface area is obviously an advantage for maximum heat dissipation. If the difference between T_e and T_f is to be small, then the total surface area S must evidently be correspondingly large. Available space and material costs are thus important factors.

The heat produced by the current in the heater elements is given by

$$W = \frac{V^2}{JR} = \frac{V^2 A}{J\rho L}$$

where V is the applied voltage, J is the mechanical equivalent of heat, R is the total resistance, ρ is the resistivity, A is the cross-sectional area of the elements and L their total length. We have seen that there is an upper limit on W (or W/S) in order to avoid overheating, as well as restrictions on element geometry. This places requirements on the resistivity, for low resistivity requires large currents and high resistivity neccessitates high voltages. Thus, in practice, values ranging from 10^{-5} to $50\,\Omega$ cm are acceptable, although $10^{-4}\,\Omega$cm is a more usual lower limit.

Except in the case of oxides, resistivity usually increases with temperature. Although a large positive temperature coefficient of resistivity allows rapid heating and introduces the possibility of self-regulating temperature control, it increases the tendency to overheat in locally reduced sections. The large variations in power consumption during heat up are also usually considered to be a disadvantage, so that low temperature sensitivity is normally favoured.

3.3.2 Conventional Materials

The most important characteristics required of a heating element material are the capacity to withstand the mechanical and chemical conditions inherent in high temperature operation, together with adequate electrical resistivity.
Table 3.3/1 gives the maximum temperature capability of the commonly used materials, as well as the type of atmosphere in which they can be used, while their electrical resistivities are shown as a function of temperature in Fig. 3.3/1.

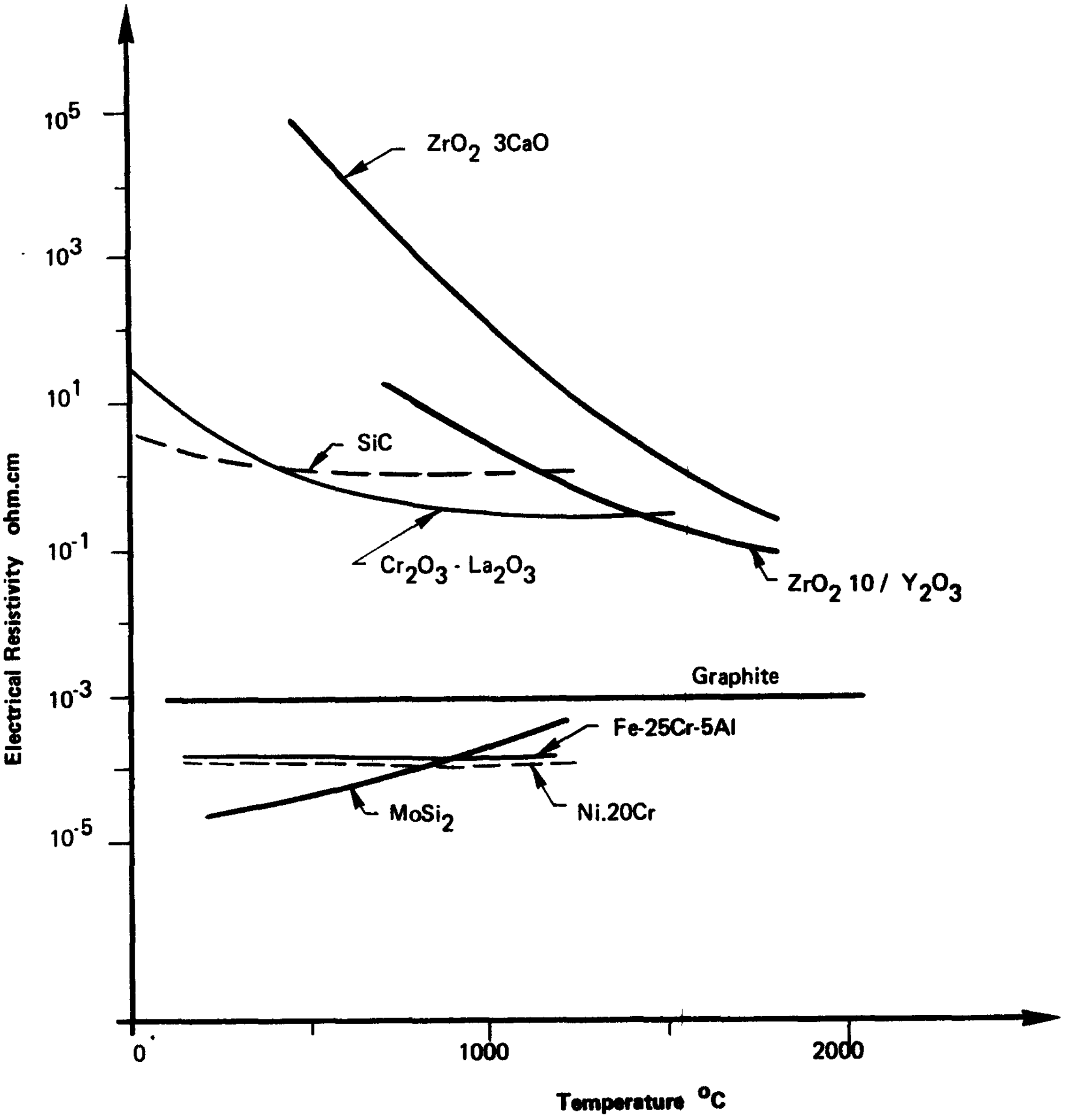

Fig. 3.3/1 Variation with temperature of the electrical resistivity of common heating element materials.

Material	Atmosphere	Maximum Temperature °C
Fe-35Ni-20Cr	Oxidising	1150
Ni-20Cr	,,	1250
Fe-25Cr-5Al	,,	1400
Pt	,,	1500
SiC	,,	1600
$MoSi_2$	,,	1750
$Cr_2O_3.La_2O_3$	,,	1900
Stabilised ZrO_2	,,	2250
Ta	Neutral, reducing, vacuum	2000
Mo	,,	2300
W	,,	2500
Graphite	,,	3000

Table 3.3/1 Maximum Temperature Capabilities of Element Materials.

3.3.2.1 Metallic Materials

By far the major part of all heating elements are made from alloys based on the Fe-Ni-Cr and Fe-Cr-Al systems. Approximate isoresistivity contours are plotted in Figure 3.3/2 for the Fe-Ni-Cr system and in Figure 3.3/3 for the Fe-Cr-Al system. The beneficial effects of chromium and aluminium, and of nickel in iron-rich alloys, are clearly visible.

Since a resistivity of about 80 to 100 x 10^{-6} Ωcm is generally considered to be a minimum value for convenient operation, the principal alloys in the Fe-Ni-Cr system are austenitic. Because of this, creep strength is not usually a problem, life being limited chiefly by oxidation-corrosion. Good environmental resistance requires at least 15% chromium, and, except in the case of sulphur-containing atmospheres, performance improves with increasing nickel content. Many of these alloys also contain 1 to 2% silicon and this increases both oxidation resistance and electrical resistivity.

Alloys of the Fe-Cr-Al system, with 20 to 30% chromium and 4 to 6 % aluminium, whose electrical resistivity is high and varies little with temperature, offer exceptional oxidation-corrosion resistance at elevated temperatures, due principally to the formation of a continuous Al_2O_3 surface film. Furthermore, the solidus temperature is in the region of 1500°C, compared with values between 1355 and 1410°C for the austenitic Fe-Ni-Cr grades. However, the ferritic structure leads to mechanical property limitations, namely low creep strength and lack of ductility. Rapid grain-growth, which sets in above 850 to 900°C, leads to embrittlement at temperatures below about 300°C after service in this range.

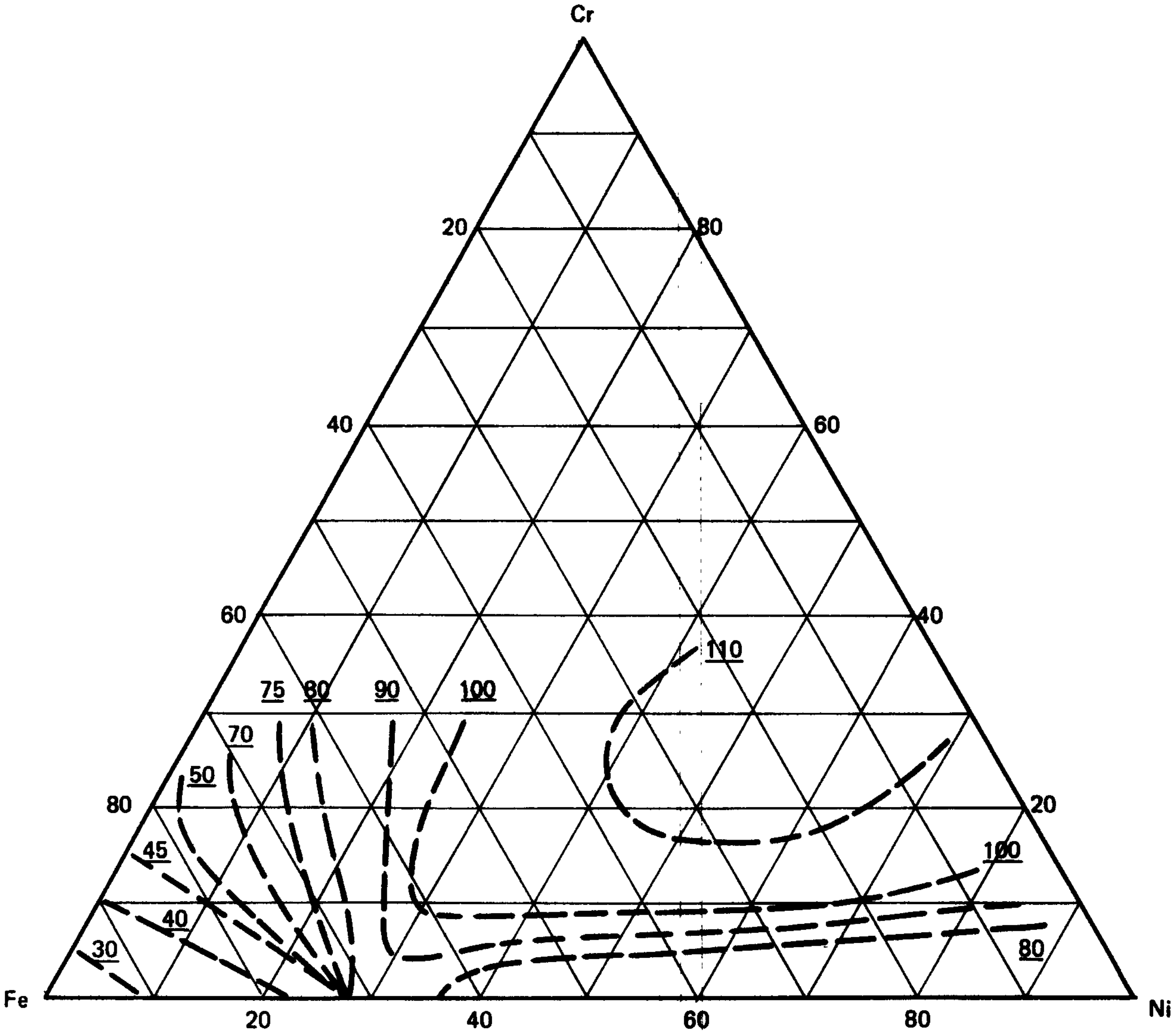

Fig. 3.3/2 Electrical resistivity of Fe-Ni-Cr alloys (μ Ωcm) at 20 °C.

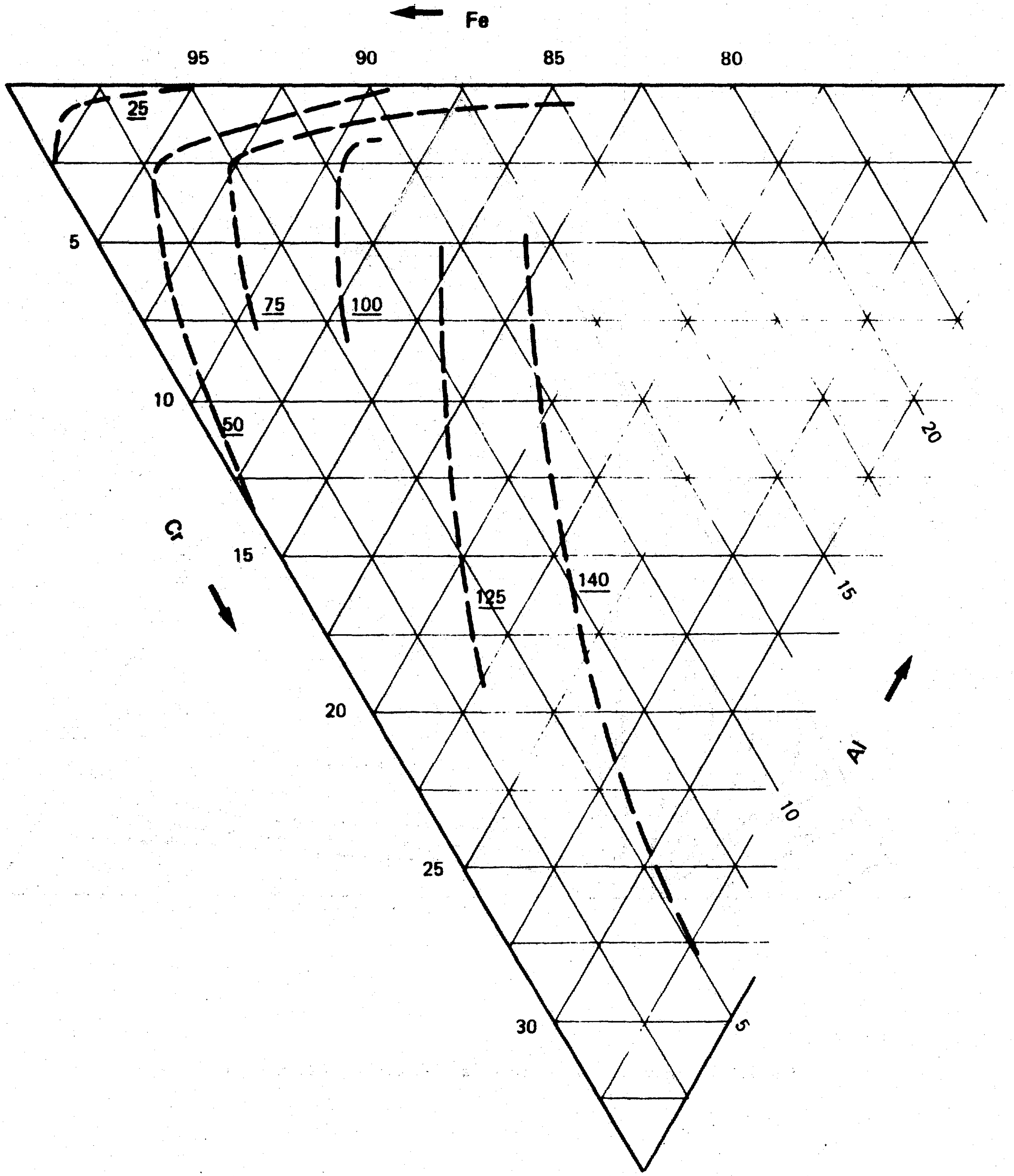

Fig. 3.3/3 Electrical resistivity of Fe-Cr-Al alloys (μ Ω cm) at 20°C

While the lack of ductility makes the Fe-Cr-Al alloys difficult to manufacture and delicate to use, particularly in heavy sections, the most common cause of failure at high temperatures is excessive creep deformation, entailing local thinning or short-circuiting. In spite of these drawbacks the ferritic alloys are widely used since they represent the highest temperature capability of the common metallic materials and because of their relatively low price.

Of the metallic heating element materials suitable for temperatures above 1375°C, namely molybdenum, tantalum, tungsten, platinum, and platinum-rhodium, only the latter two can be employed in an oxidising atmosphere, but because of their high price their use is limited to special small scale applications. This is also true of molybdenum, tantalum and tungsten, whose poor resistances to high temperature oxidation-corrosion require the use of a protective environment. Given either a neutral or a reducing atmosphere or a vacuum, these three materials can perform satisfactorily above 1600°C, molybdenum being preferable to tungsten or tantalum because of its greater ductility.

3.3.2.2 Non-Metallic Materials

Resistance heating can be extended to more extreme conditions by the use of high-melting-point non-metallic materials, such as graphite, silicon carbide, molybdenum disilicide, lanthanum chromite or stabilised zirconia. The maximum temperature capabilities and electrical characteristics are given in Table 3.3/1 and Figure 3.3/1.

The highest temperature capability of all (∿3000°C) is that of graphite, a relatively cheap and readily available material with good mechanical strength, low volatility and adequate electrical resistivity. Unfortunately its low oxidation resistance makes it necessary to provide a protective atmosphere, thus limiting its use to special, generally small scale, furnaces.

Silicon carbide is a semi-conductor which can be used in the form of rod or tube-elements produced by pressure sintering bonded powder and firing at high temperature. The maximum service temperature is 1575°C, although for a life of about a year a value of approximately 1450°C should not be exceeded. Silicon carbide elements can be used in a rough vacuum or in neutral or reducing atmospheres, provided the temperature is not greater than 1300°C. In oxidising atmospheres they are protected by the formation above 1100°C of a continuous film of SiO_2, the latter being used as a bonding agent. Although their thermal shock resistance is good and they are fairly strong in compression and in bending, their tensile strength is relatively low and they are highly sensitive to mechanical shock. Creep becomes important at very high temperatures, for which vertical mounting is preferable. A further disadvantage is the increase in resistance due to ageing, requiring the use of a transformer in order to maintain a constant power supply. This variation, coupled with the increase in resistivity with temperature above 800°C, renders series-mounted elements unstable. Parallel-mounting is therefore preferable, particularly since the good thermal shock resistance of silicon carbide enables an element to be replaced without interrupting furnace operation.

Molybdenum disilicide, $MoSi_2$ is a cermet-type heating element material. The pure compound is too brittle for practical use, so that elements are made by compression, extrusion and sintering a mixture of 90% $MoSi_2$ with 10% of other metallic and ceramic oxides which act as binding agents. Maximum temperature capability is 1700 to 1800°C, but lower values are preferable for a reasonable life ($\sim$1600°C). Like SiC, $MoSi_2$ is protected from oxidation by the formation of a glassy film of SiO_2. When working in non-oxidising atmospheres, this film has to be regenerated by periodic high-temperature exposure to an oxidising environment. Elements are usually mounted vertically because of low creep strength and generally have a single or multiple "U"-shape with both contacts at the same end for easy replacement. While the steep resistivity rise with increase in temperature (Figure 3.1/1) allows rapid furnace warm-up, it also tends to accentuate local overheating. However, the tendency to age is considerably less than for SiC, so that series-mounting of elements can be envisaged.

Lanthanum chromite, $La_2O_3.Cr_2O_3$ is a recently developed oxide semi-conductor heating element material. It is formed from a mixture of chromium and lanthanum oxides with small additions of other oxides, such as Y_2O_3, which act as doping agents and enable the electrical resistivity to be adjusted to the required value. In this way it is possible to produce composite elements with a high resistivity heating section but higher conductivity connection zones. The material shows little tendency to age in oxidising conditions, and this, together with the negative temperature dependence of the resistivity (although this is small above 600°C) leads to high stability in service. The maximum allowable temperature is 1900°C, but for a life of about a year in continuous operation, 1650°C is the approximate value. Because of low creep strength, elements should be mounted vertically for use above 1400°C. Lanthanum chromite elements are particularly suitable for oxidising atmospheres. The maximum allowable temperature decreases with diminishing oxygen partial pressure, due to the rapid rise in low-temperature resistivity caused by the tendency to equilibrate with the atmosphere. Periodic regeneration in more oxidising conditions is then necessary.

Zirconia, ZrO_2, is a refractory oxide semi-conductor whose resistivity becomes sufficiently small at high temperatures to enable it to be used for heating elements. However, pure ZrO_2 suffers a crystallographic transformation accompanied by a large parameter change. This can be overcome by stabilisation with additions of other oxides, such as CaO or Y_2O_3, which have the additional advantage of increasing the electrical conductivity, although it is still necessary to preheat the zirconia elements to about 1200°C for their resistivity to become sufficiently small. Because of this drawback, stabilised zirconia elements are restricted to special small-scale applications where their exceptional high temperature capability in oxidising environments (2200-2300°C) can justify the complex furnace design which is required.

3.3.3 Economic Aspects

Cost is one of the most important considerations determining the choice of a heating element material, and this includes not only the price of the elements themselves, but also the production losses due to furnace down-time. A highly stable electrical resistivity is an advantage from the latter standpoint, since if one element fails it can easily be replaced without the necessity of checking and matching resistances. In addition, series mounting is possible, leading to lower secondary currents. Element life requirement is usually at least 5000 to 10000 hours, although lower figures may be accepted in some extreme cases. Although non-metallic element materials are intrinsically more expensive than their metallic counterparts, this is compensated to a certain extent by their higher surface loading capacities.
Table 3.3/2 gives rough figures for the cost of heating elements per kW of output for a furnace working at a maximum temperature of 1150°C with elements operating at a temperature such as to give a 10000 hour life in air. This is included only as an example, since quite different figures would apply at different temperatures.

Material	Element temperature °C	Furnace temperature °C	Maximum Surface loading W cm^{-2}	Price $ /kW
Ni-20Cr	1200	1150	1	12
Ni-30Cr	1225	1150	1,5	8
Fe-25Cr-5Al	1325	1150	4	4
$Cr_2O_3.La_2O_3$	1650	1150	39 (10)	50
SiC	1450	1150	24 (10)	10
$MoSi_2$	1600	1150	32 (10)	30

Table 3.3/2 Economics of Element Materials for Furnace at 1150 °C.

While the higher theoretically permissible surface loading rates of the non-metallic materials enable the same heat output to be obtained with fewer elements, this can only be achieved at the expense of a less uniform temperature distribution. In addition, except in the case of very thin sections, the stresses arising from the steep thermal gradient between surface and centre become the limiting factor, so that in practice values above ∿10 W.cm^{-2} are not usually recommended and this figure has been used in the price calculation.

Furthermore, non-metallic elements are brittle and difficult to handle, so that metallic materials are generally preferred whenever conditions allow their use. Within the various metallic materials available, cost depends mainly on composition, so that Fe-Ni-Cr alloys are often preferred to straight Ni-Cr grades when operating conditions are not too severe. Although the ferritic Fe-Cr-Al alloys embrittle in service, their ductility is sufficient in the unused state and their high-temperature capability and relatively low cost ensure a wide application.

3.3.4 Future Prospects

Electric furnaces are already extensively used in industry because of their intrinsic advantages of cleanliness, temperature uniformity and ease of installation. However, electricity is not yet the cheapest form of energy. It is therefore reasonable to predict a progressive increase in the popularity of electric heating in the future, due to the rising price of fossil fuels and the relative decrease in the price of electricity, which should follow upon the introduction of other cheaper sources of energy.
The incentive for the development of more reliable, cheaper and more highly performing heating element materials is thus likely to grow.

The Fe-Cr-Al alloys represent the highest inherent temperature capability of the common metallic materials, because of their high melting points (1500°C). This, together with the comparative cheapness of their constituent elements would make them ideal materials if the problems of brittleness and low creep strength could be solved. On the other hand, the performance of the austenitic Ni-Cr and Fe-Ni-Cr alloys is limited mainly by their oxidation-corrosion resistance, so that development work should be oriented in this direction.

Because of their relatively high cost, together with their intrinsic brittleness, non-metallic elements are unlikely to replace their metallic counterparts to any great extent in applications where the latter can be used with a reasonable life expectation, but could take over in cases where fossil-fuel firing is at present employed.

Their field of application will be chiefly limited to very high temperature (> 1200°C) or to situations in which a high heat output is required in a small volume. A wider development would not be possible without a considerable decrease in price.

3.4 METALLURGICAL INDUSTRY

The metallurgical industry uses high-temperature materials in three broad classes of application for which, in general, very different characteristics are required. The first consists of conventional refractories and thermal insulating materials, used predominantly in the melting and refining of metals and alloys; these are excluded from consideration here. The second consists of components for furnaces used in the processing and heat-treatment of metals, and embraces muffles, rollers, rails, belts, baskets, etc. which usually need both high-temperature strength and oxidation-corrosion resistance to a degree depending on the application. Good thermal shock and wear resistance are also often required. The alloys used are generally solid-solution or carbide hardened. They are known as 'heat-resisting' alloys and are capable of supporting lower stresses than the "superalloys", but can usually operate at higher temperatures. Electrical heating elements are dealt with in section 3.3. The third class consists of hot-working tools for a variety of metal forming operations such as forging, pressing, hubbing, piercing, shearing, extruding, etc. The tools are usually required to sustain very high stresses; these stresses are however, imposed only for short periods of time, so that creep resistance is not a main requirement. Nevertheless the creep-resisting superalloys are finding increasing application in this area. It is convenient to deal with the two latter classes separately.

3.4.1 Furnace Components

3.4.1.1 Material Requirements

Oxidation-Corrosion resistance

Good oxidation resistance is obtained by the formation of a stable oxide film, impermeable to ionic diffusion. Most heat-resisting alloys, being based on the Fe-Ni-Cr system, owe their protection to a continuous surface film of Cr_2O_3 or of the spinel nickel chromite. BRASUNAS et al. (1) have reported the effects of composition on oxidation resistance in this system. The optimum behaviour in short time tests is obtained when the chromium content is sufficient for the formation of a continuous Cr_2O_3 layer, but in practice higher chromium levels are preferable, in order to replace losses due to spalling or evaporation in the form of CrO_3 or CrO_2.

Al_2O_3 affords better protection than Cr_2O_3 as far as oxidation is concerned, due to a smaller concentration of ionic defects, GOWARD (2). However, apart from certain superalloys and Fe-Cr-Al heating element materials, little use has been made of Al_2O_3 protection for furnace components.

Oxidation, and particularly spalling resistance, can be markedly improved by minor additions of "active" elements such as the rare-earths, but their use in commercial alloys other than electrical resistance materials is not yet widespread.

Although oxidation is the most common form of attack, corrosion by other species is often at least as important.

Carbon-containing atmospheres, either in the carburising of steel or by fortuitous contamination of furnace atmospheres by hydrocarbons, are particularly important. Nickel, which has little affinity for carbon is generally favourable.
However, the composition Ni-20% Cr is especially vulnerable in strongly carburising conditions, since the ternary eutectic in the Ni-Cr-C system, which melts are 1045°C, occurs at Ni-20% Cr-3.5% C. The liquidus temperature rises along the eutectic valley, reaching 1305°C at 32%Cr-2.2% C (3).
In general, the chromium content should be sufficient to allow for losses from the solid solution due to carbide formation. Hence Ni-Fe-Cr alloys such as Alloy 800 or Alloy 600 are widely used in installations for gas- or pack-carburising of steels. The resistance of alloys to carburisation can be appreciably increased by the inclusion of elements which have greater affinity for carbon than has chromium, e.g. titanium and niobium. Silicon is also a common beneficial addition, particularly against the effects of combined or cycled oxidation/carburisation.

Because of its relatively high solid solubility and the slow kinetics of nitride formation, attack by nitrogen is not normally a problem, but can become more severe when it is present in the nascent state as in the surface nitriding of steels. In this case, as with carbon pickup, a high nickel content is advantageous (MORAN et al. (4)).
Corrosion by other elements which could arise from fuels or other sources is normally guarded against by careful control of the atmosphere and the avoidance of external contamination. Sulphur-containing gases can be extremely deleterious, particularly under reducing conditions. This is due to the exceedingly low solid solubility of sulphur, together with the formation of low-melting-point eutectics (645°C in the Ni-S system, 877°C for Co-S, 988°C for Fe-S). Chromium, which forms a high-melting-point stable sulphide is therefore a favourable element, whereas high nickel contents are detrimental. Sulphidation resistance can be considerably improved by fairly small additions of aluminium, as shown by SCHULTZ et al. (5), and earlier by GRUBER (6) and NAUMANN (7). In extreme cases of very high sulphur-content reducing atmospheres, only the ferritic Fe-Cr or Fe-Cr-Al alloys offer sufficient resistance, although the maximum service temperature is still severely limited and the ductility and creep strength of these materials are poor.

In the case of corrosion by hot salts, of which the most severe are the halides, the main requirement for satisfactory resistance is a high chromium content, as has also been found for the combined attack by sulphur and NaCl, frequently encountered in marine turbines (8,9). The same is true for resistance to vanadium-containing ashes. All these phenomena involve fluxing of the normally protective surface oxide film.

Creep resistance

The mechanical strength required of furnace parts is in general fairly moderate, in many cases being limited to the ability of the component to support its own weight. By far the most commonly used materials are solid-solution or carbide-strengthened austenitic alloys based on the Fe-Ni-Cr system.

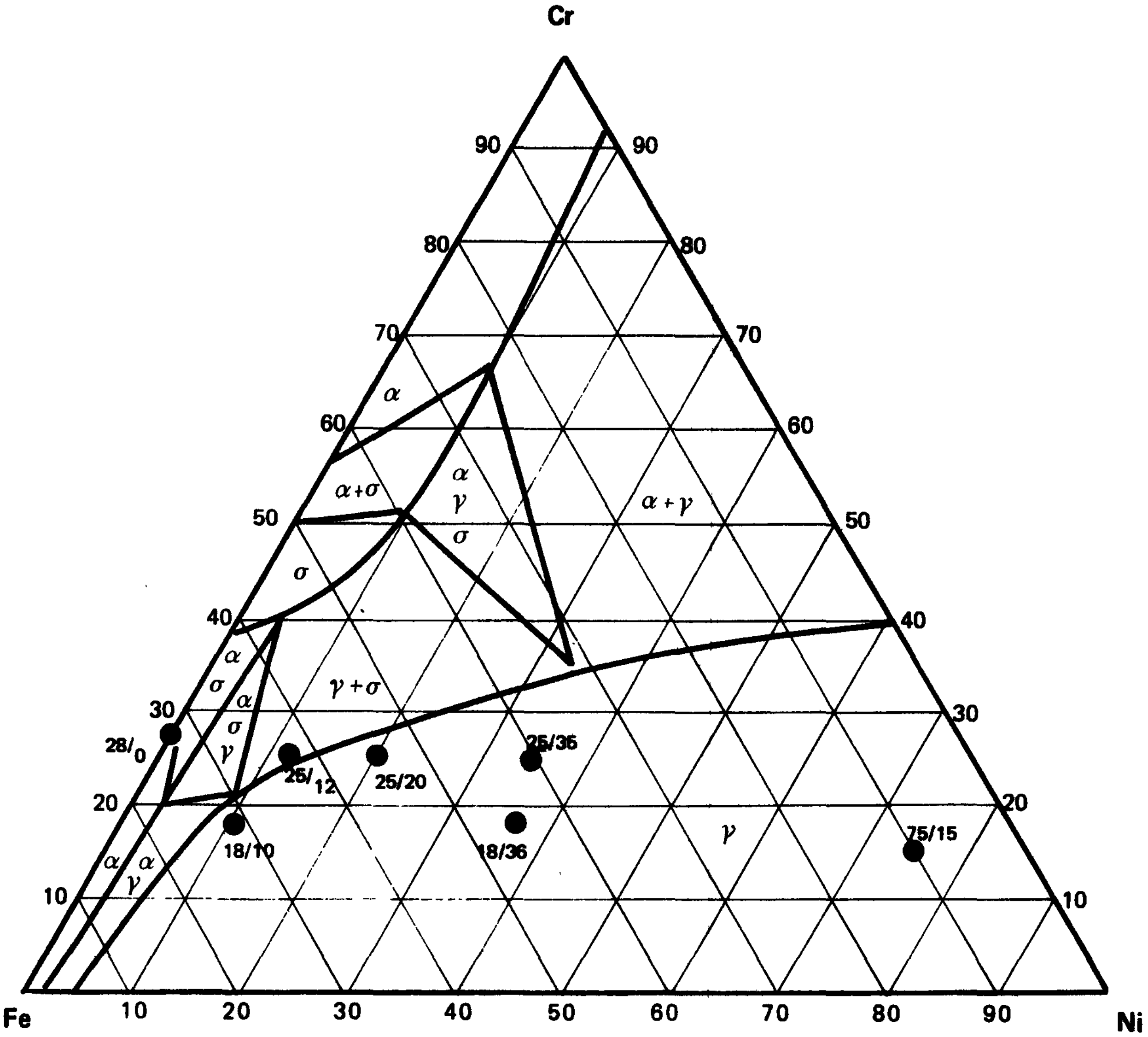

Fig. 3.4/1 *Some common heat-resisting alloy matrices based on the Fe-Ni-Cr system. (650 °C section, Metals Handbook, 1948)*

Figure 3.4/1 shows the location of some of the most commonly used matrices in the Fe-Ni-Cr system. At medium temperatures, low stacking-fault energy (compositions near the austenite phase boundary), is probably important for good creep strength, whereas.high nickel content (low diffusivity) seems to be more important at higher temperatures.

Considerable hardening is obtained by carbon additions and many heat-resisting alloys produced as castings contain about 0.4% C. Solid-solution hardening is often enhanced by alloying with elements such as tungsten, molybdenum and niobium, which also lead to the formation of more stable carbides. Cobalt probably strengthens mainly by lowering the stacking-fault energy. Total additions are limited by sigma phase formation. They can be higher in more nickel-rich matrices, but the price factor is often the major obstacle.

A number of more advanced commercial alloys, whose nominal compositions are included in Appendix Table C, are being used for a few special furnace components. Among these, the cobalt-base superalloy MAR-M-322 represents the upper performance limit of its category. The poor creep resistance of the Ni-50Cr composition, developed for use in conditions of severe vanadium corrosion, has been greatly improved by an addition of 1.5% niobium in the alloy designated IN 657, whose creep strength is comparable to that of a 25% Cr - 20% Ni steel. The UMCo-50 and UMCo-51 grades, the latter of which contains 2% niobium in the Fe-50Co-28Cr matrix, are extremely insensitive to attack by slags and molten salts and have excellent wear and thermal shock resistance. The alloy IN 643 is an alloy developed primarily for the manufacture of cast tubes for the petrochemical industry, and is a good illustration of the problem which faces the alloy designer in this field, namely that of obtaining a maximum combination of creep strength and corrosion resistance while avoiding the formation of embrittling sigma phase.

Thermal fatigue resistance

Many furnace components are subjected to rapid temperature changes or "thermal shocks". The severe temperature gradients introduced in this way give rise to stresses which can lead to rupture, or if repeated, to failure by thermal fatigue. Thermal fatigue resistance depends on a number of factors, see Section 2.2.4, and is therefore difficult to predict and has rarely been the major design criterion in alloy development for high-temperature applications. A high carbon content may be detrimental, particularly when arising from concentration gradients, as can occur in carburising atmospheres: other embrittling phases such as sigma, which reduce ductility without imparting a compensating increase in yield strength, are unfavourable.

3.4.1.2 Future Prospects

The field of furnace components is one in which there has been relatively little innovation in recent years. Unlike process plant, such as in the petrochemical industry, in which the increase in efficiency made possible by higher temperatures provides a strong incentive for alloy development, in heat-treatment furnaces the operating temperatures are clearly defined and there is no major reason why they should tend to rise. The overriding factor in materials selection is therefore the price:service-life ratio, particularly since many furnace components can be replaced relatively easily, involving comparatively small down-times.

In parts whose lives are determined by oxidation/corrosion resistance, small additions of active elements could be used to advantage, either to increase the performance of existing alloys or to enable similar lifetimes to be obtained in less expensive matrix compositions.

In creep-limited applications, on the other hand, improvements are normally only obtainable at considerable cost, by fairly large additions of elements such as tungsten, molybdenum, cobalt, etc. One of the cheapest means of increasing creep strength is to raise the carbon level and this is used in many casting alloys. However, the morphology, distribution and stability of the carbide phases could probably still be improved by an optimum combination of carbide-forming elements together with an appropriate heat-treatment. Minor additions of boron and/or zirconium, widely used in superalloys, could also be examined, particularly with a view to increasing ductility, as this is of prime importance in determining the thermal fatigue resistance.

Finally, in cases where thermal fatigue is paramount, this should be used as a design criterion in order to reach an optimum compromise between physical properties, high-temperature strength and ductility, and resistance to chemical attack.

3.4.2 Hot-Working Tools

3.4.2.1 Service conditions and material requirements

The conditions imposed on tools for the hot-working of metals vary considerably with the nature of the material being dealt with and with the particular operation, but, in general, it may be said that when the metal being processed involves temperatures above about 800°C the merits of special high-temperature materials for the tools are worthy of consideration. The characteristics required in the tool material may be summarised as follows:

1) Higher hardness at the working temperature than the material being worked.
2) Good oxidation resistance.
3) Good high-temperature strength.
4) Good impact strength and freedom from embrittlement during service.
5) Good resistance to thermal shock.
6) Freedom from distortion during heat treatment.
7) Good machining characteristics.

The relative importance of these different properties depends on the particular applications, impact strength being, for example, of prime importance in forging dies, but of much less significance in extrusion dies. Thermal fatigue resistance is of much importance in almost all cases since the contact of hot metal on relatively cool tools produces severe temperature gradients in the tool material. In very few cases, however, can a tool material be selected on the basis of its known properties, and its serviceability for any particular application can only be established by trial.

3.4.2.2 Present situation

The conventional materials for hot-working tools of all types were for many years the high-alloy tool steels containing up to 10% tungsten, chromium and molybdenum, sometimes with additions of nickel or vanadium and with carbon contents in the range 0.2 to 0.4%.
These steels are used in the quenched and tempered condition with room-temperature hardnesses in the range 450-650 HV.

With tempering temperatures between 600 and 650°C it is clear that if the tools exceed this temperature in service they are softened. In recent years nickel-base and cobalt-base high-temperature alloys have been adopted for many hot-working tools, since, although the initial hardness of these materials normally lies in the range 300-400 HV, they are resistant to softening at much higher temperatures than the tool steels. The initial cost of such materials is considerably higher than that of tool steels, but since experience shows that the life of the tool, in terms of the number of parts or quantity of material processed, may be increased by a factor of 10 - 20 or more, the economic advantage can be very great.

Since the relevant characteristics and performance depend so much on the particular application, a number of these are dealt with below:

(a) Press forging tools.

The open-die press forging of high-strength nickel-base alloys is currently carried out using anvils of a nickel-cobalt-chromium base superalloy. The optimum heat treatment is one which does not develop the highest creep resistance, but by ageing directly after forging, retains some cold work, and thus develops increased hardness.
A life 8 - 12 times that of a conventional die steel is obtained.
Thin-webbed steel forgings have been hot pressed using closed dies of a precision-cast nickel-base superalloy pre-heated to 870°C. The heated dies reduce the chilling effect on the workpiece and enable much thinner sections to be formed. Closed-die press forging of steel gear blanks is also carried out using forged and aged nickel-base superalloy dies.

(b) Drop forging tools.

Aluminium-bronze components, drop forged at 900°C, have been produced using nickel-base superalloy dies in the as-forged state. Some precipitation hardening takes place during service and a life some 6 times that of quenched and tempered die-steel tools is obtained.

(c) Extrusion dies.

Dies for the extrusion of copper sections give considerably longer life when made from a nickel-cobalt-chromium superalloy rather than a conventional die steel. Failure is due to thermal shock and hot abrasion, and for the best results the superalloy blanks should be individually forged to give a fine grain size, and only aged after forging to give a hardness above 350 HV. Extrusion of other materials, e.g. austenitic steels, copper-nickel alloys and aluminium bronze also benefits by using superalloy dies, but for brass extrusion the advantage is uncertain since zinc may have a deleterious effect on hot strength.

(d) Hubbing Tools.

In hubbing operations a tool is pressed into a metal blank to produce a shaped cavity. Nickel-chromium superalloys tools have proved most successful for hot hubbing copper at about 800°C, giving lives over 8 times that for a tungsten-steel tool. The cold-rolled and aged condition, giving maximum hardness, is preferred.

(e) Hot shear blades.

In steel mill production it is necessary for blooms and slabs to be trimmed and cut to length for subsequent working, and this is most conveniently accomplished while the metal is still very hot. With large sections (ca. 1400 cm^2) the time taken leads to the shear blades reaching high temperatures. Much improved life can be obtained using nickel or nickel-cobalt base superalloy blades.

(f) Die-casting moulds.

The die casting of metals imposes severe thermal shock on the die material, particularly on cores which are completely enveloped by the molten metal. Nickel-chromium alloys - either simple solid-solution alloys or γ'-hardened superalloys, both wrought and cast - have been succesfully used in die casting aluminium bronze, giving lives 2 to 3 times those for high-speed steel. Lower melting-point alloys, e.g. aluminium and zinc-base alloys are liable to cause intergranular attack of nickel-base alloys and for these metals conventional steel dies are to be preferred.

3.4.2.3 Future prospects

Because of the uncertain and varied technical background of this application it is likely that progress will be made by empirical trial, guided by continued practical experience, rather than by carefully planned research. It is to be expected, however, that the economical advantages of longer life will lead to increased adoption of special high-temperature materials in this field, supplanting high-alloy tool steels. The change will be of greatest advantage with more complex shaped tools involving high machining costs.

3.4.2.4 Research and development

Most materials used in this application have been developed for other purposes, but have been adapted by special processing and heat-treatment procedures. In the light of present experience it is probable that empirical developments will provide considerable further practical advance, but useful guidance could be provided by more fundamental studies of the relationships between short-term mechanical properties (hot hardness, hot yield strength, etc.), microstructure and grain morphology, and thermal fatigue resistance. Studies of hot friction, wear resistance and pressure welding characteristics in the presence of different environments and applied lubricants, would be particularly relevant to extrusion dies.

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3.5 GLASS AND CERAMICS INDUSTRY*

The melting and processing of glass is carried out in the temperature range 600-1200°C, and the sintering of refractories and ceramics at temperatures usually well above 1000°C and, particularly with the newer advanced materials, at very much higher temperatures.

The mass production of both glass and ceramic goods is generally carried out using common refractories as the containment and thermal insulating materials, and with the combustion of fossil fuels as the heat source. The stresses imposed on the structures are moderate, being only those due to the weight of the parts involved. These operations and materials are not dealt with in the present survey. There are, however, a number of operations using special high-temperature materials, usually metals or alloys, and these are noted below:

Glass Melting.

In some locations in large glass-melting furnaces the refractories may be rapidly eroded by the flow of molten glass and to counter this a cladding of thin sheet platinum or platinum-rhodium alloy may be used. Similar problems arise in automatic moulding and blowing processes.
For high-quality optical glass where contamination by refractories or other metallic oxides must be avoided, crucibles of platinum-rhodium are used. In both these applications the rhodium content may be up to 40%, the alloy being chosen to give maximum strength consistent with adequate workability. Stirrers for optical glass may be of molybdenum rod, but must be clad or sheathed with platinum to avoid oxidation. The life of such parts is limited by interdiffusion and by swelling of the coating.

Glass-Fibre Production.

Continuous glass fibre is produced by pulling molten glass through an electric-resistance-heated multi-hole bushing, normally made in platinum-rhodium alloy. Glass-fibre "wool" or "mat" is also made by a process in which molten glass is thrown centrifugally from a spinning rotor with several thousand holes in the outer rim, and blown by steam to quench it. Currently a cast nickel-base super-alloy is used for the rotor but limitations to stress and temperature restrict the process to relatively low-melting-point more expensive glasses.

Ceramics.

The lower temperature stages of ceramic production, particularly glazing, are frequently carried out in electrically heated kilns and for these the requirements for resistance heating elements are dealt with in section 3.3. One aspect of particular importance in the ceramic field is adherence of the oxide scale on the elements, since spalled particles of scale may adhere to the glaze and spoil the ware.
The ware is frequently fed through the kilns on woven-wire conveyor belts which necessarily cycle in temperature from

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*) Short unreviewed outline.

ambient to the full kiln temperature. The conventional materials for these are nickel-chromium or nickel-iron-chromium alloys similar to the electrical resistance alloys. They have a limited life, failing by low-cycle high-temperature fatigue or by stress-rupture, due to the stresses generated in pulling the belt and its load through the kiln.

Future Requirements:

Three areas are apparent in which improved materials would be beneficial:

i. Improvements in bonding and in diffusion barriers for platinum-clad molybdenum stirrers.
ii. Higher strength and temperature capability for the material for glass-fibre spinners, to permit operation at temperatures in the range 1200-1300°C.
iii. Higher strength and temperature capability for the material for woven-wire conveyor belts, to permit long-life operation at temperatures in the range 1100-1200°C.

3.6 GAS TURBINES

3.6.1 Introduction

In discussing high-temperature materials for gas turbines it is necessary to recognise that there are some significant differences between aircraft and industrial/marine applications. Aero engines utilise alloys with the most advanced strength/temperature capabilities, the high-performance short-life military engines representing the extreme case. Industrial/marine turbines can be divided into the aero-derived and heavy-duty types. The former are derated aircraft engines, usually with modified materials and the addition of a power turbine. Heavy-duty machines are purpose-built for industrial or marine applications, and historically have involved lower efficiencies, lower operating temperatures and less advanced materials than aero-derived engines. However, future designs, particularly for electric power generation, are likely to be based on a combination of the features of the two current industrial gas-turbine types.

3.6.2 Material Properties

High-temperature materials are used in gas turbines in four principal areas, i.e. the turbine discs, the turbine rotor blades, the nozzle guide vanes and finally the combustion equipment and ducting which mainly utilise sheet materials. The HP compressor in aero engines, particularly for supersonic transport and military use, may also use high-temperature materials similar to those employed in the later turbine stages.

3.6.2.1 Historical

At an early stage of development of gas turbines high-temperature steels gave way to nickel, cobalt, and nickel-iron base superalloys for critical components, except in turbine discs where steels are still used in many industrial machines. It was found that nickel-base alloys could be strengthened at high temperatures by a combination of solid-solution hardening and precipitation hardening, the γ' precipitate being outstandingly effective and stable. Nickel alloys with progressively increasing strength/temperature capabilities were developed by steadily increasing the volume fractions of γ' precipitate and the level of solid-solution strengthening. Over a thirty year period an increase in capability of about $10^{\circ}C$ per year was maintained. In consequence nickel-base alloys have been used almost exclusively in turbine rotor blading which is the application requiring peak properties. Initially all the alloys were wrought, and indeed to the present day wrought nickel-base alloys are used in many blade applications. However, workability problems limited the advances which could be made in improving the properties of wrought alloys, and it was also recognised that more substantial increases in turbine entry temperatures could be attained by means of blade cooling which is only fully realisable with cast components. Thus the later stages of nickel alloy development have involved cast alloys and these are now widely used in modern aircraft engines and in the latest designs of industrial/marine turbines.

In most applications nickel-base blading alloys are used with protective coating to combat the danger of attack by oxidation (in aircraft gas turbines) or sulphidation (in industrial/ marine gas turbines). The increases in strength in nickel-base alloys have been obtained largely at the expense of the chromium content of the alloys, so that the sulphidation or hot-corrosion resistance of the high-strength alloys is inadequate for industrial/marine applications even with the benefit of a blade coating. This has led to the development of a new series of high-chromium alloys with strength/temperature capabilities equivalent to the earlier aircraft engine alloys but with improved resistance to hot corrosion. Prior to the development of these alloys there were some instances where cobalt-base alloys, which have traditionally had good sulphidation resistance, were specified in rotating blades. However, the new high-chromium nickel-base alloys are now finding wide application in industrial and marine gas turbines.

The cobalt-base superalloys are generally hardened with carbides or solid-solution elements, and cannot match the precipitation-hardened nickel-base alloys in strength. However, carbide and solid-solution strengthening persists to a higher temperature than that obtainable from precipitation hardening, and this, together with the good corrosion resistance and weldability of cobalt-base alloys, has led to their widespread use in nozzle guide vanes. As with rotating blades, vanes have generally changed from wrought to cast materials and the relatively simple compositions of the cobalt-base alloys generally lead to good castability.

Turbine discs of course run at lower temperatures than the blades or vanes, and until recently the demands for improved materials to replace high-temperature steel have been less pressing than with the hotter components. For discs there was also a serious difficulty in developing new alloys which not only had the required very high strength but which also could be forged or otherwise hot worked into large component sizes with uniform properties. However, these problems have now been partly overcome, albeit at considerable expense, and several high-strength nickel-base alloys are now widely used in aircraft gas turbines.

The primary requirements for sheet materials for use in combustion equipment have always been oxidation resistance, fabricability and weldability. Improvements in the design and cooling of such equipment have permitted the continued use of relatively simple solid-solution alloys developed many years ago. Where higher strengths have been required, particularly in aircraft engines, several precipitation-strengthened alloys have been developed which combine a moderate increase in strength with reasonable fabricability.

In parallel with the development of nickel- and cobalt-base alloys for blades and vanes, there has been progress in the development of coatings for surface protection of these components. In aircraft engines the use of high-purity distillate fuel and high operating temperatures, together with the absence of atmospheric contamination, usually leads only to oxidation as a potential problem, and the coatings now available give good protection against this. However, some hot-corrosion problems do occur, particularly with low-flying aircraft, and also the protective coatings can occasionally introduce problems by reducing creep or fatigue strength. Moreover, in industrial and marine engines conditions are such that hot corrosion or sulphidation can readily occur, and although improved coatings have been developed they do not give adequate protection against this form of corrosion, particularly in the very much longer operating lives required for industrial and marine engines compared with aero engines.

3.6.2.2 Present Situation

Advanced air-cooling techniques can hold component metal temperatures as much as 300°C below gas temperatures.

Blades Stress/temperature requirements in rotating blades for aircraft engines can reach 140N/mm^2 at 950°C or 250N/mm^2 at 750°C, with significantly higher stresses in the blade roots which are usually below 750°C. In industrial and marine turbines the operating temperatures are lower and stresses generally do not exceed 120N/mm^2 in the hot part of the blade, being consistent with expected lives of many tens of thousands of hours whereas a few thousand hours can be acceptable in aircraft engines. Degradation can occur by creep, fatigue, or thermal fatigue. Also , in aircraft engines oxidation may occur, particularly if the surface coating is damaged. More significant is the degradation by hot corrosion in industrial and marine gas turbines and this is increasingly proving to be a life-limiting factor. Many other factors must of course be considered in selecting alloys. For example structural stability is most important and theoretical phase composition control is always utilised in alloy development and is followed by long-time testing to confirm that properties do not deteriorate. Density is also important because in rotating machinery specific strength is the important parameter. Also, since gas-turbine components must be made to very close tolerances low expansion coefficients are usually desirable. Amongst the materials commonly used in the leading stages of aero turbines are the cast alloys B1900, IN-100 and MM002. In industrial and marine turbines the older alloys Udimet 500 and 700 and Alloy 713 are currently being replaced by the high-chromium alloy IN-738. In the later turbine stages and in power turbines the wrought alloys in the 'Udimet' and 'Nimonic' series are still widely used. Further examples are shown in Table 3.6/1.

Nozzle Guide Vanes Vanes see higher temperatures than blades (e.g. up to about 1100°C in aircraft engines and 950°C in industrial turbines), but normally are subjected only to gas bending stresses amounting at the most to 30-60 N/mm^2. Degradation can occur through oxidation, thermal fatigue and, in industrial and marine engines, through hot corrosion. In terms of temperature and environment the first row of nozzle guide vanes see the worst conditions in the turbine. The alloys most commonly used are the cobalt-base materials X45, MM509 and FXS414. In some industrial engines where unusually high vane stresses occur, or where uniformity of materials is desired, manufacturers have specified the nickel-base blading alloy IN-738 for vanes. See Table 3.6/1 again.

Turbine Discs Discs may be subjected to temperatures up to about 750°C at their edges and to stresses up to 500N/mm^2 near the centre. High-temperature tensile and fatigue properties are critical. Many industrial and marine turbines still make use of steels such as A286 and Discaloy but in aircraft and more advanced land-based engines nickel-base alloys such as Waspaloy, Astroloy and René 95 are now used as shown in Table 3.6/1. As indicated above these alloys require expensive melting, forging and machining routes in order to achieve uniform and satisfactory properties, and there is a considerable incentive to find other production routes which will be more economic. In small turbines for helicopter or land-based operation integrally-bladed discs are sometimes cast in one piece, and the alloys employed may be either conventional disc alloys or certain blading alloys such as Alloy 713. Outstandingly good castability is essential for this production route.

Sheet Materials Sheet alloys may be subjected to temperatures of 1000-1100°C in aircraft engines but are usually operated at only 800-900°C in industrial and marine engines. Stresses are usually very low, e.g. less than 20N/mm^2. The life-limiting factors are usually thermal fatigue, oxidation or even melting due to local overheating. Industrial and marine engines still utilise the solid-solution alloys Nimonic 75 and Hastelloy X, while aircraft engines make use of the precipitation-hardened alloy C263. Various other alloys listed in Table 3.6/1 are used to a lesser extent.

Data Required Information is normally required on tensile and stress-rupture properties (including notch sensitivity), creep, fatigue (including low-cycle fatigue), thermal fatigue, structure and structural stability, oxidation resistance (both static and dynamic), corrosion resistance, castability, weldability, machinability and expansion coefficient. Fracture mechanics data are now needed for rotor disc materials. In addition the effect of joining and coating treatments on structure must be understood, and heat treatments may need to be re-optimised to permit use of particular joining or coating procedures. The increasingly long life expected with industrial turbines magnifies the difficulties involved in relating laboratory data to service behaviour. Very long-time data on creep properties and stability are now sought by designers; corrosion testing presents an even greater problem because in addition to the long service times envisaged it is impossible to specify accurately the corrosion conditions which materials will meet in all the varying turbine applications and locations.

Gross Material Consumption The production of superalloys for all gas turbines in Western Europe in 1975 is estimated as approximately 5750 tonnes wrought and approximately 1000 tonnes cast, on a mill product basis. This does not take account of a significant quantity of materials and components bought from the United States by European licensees of American turbine-building companies. The ratio of aircraft engine materials utilisation to that in industrial and marine turbines is roughly 3:1. Although there is currently a recession in turbine business it is expected that it will again grow towards the end of the decade, so that by 1985 alloy production will be at least 25% higher than the above figures.

	Rotating blades	Nozzle guide vanes	Turbine discs	Combustion equipment
Aero	B-1900 IN-100 Mar M-002 Inconel X-750 IN-792 Nimonic 115 René 77 René 80	X-45 Mar M-509 FSX-414 M-21 C-130 C-242 C-1023	Incoloy 901 Waspaloy Astroloy René 95 Inconel 718	Nimonic 75 Hastelloy X C263 C242 C1023 Haynes 188 Inconel 617 Inconel 718
Industrial & Marine	Nimonic 105 Alloy 713 Udimet 500 Udimet 700, 710 IN-738 S-816	Crown Max. X-40 X-45 FSX-414 Nimonic 105 IN-738 L-605	A286 FV448 FV 535 Discaloy Alloy 713	N-155 L 605 Nimonic 75 Hastelloy X RA-333

Table 3.6/1 Some typical high-temperature materials used in gas turbines.

3.6.2.3 Future Prospects and Forecasts

a) Short Term (5 years) Turbine blades will continue to be made almost exclusively from nickel-base alloys. These will go through the final stages of development , involving composition and process changes, which may not raise the maximum operating temperature significantly but which will enable greater reliability to be attained. In particular hot isostatic pressing of cast components may become widely used, giving significant improvements in properties, notably fatigue. Directionally-solidified blades (see below) will be specified in advanced military aircraft engines.

Recently developed high-chromium nickel-base alloys (e.g. IN-939) will be adopted for both blades and vanes in industrial and marine turbines. Possibly further alloys of this kind may be developed to permit industrial and marine turbines to be operated closer to the temperatures prevailing in aircraft engines whilst resisting degradation by hot corrosion. Achievement of this objective will be aided by development of improved coatings resistant to hot corrosion (and possibly also by use of corrosion-inhibiting additives to the fuel).

Similarly, in aero-engines vanes are likely to use the most recently developed cobalt-base alloys with improved oxidation resistance. Vanes may also soon be made from sheet alloys (probably nickel-base) in order to take advantage of developments in dispersion strengthening.

Current investment and development work with powder alloys is likely to lead to substantial use of turbine discs made by the powder route. The driving force here is the substantial economic saving which can be made by cutting down material requirements by direct fabrication of finished shapes, and also the improved uniformity of composition and properties which can be attained by the powder route.

A number of sheet alloys already exist with superior oxidation resistance and other properties to the materials generally used in current turbines. The next five years will see full evaluation of these materials (eg. IN-586) and materials currently under development (eg. Nimonic MA956).

b) Medium Term (5 to 20 years) One interesting possibility is that the development of water cooling in gas-turbine components could permit the use of current superalloys for a much longer time than has generally been expected. However, this may only apply to industrial and marine turbines.

In high-efficiency engines blades are likely to be made from directionally-solidified materials and possibly from single crystals, thus eliminating the transverse grain boundaries which are a source of weakness in current components. Further significant advances to meet the complex high-temperature requirements of gas-turbines are unlikely to be made with single metallic alloys. The nickel- and cobalt-base systems are obviously limited by their melting points. Chromium appears to be the next most promising metal base, but the failure to overcome its inherent brittleness makes it difficult to envisage practical use; the other more refractory metals also suffer from serious problems in environmental resistance, brittleness, etc.

It will, therefore, be necessary to develop successful composite systems or to turn to non-metallic materials. Directionally-solidified eutectics are a form of composite receiving much attention. However, the greatest strengths have been achieved with tungsten alloy filaments reinforcing metal matrices, including niobium alloys. There are still difficult problems with thermal fatigue and oxidation resistance, but it is possible that complex composites involving new alloys based on refractory coatings, could become a practical possibility. The main alternative is to use ceramics, which offer high specific strengths at high temperature with potentially adequate environmental resistance, combined with the great advantage of low cost and good availability of raw materials. Their drawback is in ductility and impact resistance, but progress has been made with laminated, crack-inhibiting structures, particularly by moving from simple materials such as silicon nitride to more complex ceramics, e.g. Sialon. In the medium term it is likely that vanes and combustion equipment in some industrial engines will utilise such materials.

c) Long Term (beyond 20 years) In the long term aircraft and industrial/marine gas turbines are likely to need quite different materials, since it is probable that high-purity distillate fuels will be reserved for aircraft use, while other machines will have to operate on relatively low-grade fuels or on gaseous products obtained from coal. Thus, although the demands of aircraft engines may not be very different from now, the industrial/marine type will require materials which will resist severely corrosive or erosive conditions. This might limit, or even cause a reduction in, the operating temperatures of industrial/marine engines.

The above forecasts are summarised in Table 3.6/2

Table 3.6/2 Summary of Future Prospects

Short term (5 years)

Improved nickel-base alloys

- greater sulphidation resistance (for industrial/marine)
- hot isostatic pressing of castings
- directional solidification (military aircraft)
- dispersion-strengthened sheet (military aircraft)
- greater oxidation resistance (sheet)
- disc alloys from powder

Improved cobalt-base alloys

- greater oxidation resistance (cast and sheet alloys)

Medium term

Directional solidification of nickel alloys (general use)
Single-crystal nickel alloys
Directionally-solidified eutectics
Ceramic vanes and sheet alloys (land-based turbines)
? Chromium alloys ?
? Ceramic blades
? Alloys of refractory metals (closed-cycle turbines)
? Fibre/wire reinforced composites involving advanced refractory-metal alloys.

Long term

Nickel/cobalt alloys to resist more severe corrosion/erosion
? Alloys of refractory metals (general use) ?
? Ceramics (general use)
? Metal or metal/ceramic composites (general use)

3.6.3 Lines of Material Research and Development Being Followed

As indicated above much research and developmental effort is being applied to directionally-solidified materials and to single crystals, This work is already leading to superior properties in turbine blades but the problem remains of making the process economically feasible for widespread application particularly in components with internal cooling passages. Work also continues on dispersion strengthening, and on materials combining the virtues of dispersion strengthening with precipitation strengthening. However, such materials are essentially wrought and suffer from the disadvantage of all wrought materials in that it is almost impossible to incorporate the advanced cooling which has been developed with cast alloys. Thus a very great advance in temperature capability is required in the material before a genuine advance can be obtained in the fabricated component. The most fruitful area for dispersion strengthening currently appears to be in sheet alloys. Developmental work on ceramic materials is currently aimed at either large industrial turbines or small turbines for automotive applications where very high temperatures are required in order to achieve the necessary efficiency and economy. Static components such as combustion chambers are being evaluated first. Sample blades have been made in composite materials, particularly directionally-solidified eutectics, but process economics are critical. Development of practical filament-reinforced composites requires satisfactory component alloys with mutual compatibility.

Many conventional and advanced metallic materials are being subjected to evaluation in impure helium, having in mind the possibility of operating closed-cycle gas turbines in connection with the helium-cooled high-temperature reactor. This application may ultimately lead to a demand for a combination of high operating temperature and very long life which is beyond the capability of available metallic materials.

The current activity in powder alloys for turbine disc applications has also been mentioned above, and it should be added that there is much effort being applied to thermo-mechanical processing of such materials in order to achieve improved properties.

3.6.4 Outstanding Basic Problems and Suggestions for Reseach

With conventional superalloys there is a need for

(i) Investigation of superimposed creep and fatigue conditions, and crack-growth rates. Fracture-toughness concepts must be more widely applied to superalloys.

(ii) Improved creep and thermal-fatigue properties in thin wall section for advanced blades.

(iii) Better and more uniform tensile, creep, and low-cycle fatigue properties, combined with more economic manufacturing techniques, in alloys for aircraft-engine turbine discs.

(iv) Improved resistance to hot-corrosion and erosion in alloys for industrial and marine turbines, to be combined with mechanical properties as good or better than those of current materials. (This problem will continue and increase as gas turbines become widely used in association with high-temperature reactors, coal-gasification plant, and other chemical processes, and as the purity of available liquid fuels deteriorates).

(v) Investigation of the interaction of corrosive environments with creep, fatigue, impact properties etc.

(vi) Improved and standardised computational techniques for predicting long-term structural stability. (Currently there are conflicting techniques for sigma phase prediction and virtually no accepted techniques for other phases).

(vii) Further investigation of trace element effects (despite the considerable amount of work already done).

(viii) Improved joining methods both for precipitation-strengthened and for dispersion-strengthened materials.

(ix) Investigation of effects of surface oxide growth on efficiency of advanced metal cooling systems, and development of coating techniques for internal cooling passages.

(x) Development of coatings specifically for protection against hot corrosion (as opposed to existing oxidation-resistant coatings), using techniques compatible with normal heat-treatment of the material.

(xi) Investigation of the effect of coatings on mechanical properties and on the structure of the substrate in long service exposures.

In order to introduce <u>new classes of high-temperature materials</u> there is a need for:

(i) Development of economic techniques for mass production of cooled components using directionally-solidified alloys and eutectics, together with improved transverse properties in such materials.

(ii) Improved oxidation resistance and ductility in alloys of the refractory metals. (Coatings may not provide sufficient protection in long-life applications).

(iii) Broad research on fibre-reinforced materials involving development of component alloys with specific properties and mutual compatibility leading to stable high-performance composites.

(iv) Improved ductility and impact resistance in ceramic materials.

(v) Development of test methods and statistical evaluation of the behaviour of low-ductility materials, to permit prediction of the performance of an assembly of, for example, ceramic components.

(vi) Revised engineering design methods to permit use of low-ductility materials.

It must of course be recognised that solution of the basic problems with refractory metals or ceramics would lead to many more detailed requirements of the kind listed above for conventional alloys.

Note: The compositions of the alloys referred to in this chapter are shown in Appendix Table C.

3.7 HIGH-TEMPERATURE NUCLEAR REACTORS

3.7.1 Introduction

Ever since its original concept in the 1950's the helium-cooled high-temperature reactor has been heavily dependent on materials innovation and development. In the first instance, the whole concept depended on the development and application of a core capable of delivering coolant at temperatures well above those available from other nuclear reactors, and, in the light of the results of much materials testing and the operation of prototype reactors, there is now little doubt that existing alloy specifications are entirely adequate for the introduction of the high-temperature reactor as an economic heat source in large commercial steam-cycle plants for electricity generation.

Even in the early days, however, it was realised that its use in conventional steam-raising with a helium outlet temperature of about 750°C, was but a stepping stone to more efficient and varied applications. Early attention was directed towards the closed-cycle helium turbine (1) and more recently the potential of the HTR as a source of process heat is being vigorously pursued (2 and 3). Study of the system from the viewpoint of these more advanced applications involving core outlet gas temperatures above 750°C shows that although continuing work is needed on the fuel and core materials, considerably more emphasis is needed on the structural materials and components of the primary circuit and of associated process plant to ensure successful development and exploitation.

These two advanced systems are quite different, but largely because of the high operating temperatures and long service lives required, demands on materials have much in common. For this reason it is convenient to examine materials at the same time for both types of plant, particularly in the early stages of evaluation.

At first it was generally considered that the use of high-purity helium would eliminate corrosion problems or at least reduce them to a point where they would not cause embarrassment to designer and operator. However, the possibilities of interaction between the impurities in the coolant and metals and alloys used for the primary circuit were fully appreciated as far back as 1956, and much work has been carried out as part of the Dragon Project Metals programme.

3.7.2 The Helium Gas Turbine

The direct-cycle helium gas turbine has been the subject of many design studies over the last ten years. At a Dragon Project Colloquium in 1965 (4) the basic arguments favouring the direct cycle were stated, and several proposals for HTR gas turbines (HTR-GT) were discussed. In 1966 Bohm (5) presented a design for a prototype 22 MW(e) system with helium entering the turbine at 675°C, and suggested that his basic scheme was suitable for power plant in the 1000 MW(e) range. Later, Hosegood et al. (6) reported studies on the direct cycle HTR, giving their detailed design for a 980 MW(e) power station with a helium temperature of 967°C. This report has been followed by studies by GEC Gas Turbines Ltd. in the UK (7), by General Atomic Company in the USA (8, 9, 10) and by the HHT project in Germany (11). These designs proposed turbine inlet temperatures in the range 800-850°C and the main details of each design are shown in Table 3.7/1.

It is likely that an early direct-cycle HTR would operate at lower temperatures than those suggested by Hosegood et al. and attention is now directed to the development of systems with turbine inlet temperatures of 900-950°C.

	DRAGON (1970)	GEC (1972)	HHT and GA (1975)
Thermal Output (MW)	2208		3000
Electrical Output (MW)	980		1070
Overall Efficiency (%)	44.4	41	36
No of Turbine Loops	4*	4	3
Orientation of Turbomachinery	Vertical	Vertical	Horizontal
Rating of each generator (MW)	500	300	370
H.P. Turbine Inlet Temperature (°C)	967	827	816-850
H.P. Turbine Outlet/ Recuperator Inlet Temperature (°C)	549	502	548
H.P. Turbine Outlet/ L.P. Turbine Inlet Temperature (°C)	762	657	
H.P. Turbine Inlet Pressure (bar)	59	49	60-70
H.P. Turbine Outlet/ L.P. Turbine Inlet Pressure (bar)	37	30	
L.P. Turbine Outlet/ Recuperator Inlet Pressure (bar)	20	18	31

* 2 double flow units

Table 3.7/1 Main Design Features of Commercial HTR-GT Proposals (Dry Cooled)

3.7.3 The HTR as a source of Process Heat

Apart from safety aspects, the main problem with nuclear process heat is essentially one of scale. The output of a 3000 MW nuclear reactor is ten times greater than the maximum power requirement of the largest ammonia plant in the U.S.A. The other factor that would make it difficult to supply heat directly to the chemical process industry is the time that a nuclear reactor is out of service. Nuclear reactors are reliable compared with conventional power stations, but even an outage rate of 20% can lead to unacceptable cost increases for most chemical processes.

These problems of scale and availability are by-passed if the nuclear heat is used to produce a secondary fuel. Of several possible process-heat applications for the HTR, three have received considerable attention:

a) production of hydrogen by reforming reactions between water and hydrocarbons, particularly methane;
b) Steam- or hydro-gasification of coal;
c) production of hydrogen by thermal decomposition of water.

These processes were discussed recently in a series of papers presented at conferences in Paris (12), London (6) and Jülich (13). Publications by Kugeler et al. (31, 32, 33) have also reviewed the problems arising in the design of such plants.

a) Methane Reforming and Steel-Making

The use of nuclear heat in the steel industry was studied by Hosegood et al. (14) and a later paper by Finniston (15) discussed in broader terms the integration of nuclear power into a large steel works.

In the schemes envisaged the nuclear reactor provides heat for the steam reforming of methane (natural gas) to produce a reducing gas mixture:

$$CH_4 + H_2O \dashrightarrow 3H_2 + CO$$

This mixture may subsequently be transformed by a water shift reaction:

$$3H_2 + CO + H_2O \dashrightarrow 4H_2 + CO_2$$

to produce pure hydrogen. The reactor heats the steam and methane needed for reforming and may also be used to reheat the product gas. The hot gas is passed into a shaft furnace while small pellets of ore are fed through in the other direction. The gas reduces the ore to sponge iron which is a suitable feed for electric arc furnace melting. These processes require temperatures of about 800°C both for reforming and for reheating the product gas. The heat available at lower temperatures would be used to generate electricity for the electric arc furnaces.

In conventional direct reduction processes, the heat for producing the reducing gas is normally provided by combustion of natural gas or naphtha, and Finniston notes that in nuclear steel making approximately half of the total hydrocarbon requirements are replaced by nuclear heat.

In 1973 the European Nuclear Steelmaking Club (ENSEC) was formed (16) to define a strategy for the application of nuclear energy to steelmaking. The Club has three working parties studying:

(i) possible process routes and their energy requirements;
(ii) the production of reducing gases using nuclear energy;
(iii) the temperature and environmental limitations of materials for heat exchangers in nuclear steemaking plants.

b) Coal Gasification

A number of countries have large reserves of both hard coal and lignite, and are faced with the increasing cost and dwindling supply of crude oil and natural gas. It is not surprising, therefore, that there is considerable interest in using these coal reserves more effectively. An indication of this can be seen in the programme on nuclear process heat for coal gasification that is being established by the German Federal Government, industry and KFA Jülich (17, 18). Conventional routes for coal gasification use 30 to 40% of the calorific value of the coal to convert the coal to gas. If this is replaced by nuclear heat, readily available resources of coal will last longer and the price of gas will be less dependent on the cost of coal. Atmospheric pollution should also be greatly reduced.

Three systems for gasification plants linked to HTR's have been described. Two are discussed principally as means of converting lignite to methane (18, 19); the other system is basically for water-gas production from hard coal (20, 21).

The first system relies on the steam reforming of methane. Application of an HTR is therefore essentially as described above, requiring temperatures in the region of 800°C. The hydrogen produced reacts with lignite to give a mixture of CH_4, H_2, CO, H_2S and CO_2. After cleaning and separating, the net product is methane, some of which is fed back to the reformer.

In the second system a mixture of H_2, CO and H_2O is preheated to about 900°C by an HTR and then reacted with lignite to give a mixture largely consisting of methane as above. This method is simpler and more direct than the first, but has the major disadvantage that a higher temperature is needed.

The third system is even more direct. Steam and pulverised coal are fed into a fluidised bed which is heated by a secondary helium loop of the HTR. Juentgen et al. (20) described an industrial gas generator, and alloys for the heat exchanger are currently being tested in a small coal/steam fluidised bed at atmospheric pressure (22, 23). The product of such a system would be a mixture essentially of hydrogen and carbon monoxide and in that form could be used for heat generation or reduction processes. Alternatively, it could be converted to hydrogen, town gas, methanol (for motor car fuel) or synthetic "natural gas".

As with the direct-cycle helium turbine, the efficiency of process-heat installations increases rapidly with temperature. The minimum temperature for steam reforming methane is about 800°C, but significantly higher temperatures are needed for the direct gasification of coal. These temperatures are similar to those required by the most recent proposals for direct-cycle gas turbines (Table 3.7/1), but the need for an intermediate heat exchanger would increase temperatures in the primary circuit to well above 850°C. On the other hand, the absence of moving parts exposed to high temperatures in process-heat systems means that many components need not normally be highly stressed at operating temperatures.

3.7.4 Environmental Conditions in HTR Systems

Material behaviour in HTR systems will be a strong function of the working environment, which may be divided into three regions:

i) the primary circuit;
ii) the intermediate circuit;
iii) the process gas.

In essence i) and ii) are very-high-purity helium and although its nuclear and "working fluid" properties are unaffected by the traces of impurities present, they dominate and control its chemical properties.

In addition to residual air and other contaminants on reactor start-up, these impurities may originate from in-leakage of air and water from the atmosphere, cooling circuits or process streams; from out-gassing of insulating materials and graphite; and from reduction of metal oxides. Hydrogen may diffuse in from waterside corrosion of boiler tubes, or from process streams. Oil vapour may arise from lubricated bearings or diaphragms and will pyrolyse in the core to give hydrogen and methane. Maintenance and refuelling operations will introduce further impurities to the circuits. In the primary circuit these impurities react with the hot graphite to produce an atmosphere in which hydrogen and carbon monoxide are the predominant impurities, but with a significant level of methane. The operational efficiency of the continuous purification plant must be considered for each chemical species, in order to estimate the equilibrium levels of impurities.

The basic thermodynamic and kinetic data were surveyed by Everett, Kinsey and Rombert (24) as early as 1965 and a simple mathematical treatment for the dominant primary circuit chemical reactions was evolved. Later information on a realistic experimental basis has been derived from operation of the prototype reactors and from impurity injection experiments which have been summarised by Keep (25).

Graphite corrosion has been reviewed by Ashworth (26) and thermodynamic equilibria have been calculated by Hales (27), Pearce (28) and Kofstad (29). These show that for metals the oxidation potential of the gas can be related to the P_{H_2}/P_{H_2O} and P_{CO}/P_{CO_2} ratios and that the carburisation potential can be related to the $P_{CH_4}/P^2_{H_2}$ and P^2_{CO}/P_{CO_2} ratios.

It is important to note that oxidation potentials are not pressure dependant whilst carburisation potentials are.

The evidence gained from experimental prototype reactors has enabled realistic estimates to be made of the impurity levels to be expected in the primary circuits of a range of HTR power reactor designs, and the essential factors are given in Table 3.7/2. The subjective aspect of these estimates and their dependance on engineering design features has to be taken into account until more experience is directly available from power reactors. In general it can be said that the chemical ratios can be forecast with much more certainty than the absolute levels.

In process heat systems, the process gas picks-up its heat either from the reactor primary circuit directly or through an intermediate circuit. Generally speaking, process temperatures might be expected not to exceed those experienced in normal industrial conditions. However, the main issues from the materials viewpoint revolve around the lifetime, which may have to be much longer than might be acceptable in more conventional plant due to the high cost of outage time in the nuclear system. Aspects of requirements from the process-gas side are similar to those referred to in section 3.2.

			Steam Generating Reactor			**Process Heat Reactor**	
			Normal	**H_2O Leak**	**HTGR-GT Direct cycle**	**No Intermediate Circuit**	**With Intermediate Circuit**
H_2		μatm	200	500	200	200 - 1000	100
H_2O		μatm	1.5	15	0.5	1 - 5	0.5
CO		μatm	40	300	20	20 - 100	20
CO_2		μatm	1-2	1 5	1	1 - 2	1
CH_4		μatm	20	25	20	20 - 30	15
M_2		μatm	5-10	5-10	5 10	5 - 10	5 10
Oxidation Ratios	$\frac{P_{H_2}}{P_{H_2O}}$		130	33	400	200	200
	$\frac{P_{CO}}{P_{CO_2}}$		20 - 40	60 - 300	20	20 - 50	20
Carburising Ratios	$\frac{P^2_{CO}}{P_{CO_2}}$	atm	0.8 1.6 x 10^{-3}	9 x 10^{-2} 1.8 x 10^{-2}	4 x 10^{-4}	4 x 10^{-4} 5 x 10^{-4}	4 x 10^{-4}
	$\frac{P_{CH_4}}{P^2_{H_2}}$	atm^{-1}	5 x 10^2	10^2	5 x 10^2	5 x 10^2 - 30	1.5 x 10^3

Table 3.7/2 Suggested Helium Impurity Levels and Chemical Ratios in Primary Circuits of Power Reactors.

3.7.5 Operating Temperatures and Stresses

A proper assessment of the requirements for materials from the viewpoint of temperatures and stresses requires close cooperation between designers and materials experts. The extended lifetime requirement in a high-capital-cost situation, stretches the ingenuity of the engineer and technologist to the full, and high emphasis is placed on fault conditions which may cause plant outage. In these circumstances it is not possible to give precise operating values for the various high-temperature components.

As a very general guide to the range of conditions which might occur in gas turbine and process heat systems, Table 3.7/3 is presented. It must be emphasised, however, that in quoting these values a correspondence between the operating stress or pressure and the temperature is not necessarily implied. For example, turbine components may be cooled and in the case of hot gas ducting, designs can be adopted which could separate the functions of withstanding high temperatures and high pressures.

System	Component	Temperature (°C)	Stress (N/mm²) or Pressure Difference (bar)
HTR-GT	Turbine blades	805-970	140 N/mm²
		(Root) 700 min	420 N/mm²
	„ discs	535 min	
	„ nozzles	805-970	
	„ ducts and casings	805-970	
	Core outlet duct	805-970	~ 60 bar
	Core inlet duct	~ 500	~ 60 bar
	Recuperator	~ 525	~ 30 bar
Process heat with intermediate heat exchanger	Core outlet duct	900-1000	40 - 80 bar
	Intermediate heat exchanger	900-1000	0 - 40 bar
	Duct to process	850 - 950	40 - 80 bar
	Reformer/ secondary heat exchanger	800 - 950	0 - 40 bar

Table 3.7/3 Major Elevated Temperature Components of Advanced HTR-GT and Process-Heat Installations.

3.7.6 Materials Requirements.

Apart from the usual aspects of corrosion, stress and fabricability, materials for nuclear installations require the consideration of additional factors. For the HTR a particular material must be assessed in terms of:

a) Corrosion by the impure helium coolant and its effects on properties;

b) Accessibility of components and the consequent service life; and
c) The requirement not to release into the coolant species which would become highly radioactive during passage through the core.

An important factor is the one of the reliability and the access to circuit components for maintenance. Components such as ducts, intermediate heat exchangers, rotating machinery, should be designed for service lives much longer than those required in conventional plant, i.e. 100,000 to 300,000 hours.

Requirements c) means giving special attention to the behaviour of certain alloying elements. Cobalt and tantalum are commonly added to high-temperature alloys or may be present as impurities; cobalt in particular gives good solid-solution strengthening in nickel-base and iron-nickel alloys. Unfortunately, they both become intensely radioactive in the core of a nuclear reactor. If oxide particles containing these elements were carried through the reactor by the gas stream, then pockets of highly radioactive dust could accumulate. Thus it is inadvisable to use alloys containing cobalt or tantalum in the primary circuit. If they were used, their oxidation and spalling characteristics would have to be thoroughly understood and protective coatings of other materials might be needed.

3.7.7 Surface Reactions of HTR helium with metals and alloys

Thermodynamic data for a number of elements commonly present in high-temperature alloys show that the oxidation potential associated with atmospheres of the type given in Table 3.7/2 results in metals such as manganese, chromium, silicon, aluminium and titanium being oxidised whilst iron, nickel, cobalt, copper,etc. are reduced. In practice, niobium, tungsten and molybdenum are not found in the oxides due probably to a combination of the low oxygen potential (of the order of 10^{-25} atm) and their low concentration in solid solution in the alloys in the presence of excess carbon. It is noteworthy that the volatile MoO_3 oxide is never formed at the oxygen potential prevailing in the coolant gas. The stable oxidation product is MoO_2, an oxide resembling ZrO_2 in structure.

With the exception of the plain-carbon and chromium-free low-alloy steels all alloys likely to be found in the primary circuit of an HTR contain elements that are selectively oxidised by the coolant. Although the total concentration of impurities may be less than 1.0 vpm, this is sufficient to react with the metal and affect significantly the behaviour of certain alloys.

When a material such as an austenitic stainless steel or a nickel-base high-temperature alloy is exposed to HTR helium at a temperature in excess of 350°C its oxidisable components react to form a film. This film or scale is characterised by the absence of elements such as iron and nickel; it consists almost entirely of Cr_2O_3- with traces of titanium, manganese and silicon when these are present in the alloy. it is noteworthy that aluminium, although oxidised below the surface, is not usually present in the surface film. Unfortunately these films are less protective than those formed in air: they become porous and in some cases are able to spall. Furthermore the rate of film growth is controlled not only by diffusion of chromium (and other oxidisable species) through the film but also by the rate at which chromium can diffuse through the underlying metal to the metal/oxide interface. If the rate of reaction at this interface is greater than the rate at which the chromium is replenished, a stage will be reached when the activity of the chromium will fall below that required for oxidation: oxygen will then be free to enter the metal and to react internally. It is important to appreciate that, at this stage, the surface reactions are characteristic of a chromium-free alloy. Internal oxidation is a diffusion-controlled phenomenon, the depth of attack being dependent on the diffusion of oxygen into the metal, which in turn is dependant on the concentration of oxidising species in the coolant gas.

Although oxide film formation and internal oxidation both play a vital role in the behaviour of all conventional high-temperature alloys, in the HTR carburisation is a more important factor. With many hundreds of tons of graphite in the core of a reactor, and with oxygen- and hydrogen-containing impurities in the helium coolant, carbon can be transported and incorporated into the alloy by two basic mechanisms, one involving methane, the other carbon monoxide and water. The latter is probably the most effective.

Whatever the thermodynamics of the reactions, experience in operating reactors and in laboratory facilities demonstrates that selective internal oxidation and carburisation occur simultaneously, the extent depending on the composition and concentration of the impurities, alloy composition and on temperature.

A wide selection of metals and alloys has been studied as part of the Dragon Project Metals programme; in addition to their creep properties a major effort has been directed to a study of microstructural changes, particularly those adjacent to the surface. It has been possible to correlate the creep behaviour - particularly any differences in creep rate observed between tests in air and in HTR helium - with the microstructure. With this information assessment of the effects of each alloying element on the load bearing capacity of the alloy as been possible (30).

The alloys studied have mainly been based on the iron-nickel-chromium and nickel-chromium systems, ranging from normal stainless steels to precipitation-hardened nickel-base super-alloys. The reactions of all these alloys with HTR helium are governed by the same principles and it is possible, therefore, to discuss the behaviour of the individual elements in a general manner although the significance of each reaction may depend on other elements present.

Fe, Ni and Co - these elements are noble to both oxygen and carbon in HTR helium and hence can be considered stable.

Cr - this element is unstable to both oxygen and carbon. A surface film of Cr_2O_3 is formed, followed by internal oxidation and a chromium-impoverished zone. Immediately below this, chromium carbides are formed either inter- or intra-granularly, and these may affect the mechanical properties of the alloy, particularly impact strength.

Al, Ti, Si, Mn - these elements are all oxidised in HTR helium, forming surface or internal oxides. The surface films are not protective and internal oxides may be deleterious to strength. Although titanium and aluminium are essential for precipitation-hardening alloys, they may not be satisfactory for long-term strengthening.

Mo, W, Nb - important solid-solution strengtheners, and niobium also aids precipitation hardening - all are favourable for HTR service.

Zr, Hf, B - minor constituents affecting grain-boundary properties and high-temperature ductility. No direct evidence of effects in HTR helium.

Molybdenum and its alloys are worthy of special mention since they are unaffected by the HTR helium environment. There is no possibility of producing the volatile MoO_3 oxide at the oxygen potentials prevailing in the primary circuit, and since recrystallisation and diffusion of the alloying elements (usually zirconium and/or titanium) is negligible below about 1000°C, the alloys are entirely stable. Provided difficulties of fabrication can be overcome economically, there is little doubt that molybdenum alloys will play a major role in the development of advanced HTRs.

3.7.8 Selection of Materials

As far as choice of alloy specification is concerned the objective must be to achieve metallurgical stability under operating conditions. Whereas it is possible to design and build an initial steam-cycle HTR using metals and alloys presently in commercial use and having formal specifications and codes of practice, there is little doubt that, for applications involving continued operation at temperatures much in excess of 750°C, prevailing industrial alloys do not offer adequate integrity. A major effort will be required to specify alloys for service at 850°C, particularly where high pressure, and therefore high stresses, are concerned.

In considering the choice of materials for the NPH application, there are some fundamental differences of design philosophy between the nuclear and the chemical industries. These are primarily associated with radiation, fission products and induced activity, the effects of which dominate maintenance. For example, the standards of reliability presently accepted for a conventional methane-reforming plant are totally unacceptable for a nuclear plant, as the cost of maintenance would be prohibitive. Furthermore, since significant contamination of the reactor primary circuit by process gases, or of the process gases by fission products ,is again unacceptable, the designer and metallurgist are faced with a major problem.

Although the work carried out to date indicates relatively small effects on the creep characteristics of the conventional high-temperature alloys (not exceeding about 20% in effective strength) significant structural changes have been observed as a result of corrosion which would be expected to influence surface-related failures. Particular attention must be paid to fatigue as it is predictable that the surface reactions observed on the majority of existing alloys would stimulate crack initiation. This applies to both conventional (high frequency) and low-cycle fatigue. Furthermore the absence of stable oxide films directs attentions to problems of friction, fretting and wear. In this respect the importance of carrying out tests in the appropriate environment needs no emphasis.

The use of alloys inherently noble to the environment has many attractions. Molybdenum alloys and nickel-molybdenum based alloys are two examples which may well prove ideal for certain components. However, self-welding with such alloys is a certainty at temperatures above 750°C and provision for this would have to be made in the design. Furthermore, such alloys are unlikely to act as barriers to hydrogen diffusion, a point of particular importance for any process-heat application.

The possible contamination of the primary circuit by hydrogen resulting in excessive methane formation is one of the major metallurgical problems to be faced. Oxide films (particularly alumina and silica films) have an inherent ability to resist hydrogen diffusion and it would seem that the formation and preservation of such films on all metallic surfaces of an intermediate circuit might provide a satisfactory solution. If the normal spinel formed on iron-nickel-chromium alloys was ineffective, it might be necessary to consider the use of duplex tubing.

By using an iron-chromium-nickel or nickel-chromium base, with appropriate quantities of tungsten, molybdenum and niobium as solid-solution strengtheners, alloys having adequate properties for the introduction of the process heat HTR should become available within a reasonable period.

3.7.9 Conclusions

In conclusion the present positions of the three main fields of application of the HTR are summarised:

a) Steam cycle

Since there is no necessity for any metallic components to operate at high stress in excess of 600°C and at low stress much above 700°C it would seem that no problem associated with creep phenomena would be expected, provided the knowledge presently available is taken into consideration in the choice of material specifications and design alternatives. Further information on high- and low-cycle fatigue, friction and fretting is required to overcome problems of "acoustic noise" and thermal-stress cycling. However effects can be reduced to a minimum by using appropriate materials and designs, it is unlikely that any major materials problems will limit the successful introduction of the steam-cycle HTR.

b) Direct-cycle gas turbine

Here it is primarily a question of temperatures and stresses. At present alloys can be produced that should operate satisfactorily at temperatures in the 800-850°C range, depending on the stress required. Whilst creep is not expected to be a serious problem, surface-related failures, i.e. high- and low-cycle fatigue, friction and fretting require further investigation. Prevailing alloys may need modification since most high-strength nickel alloys contain significant quantities of cobalt and tantalum.

c) Process heat

The minimum temperatures required in this application are such that significant alloy development will be necessary before its feasibility can be assured. At the present time it would be unwise to assume that any metallic materials are available capable of utilising gas outlet temperatures in excess of 900°C. Corrosion problems which would arise on the process-gas side have not been considered in this section.

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3.8 FUSION REACTORS

3.8.1 Introduction

Though many plasma-physics problems still need to be solved, controlled thermonuclear-fusion research, started in the early fifties, has reached the stage of conceptual design studies of fusion-reactor power plants. The fusion concepts mostly considered in these design studies are the tokamak, mirror and theta-pinch concepts with an electromagnetic confinement scheme, and the inertially-confined laser-pellet concepts. An important difference between these concepts is their mode of operation, being steady-state in the mirror, and pulsed in the case of the theta-pinch and laser-pellet concepts. Excellent review papers, describing current conceptual design, were recently published by Steiner (1) and Ribe (2). Table 3.8/1, stemming from Steiner (1) summarizes some of the working conditions of currently envisaged conceptual designs.

	Mirror	**Theta-Pinch**	**Laser-Pellet**	**Tokamak**
First Wall Material	Stainless Steel	Al_2O_3 + Niobium	Lithium-Wetted Niobium	Stainless Steel
First Wall Thickness (mm)	1	0.3 + 1	10	4
Neutron Wall Loading (MW/m^2)	1.6	2	2.6	1.25
Timescale for Energy Deposition	Continuous	80 x 10^{-3} seconds	10^{-7} - 10^{-11} seconds	Continuous
Energy Deposition:	watts/cm^2	J/cm^2.pulse	J/cm^2.pulse	watts/cm^2
i. Neutron-induced	0.9	6.6 + 20.7	7.0	5.2
ii. Plasma-radiation	5.0	43 + 29	2.8	22.0
iii. Particle fluxes	100.0	Negligible	60.6	1.0

Table 3.8/1

Because of its high reaction rate at relatively low temperatures the deuterium-tritium-lithium (D-T-Li) fuel cycle is considered to be the most feasible for the first generation of controlled thermonuclear reactors (CTR). Deuterium and tritium are the reactants, whereas lithium is required for tritium generation. The energy extracted from a fusion reactor appears as heat, generated by neutrons, plasma radiation and charged particles in the first wall and blanket structures, and would be recovered by a thermal-energy conversion system. In some concepts direct energy conversion of the charged particles to electrical energy is a possibility. The timescale for peaceful application of fusion energy is marked by experiments that, nowadays, are beginning to enter the scientific-feasibility phase. The subsequent experimental-reactor phase will be followed by a demonstration-reactor phase. In the U.S.A. it is believed that fusion power, under either pessimistic or optimistic conditions, can be demonstrated in the time range of 1990 to 2014 (3).

High-temperature materials are first of all required as constructional materials for the first wall or vacuum envelope of the plasma and for its supporting and cooling structures. Other applications are in non-structural components, insulating materials being an important example. Another area of application is in liners, limiters and diverters, reducing the ion impact on the first wall, and in spectral shifters and energy converters meant to reduce first wall erosion and to soften the neutron spectrum.

Metals and alloys currently considered for application as structural and non-structural materials in fusion reactors are nickel-base alloys; austenitic stainless steels; the refractory metals niobium, vanadium and molybdenum and some refractory metal-base alloys; SAP, silicon carbide and graphite (4). Candidate insulators are some metal oxides such as Al_2O_3 and BeO, as well as nitrides.

The properties required for the successful application of high-temperature materials in fusion reactors depend on the fusion-reactor concept, although most of the problems are, at least to some degree, common to all of them.

3.8.2 Operational Conditions

3.8.2.1 Materials Environment

The radiation environment in a CTR consists of neutrons, electrons, ions and neutral particles, all except the neutrons being stopped at the first wall surface. The neutron energy spectrum at the first wall of a CTR is significantly harder than that in the core of fission reactors as a result of the 14.1 MeV neutrons generated in the D-T reaction (1). The higher energy of the neutrons causes both the cascade size and the number of displacements per atom to be considerably larger in the first wall of the fusion reactor as compared to fission reactors. Non-elastic collisions were reported to dominate the damage production under 14 MeV bombardment (5). Time averaged fast-neutron fluxes at the first wall are typically $\sim 3.10^{14}$ n/cm^2.s at a wall loading of 1 MW/m^2. In reality wall loadings as encountered in current conceptual designs are in the range ~ 1 MW/m^2 to $\sim$ 10 MW/m^2). Instantaneous neutron fluxes are expected to be much higher in some cases because of the pulsed nature of many concepts (see Table 3.8/1), resulting in instantaneous defect production rates that are several orders of magnitude higher than in fission reactors. The average defect production rate in CTR's at 1 MW/m^2 is $\sim$ 10 dpa/yr, being relatively insensitive to the choice of the first wall material and being comparable to the defect production rate in fast fission reactors.

The harder spectrum in CTR's causes high transmutation reaction rates (6). Helium and hydrogen production rates depend strongly on the type of material irradiated but are generally one to two orders of magnitude higher at 1 MW/m^2 wall loadings than in fast fission reactors. The generation of non-gaseous transmutation products in materials exposed to the high-energy neutron environment will not be negligible either and may result in quite important changes (7).
The first wall will also be exposed to a flux of mainly deuterium, tritium and helium ions and atoms escaping from the plasma. Total particle fluxes expected are of the order 10^{13}-10^{14} particles/cm^2.s having an energy spectrum ranging up to 3.5 MeV but with the majority of the particles having an energy well below 20 keV (7). In view of the energies involved particles will be stopped at the first wall after having reached maximum penetration depths of some micrometres. Whereas the inner surface of the first wall faces a vacuum, its outside surface and the cooling and supporting structures are in contact with a cooling medium (1), causing compatibility problems. In current conceptual designs the coolant is liquid lithium, a lithium-containing fluoride salt or helium gas.

3.8.2.2 Temperatures and Stresses

Temperatures and stresses in the first wall and other structural parts depend on such factors as wall loading, design, cooling pressure, etc., and are characterized by a non-uniformity in space and time.
Due to the pulsed nature of the energy deposition (see Table 3.8/1) in several conceptual designs, large temperature transients will occur. In the theta-pinch concept, for example, transients of 300°C are expected (2).
Maximum operating temperatures in current conceptual designs using stainless steel are in the range 500-600°C. Designs in which refractory-metal-based alloys are considered are planned to operate at temperatures near 1000°C. Stresses arise as a result of coolant and/or breeding material pressure, temperature differentials, self-weight, etc. The exact stress levels depend on the design and are estimated (4) to be in the range 10-100 N/mm^2. Of more concern is the inhomogeneous stress distribution in space and in time resulting from the neutron flux and temperature gradients, and their cyclic nature. Stress cycling, resulting in a fatigue-creep interaction in the structural materials, is considered to be one of the most difficult problems to be dealt with in CTR design.

3.8.3 Materials problems

The phenomena associated with radiation effects on materials are considered to be the limiting factor in the lifetime of a material in a CTR environment. The following sections are therefore primarily concerned with radiation effects in the bulk and on the surfaces of material components exposed to radiation.

3.8.3.1 Dimensional changes

Radiation-induced swelling stems from the accumulation of vacancies into voids and of gas atoms into bubbles respectively. Void swelling, recently reviewed by Norris (8,9) and Eyre (10), occurs after a dose threshold has been reached in the temperature range ~ 0.20 to ~ 0.55 T_m (T_m = melting temperature in K) with a maximum around 0.45 T_m. Void swelling is strongly influenced by external parameters (temperature, dose, dose rate) and internal material variables (presence of interstitial and substitutional impurities and of alloying elements, metallurgical state). A key irradiation/material parameter influencing void swelling is the (n,α) reaction rate. Of the material parameters, coldwork has been shown to be a particularly important variable. Void swelling may increase up to large values (swelling values of 30% have been reported (11))before saturation effects may set in. Such figures demonstrate the technological importance of void swelling, causing distortions in components subjected to inhomogeneously distributed neutron fluxes and temperatures.

Swelling as a result of gas-atom coalescence is primarily caused by helium, introduced into the lattice as a result of (n,α) transmutation reactions and of radioactive decay of tritium diffused into the lattice from the environment.

Helium-bubble formation during helium bombardment has been observed at temperatures as low as room temperature (12). Thermal release of helium atoms out of structural candidate materials for CTR's may start at rather low temperatures (about 700K has been reported for niobium (13)). The amount of swelling due to helium gas bubbles is believed to be within the 1-10% range for the helium gas concentrations generated in CTR high-temperature components (14).

3.8.3.2 Mechanical Properties

The mode of deformation in the CTR components operating at high temperatures will be creep with superimposed fatigue due to the cyclic nature of the stresses. At low temperatures, in the range 0.3 - 0.5 T_m, irradiation creep dominates over thermal creep. It is believed to be due to the irradiation defect-assisted climb of dislocations over glide obstacles (15). Radiation creep has been studied on a rather limited scale in the context of fast-breeder reactor programmes on some austenitic steels, nickel alloys and graphite. Almost no data exist for other candidate materials such as the b.c.c. metals and their alloys (16). At temperatures >0.5 T_m thermal creep takes over as the dominant process. Crack nucleation will generally be accelerated by neutron irradiation whereas the crack propagation rate could be affected both positively and negatively depending on the testing temperatures (17, 18). Virtually no information exists regarding the effect of superimposed creep-fatigue stress combinations on materials in the irradiated condition.

It is important to note that data obtained from fast-breeder reactor programmes may not be applicable to CTR's, having higher neutron energies as well as higher helium and hydrogen

gas-generation rates.
Loss of ductility is considered to be a serious problem in CTR's (4). At temperatures above ∿0,5 T_m the major cause of embrittlement is the production and aggregation of helium into bubbles at grain boundaries, leading to enhancement of intergranular fracture. Indications are that f.c.c. iron- and nickel-base alloys are very sensitive to helium embrittlement (19) whereas with b.c.c. metals and alloys this appears to be less so (20). Virtually no experimental information is available concerning hydrogen embrittlement of CTR candidate materials at high temperatures. Hydrogen and its isotopes, resulting from nuclear transmutation reactions and present in the blanket as well, may seriously affect the mechanical properties of structural materials at low temperatures. Metals forming stable hydrides have been observed to be severely embrittled near room temperature (21). The situation with regard to embrittlement of non-hydride-forming systems is less clear.
The ductile - brittle transition temperature of b.c.c. metals has also been observed to be raised to above room temperature as a result of even modest neutron doses (4). The DBTT is of importance because brittle failure may be iniatiated upon lowering of the component temperature during normal cycles or for maintenance.

3.8.3.3 Surface Effects

Problems associated with surface radiation effects are likely to be limited to the first wall. Plasma particle and neutron irradiation lead to sputtering and blistering, resulting in erosion of the radiation exposed surfaces. Wall erosion is considered an important problem in CTR's, not only from the viewpoint of structural stability but also because of plasma contamination effects.

The sputtering yield is determined by the bombarding particle parameters (energy, mass, angle of incidence) and by the target parameters (material, target temperature, surface conditions) (22). The sputtering yields for fast neutrons on CTR candidate materials have been an area of controversy, but the situation has been considerably clarified recently (23). Experiments and calculations point to neutron sputtering yields of the order of 10^{-3} - 10^{-6} atoms ejected per incident neutron for sputtering of single atoms; upper limits for sputtering yields due to chunk emission under 14 MeV neutron bombardment are around 10^{-3} atoms/neutron. Chemical sputtering can be an important mechanism of wall erosion in non-metallic materials (24). Blistering occurs as a result of coalescence of gas particles originating from the plasma, penetrating the surface and forming stable bubbles in near surface layers of the first wall, even at room temperature.
The blister size, shape and density depend on a large number of incident particle and target parameters (25). At sufficiently high temperatures, bombarding energies and gas pressures the blister skin ruptures, leading to wall erosion by flaking. Indications do however exist that under CTR conditions blistering may be completely avoided (26).

Since the experimental evidence related to sputtering and blistering under CTR conditions is limited, and the fluxes of plasma particles are uncertain, wall-erosion rates are difficult to estimate.

3.8.3.4 Corrosion Effects

Corrosion of surfaces may occur as a result of exposure to the cooling media proposed for current conceptual designs. Helium, being an inert gas, is not corrosive but the "corrosive" character of a helium coolant is due to impurities continuously introduced into the cooling medium from outside sources. Numerous experimental data concerning liquid-metal and liquid-salt corrosion have been obtained in fast-breeder reactor research programmes. Because of aggravating factors such as MHD effects (possibly leading to galvanic corrosion) and neutron-induced transmutation reactions in the coolant (possibly influencing corrosion reaction kinetics and the nature of reacting species at the container surfaces) (27) these data may not be directly applicable to CTR conditions. The theoretical understanding of corrosion phenomena under CTR conditions is inadequately developed and extensive testing is required to define liquid-metal, molten-salt and helium corrosion under the operating conditions and radiation environment of fusion reactors. Except for the case of nickel-based alloys, however, corrosion is not believed to be the limiting factor in the temperature of operation of CTR's.

3.8.3.5 Physical Properties

Physical properties of prime importance in CTR applications are thermal and electrical conductivity, thermal expansion coefficient and elastic constants.
For metals the changes in physical properties upon neutron irradiation will generally be much smaller than those of the mechanical properties, especially in the temperature range where most of the displacement damage anneals out.
Ceramic materials, including insulators, may undergo quite large changes in thermal and electrical conductivities upon irradiation, the extent of the change being generally smaller the higher the irradiation temperature (see e.g. 28, 29).

An area of considerable interest is the solubilities and diffusivities of gases like hydrogen, helium and their isotopes in CTR candidate materials with "technical" compositions and structures. The knowledge of these properties, especially in the presence of radiation fields, is very restricted.

3.8.4 Problem areas and Research Trends

From the previous sections it appears that main research areas being explored at present in relation to the technological application of high-temperature materials in CTR's are dimensional stability, mechanical property changes and surface erosion.
Due to the non-existence of a CTR test facility the fusion reactor environment has to be simulated to study the problems. Simulation tests are performed using fission reactors and

particle accelerators. For the near future intense 14 MeV neutron sources are proposed which will match more closely the irradiation environment typical for CTR's. Such sources will also have the advantage of generating uniform damage in small bulk specimens, enabling a wider range of more realistic experiments to be carried out than by using charged particle bombardment. However, due to the limited volume available for experiments and to the limited fluxes obtainable, such 14 MeV neutron generators will have to be used in a very selective manner (30).

For these reasons simulation with fission neutrons and charged particles will remain an important means for pre-selection of CTR candidate materials. Charged-particle irradiations have the advantage of being characterized by the possibility of achieving high damage rates. Charged-particle irradiations have proved successful in simulating the plasma particle-surface interaction conditions expected in fusion reactors. The situation with regard to bulk radiation damage simulation is more complicated, due to the inherently different interactions of charged particles with matter as compared to high-energy neutrons (different recoil energy spectra and spatial distribution of damage, rate effects, etc.). Charged-particle bombardment has been used rather successfully for studying swelling phenomena in the context of fast-breeder reactor programmes. Close simulation of CTR conditions by particle bombardment is more difficult mainly due to the high gas-generation rates, higher neutron-recoil energies and cyclic character of the neutron fluxes in the CTR's. The correlation of charged-particle damage with neutron damage on both the theoretical and experimental levels represents an important research activity when such simulation studies are to provide a realistic means for anticipating fusion neutron-damage effects.
There is, however, a trend to devise more sophisticated experimental facilities in order to cope with some of these difficulties. For example, experimental arrangements have recently been devised allowing simultaneous ion-radiation damage and helium-ion injection in dual accelerator facilities in order to study synergistic effects of helium on void swelling (31). Other examples are radiation creep testing in proton beams (32, 33) and surface blistering studies by helium using broad energy and angular distribution spectra matching more closely CTR conditions (29).
Up to now there is a clear lack of studies simulating changes in mechanical properties by charged-particle irradiations.

In relation to the previously mentioned high-temperature materials problems a better understanding, experimentally as well as theoretically, should be developed concerning:

(i) the changes in mechanical properties caused by radiation simulating CTR conditions, of structural and other CTR candidate materials such as insulators, with particular emphasis on creep, stress rupture, fatigue life, creep-fatigue interaction and ductility. The influence of helium and hydrogen on these properties is of special importance.

(ii) the dimensional stability of materials.

The mechanisms responsible for nucleation and growth of voids and dislocation loops, as well as the void-growth saturation mechanisms, deserve more attention. Given the extreme sensitivity of void swelling to target parameters, studies on model f.c.c. and b.c.c. alloy system specimens having well-characterized chemical composition and micro-structural states are indispensable. The influence of hydrogen and helium and the influence exerted by stress fields is of particular importance.

(iii) the interactions between plasma particles and neutrons with surfaces of well-characterized specimens. These interactions should be studied from the point of view of wall erosion and surface structure, as well as from the point of view of radiation enhancement of surface rate processes (diffusion, chemical reactions, precipitation, etc.) which may alter the mechanical properties of the wall.

(iv) gas trapping, gas solubility and diffusivity in CTR candidate materials as well as the charge state, energy and angular distributions of back-scattered particles which are of prime importance to the particle balance of the plasma.

A detailed list of recommendations concerning these research topics has recently been issued by the American Physical Society Study Group on physics problems relating to energy technologies (34).

As a final consideration, the importance of chemically and microstructurally well-characterized samples for this kind of research must be stressed. A meaningful comparison of results obtained by different research groups using similar or different simulation techniques is only possible when standardized samples are used. Perhaps an international organisation such as Euratom could undertake the task of supplying standardized specimens.

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3.9 MAGNETOHYDRODYNAMIC ENERGY CONVERTORS

3.9.1 Outline of Process

3.9.1.1 Physical Principle

Electrical power generation by magneto-hydrodynamic (MHD) or magneto-gasdynamic (MGD) convertors consists in driving a conducting fluid at high speed through a perpendicular magnetic field, generating a direct current. The combination of this principle with classical thermal processes has a potential gain of energy conversion efficiency of about 45% to 60%. The power generated by MHD is:

$$P \propto V^2 B^2 \sigma$$

where σ is the specific conductivity of the fluid, V is its speed and B is the magnetic field. σ is high for fluids at high temperature but, in general, is not sufficient for MHD. It is necessary to add potassium and caesium, both with a low ionization potential. As caesium is costly, potassium is preferred, either as KOH, K_2SO_4 or K_2CO_3. To increase the magnetic field B, the solution lies in the use of superconducting materials. In a gas with 1 mole % of potassium salts, the gas speed reaches 1000 to 1500 ms^{-1}.

3.9.1.2 The Technical Systems

The MHD and MGD processes are classified into three systems depending on the fluids used (Table 3.9/1). The open gas cycle operation uses energy from coal, oil or natural gas. To make the gas conductive potassium or caesium is added. The temperature is high and the fluid is rich in oxygen. The closed gas cycle uses an inert gas such as helium or argon, heated in a nuclear reactor, and the temperature is not as high as before. The liquid-metal cycle uses liquid metals instead of gases; because the electrical conductivity of metals is high, this system does not need a high speed of fluid or a high magnetic field.

System	Fluid	T, °C	
		Max.	Min.
Open cycle	Combusted coal, oil or natural gas	2400	1800
Closed cycle	He, Ar heated by nuclear reactor	1700	800
	Fused metals (Na, Hg, NaK)	900	700

Table 3.9/1 M.H.D. and M.G.D. Processes.

3.9.2 Operational Conditions and the Material Requirements

Material problems at high temperatures exist for the structure of the combustion chamber of the MHD channel and of the heat exchanger, but the main problem is related to the life time of the electrodes.

At present the system's gas temperatures are operating at about 2500°C. For the cold-channel operation the temperature of the cooled metal wall reaches 500°C. For the semi-hot operating system the wall temperature rises to 1800°C and its material requirements will be discussed in some detail.

In general the wall material must have the following properties:

high melting point and low vapour pressure,
high resistance to abrasion resulting from the plasma jet,
high resistance to corrosion due to the insemination agents,
high oxidation resistance at high temperature,
high thermal-shock resistance.

For the electrode material also some specific requirements have to be met:

high electrical conductivity, together with a high electronic transfer even at low temperature,
high thermionic emission at high temperature.

For the structural material of the insulating walls the requirement is:

low electrical conductivity.

A single material, which satisfies all these requirements does not exist, thus a quite difficult choice has to be made.

3.9.3 Discussion and Assessment of the candidate materials

3.9.3.1 Insulating Materials

The candidate materials are magnesia (MgO), thoria (ThO_2), beryllia (BeO), yttria (Y_2O_3), magnesia-alumina spinel ($MgAl_2O_4$) and zirconates. However, all oxides become conductive at high temperatures. This temperature dependence requires, that the temperature of the walls should not exceed 1500°C, at which temperature the electrical resistance is between 10 and 10^3 Ω cm.

Among the oxides thoria, ThO_2 ($T_m = 3200^\circ$) has the highest melting point, high refractoriness, good corrosion resistance and good insulation properties. However, it is a radioactive material of high cost, and its application does not seem possible.

Magnesia, MgO, is still stable at 2300°C. resulting in a very good insulating material, and is often used in MHD conversion. The performance of magnesia depends on its purity, more than 2% of Fe_2O_3, CaO or SiO_2 not being aceptable. Forsterite (2 $MgO.SiO_2$), montincellite ($CaO.MgO.SiO_2$) or magnesia ferrites ($MgO.Fe_2O_3$) are formed in the grain boundaries and these materials have poor corrosion resistance to alkalies. A good result is obtained by using blocks of electrically-fused magnesia. The deterioration of the insulating properties of electrically-fused magnesia due to the penetration of seed materials is considerably less than for other materials, since the magnesia block is very dense and has no open pores. The blocks are tailored in such a way that the <110> direction of the periclase is parallel to the direction of the plasma flux. Volatility is the weakness of magnesia, and it is difficult to use above 1500°C, since it reacts with ZrO_2 or ZrB_2 electrodes.

Alumina, Al_2O_3 (T_m = 2040°C) is a very refractory material. Attractive properties are: good mechanical strength corrosion resistance,thermal and chemical stability, and high electrical resistance. Unfortunately, alumina reacts with potassium ions to give aluminates (βAl_2O_3), which are ionic superconductors; thus this oxide is more useful for a cold wall. However. a possibility is to arrange a magnesia wall upstream of the alumina one,allowing magnesia to volatilize and form a surface layer of spinel on the alumina with good resistance to potassium ions.

Beryllia, BeO (T_m = 2600°C) has a thermal conductivity similar to that of metals. Its electrical resistivity is high and it has a high resistance to thermal shock. The problem of beryllia is its toxicity, thus confining this material to the cold system.

Strontium zirconate, $SrZrO_3$ (T_m = 2740°C) is a good electrical insulator, but compounds with good properties are only found in a narrow range near to the stoichiometric composition. Other possible zirconates are those of calcium, $CaZrO_3$ (T_m = 2340°C), barium,$BaZrO_3$ (T_m = 2700°C), or silicon,$SiZrO_4$ (T_m = 2420°C).

For wall construction corrosion due to potassium must be prevented. The use of dense materials could be a solution, but such materials suffer brittle fracture. Therefore, the hot insulating walls may be built from metallic elements separated from each other by refractory ceramic layers. Cooling will be required for the insulating material. The inner temperature of the walls is 1650°C to 1700°C, and to conduct the heat to the water-cooled surface, the thickness of ceramic material has to be adjusted for appropriate heat flow, for example as in Table 3.9/2.

Test Plant	Thermal Flux $W.cm^{-2}$	Thickness of ceramic mm
Laboratory, 200 kW	6 - 7	35
Pilot facility, 8 MW	50	6 - 7
Power station, 500 MW	400	0.8 - 0.9

Table 3.9/2

The wall structure described offers a possible solution and the maximum size depends on the temperature of the front face. Lamellae of magnesia or strontium zirconate joined by cement may be used, with stainless steel to prevent migration of the potassium compound and to assure heat removal. The cooling of walls may cause not only a large heat loss but also many other undesirable phenomena, such as the generation of arc spots, which may cause serious damage to electrodes, or a drop of potential of the electrodes which reduces the effective power. It may therefore be necessary to keep the temperature of the channel walls as high as possible.

3.9.3.2 Electrodes

The following three material groups were selected as candidate materials for electrodes: alloys, refractory metalloids and oxides.

Alloys have very good mechanical strength but very poor oxidation resistance. Alloys belonging to the Ni-Cr system seem to be good but cannot be used at high temperatures. Some additions (Ta, Mo, Al_2O_3) improve the operating temperature but such electrodes are not satisfactory at high enough temperatures.

Some carbides have been tested e.g. ZrC and SiC. Silicon carbide has been tested in the Soviet Union at 1500°C at a gas velocity of 500 m s^{-1}. It behaved well for 50 hours but has far to go to reach 10,000 hours. Oxidation has been tested on several borides and hafnium and zirconium borides are promising at 1350°C. Their oxide films have a high melting point and considerably high conductivity at high temperature. Nevertheless the oxidation rate becomes high above 1150°C with the activation energy changing from 35 kcal/mol to 60 kcal/mol. 10% $MoSi_2$ or CrB added to zirconium boride improves the oxidation resistance.

It is important to obtain information on the processes at the electrode surface in order to develop materials for practical use. Preliminary tests show that if the lower electrode surface temperature is below 500°C, then no electric current is observed up to an applied potential of 200 volts between the electrodes. At higher operating temperatures the current increases rapidly. For example, cobalt or niobium carbide give 15 to 20 A cm^{-2}. For stable operation employing pure zirconium boride, it is necessary to keep the temperature of the electrode surface above 1200°C.

Among oxide ceramics zirconia (T_m = 2700°C) seems possible but this material has a crystallographic transformation with some dimensional change (4). If oxides such as MO or M_2O_3 are added some oxygen vacancies appear and the cubic structure can be stabilized even at a low temperature: it is then called stabilized zirconia.
The best stabilizers are Y_2O_3:

$$Zr^{4+}_{1-x}Ca^{2+}_{x}\ O^{2}_{2-x}\ \square_{x}$$

$$Zr^{4+}_{1-2x}\,Y^{3+}_{2x}\,O^{2}_{2-x}\,\boxed{}_{x}$$

Stabilized zirconia has good chemical inertness, low vapour pressure (10^{-6} bar at 1700°C), a dissociation pressure of 10^{-12} bar at 1700°C and very good electrical conductivity above 1100°C. A problem with this material is its ionic conductivity. The assembly of current collector, electrode and plasma forms an electrochemical cell with the ionic material as electrolyte. At the anode there is an oxidation reaction and at the cathode a reduction reaction. At the cathode, the ceramic-to-metal contact becomes poorer in oxygen; many vacancies appear, the zirconia becomes black and friable and the electrode is destroyed. The behavior of this electrode can be improved with a flow of oxygen or carbon dioxide near the electrode. Attempts have been made to make electronically conducting zirconia with additions of 30% ceria. The couple Ce^{4+}/Ce^{3+} is the reason of this electronic contribution (70%). Studies have also been made with other rare-earth oxides. Another problem with zirconia is the low electrical conductivity below 1000°C. Many solutions have been sought; some with cermets such as zirconia-Inconel, and some using platinum, which is expensive. It is possible to insert wires into the ceramic, but the technology is not easy. Thus zirconia has two main disadvantages: ionic conductivity and low electrical conductivity below 1000°C.

Lanthanum chromate, $LaCrO_3$ (T_m = 2490°C) is a new material with very good electrical conductivity, which is electronic even at low temperature. As $LaCrO_3$ has poor corrosion resistance to K_2SO_4, some composite materials have been tested. Some excellent materials are:

$69\%ZrO_2 - 12\%CeO_2 - 19\%CaO$	70 weight-%
$(La_{0,95}Ca_{0,05})CrO_3$	30 weight-%
B_2O_3	1%

It is recognized that B_2O_3 not only functions effectively as a sintering accelerator but remarkably improves the electrical conductivity.

Lanthanum chromate has poor corrosion resistance. Penetration of potassium into the electrode and loss of lanthanum and chromium from the ceramic are observed with both electrodes, but the former is more noticeable at the cathode and the latter more severe at the anode.

Spinel electrode modules are possible. The electrical conductivity of $FeAl_2O_3$-Fe_3O_4 solid solution is totally electronic. With 30 mol percent Fe_3O_4 the conductivity at 1600°C is 1 mho cm^{-1} and has no temperature dependence. Some coal slags containing Fe_2O_3/Al_2O_3 are also valuable.

3.9.4 Future prospects and research opportunities

The MHD hot-channel operation has not yet reached 1000 h (table 3.9/3), but the research has given some spin-off for other applications. The high conductivity of zirconia and lanthanum chromate is useful for heating elements for furnaces in oxidizing atmospheres; the ionic conductivity of zirconia is useful for oxygen gauges, or water electrolysis.

Electrode Material	Life hours
Metals	10
Intermetallic	100
Oxides	1000
Requirement	10 000

Table 3.9/3 Approximate Lives of MHD Electrodes.

Three types of problem must be solved in the future: the first is the corrosion by potassium ions; the second the development of new structures with high resistance to thermal shock; and the third, the improvement of the service life of materials.

a) Short term: corrosion

The discovery of a new technique for obtaining information on the first atomic layer of a solid would offer important prospects. It would permit the examination of the penetration of potassium, and lead to an understanding of the influence of adsorption on the surface energy, of the transition between the first atomic layer and the next, and of electronic and ionic transfers, which are responsible for corrosion.

b) Medium term; microstructure

The relation between the structure of ceramicsand their properties is not well understood. The main characteristics of the microstructure are the spectra of spatial distribution of crystalline defects, the porosity, the phases present, and the chemical segregation. It is well known that control of the microstructure can lead to improvement of properties by a factor of 1 to 100. The microstructure depends mainly on the history of the material, so that it is convenient to analyse carefully the mechanism of the microstructure evolution, homogeneity of the powder, thermodynamic stability and crystalline growth.

c) Long term: long lifetime

The fabrication methods of ceramics must be revised, after the different steps are better understood. Classical methods must be given up in favour of methods permitting better control of the very reactive materials. Research in the space field may help to find new solutions and new materials with better performance. Protective coatings will be improved to give a solution of the corrosion problem. These studies on materials depend on progress in interfacial science and fibre-matrix chemical interaction.

3.10 PRODUCTION OF HYDROGEN BY WATER DECOMPOSITION

3.10.1 Background and present situation

The main uses, in Europe and all over the world, of hydrogen today are in the chemical industry and in oil refining. It has to be considered principally as a chemical feedstock and it is generally produced from fossil fuel sources.
Table 3.10/1 gives, in million tonnes, the hydrogen consumption worldwide in the year 1970; these figures are not very recent, but the percentages of the various processes have not changed significantly.

Process	**W. Europe**	**%**	**N. America**	**%**	**Other W. World**	**%**	**Eastern Countries**	**%**	**Total World**	**%**
Chemicals:										
Ammonia	2.2	56	2.6	37	1.7	58	2.9	78	9.4	54
Methanol	0.4	11	0.5	7	0.3	10	0.2	5	1.4	8
Other Chemicals	0.2	5	0.6	9	0.2	7	0.1	3	1.1	6
Refinery :										
Desulphurisation	0.5	14	1.6	23	0.5	17	0.2	6	2.8	16
Hydrocracking	0.06	2	1.3	18	0.04	1	0.03	1	1.5	9
Excess Hydrogen as fuel	0.3	8	0.2	3	0.02	7	0.2	5	0.9	5
Miscellaneous	0.06	2	0.2	3	0.04	1	0.03	1	0.3	2
Total	3.7		7.0		3.0		3.7		17.4	

Source: Shell International

Table 3.10/1 Hydrogen Consumption Worldwide 1970 - Million Tonnes.

Table 3.10/2 gives a more detailed analysis of hydrogen consumption in the countries of the European Community in the year 1973; in the table the figures refer to hydrogen consumed in primary uses and the hydrogen content of the end products. The figures for Western Europe can be considered very similar to those reported here.
Concerning the production of hydrogen, the feedstocks used in Europe are reported in Table 3.10/3; the partition of the different raw materials varies from area to area; those areas close to natural gas supplies tend to operate more on natural gas. The present situation of hydrogen production processes will probably change in the future, due to the variations in the overall structure of the energy market. Hydrocarbons are increasing in cost and, even if the estimates may be changed. a decline in reserves is considered certain. There is the opinion that coal will again increase in importance; nuclear energy will also have an increasing role.

		Proportion of Hydrogen Consumed in									
		Primary Uses %					End Uses %				
Country	**Total Hydrogen Consumption '000 tonnes**	**Ammonia** %	**Methanol** %	**Other Chemical** %	**Miscellaneous** %	**Refinery** %	**Fertiliser** %	**Plastics** %	**Textiles** %	**Miscellaneous** %	**Refinery** %
United Kingdom	540	48	13	8	2	29	49	6	6	10	29
W. Germany	860	50	17	13	2	18	44	14	13	10	18
France	660	62	5	6	2	25	56	6	3	10	25
Netherlands	600	73	3	5	2	17	67	4	2	10	17
Belgium & Lux.	180	66	1	9	2	22	65	3	2	10	22
Italy	535	56	7	3	2	32	48	6	4	10	32
Denmark	15	23	-	-	2	75	23	-	-	2	75
Ireland	12	58	-	-	2	40	58	-	-	2	40
Total EEC	3,402	59	9	7	2	23	55	8	4	10	23

Source: Consult-Eur.

Table 3.10/2 Hydrogen Consumption by Countries in the EEC 1973.

Feedstock	**Overall** %	**Ammonia Synthesis** %
Natural gas	60	71
Naphta	26	26
Heavy fuel oil	5	
Coke/coal	9	3
Electrolytic	neg	-
Total	100	100

Source: Consult-Eur, ECN

Table 3.10/3 Raw Materials for Hydrogen Production in Europe

The probable variations which will occur in the partition of the primary energy sources in the medium and long term will certainly have an influence on the methods for hydrogen production, at present mainly based on hydrocarbons. For these reasons attention is now given to all possible methods for producing hydrogen from other sources, methods which could be useful in the short, medium or long term.

Principally hydrogen is produced using water in connection with another raw material or an energy source; we can make a subdivision of the methods of production according to this second element used with water:

- hydrogen from hydrocarbons
- hydrogen from coal
- hydrogen with electricity
- hydrogen using high-temperature heat

In the present report hydrogen production from hydrocarbons is not considered because these are conventional processes already extensively used in the chemical industry. Also production methods using electricity through convential water electrolysis are not taken into account, because these processes are operated at low temperatures (present electrolytic cells at 60-80°, advanced cells at 120-150°C).
We will consider hydrogen from coal and hydrogen using high-temperature heat.

3.10.2 Future prospects and forecasts

Large applications of new, non-conventional processes will be effective only in the medium and long term. We can consider that processes for production of hydrogen from coal could be applied in the medium term: technologies are already known and plants operated. Only in the long term, if we consider large industrial use, will hydrogen be produced from water using only heat: the method is still in a research phase and competitive processes have to be selected.

Taking into account the reactions, or the processes, operated at high temperature, we have the following list:

processes using coal

- steam gasification of coal (ab. 900°C)
- steam reforming of methane for coal gasification (ab. 900°C)

processes using water and heat:

- thermochemical processes for water decomposition (800-900°C)
- water-vapour electrolysis (800-900°C)

3.10.2.1 Medium-term processes

We mention here for the sake of completeness hydrogen production from coal. but without taking into consideration the method for defining lines of materials R and D. The process is based on the endothermic steam-carbon reaction:

$$C + H_2O = CO + H_2$$

The heat required can be supplied by nuclear energy. The method is not described and analyzed here, but some potential materials problems are mentioned:

-erosion from coal particles
-oxidation
-sulphidation

A variant for hydrogen production from coal is given by hydrogenation of coal to methane and successive reforming: the hydrogen produced in this endothermic process is partly recycled (2/3) and partly (1/3) is available. The problems of steam reforming of methane (700-850°C) are those of the steam-methane reaction used for the production of hydrogen from natural gas.

3.10.2.2 Long-term processes

Methods of production of hydrogen from water, by thermochemical processes which use heat drawn directly from a high-temperature nuclear reactor (or may be from a solar furnace) are considered here.
Because of temperature limitations of nuclear reactors ($\leq$ 1000°) and of materials technology the direct, singlestep water dissociation, which requires temperatures higher than 2000°C, cannot be achieved.
However, a sequential chemical reaction series can be defined in which hydrogen and oxygen are produced, water is consumed, and all other chemical compounds are regenerated and recycled. Theoretically the system is the same as electrolytic decomposition of water: a system in which heat and water are the input and hydrogen and oxygen the output.
The potential practical high efficiency of this method is a motivation for research to identify and develop thermochemical processes; various investigators have proposed numerous chemical sequences and laboratory testing of reaction steps has been made in some cases. The scientific feasibility has been demonstrated but no industrial plant has been realized at the moment. It must be mentioned that in some cases, the so-called hybrid cycles, one of the reactions is a chemical-electrolytic reaction.

At least one of the chemical reactions in these processes is operated at high temperatures: 700-900°C. From the point of view of constructional materials we have two kinds of problem: corrosion and hydrogen embrittlement.

(1) Corrosion

Many of the thermochemical cycles being studied at various laboratories involve handling corrosive reagents at high temperature and high pressure, particularly salts and acids. For the most part, the reactions are being studied at present in glass and quartz laboratory apparatus. Few of the programmes have reached the stage where materials for scaling-up a process have been selected.

Material compatibility programmes to support the development work for thermochemical processes are made in some laboratories with screening tests designed to evaluate materials under conditions which correspond exactly to thermochemical process conditions.
According to the cycle, the reaction(s) operated at high temperature can have quite different characteristics.
A general subdivision can be made into reactions in reducing atmosphere or reactions in oxidizing atmosphere: different classes of materials can be chosen for these different conditions.
Another typical characteristic is that in many of the reactions a halide is present, in combination with hydrogen: a possible synergistic effect of these two elements (hydrogen

and a halide) is an unexplored subject.

If one examines a list of the reactions under study and the materials being used to contain them, it may seem that ceramic materials have more to offer than metals and alloys for scaling-up thermochemical processes. However, there is a reason why metals and alloys should be used for at least part of the equipment: heat exchangers must be used if the processes are to be efficient, and only metals and alloys, apart from some graphites and carbons, have thermal conductivities that are high enough for heat-exchanger hardware.

(II) Hydrogen Embrittlement

Hydrogen production processes, as well as other advanced energy conversion systems such as coal gasification, involve hydrogen as a product of one of the reaction steps. In all the cases where hydrogen is present at temperatures up to 1000°C containment of hydrogen at these temperatures and at pressures up to 40 atm is an important design consideration.

In a recent NASA report (JPL 5040-1, December 1975) the following statement is made:

"Fortunately, the requirements for hydrogen containment at high temperatures and pressures have existed for a number of years in the ammonia and petroleum hydrorefining industries. Much technology has been developed which, at least partially, may be applicable to the anticipated requirements for hydrogen production. However, there are strong indications that the Nelson curves used to design against elevated temperature hydrogen attack are inadequate. The Nelson curves are constructed from plant failures and data on satisfactory operating regions, accumulated over many years of practical experience. These curves delineate the safe and unsafe hydrogen pressure-temperature regimes for carbon and alloy steels in a purely empirical way.
The hydrogen gas environments are those used in the petrochemical industry and are far from pure."

A process which is conceptually similar to the thermochemical decomposition of water is high-temperature gaseous-water electrolysis: the process is oriented to use heat from a high-temperature source as much as possible instead of electricity. The method is not yet developed to industrial realization and one of the main difficulties is in the materials to be used at high temperature.

3.10.3 Lines for materials research

Important material problems have to be solved in the development of industrial processes for hydrogen production by thermochemical decomposition of water. The method is in the research phase and selection of promising processes has to be made; application is foreseen in the long term.
Development of materials will be necessary, but at this moment it is too early to start because the detailed conditions of processes have yet to be defined.
Exploratory research and screening corrosion tests are necessary and important for the orientation of the study, and as

criteria for the selection of processes. Conditions for the corrosion environment(temperature, chemicals, concentrations, impurities) are strongly dependent on the selected process. General conditions are the following:

- range of temperature: 600-950°C
- two classes of environment: oxidizing atmosphere
                                                   reducing atmosphere

Another aspect is the presence of hydrogen, from the point of view of embrittlement, in corrosive conditions at high temperature.
Besides the thermochemical processes for water decomposition high-temperature gaseous-water electrolysis could be developed in the long term. Specific material problems have to be solved for this process also.

3.11 COMBUSTION ENGINES *

Internal or external combustion engines involve a few components operating at high temperatures and for these specific characteristics are required.

Exhaust valves.

In internal combustion engines these operate at temperatures which may reach 800-900°C maximum, and suffer mechanical and thermal stresses, corrosion and erosion. Failures, when they occur, are usually at the valve seat and may be due originally to oxidation or to thermal or mechanical fatigue, but are aggravated by severe erosion by leaking combustion gases. The corrosive effects of lead oxides arising from fuel additives are additionally important. Special high-chromium and high-silicon ferritic steels, and austenitic steels strengthened with tungsten additions have been developed for this service, but nickel-base superalloys of the simpler type are now being adopted for higher-duty engines. Continued improvements, with economics playing an important role, are expected.

Spark-plug electrodes.

These operate at temperatures up to about 800°C and suffer a combination of corrosion and electrical erosion. A ductile material readily drawn to wire and capable of being adjusted for gap-setting is required. The conventional materials are nickel alloys with additions of silicon and manganese to control oxidation and corrosion. For aero-engines and other highly-rated engines platinum alloy electrodes (platinum-iridium or platinum-tungsten) are used.

Pre-combustion chambers.

Some compression ignition engines have pre-combustion chambers into which the fuel is injected and where combustion is initiated. Temperatures may reach 800°C or more and fluctuate widely, leading to thermal fatigue failures and severe erosion. Cast nickel-base superalloys are widely used for these components.

Other forms of combustion engine, e.g. Stirling, Wankel, present special material problems, which sometimes involve high-temperature conditions.

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* Short unreviewed outline

4. MATERIALS

4.1 METALS AND ALLOYS

4.1.1 Ferritic Steels*

This group of steels includes all those with a basically body-centred-cubic structures, i.e. consisting of ferrite or the various decomposition products of austenite. The compositions range from plain carbon or low-alloy steels, with alloy additions usually not exceeding about 5% in total, to steels with up to about 30% chromium. In all cases the strength, both at normal and elevated temperatures, depends largely upon the carbon content and the heat treatment applied. The steels are economical and hence are chosen if their properties are adequate.

The low-alloy steels are unsuitable for service in oxidising atmospheres at temperatures above about 550°C because of scaling. Nevertheless special steels have been developed with high creep strength at temperatures up to this level and are widely used in the steam power industry. The principal steels of this group are those with additions of chromium up to 2 1/4 % and molybdenum up to 1 % and sometimes also with about 0.2 % vanadium. They are usually used normalised and tempered at 600 - 700°C. However, because of the scaling limitation they do not fall within the present remit.

For adequate resistance to high-temperature corrosion and oxidation higher chromium contents are required than in the above steels. For different service conditions steels with chromium contents ranging from 5 % to as much as 30 % are used, often also with additions of aluminium or silicon further to improve the oxidation resistance.
Unfortunately increasing chromium content almost invariably leads to reducing high-temperature strength and at the same time increases the tendency to embrittlement at lower temperatures. The formation of sigma phase on heating the higher-chromium steels in the temperature range 500 - 900°C may also lead to embrittlement.
Austenitic steels with their higher creep strength at temperatures above 600°C associated with higher ductility are therefore preferred for stress-carrying applications above this temperature.

The types of ferritic steel used primarly for oxidation resistance at high temperatures are as follows:

5 - 6 % chromium:	oxidation resistance to about 650°C, or with aluminium and silicon additions to 800°C. Used in petrochemical plant.
7 - 10 % chromium:	oxidation resistant to about 750°C, and with silicon additions (2 %) are used for internal combustion engine valves. With 1 - 2 % aluminium oxidation resistance is satisfactory up to about 900°C, and the steels are used in the petrochemical industry and for furnace components.

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* short unreviewed outline

13 % chromium:	Steels of this type are mainly used for corrosion resistance at normal and moderate temperatures, particularly for steam turbine blading. With additions of silicon and aluminium they are resistant to oxidation at temperatures up to 1000°C.
20 % chromium:	Steels with additions of up to 2 % silicon and about 1 % nickel have been used for internal combustion engine valves because of their good resistance to hot corrosion. A high carbon content (about 0.75%) is required.
25 - 30 % chromium:	These high-chromium steels are used in both wrought and cast forms for various furnace parts and heat-treatment equipment where scaling resistance at temperatures up to 1100°C is required. With additions of about 5 % aluminium the highest oxidation resistance is achieved, making the material serviceable at temperatures up to 1250 - 1300°C. Such materials are used for electrical heating elements, see section 3.3.

The creep resistance and stress-rupture strengths of most of these classes of steel can be improved by small additions of molybdenium, vanadium, tungsten or niobium, and by appropriate thermal treatments, so that useful strength can be obtained at temperatures up to about 600°C. Many commercial steels are available.

For higher temperature service with appreciable mechanical strength one is forced to turn to austenitic steels.

4.1.2 Austenitic steels

4.1.2.1 Ranges of composition of major groups

The steels considered in this section are the ferrous alloys containing chromium and nickel to such an extent that the matrix is completely austenitic over a wide temperature range from sub-zero temperatures up to service temperatures of the order of 1100°C. In many cases the austenite is stable up to the solidus temperature.

The austenitic matrix gives these types of steel their characteristic mechanical properties. The presence of chromium and nickel also determines the ability of steels to resist the attack from corrosive environments. The basic mechanical and corrosion properties are thus governed by the chromium and nickel contents but they can be further improved by additions of other alloying elements, e.g. carbon, which gives rise to strengthening due to the precipitation of carbides, and silicon, which improves the oxidation resistance by forming protective surface oxides. Although such additional elements may prove beneficial to the properties of the finished product when added in large amounts, there is often an upper limit set by the manufacturing procedure because of adverse effects on deformability, machinability etc.

Among the steels used at high temperatures in the power and chemical process industries certain groups can be distinguished. The groups are characterized by the chromium and nickel contents and may be described accordingly.

(i) 18Cr 10Ni steels

This group comprises the plain 18/10 material (AISI 304, Werkstoff No. 1.4301), the molybdenum-alloyed variant (AISI 316, Werkstoff No. 1.4401) and the steels containing the strong carbide-formers titanium (AISI 321, Werkstoff No. 1.4541) and niobium (AISI 347, Werkstoff No. 1.4550). The standardized wrought steels given in parentheses are the most common types but there exist a large number of commercial alloys with 16-20 % Cr, 8-14 % Ni and various additions of molybdenum, titanium and niobium.

The high-temperature strength of these steels increases with the carbon content. In contrast to the stainless steels intended for low-temperature applications, the high-temperature versions contain the maximum allowed carbon content which falls in the range 0.08-0.15 % (e.g. AISI 304H, 316H etc., Werkstoff No. 1.4878) and are furthermore solution heat treated at a higher temperature, viz. about 1100°C.

Cast heat-resistant steels belonging to this group (ACI type HF, Werkstoff No. 1.4825) are characterized by having a higher carbon content, typical range 0.20-0.40 %, and higher silicon than the wrought variants. The increased amount of these elements, resulting in higher creep strength and better oxidation resistance, extends the useful temperature range towards higher temperatures.

(ii) 23Cr 13Ni steels

To this group are referred steels, eg. 20/12, 23/13 and 25/12, with increased chromium content as compared to (i) and also slightly increased nickel to counteract the tendency to form ferrite. A high silicon content, i.e. about 2%, is a common feature which in conjunction with a higher chromium content makes these steels considerably better than the group (i) steels in terms of oxidation resistance. The carbon content is usually 0.15-0.20% in wrought products (AISI 309, Werkstoff No. 1.4828) but may be as high as 0.50% in castings (ACI type HH). There also exist variants with additions of strong carbide-formers (e.g. niobium in Werkstoff No. 1.4885) to increase creep strength.

(iii) 25Cr 20Ni steels

Some of the most common types of heat-resistant wrought and cast alloys belong to this group. The wrought alloys with 24-26% Cr and 19-22% Ni are available both with low silicon (AISI 310, Werkstoff No. 1.4845) and high silicon (AISI 314, Werkstoff No. 1.4841), the latter having a higher oxidation resistance. The carbon content also varies but usually falls in the range 0.10-0.20% to ensure that the creep strength is retained up to temperatures in the range 900-1000°C. The oxidation resistance in air is good up to 1100-1150°C.

The cast alloys (AIC type HK, Werkstoff No. 1.4848) display slightly larger variations in chromium (24-28%) and nickel (18-22%) and often contain up to 0.40% carbon. As silicon normally is high, the creep strength as well as the oxidation resistance of these alloys is superior to their wrought counterparts.

(iv) 20Cr 25Ni steels

In comparison with group (iii) the 20/25 alloys are less common. They offer an increased austenite stability at the expense of the oxidation resistance, which limits the maximum useful temperature in air to 900-1000°C. The carbon content of wrought products (AISI 311) is maximized to about 0.25% while castings (ACI type HN) may contain up to 0.50%. Due to the thermodynamic stability of the matrix a high creep resistance may be attained, particularly when adding strong carbide-formers such as titanium and niobium which produce precipitation strengthening.

(v) 20Cr 32Ni steels

These alloys, which are sometimes referred to as nickel-base alloys, are the most highly alloyed considered in this section. The thermodynamic stability of the austenite is excellent, due to the high nickel content in relation to chromium. Additions of carbon, titanium or niobium contribute to the creep strength. Wrought alloys with carbon maximized to about 0.10% (Alloy 800, Werkstoff No:s 1.4861 and 1.4876) retain their strength up to approximately 1000°C. With an increase in carbon content up to 0.4% (Alloy 802) the temperature limit is pushed further upwards and the oxidation resistance may then become the critical property. Cast alloys are available with low carbon and niobium additions (Werkstoff No. 1.4859) and with high carbon and increased silicon to improve the oxidation resistance.

Apart from these major groups of steels there exist a number of alloys with other combinations of chromium and nickel, e.g. 16/13, 15/15, 25/25, etc. Additions of other alloying elements than those mentioned explicitly in the text are also utilized to improve the creep strength (boron, nitrogen, vanadium, cobalt, tungsten) and oxidation resistance (aluminium, rare-earth metals). Precipitation strengthening is not always based on the precipitation of carbides but may also be achieved by intermetallic compounds such as γ'-$Ni_3(Al,Ti)$. Although the classification is based on the nickel content it should be remembered that, in some alloys of the 18/10 type, manganese partly replaces nickel as an element which stabilizes the austenite.

4.1.2.2 Availability of raw materials

Only a few remarks will be made regarding the availability of raw materials for the production of the stainless steels considered here. Although a considerable growth in the consumption of these steels is foreseen for the next decade the mineral reserves from which the principal elements iron, chromium and nickel can be profitably extracted using existing technology are reassuringly large. Yet they represent only a part of the mineral resources which may eventually become available. However, the major part of the reserves are located in developing countries and in areas with political unrest which may influence the market situation and availability in the near future.

Besides the use of virgin raw materials the recycling of scrap is an important source of supply, particularly when aiming at a more efficient use of the total world resources. Extensive recycling, however, calls for efficient methods of removing all sorts of contaminants from the scrap, which otherwise cause production problems and deterioration of the properties of the finished product. Scrap refined by high-vacuum remelting is already being used for the production of some cast alloys.

4.1.2.3 Forms available

As already mentioned in section 4.1.2.1 all major combinations of chromium and nickel are available in both wrought and cast forms. The low-carbon varieties are, with few exceptions, hot and cold worked into sheet, bar, wire and tubular products as well as forgings, i.e. the forms utilized in the construction of process equipment such as tube or plate heat-exchangers and reactors, piping, valves, tube fittings, etc.

The high-carbon varieties on the other hand are usually not so easily workable and are primarily used as-cast. Centrifugally cast tube is one of the major products which is made extensive use of in the construction of furnaces for the petrochemical and metallurgical industries. Other furnace details are produced primarily in the high chromium-nickel variants as static castings to serve as tube bends, fixtures, baskets and carriers.

Some high-carbon steels, e.g. 25Cr 20Ni (AISI 310H, ACI type HK 40) and 20Cr 30Ni (Alloy 802), are available in wrought form as hot extruded tubes and hot- and cold-worked wire, the latter being used for the manufacture of welding consumables among other things.

4.1.2.4 Workability and machinability

Stainless steels with carbon limited to about 0.15% are inherently ductile within a sufficiently large temperature interval around 1200°C to allow hot working, i.e. forging, rolling and extrusion, to be carried out. The temperature range is narrower for the most highly alloyed grades because of a lower solidus temperature, a decrease in ductility at 1000-1100°C and a higher deformation resistance. As a result, larger forces are required to arrive at the same degree of deformation in each pass, e.g. in an extrusion press, otherwise the size range diminishes. This effect is particularly obvious when the carbon content is raised because of the high potential of carbon as a strengthener. Hence most high-carbon alloys are being used in the as-cast condition.

The higher the alloy content the more prone the material becomes to hot shortness caused by impurities, i.e. residual elements such as sulphur and heavy metals (lead, bismuth,etc.). The harmful influence of these elements is usually counteracted by the addition of minor alloying and trace elements (boron, zirconium, rare earths) which in many cases act as efficient grain-boundary refiners. Special melting practices, e.g. high-vacuum- or electroslag-remelting sometimes have to be adopted.

Cold working does not normally cause any problems but the high deformation hardening rate of austenitic alloys has to be taken into account as it limits the degree of deformation obtainable with any given process equipment.

Large-scale machining is used to manufacture components out of both wrought and cast materials. One example is pull-boring of centrifugally cast tubes. Such operations are technically feasible although the maximum allowable cutting speed is 10-20% lower for the high-chromium-nickel, high-carbon steels than for the standard 18/10 material. The higher tool wear, which is associated with the toughness and high deformation-hardening rate of the austenitic matrix, is counteracted by switching from high-speed steel to cemented carbide tool tips, which also allow higher cutting speeds.

4.1.2.5 Joining

Electric welding is the most extensively used method of joining austenitic steels in the construction of high-temperature equipment. Suitable fusion-welding methods are manual metal-arc and gas-shielded arc welding, the latter with or without filler metal. Welding consumables for manual processes (coated electrodes and rods) and automatic processes (wire and strip) are available in matching compositions for most of the alloys.

Austenitic steels in general can be welded without pre-heating as they are inherently ductile and produce no hard transformation products during the welding operation. Since they have a low thermal conductivity and high thermal expansion the heat input must be kept low to avoid local deformation of the welded joint. The high-strength high-carbon grades are particularly sensitive in this respect.

In order to get the same creep strength and corrosion properties in the weld as in the parent metal, filler metals with a similar chemical composition are often chosen, which implies that they produce fully austenitic welds. A well known characteristic of such a weld metal is its sensitivity to solidification cracking and reheat cracking in multipass weldments, which calls for careful inspection during welding. A low heat input and careful control of the weld-metal chemistry to keep impurities such as phosphorus, sulphur and trace elements down to a minimum are means to combat this problem.

For steels having chromium and nickel contents in the range 20-30% it is not always possible to get acceptable welds with filler metals of matching composition and a high-nickel filler has to be used instead. This usually means that the creep strength of the weld is inferior to that of the base metal at the highest temperatures.

4.1.2.6 Mechanical properties - availability of data

The elastic and short-term mechanical properties such as Young's modulus, the yield strength at 0.2 and 1.0% off-set, the tensile strength and the fracture elongation, are well established for all standardized austenitic steels and are usually given for temperatures up to 600°C including the influences of product form and size and heat treatment.

The creep properties are, with a few exceptions (viz. alloys specified for moderate temperature applications in the nuclear power industry), less well known. The strength is described by the stress to produce 1% creep strain and rupture in a certain time and at a certain temperature. Only rarely is detailed information on the creep behaviour available such as creep strain rate as a function of stress and temperature or isochronous creep curves. The long-term rupture strength is usually extrapolated from tests of much shorter duration and it is only for the most widely used 18/10 steels and some of the others that testing times approach those encountered in service, e.g. 100000 h. The wide scatter observed when compiling test results on the most extensively tested alloys is an inherent problem when analysing creep data collected on an international basis.

The influence of cyclic conditions (load and temperature variations) on the accumulation of damage at high temperature is receiving increasing attention but there is still a lack of information on the interaction between creep and fatigue.

The relationship between the short-term mechanical properties and parameters such as alloy chemistry, production method and microstructure are generally well understood. This does not hold true for the long-term properties, as the scatter in test results tends to disguise the true influences and makes the evaluation much more difficult. As a consequence large safety margins are rather arbitrarily applied and the alloys are seldom utilized to their full capacity.

4.1.2.7 Corrosion properties - availability of data

The oxidation resistance is mostly described by a scaling temperature or maximum recommended service temperature in air. These figures are normally arrived at by short-term testing and the testing technique, as well as the criterion used in the evaluation, is only rarely specified. It is well known, however, that the rate of oxidation is very sensitive to parameters such as temperature variations and deformation rates, as well as to the alloy chemistry and surface treatments, but details of such influencies are seldom found in the description of specific alloys.

The oxidation resistance in other media such as high-temperature steam and carbon dioxide has been extensively studied particularly for steels of the 18/10 type in the development of conventional and nuclear power systems. Some austenic steels (18/10, 20/25, 20/32) have been exposed to media with low oxygen potentials, e.g. helium containing small impurities, and liquid sodium. In those circumstances the findings are related to specific systems and cannot always be generalized.

The carburization resistance is of prime importance for components which come into contact with hydro-carbons at high temperature, e.g. in petrochemical and metallurgical furnaces. Results from laboratory test are available for several of the 25/20 and 20/32 alloys considered here which demonstrate the influence of alloy chemistry, surface condition, etc. Because of the many parameters involved more information is required in order to be able to predict the 'rate of material destruction during specific service conditions. Examination of damaged components is often used as a means to overcome this problem resulting in rules of thumb for the choice of materials for specific purposes.

What has been said about oxidation and carburization holds true also for other types of corrosion attack, e.g. in combustion gases, nitrogen, chlorine and hydrogen chloride, hydrogen sulphide, corrosive slags and molten salts. For most austenitic steels there exists an estimate of the maximum corrosion rate in these media, and a maximum service temperature is recommended, but there is a general lack of information about the influence of materials and process parameters.

4.1.2.8 Physical properties - availability of data

Data are in general available to describe such properties as density (at 293 K), magnetic permeability (at 293 K) electrical and thermal conductivity, specific heat (at 293 K) and thermal expansion. The values given are usually based on actual measurements with the exception of thermal conductivity which is calculated from the electrical conductivity data by means of the Wiedemann-Franz-Lorentz relation and should be regarded as mere estimates. The data are referred to a certain nominal chemical composition and variations due to varying composition, treatment, and product form are ignored.

Changes in the properties which occur during high-temperature service are sometimes indicated, e.g. a density change due to ageing which cause a change in dimensions, or an increase in the magnetic permeability due to oxidation and or carburization.

4.1.2.9 Shortcomings and outstanding problems

In order to make the choice of material for high-temperature components intended for long-term services it is important to have detailed information on the time-dependant damage processes, which can be expected in a certain environment. It must be possible to quantify the damage rate due to plastic deformation and corrosion, as well as the interaction between such processes, to arrive at a valid prediction of the service life. This is essential for components operating at high pressures or carrying potentially dangerous compounds because of the catastrophic consequencies of a failure.

The mechanical properties are mostly assessed by short-term testing in air with a uniaxial stress state. The findings are then extrapolated to longer times, other temperatures and other stress states and environments. As there is no equation of state available which can be generally applied, such extrapolations to other service conditions are very uncertain. This complicates the choice of material and necessitates the application of large safety margins. It also makes it difficult to introduce more sophisticated design methods based on advanced stress analyses as they require detailed information on the creep behaviour, e.g. primary creep, steady state creep rate, influence of a triaxial stress state and of constraints. The interaction between monotonic creep and fatigue is another example of an area where very limited information is available today. These remarks are not only related to more exotic steel grades but to most materials.

When it comes to the chemical resistance of the alloys the problems are even more complicated. The influence of material parameters on the resistance to oxidation, carburization, etc. are often investigated in laboratory tests simulating the conditions prevailing in actual process equipment. Even under those simplified conditions the effects of alloy composition, heat treatment, surface conditions, etc. involve so many parameters that the evaluation becomes complicated. To refer the results back to the performance under actual service conditions is often not possible and this is the reason for analysing components damaged during service. There is a need for more systematic studies of this kind.

4.1.2.10 Current research

The research work on a certain type of material is most often closely linked to the development of new systems for power production or new chemical processes. As part of the development of the fast breeder reactor some of the 18/10, 20/25, and 20/32 alloys are being extensively studied in order to collect detailed information on creep properties, creep-fatigue interaction, swelling induced by neutron irradiation, and the interaction between the material and the coolant. The same types of alloys have been selected for the high-temperature gas-cooled reactor for which similar programmes are carried out, to a large extent on an international basis. The results will be used as a guide in the final selection of materials, to form the basis for a correct specification of the material parameters, and to furnish the data necessary for a design based on detailed stress analysis.

Concurrently with this applied research, more fundamental studies of mechanical and corrosion properties are conducted. The interaction of creep and fatigue and the concept of damage are examples of work which is of interest both from a solid mechanics and a physical metallurgy point of view.

The high-temperature corrosion properties are critical for petrochemical processes and large efforts are being made to find materials which are resistant to oxidation, carburization etc. under the conditions prevailing in cracking furnaces, methane-steam reformers, gas heaters, etc. A lot of these activities are geared to collect information on the basic influence of alloying elements. Beside the influence of alloying elements other means of combating corrosion are tested, such as surface treatments and surface coatings.

4.1.3 Nickel-base alloys

4.1.3.1 Ranges of composition of major groups

In accordance with their composition, three major groups can be differentiated:

a) Iron-nickel-chromium alloys with nickel contents of 32-42% of the Alloy 800 type (Appendix table C). Typical alloys of this group have high strength combined with good heat and corrosion resistance, and are the standard materials for many applications in the petrochemical field and for furnace parts.

b) Nickel-chromium-iron alloys with nickel contents of 60-75% of the Alloy 600 type (Appendix table C). Due to their high nickel and chromium contents and low iron content, the alloys show high resistance against oxidation and carburization. Typical fields of application are heat exchangers, process piping, carburizing fixtures and retorts, furnace and reactor components.

Some of the alloys of this group are age-hardenable by precipitation and exhibit high creep strength, so that they can also be classified as superalloys of group c).

c) Nickel-chromium superalloys with nickel contents of 55-75% and containing precipitation-hardening additions, mainly aluminium and titanium (Appendix table C). These group c) alloys have been developed to give high creep strength and high-temperature oxidation resistance for critical components of aerogas turbines. In addition, structural stability over long service times, fatigue and thermal-shock resistance, combined with ease of fabrication, have been required. Over the years, the application of superalloys has been extended to include industrial gas turbines, nuclear power, space vehicles, petrochemical equipment and other elevated temperature applications.

These alloys have a stable, face-centered-cubic phase with a high solubility for other elements in the austenitic matrix. The majority of such nickel-base alloys are strengthened by the precipitation of a γ' phase, an intermetallic compound of the $Ni_3(Ti, Al)$ type which is stable to relatively high temperatures. This phase has an ordered face-centered-cubic crystal structure which is coherent with the face-centered-cubic matrix, and therefore has a low surface energy, giving good long-term stability at elevated temperatures. In addition, γ' is reasonably ductile and does not therefore cause embrittlement (for further details see ref. 7).

In some alloys, Ni_3Nb is the hardening phase. This has an ordered body-centered-tetragonal crystal structure and, like γ', niobium is used as an alloying addition in those alloys which are used in welding applications and must be free of hot-cracking.

The structure of the grains and the grain boundaries of these superalloys is a determining factor in their creep resistance and creep ductility. Insufficient hardening of the grain boundaries leads to high creep rates while too much hardening will lead to poor creep ductility. The control of grain-boundary structure is largely practised through precipitation of carbides, principally chromium-carbides, but sometimes also with refractory metals. The trace elements boron, zirconium and magnesium also play an important rôle in some alloys, where they are segregated to the grain boundaries due to their atypical size (ca. 25% over or undersize). The mechanism of these trace additions is still not clear.

The relationship between volume fraction of precipitate and the high-temperature properties of superalloys represents a major design consideration. An increase from 14 to 60% in γ' can quadruple the stress-rupture properties. This has been accomplished by increasing use of aluminium, titanium, niobium and tantalum and adjusting the γ' solubility with cobalt, iron and chromium. This increase in γ' volume fraction has extended the range from general purpose wrought age-hardenable alloys such as Nimonic 80A and Inconel X-750 (14%) to investment-cast alloys such as IN-100 (60%). Over the years, the high-temperature capability of nickel-base alloys has been progressively improved by increasing the stability and volume fraction of γ' and the strength of the alloy matrix by raising the level of alloying additions.

The complexity of chemical compositions leads to heterogeneous structures which, because of the wide range of melting points of the constituents, makes the hot working of many complex alloys in large ingots extremely difficult. Consequently at present, the strongest alloys can only be produced as finished-shape castings.

In terms of properties for aircraft gas turbines, the nickel-base cast alloys have allowed a 50-75°C advance in metal temperature compared with the best wrought alloys. However the advance in turbine inlet temperature has been even greater as improved casting technology has allowed the incorporation of cooling passages in cast components.

The compositions of some typical cast alloys are included in Appendix table C. Their chemical compositions show significantly increased titanium and aluminium contents compared with the wrought alloys, plus major additions of tungsten and other refractory metals.

A further 30-80°C advance in metal temperature compared with the conventionally cast alloys can be achieved by directional solidification (columnar crystals) or by single crystal components. In this way the problem of impairing the grain-boundary ductility by further strengthening the matrix can be avoided. However, this development is still in the experimental stage.

For the same reasons which led to development of cast alloys, i.e. to overcome problems of forgeability and machinability of the wrought materials, powder-metallurgy methods have been applied with the further advantage that the scatter in properties obtained in precision castings is avoided. However, all cold pressing processes are basically unsatisfactory, as practically no green strength is achieved and the compact shows a high degree of inter-particle porosity (only 60% of theoretical density). The most promising methods currently developed are vacuum hot-pressing, "pancake" hot-press forging, as well as extrusion and hot isostatic pressing.

Dispersion-hardened alloys such as thoria-dispersed nickel (TD-Nickel) have good high-temperature properties but poor intermediate temperature properties, due to absence of γ'-forming elements. A process known as mechanical alloying (ref.8) has recently allowed the production of alloys which combine the best features of γ'-hardened and dispersion-hardened materials. It is essentially a dry, high-energy ball-milling process.

IN-853 (20 Cr, 2,5 Ti, 1,5 Al, 1,3 Y_2O_3, bal. Ni) was the first dispersion-strengthened superalloy produced by this process and is now marketed as MA 753. Below 760°C, the rupture strength follows the curve for the γ'-strengthened Nimonic 80 A closely, while above 815°C, the rupture strength follows the curve for the dispersion-strengthened TD Nickel. In addition, the rupture life curves of IN-853 are flatter than those of conventional superalloys and therefore offer a significant increase in rupture strength at longer times. This is of importance in the selection of materials for industrial turbines, where long-term property stability is required.

A further advantage of the oxide dispersion-strengthened alloys is their improved corrosion behaviour. After a fused salt corrosion test on IN-853, only general surface attack occurred whereas Nimonic 80 A in addition suffered heavily by intergranular corrosion.

4.1.3.2 Availability of raw materials and costs

The annual growth rate of nickel consumption from 1947 to 1975 was about 6,5%. This figure can also be assumed in the future for the total consumption. There are sufficient ore deposits to allow this rate to continue in the foreseeable future. The ocean mining of manganese nodules containing up to 2% Ni will be of interest in the long term. The economics of this process will determine at what time ocean mining will be introduced. Finally, there are enormous amounts of nickel (ca. 10^{12} tons) contained in the ultra basic rock "peridotite". However, due to its lower concentration (approx. 0,2% Ni), a new form of low-cost processing would be required.

During the period 1966-76, the price of nickel has nearly tripled, and by the end of 1975, had reached almost $ 5/kg. An appreciable proportion of this price rise is due to rising production costs as a result of inflation. Another factor is that investment costs for creating new mining capacity have soared. Whereas in 1965 $ 4/kg nickel products were necessary to finance new mining projects, now $ 20/kg are required. Finally, it will be necessary to resort in future to deposits with lower nickel contents which will lead to higher production costs if it will not be possible to develop more economic production methods. These three factors - inflation, rising investment costs and the need to work with poorer ores - apply in general also to all other metals, so that similar price increases can be expected (perhaps with the exception of iron and aluminium).

Apart from the cost factor, it is unlikely that nickel will be substituted in high-temperature alloys due to its specific properties. This does not preclude the use of cheaper alloys e.g. Cr-Mn-Fe alloys, in the lower temperature range.

It is interesting to note that the increase in the nickel price is not reflected fully in the price of high-temperature alloys, as a price comparison for Nimonic 80 A between 1967 and 1976 shows. The price of this alloy rose only by 60% against more than 200% for electrolytic nickel in this period.

4.1.3.3 Forms available

The majority of wrought nickel-base alloys are produced initially as forged or extruded stock and may then be further worked to any of the common forms, e.g. bar, section, tube, sheet, etc. The casting alloys are normally supplied for remelting as cast sticks with a ground finish. Some are air-melted whereas the more sophisticated ones are vacuum melted.

4.1.3.4 Workability and machinability

a) Hot-working

With the development of alloys for higher strength at higher temperatures, hot-working operations have become more difficult, although they are carried out at temperatures where the hardening phase has been taken into solid solution and the alloys show an increased ductility. However, with the increase of the precipitation-hardening elements, the solution temperature for γ' is increasing, so that the hot-working temperature range is decreasing. For the more complex alloys, the working range may be as narrow as 10-20 deg.C. For this reason, hammer-forging has become impracticable, and usually extrusion by the glass-lubrication technique or press forging are applied to break down the ingot structure. Using wrought stock material, the majority of the alloys can be successfully hot-rolled to produce bar.

Die-forging is used for the production of discs and blades from wrought billet and bar stock. A number alloys tend to exhibit critical grain growth if deformation is insufficient, so that careful design of forging sequences and deformation steps is essential.

b) Cold-working

Nickel-chromium base alloys strain-harden appreciably on cold working. Hence in addition to the usual advantages of cold-working, i.e. improved surface finish and better gauge control, better properties and/or structures can be achieved. If, for instance by cold-rolling, a section is reduced in thickness by 10% and then given a suitable solution treatment, the whole section can be recrystallized to a uniform and fine grain size with carbide precipitates both within the grains and at the grain boundaries. Such a structure exhibits improved mechanical properties and resistance to thermal cracking.

For the production of cold-drawn wire and cold-rolled sheets, conventional methods are applied.

c) Machining

In common with austenitic steel, most nickel-base alloys exhibit a propensity to work harden readily. In practice, it has been found preferable to carry out certain machining operations, such as rough turning, in the solution-treated condition, and other operations, such as finish turning or grinding, in the annealed state.

In order to obtain efficient metal removal, the machine tools should have ample power, low-speed cutting capability, rigid construction and freedom from backlash. The cutting fluid should have extreme pressure characteristics to minimize build up on the tools. Many lubricants have a high sulphur content. Machined components should therefore be well cleaned before heat treatment, to avoid corrosion by sulphur attack.

If the above guide lines are observed, other machining operations such as milling, boring, drilling, broaching, tapping and reaming can be executed satisfactorily. (For details, see ref. 1). Also grinding, polishing, buffing or brushing do not pose any problems if pressure and speeds of finishing equipment are properly controlled.

4.1.3.5 Joining

Whereas high-temperature brazing can be applied to most alloys, there are limitations imposed by the materials on the use of some welding processes. Most of the age-hardenable alloys can be welded by the gas-tungsten-arc process. However, the propensity for cracking in the heat-affected zone of the base metal depends on how quickly precipitation takes place during welding. As titanium and aluminium are the main precipitation-hardening elements in these alloys, it is obvious that with increasing amounts of these two elements, the danger of hot-cracking increases. In alloys with 6% aluminium plus titanium, cracking occurs readily in thin-section material, making this material practically unweldable.

The addition of niobium to the aluminium- and titanium-hardened alloys delays the precipitation reaction and reduces the tendency to hot-cracking. Thus, Inconel 718 with about 5% niobium is one of the most weldable of the high-temperature materials in the annealed or solution-treated condition. On the other hand, the addition of boron and zirconium which improves the creep and stress-rupture properties of these alloys raises the tendency for weld metal and heat-affected zone cracking, as both elements segregate to the grain boundaries and may lower the melting point enough to give liquation-type cracking in the fusion zone. In confirmation of this, Nimonic C 263 which is free from boron and zirconium, is also free from hot cracking.

The problem of weld and heat-affected zone cracking can be overcome by the flash-butt welding process, where the material heated close to or above the solidus temperature is expelled into the flash during the upsetting process.

The provision of crack-free welds must be accompanied by satisfactory point properties. Even with butt points, notches can be produced at the edge of the weld simply by poor weld profiles. Normally 5 to 10% reinforcement is tolerable. Where this is exceeded, weld dressing should be applied to remove the resultant notch effect.

Weld properties are probably most seriously affected by post-weld heat-treatment, and materials suppliers make appropriate recommendations. (For further details, see ref. 1).

4.1.3.6 Mechanical properties - availability of data

Originally nickel-base superalloys were developed and used for creep and heat-resistant applications, especially gas-turbine blading and flame tubes, so that other mechanical properties were only of secondary interest. However, with the increasing importance of these alloys in other industries and applications, for instance for nuclear reactor components, a wider study of mechanical properties became necessary. For the more widely used alloys, quite extensive compilations of data embracing short- and long-time tensile, fatigue, creep and impact tests at a wide range of relevant temperatures are available. It is not possible to review them in detail in this chapter, and the data are available in references 1, 2 and 3, and from the manufacturers of these and similar alloys.

4.1.3.7 Corrosion properties - availability of data

The most common forms of corrosion of nickel-base alloys encountered during service result from attack by oxygen, sulphur or carbon in the working environment.

Within the field of aerospace application the predominant corrosion process is oxygen attack and substantial efforts have been made to improve oxidation resistance by alloying and by the application of protective coatings (Refs. 11, 12 and 13 and Sections 4.5). Current technology appears to favour the formation of an aluminium oxide (Al_2O_3) outer scale. Recent attempts to improve the adherence of this protective scale to the substrate, both at continuously high temperatures and during thermal cycling, have included the addition of small concentrations of rare-earth elements, e.g. yttrium, lanthanum, cerium (see Section 2.1.3.).

Some typical oxidation test data in air are given in ref. 1. The alloys were subjected to thermal cycling to simulate service conditions.

Alloys required for land-based, low-altitude or marine applications are also exposed to sulphur- and/or carbon-containing environments. The general phenomenon of high-temperature metallic sulphidation, usually in conjunction with attack by certain aggressive fossil-fuel impurities e.g. sodium, vanadium or chlorine gas, is loosely termed "hot corrosion". In the case of nickel alloys, this may for example result from reaction with sulphur and sulphur coumpounds to form a nickel/nickel-sulphide eutectic which melts at temperatures as low as 645°C. The attack, mainly from sulphur-bearing gases such as sulphur dioxide, trioxide and hydrogen sulphide, but also from surface contamination by sulphur-bearing mineral oils, proceeds by penetration of the metal grain boundaries, faciliting intergranular cracking. Resistance to corrosion by hydrogen sulphide is greatly improved by raising the chromium content, especially to approximately 35%. By comparison, the attack by sulphur dioxide is less than by hydrogen sulphide.

In discussing carburisation, it is important to consider carbon diffusion rates and carbon solubility in nickel-iron-chromium alloys. With increasing nickel content, the carbon diffusion decreases, and the rate of carbon pick-up in carburizing atmospheres decreases. On the other hand, high-nickel alloys have very little solubility for carbon between ambient temperature and 900°C, so that high-nickel alloys precipitate chromium carbides more readily during cooling and are therefore more easily embrittled than iron-nickel-chromium alloys.

In general, in a combustion atmosphere with excess of air, no carburization takes place; so that heating of nickel-chromium alloys in carbon dioxide gives less corrosion than in air.

The mechanism of hot corrosion by fuel ashes is extremely complex, but apparently involves the formation of a molten deposit on the alloy surface, which fluxes the protective scale, thus allowing rapid penetration of sulphur, carbon etc. into the metal. Attack is extremely severe in the temperature range 700 to 850°C, where sodium sulphate is molten. As with simple sulphidation, fuel-ash corrosion decreases with increasing chromium content.

4.1.3.8 Physical properties - availability of data

As long as nickel-chromium alloys were mainly developed for gas-turbine applications, mechanical and chemical behaviour at elevated temperature were of much higher interest than physical properties. However, the extension of the use of these alloys into other industrial fields, especially for nuclear reactor components, has widened the interest in their physical properties.

Values for physical properties, such as density, thermal conductivity and expansion, specific heat, electrical resistivity, elastic moduli, and melting ranges are readily available in producer brochures (ref. 2, 3 and 5). Some notes on optical and magnetic properties are given in ref. 1 and 4.

Information relevant to the application of nickel-base alloys in the nuclear field under irradiation is given in ref. 4 and 14. High-nickel alloys suffer embrittlement by irradiation at 500°C whereas nickel steels are only affected above 600°C. This effect is due to a nuclear transformation and cannot therefore be remedied by heat treatment. It is interesting to note that Nimonic PE 16, which withstands significant doses of irradiation, has a nickel content below 50%.

4.1.3.9 Shortcomings and outstanding problems

The development of wrought nickel-base alloys for higher and higher temeperatures and longer life has reached a natural barrier as the increase in alloy additions for increasing the volume fraction of γ', as well as for stiffening the matrix, has decreased the melting temperature, with a drastic reduction in the hot-working range.

However, it should be possible by better control of harmful trace elements such as tellurium, bismuth, lead and silver, and better understanding of the rôle of beneficial trace elements such as boron, zirconium and magnesium and of their effect on the morphology of the grain-boundary carbides, to improve the ductility and strength of superalloys. In addition, by better understanding and control of the metallurgy of these superalloys, and by improved processing methods, it should be possible to lower their production costs.

The pressure to use more economic alloys will stimulate further development work, for instance of alloys with higher iron content as exemplified by the use already of Incoloy 910 and Nimonic 942.

Another outstanding problem is the development of improved hot corrosion resistance against vanadium, which is present in residual oils, so that the life of these superalloys in industrial gas turbines would be greatly lengthened and this application made more economical.

Although some improved strength and ductility have been attained by directional solidification, there is still ample room for further development of this process to produce more cheaply both stronger and more corrosion-resistant materials for turbine blades.

4.1.3.10 Current research

Due to the difficulties of hot working of the higher alloyed superalloys, major effort has been directed to produce gas-turbine components by powder-metallurgical technology. Whereas the first step, to obtain the necessary density, was successfully achieved by applying hot isostatic pressing, the ductility of these compacts is still not satisfactory. It remains to be seen if it is possible to improve this property without further hot working; otherwise the advantage of sintering to finished shape would be lost.

Work will continue on the development of dispersion-hardened alloys by mechanical-alloying processes, producing bar and sheet material of the same strength but with better corrosion resistance than that of the advanced cast super-alloys. This material, which will necessarily be wrought, should possess acceptable fabrication and machining characteristics. It should be economical to produce special sections by extrusion or rolling close to that of the finished parts (ref. 9).

The evaluation of Incoloy 800, Inconel 617, Hastelloy X and other alloys of various compositions for application in the impure helium environment of the high-temperature gas-cooled reactor will continue, as well as wear and friction testing for moving metal parts in the same environment (ref. 6).

The continual requirement for creep materials of higher temperature capability for use in gas turbines has stimulated a small activity in the field of in-situ composite materials. It is hoped that these alloys derived by the directional solidification of intermetallic, and metal/refractory eutectics, will combine the high-temperature strength and stability of refractories with the ductility and toughness of nickel-based superalloys.

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4.1.4 Cobalt-base alloys

4.1.4.1 Composition

The development of heat and creep-resistant properties in cobalt-base alloys largely depends on carbide hardening and solid-solution strengthening, with the former providing the major contribution. Most creep-resistant alloys (commonly designated 'superalloys') are complex combinations of elements intended for applications in which strength is important; whereas alloys of the type UMCo 50 developed for high-temperature low-stress conditions (furnace fittings) are compositionally simpler.

The carbide-forming tendency depends on the alloying element added and each of the following will contribute individually or in combination: niobium, zirconium, tantalum, tungsten, titanium, chromium and molybdenum. Carbide stability depends both upon temperature and carbide composition.

Solid-solution strengthening is provided by tantalum, tungsten, niobium, chromium and less commonly molybdenum. Since these elements also form carbides, their effectiveness as solid-solution hardeners depends upon the amount of these hardeners, the carbon content and the carbide composition. They also differ in the degree of solid-solution strengthening effected. Other advantages are obtained such as the extremely important contribution to the hot-corrosion and oxidation resistance made by chromium.

Element	Effect
Chromium	Improves oxidation and hot-corrosion resistance, produces strengthening by formation of M_7C_3 and $M_{23}C_6$ carbides.
Molybdenum Tungsten	Solid-solution strengtheners; produce strengthening by formation of intermetallic compound Co_3M and M_6C carbide.
Tantalum Niobium	Solid-solution strengtheners; produce strengthening by formation of intermetallic compound Co_3M and MC and M_6C carbides.
Aluminium	Improves oxidation resistance; produces strengthening by formation of compound CoAl.
Titanium	Produces strengthening by formation of MC carbide and intermetallic compound Co_3Ti; with sufficient nickel produces strengthening by formation of intermetallic compound Ni_3Ti.
Nickel	Stabilizes FCC form of matrix; produces strengthening by formation of intermetallic compound Ni_3Ti; improves forgeability.
Boron Zirconium	Produce strengthening by effect on grain boundaries and by precipitate formation; zirconium produces strengthening by formation of MC carbide.
Carbon	Produces strengthening by formation of carbides MC, M_7C_3, $M_{23}C_6$ and possibly M_6C.
Yttrium Lanthanum	Increase oxidation resistance.

Table 4.1.4/1 Effects of several Elements in Cobalt-base Superalloys.

Table 4.1.4/1 summarises some of the effects produced by element additions although not all these effects necessarily occur simultaneously in an alloy.

4.1.4.2 Raw material availability

Cobalt is largely produced as a by-product of copper mining operations in Zaire and Zambia with lesser amounts as a by-product from several nickel mining operations. Production figures for the years 1972 - 1975 are listed in Table 4.1.4/2 with the year-end price in U.S. dollars per kilogram.

Country	1972		1973		1974		1975	
	Tonnes	$/Kg	Tonnes	$/Kg	Tonnes	$/Kg	Tonnes	$/Kg
Zaire	13,043	6.1	15,052	7.2	17,545	7.9	13,638	8.7
Zambia	2,053		1,944		1,962		2,108	
Canada	1,549		1,854		2,084		1,527	
Morocco	1,529		1,378		1,644		1,891	
Finland	803		1,010		812		1,084	

Table 4.1.4/2 Metric Tonnes of contained Cobalt and Year End Price.

The drop in production in Zaire reflects the general economic recession during this period. Based on the average consumption growth rate of 6.5 per cent per year over the period 1960 - 1973 forward predictions indicate that a consumption total requirement of 36 - 40,000 tonnes by 1980 can be met based on the increased production potential of existing producers and the newer nickel mining operations in Australia, New Caledonia and the Phillipines. The possibility of the exploitation of marine deposits containing cobalt ensures adequate supplies of the metal for the foreseeable future.

4.1.4.3 Available forms

The majority of the commercially available cobalt alloys are casting alloys. They are obtainable as cast ingots or investment castings. The more recently developed alloys e.g. MAR-M 302, MAR-M 509, AR 215 require vacuum processing because of their high reactive element content. They are available as vacuum melted ingots or vacuum cast-to-shape components. The application of vacuum processing techniques to the earlier alloys e.g. X 40, WI 52, HA 25 does not result in sufficient rupture strength improvement to warrant, in all cases, the increased manufacturing costs. Generally, vacuum processing leads to an increase in ductility regardless of the type of alloy.
The wrought alloys e.g. HA 25, L 605 and HA 188 are available as billet and forging stock, bar, plate, sheet, wire and welding rod.

The application of powder metallurgy techniques to the processing of high-temperature materials has recently made significant advances and the material property claims are promising. Prealloyed powders with the nominal compositions of alloys such as X-40, HA 25 and S 816 have been produced.

4.1.4.4 Workability and machinability

a) Workability

Cobalt-base alloys have been developed and traditionally used either cast or wrought, and little definitive work has been carried out to compare the properties of a specific composition in both forms. Although many of the casting alloys can be hot worked with care, the resulting mechanical properties, particularly creep strength, are adversely affected, the more so as the complexity of the as-cast structure increases - hence the reduction in creep strength of hot worked MAR-M 509 (compared with the as-cast properties) is more drastic than with the less complex structured alloy X 40.

The wrought alloys HA 25, L 605 and HA 188 are readily hot worked within the temperature range 950 - 1230°C. They are all cold formable but the work-hardening rate is greater than that experienced in austenitic stainless steels and many nickel-base alloys. As a result more intermediate annealing between stages of cold forming may be required to produce the final shape. Annealing at 1175°C followed by rapid cooling will restore the original ductility. The alloys also exhibit strain-rate sensitivity which varies with the method of forming, so that generally relatively slow operating speeds are recommended, as for nickel-base alloys. The strain introduced during any cold-forming operation should exceed at least 10 %. Lower percentages may reduce the grain nucleation rate, yielding abnormally large recrystallized grains during the subsequent annealing operation.

b) Machinability

Cobalt-base alloys exhibit several characteristics that contribute to difficulty in machining and cause rapid tool wear and high machining costs.These characteristics are:-

1. high shear strength which causes high forces at the cutting edges of the tools
2. high capacity for work hardening
3. presence of hard abrasive carbide and intermetallic compounds in the microstructure
4. low thermal conductivity resulting in heat concentration in the cutting area

Machinability ratings based on cutting speed or metal removal rate have limited utility. Manufacturing ratings involving machining costs and production loading schedules are more useful. The manufacturing programme for aerospace components frequently requires identical structural parts to be produced from different alloy compositions which provides useful comparative data. Based on these and much general experience, specific data on tool design and feed rates are available and should be consulted before undertaking critical machining operations.

4.1.4.5 Joining

a) Welding

Wrought cobalt-base alloys are amenable to joining by several conventional fusion welding techniques - gas tungsten-arc, gas metal-arc, shielded metal-arc, electron beam and resistance welding. Where the application requires very high reliability gas tungsten-arc and gas metal-arc welding are recommended.

From the little information available welding becomes more difficult as the carbon content of the alloys increases and this is borne out by the problems associated with the welding of the cast cobalt alloys. Great care must be exercised with alloys such as X 40, HS 21, HS 36. However, other than repair welding, there is usually little need to weld most castings.

Joint design to allow full penetration, and weld grooves machined to assure proper fitting, are essentially the same as for nickel-base alloys.

The weld joint and adjacent area must be thoroughly cleaned, foreign matter removed by grinding, machining or wire brushing with stainless steel (sand and shot blasting should not be used because of the likelihood of serious contamination).

Cobalt-base alloys are welded in the solution-treated or annealed conditions as this has been shown to reduce the possibility of heat-affected-zone hot cracking. Jigs and fixtures may be employed to facilitate welding and reduce warping, but hold-down clamps (if used) should be positioned a sufficient distance away from the weld fusion line to permit the welding heat to dissipate slowly to minimise cooling strains. Excessive restraint during welding and surface contamination by metallic copper (from the copper welding fixtures) should be avoided. Copper contamination promotes severe heat-affected-zone cracking. This situation can best be prevented by chromium electroplating all copper jigs and fixtures.

b) Brazing

The choice of alloy for brazing cobalt-base alloys will depend on the service temperature and environment. In the majority of applications this necessitates the use of filler metals of the Ni-Cr (AWS Classification B Ni-1,-3,-5,-7) and Au-Ni (AWS B Au-4) type as well as various proprietary cobalt-base compositions. Furnace brazing under controlled atmospheric conditions (argon, hydrogen or vacuum) is generally the preferred method. Careful precleaning procedures must be adopted to remove grease, refractory and adherent oxides and base-metal inclusions and surface contaminants. The procedures adopted for stainless steel and nickel-base alloys apply in the majority of cases.

4.1.4.6 Mechanical properties

The characteristic hot tensile and creep-rupture strengths of cobalt-base alloys are available from manufacturer's publications, and some data are given in the appended references. The data generally cover the temperature range up to 1000-1050°C, and are usually average values for the alloys in their most common conditions.

4.1.4.7 Corrosion properties

Elevated temperature attack may be due to direct oxidation or may be the result of attack by other elements, principally sulphur. Sulphidation may be described as an accelerated attack by oxygen brought about by the presence of sulphur and alkali-metal salts in the atmosphere. The attack is particulary severe in the temperature range 760-1000 °C. There is general agreement that condensed alkali metal salts, notably Na_2SO_4 are a prerequisite to such corrosion. The source of these salts may be 1) direct ingestion of sea salt in a marine environment, 2) formation of Na_2SO_4 during the combustion of fuels containing both sodium and sulphur, and 3) formation of Na_2SO_4 during combustion from sodium-contaminated airborne dust and sulphur in the fuel. Since the life expectancy of a stressed gas-turbine component may be limited by its hot-corrosion resistance rather than by its stress-rupture strength there are considerable economic incentives for preventing or reducing hot corrosion attack.

Cobalt-base alloys appear to be intrinsically more resistant to this form of attack than nickel alloys; for example in sulphidising atmospheres or in crucible tests Co-20Cr is more resistant than Ni-20Cr. The high melting temperature of the $Co-Co_4S_3$ eutectic (877 °C) compared with $Ni-Ni_3S_2$ (645 °C) has been suggested as one reason for their better performance. In addition the diffusivity of sulphur in a cobalt alloy is approximately 100 times slower than that in nickel. Similarly commercial cobalt-base alloys are generally recognised as more hot-corrosion resistant, but less oxidation resistant, than complex nickel-base alloys. These alloys are strengthened primarily by $Cr_{23}C_6$ carbides and therefore usually contain a relatively high concentration of chromium. It has been established that the optimum level of chromium is in the range 25 - 30 % by weight.

The roles of various addition elements have been studied in some detail and there is now a measure of agreement on the probable role of each element although synergistic interactions among elements and between composition and test parameters must be expected. Chromium and yttrium have been identified as beneficial. The refractory metals (added as matrix strengtheners and carbide formers) with the possible exception of tantalum, decrease hot-corrosion resistance. It has been suggested that their role is related to the formation of compounds such as Na_2MoO_4 and also their tendency to segregate to the dendrites of cast alloys, thereby providing potential sites for localised attack. The role of the rare-earth metals or oxides appears to be related to their beneficial effect on scale adherence and their involvement in the precipitation of complex sulphides or oxysulphides in the alloy-depleted zones.

Data on the corrosion resistance of cobalt-base alloys is widely disseminated through the literature. The references provide a useful range of available data.

4.1.4.8 Physical properties

The density of cobalt-base alloys falls within the range 8.3 to 8.9 $g.cm^{-3}$. The high refractory metal (tungsten and tantalum) content in the majority of alloys contributes significantly to these values.
The dynamic modulus of elasticity is similar for alloys of a given base and the average values for cast cobalt-base alloys are typically:

Temperature °C	20	650	760	870	980
Modulus 10^8 Nmm^{-2}	2.25	1.78	1.65	1.55	1.37

Thermal expansion coefficients are similar to those of nickel-base alloys and are typically:

Temperature Range °C	20-200	20-650	20-760	20-870	20-980
Coefficient 10^{-6} per °C	13.1	15.3	15.8	16.2	16.6

Thermal conductivity of the alloys is of the order of 85 % less than that of pure cobalt taken as 92 watts/metre K. The values for HS31 are tabulated below:

Temperature °C	100	200	320	430	540
Conductivity W/m.K	13.7	15.8	17.7	19.7	21.7

4.1.4.9 Shortcomings and outstanding problems

Cobalt-base alloys are generally strengthened through solid-solution hardening and carbide precipitation. The former ensures hardening of the matrix while the latter retards slip and grain-boundary migration. In high-carbon alloys part of the applied stress is supported by the intergranular carbides which in this case, form a rigid skeleton.

The alloys are generally used in the un-heat-treated as-cast condition although some attempts have been made to increase the strenthening efficiency of the carbides through solution and ageing heat treatments. These treatments modify the morphology of the as-cast grain boundary precipitate and result in reduced ductility. Also the intragranular precipitates which develop are complex, relatively unstable, carbides of the $M_{23}C_6$ and M_6C types which tend to overage at temperatures within the range 760-870°C, and therefore make little contribution to alloy strength at higher temperatures. Much of the research work on carbide reactions in conventional alloys was carried out between 10 and 35 years ago and there is a need to generate more information along the lines developed for nickel-base alloys where the suppression or elimination of secondary carbide reactions has been achieved.

Most of the available information on hardening by intermetallic compounds has been obtained from ternary and quaternary alloys. Results show that above 870°C this type of hardening becomes largely ineffective because of overageing. The types of compounds precipitated are Co_3Ti, Co_3Ta, Co_3Mo, Co_3W and Ni_3Ti. Whereas these geometrically close-packed phases are vital strengtheners in nickel alloys they do not form easily in cobalt alloys. When formed, the lattice parameter mismatch is of the order of 1.0 % as compared with the highly effective -0.1 % to +0.5 % in nickel alloys. Intensive effort in recent years has identified some of the stabilising mechanisms involved with these precipitates without extending their stability sufficiently to offer strengthening in the temperature range currently shown by nickel-base alloys. At the medium temperature level the effectiveness of γ'-strengthened L-605 has been demonstrated with significant strength and ductility improvements. Further studies on the role of Co_3Ta (particularly the stabilisation of the FCCα-Co_3Ta as opposed to the conversion product HCPβ-Co_3Ta) and ordered HCP Co_3W and Co_3Mo, and possibly Laves phases such as Co_2Nb and Co_2W, are required.

Although there are significant gaps in our understanding and knowledge of carbide reactions and interactions, and of the factors affecting the constitution, structure and stability of various intermetallic compounds and of the surrounding matrix, the rôle of alloy processing parameters offers the possibility of improved material utility. Some of the ways of affecting properties are itemized in Table 4.1.4/3.

Mechanism	Comments
1 Grain structure (directional, single, fine)	Directional solidification yields better thermal fatigue properties and ductility, but higher cost because of special processing. Fine-grained more ductile, possible better fatigue but poorer creep resistance (powder metallurgy).
2 Dispersoids (ThO_2, other oxides, carbides)	Expensive, technique very critical; no outstanding alloy yet developed.
3 Eutectics (intermetallics)	Requires further investigation, offers promise of high-temperature stability and good strength.
4 Fibre reinforcement	Encouraging results being obtained with cobalt-tantalum-carbide systems but more information required.
5 Combinations of the above	Adds to expense so that properties developed must be improved enough for economic justification.

Table 4.1.4/3 *Some strengthening mechanisms.*

4.1.4.10 Current research

Some of the principal areas of research and development are described below.

a) Hot-corrosion resistant alloys for protective coatings - work carried out in the U.S.A. on Co-Cr-Al-Y alloys, and in Europe on Co-Cr-Ni-Ta-Al-Y compositions, has demonstrated the exceptial hot-corrosion resistance that may be obtained. The compositions and the techniques of applying the alloys as protective coatings are under active development.

b) Directional solidification - the application of this technique has shown that the properties developed with columnar X-40 are practically equivalent to equiaxed MAR-M 509 in stress-rupture strength (the strongest cobalt-base alloy currently available) with superior ductility and thermal shock resistance. Further investigation to optimise alloy compositions specifically for this technique is of considerable interest.

c) A special case of directional solidification is that presented by composites where the matrix is a cobalt-base solid solution and the strengthening fibre is a refractory metal carbide such as TaC or NbC. The type of alloy designated COTAX-3, developed by Bibring et al, exhibits many properties which are superior to those of the best superalloys.

d) It has been established by recent research and development programmes in the U.S.A. and Europe that the application of powder metallurgy techniques markedly enhances the tensile properties (strength and ductility) of superalloys up to about 800°C. The alloy compositions used in these investigations have been derived from existing alloys which were developed for use in the cast or wrought form; again there is a need to develop compositions specifically for the process.

e)General alloy development directed towards improved all-round performance, both in the cast and wrought forms, is continually under active consideration by many superalloy producers and aero-engine manufacturers in the U.S.A., France and the United Kingdom.

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4.1.5 Refractory Metals

If the refractory metals are considered as those with melting points above 2000°C, one has ten metals. From these the elements molybdenum, tungsten, niobium, tantalum and rhenium in metallic form have gained considerable technical significance, while the metals hafnium, osmium, ruthenium, iridium and technetium are up to now only of significance for some special fields of application. For the sake of completeness the metals chromium, vanadium, zirconium and titanium, having melting points slightly below 2000°C, are shortly considered in the appendix, section 4.1.5.8..

The properties of the aforementioned technically important refractory metals can briefly be characterized as follows: high strength as indicated by their high melting point, high-temperature and long-time rupture strength, high recrystallization and ductile-brittle transition temperature, and accordingly, difficult forming and working. In addition low vapour pressure, high modulus of elasticity and low coefficient of thermal expansion. Unfortunately, a very significant characteristic of these metals is the poor oxidation resistance at temperatures as low as 400 - 700°C.

Detailed mechanical, oxidation and thermal properties and descriptions of applications of molybdenum, tungsten, tantalum, niobium and rhenium are contained in the literature (1 - 12). The following notes provide general information on these metals.

4.1.5.1 Molybdenum

Melting point 2610°C. High modulus of elasticity and due to its relatively low density (10.22 g/cm^3) excellent strength-to-density ratio at high temperatures. Poor low-temperature ductility compares badly with tantalum and niobium. Oxidation resistance is poor; above 500°C MoO_3 forms and sublimes rapidly at 600°C. Molybdenum can be used at high temperatures in hydrogen or inert gases or a vacuum. Silicide diffusion coatings provide short-term protection against oxidation.

Supplies of ore are good and relatively cheap. Production of molybdenum concentrates in the Free World was 75 million kg contained molybdenum in 1974. The price in 1976 is about 6.6 U.S. dollars per kg of contained molybdenum plus freight from the mine.

Molybdenum powder is consolidated by powder metallurgy or by arc melting. Alloys can be produced by both methods but the arc-melted product gives better welding properties. Electron-beam welding is preferred but the result is still on the brittle side.

Molybdenum is available in most forms - sheet, rod, wire and tube. Liners for chemical tanks can be produced by joining sections by rivetting, followed by plasma spraying the joints with molybdenum.

The most common alloy is TZM containing 0.5 % Ti and 0.08 % Zr. This is usually produced by arc melting. If the application depends upon physical or chemical properties unalloyed molybdenum is used; if good mechanical properties are required TZM is used.

Molybdenum is resistant to molten glasses and fused salts as well as acids and alkalis and also liquid metals at high temperatures.

Molybdenum and its alloys have a multiplicity of uses in the electronics industry; also as electrodes in glass melting. Applications in aerospace and nuclear industries have been examined. TZM has found application in the die casting of aluminium- and copper-base alloys where it is used as cores and inserts. TZM is also being investigated as a material for power generation, including closed-cycle turbine power plants. There is an increasing use in the chemical industry. Molybdenum is also used in the construction of high-temperature furnaces for operation in hydrogen.

4.1.5.2 Tungsten

Highest melting point (3410°C) of the refractory metals. Very high strength at high temperatures. Main drawbacks are its poor oxidation resistance and lack of ductility at lower temperatures. It can be used at high temperatures in hydrogen or inert gas or in a vacuum. Good heat and electrical conductivity. Its high density (19.35 g/cm^3) is a disadvantage.

Tungsten minerals are widely distributed and relatively abundant. In 1970 reserves in the Western World were estimated to be 226,000 metric tonnes of tungsten contained. Reserves in U.S.S.R., China and North Korea were believed to be four times as much. In 1974 the Western World's consumption of tungsten ore was estimated to be 29 million kg of tungsten contained. The price of the ore varies with demand; in 1974 it was about 14.5 U.S. dollars per kg of tungsten contained and in 1975 it was 11 dollars.

The metal powder is consolidated by the powder metallurgy process. Solid metal may also be produced by arc and electron-beam melting but the ingots produced have large columnar grains unsuitable for working.

The metal is available in most forms - sheet, rod, wire, and it may also be hot spun to produce nozzles.

Tungsten is used for the production of lamp filaments, heating elements, X-ray anodes, welding electrodes and equipment for high-temperature furnaces. Aerospace applications have been investigated but the good high-temperature properties are marred by the lack of resistance to oxidation and also, to a certain extent, the high density. Alloying has failed to improve oxidation resistance. Protective coatings have achieved some improvement but none is completely satisfactory in providing resistance to oxidation, abrasion, alternative heat and cold and impact. Tungsten nozzles have been used for rocket motors, often in the form of porous sintered tungsten infiltrated with silver.

4.1.5.3 Tantalum

Melting point 2996°C. Combines excellent high-temperature strength, even above 1650°C, with excellent ductility below -200°C. Main disadvantage is its relatively low oxidation resistance at low temperatures. Unlike molybdenum and tungsten it absorbs oxygen at temperatures as low as 500°C with subsequent embrittlement. Its density is high at 16.6 g/cm^3.

Supplies of tantalum minerals are restricted, not nearly as abundant as niobium, molybdenum or tungsten. The ores are very expensive, as is the processing from the ore to the metal. The total amount of tantalum manufactured products in the major consuming countries was about 0.9 million kg in 1974. The price of tantalum concentrates in 1975 was about 59.5 U.S. dollars per kg of tantalum contained. At the same time tantalum powder sold for 77-99 U.S. dollars per kg. Once the trade recession is over the usage of tantalum is expected to increase by about 10 % per year and with no new sources of raw materials developing, and the gradual decline in production from existing sources, the price of concentrates will increase.

Tantalum powder was originally consolidated by the powder-metallurgy process but all metal is now produced by electron-beam melting. High-purity metal is produced by this process and scrap can also be recovered by the refining action of electron-beam melting. The metal is worked cold, any annealing which might be required being done at 1300 - 1400°C in a vacuum or inert gas.

Tantalum is available in most forms including sheet, rod, wire and tube. A recent development is the explosive cladding of tantalum on copper and on steel.

An outstanding property of tantalum is its complete resistance to some corrosive media, e.g. it is inert towards hydrochloric acid. This property results in tantalum being used in many chemical processes despite its high price. The largest application is for capacitors. Tantalum is also used for the production of parts for high-temperature furnaces.

4.1.5.4 Niobium

Niobium has a number of properties which make it suitable for high-temperature applications - high melting point (2470°C), low density (8,57 g/cm^3), good low-temperature ductility, excellent high-temperature strength. It also has properties of special interest for nuclear applications, viz. low thermal-neutron-capture cross-section (1.15 barns/atom) and good resistance to liquid-metal corrosion at moderate temperatures. Its low modulus of elasticity is a disadvantage. Resistance to oxidation is poor. Contamination by oxygen reduces ductility. It also adsorbs hydrogen. It can be used at high temperatures in a vacuum or inert gas atmosphere.

Supplies of niobium minerals are relatively abundant but processing to metal is expensive. The U.S. consumption of niobium in 1975 was nearly 2.5 million kg. The principle ore used is pyrochlore which sold in 1976 for about 5.5 U.S. dollars per kg of contained niobium.

Niobium like tantalum is readily electron-beam melted.

Alloying has improved its high-temperature strength and its oxidation resistance but not sufficiently as regards oxidation resistance. Attempts to protect the metal by coatings have not been entirely successful.

Niobium is a metal which has shown great promise both in the nuclear and high-temperature materials fields but never achieved anything lasting. Work on the possibility of using niobium for turbine blades has been going on for many years. The best performance achieved has been 100 hours at about 1400°C which falls far short of the objective. It is now considered useless for use in jet engines by all the large U.S. producers of gas turbines. One new but limited use which has passed development tests is for heat exchangers in chromic acid solution. One possible fairly large use could be in alloys for superconducting materials.

4.1.5.5 Rhenium

Melting point 3180°C, exceeded only by tungsten; density 20.53 g/cm^3.

Strength at high temperature greater than any other refractory metal up to 2000°C. Good room-temperature ductility in the recrystallised condition.Oxidation resistance is poor.

Use is restricted by supply limitations and high cost. The supply is variable as it depends upon recovery from the roasting of molybdenite produced as a by-product from copper ore. World output is normally about 4500 kg of metal per year, but as the usage of copper is down, so is the molybdenite from the copper mines and in 1975 the output of rhenium was only 2300 kg. The price of rhenium powder in 1975 was 1300 U.S. dollars per kg.

Rhenium powder is consolidated by powder metallurgy. The metal work hardens rapidly and requires annealing at high temperature in hydrogen. Annealing is required after about 5 % reduction. Rhenium-tungsten alloys are more readily worked.

The main applications for rhenium are bimetallic platinum-rhenium catalysts, and thermocouples. It is also used for X-ray tubes. About 80 % of the rhenium is used for catalysts.

4.1.5.6 Processing

Machining

Tungsten is difficult to machine. Use cemented carbide tools, Small holes (less than 3 mm) are made by spark machining.

Molybdenum machines as easily as cast iron but is much more abrasive. Use cemented carbide or high-speed steel tools.

Tantalum machines easily provided correct procedure is used. Cemented carbide tools must not be used - the tantalum tends to weld to the carbide. Use high-speed tools and a lubricant such as "Inhibsol" (I.C.I.). Carbon tetrachloride is satisfactory but not permissible because of its toxicity.

Niobium machines as tantalum.

Working

Tungsten	can be worked at about 200°C or above. It is brittle at about 150°C and below.
Molybdenum	works comparatively easily.
Tantalum	works easily and normally does not require annealing.
Niobium	as for tantalum.

Spinning.

Tungsten -spin hot but do not exceed 1000°C.

Molybdenum-spin hot but do not exceed 850°C - oxide formed acts as lubricant.

Tantalum -spin cold - use aluminium bronze tools to avoid sticking.

Niobium -as for tantalum.

The above comments were made by operators with many years experience.

Joining

Molybdenum and tungsten are weldable within certain limitations, i.e. the strength of the welds is low. Tantalum and niobium can be joined by several welding techniques, most simply by tungsten-arc inert-gas welding.

New welding techniques, in particular electron-beam welding, have been shown to be an improvement especially in welding molybdenum alloys, which behave significantly better than unalloyed Molybdenum.

Comparative prices for 0.75 mm refractory metal sheet.

Tantalum : 110 U.S. dollars per kg.
Tungsten : 57 U.S. dollars per kg.
Molybdenum: 38 U.S. dollars per kg.

4.1.5.7 Research and Development required.

On the basis of the aforementioned properties and of the state of the art of actual techniques of production and application, several areas of research and development can be defined, which may bring about a progressive improvement of refractory-metal technology.

Oxidation Protection:

The effective protection of molybdenum and tungsten against atmospheric influences has for long been the subject of numerous research efforts. Silicide diffusion coatings, one of the most promising, protects molybdenum for one hour at 1650°C and up to several hours at lower temperatures. Although the more widespread use of molybdenum and tungsten depends largely on an effective means of protection against oxidation at high temperatures, the chance of achieving success must be considered to be minimal.

Ductility and Plasticity.

One of the most important themes of research effort has been the problem of forming body-centred-cubic metals.

The hot working and shaping of molybdenum and tungsten is especially difficult because of their high melting points.

The causes of brittleness and susceptibility to cracking must be sought in the effect of dissolved or undissolved impurities precipitated at the grain boundaries, on the structure formation, the subgrain- and grainboundary structure and the structure adjacent to the grain boundary. The influence of interstitially dissolved elements such as oxygen, nitrogen or hydrogen on the ductility in the temperature ranges of interest is not yet understood, but working hypotheses are being discussed. The understanding about the effects of carbon is being further developed. Apart from these small-atom-radius elements, the effect of various other elements present as impurities in molybdenum and tungsten, but also in ductile tantalum, is not yet fully explained. The effect of the impurities is closely connected to the structure formation which, during processing, is influenced not only by the type of forming but also by the heat-treatment procedures followed (through recovery, recrystallization and continuous or discontinuous grain growth).

The ductility may be improved (resulting in a decrease of the brittle-ductile transition temperature and an increase in the degree of deformation) during the forming operations by combining the forming methods and extent of deformation with appropriate heat treatments in order to obtain optimal structures. Determination of the effect of impurities or alloy elements on the slip mechanisms and on the grain-boundary strength is of importance. Together with negative effects of most impurities, positive effects are also to be expected. Structure formation and impurities mutually influence each other.

It may be mentioned in this context, that problems of superplastic behaviour of high-melting-point alloys have not yet been solved completely.

Materials for very high-temperature applications.

Technical progress demands materials for application at higher and higher temperatures. Therefore the long-time rupture strength of the refractory metals becomes of particular importance. One way to achieve this objective is the development of new alloys based on the refractory metals; a second is the improvement of existing ones.

Knowledge concerning creep mechanisms indicates that it might be possible to improve the creep properties of the refractory metals by optimizing the structure and by the correct choice of alloy elements, thus increasing the slip resistance in the lattice or grain-boundary region.

Oxide or carbide dispersion-hardened alloys take a promising position, the temperature of interest in this context being above 1000°C.

Joining techniques.

In this field further improvements are to be expected as a result of systematic examination of the parameters of new welding processes. Moreover, improvements of the strength of the weld are to be expected in the light of the factors mentioned above in connection with ductility and plasticity.

Next to fusion welding, success has been achieved in diffusion bonding and friction welding of molybdenum and tungsten, but these techniques have dimensional restrictions.

Another joining technique, which has not yet reached the same level as for other metals, is brazing. As brazing materials the reactive metals are used as additions to those metals and alloys the melting point of which makes them suitable for high-temperature brazing. When joining molybdenum and tungsten with other metals, the main difficulties arise from the large differences in coefficients of thermal expansion. Technical difficulties result from the necessity to work under a vacuum or under a protective gas at high temperatures and from the dimensions of the parts to be joined.

Corrosion Behaviour:

In relation to the applications of refractory metals numerous investigations have been carried out out on corrosion behaviour, both at normal and at elevated temperatures. The resistance of tantalum against chemical attack is well known. For molybdenum and tungsten data on the behaviour under chemical attack, on resistance against metallic melts, and on corrosion losses in contact with liquid oxides and ceramics are of interest. Very little is known about the wear-behaviour of refractory metals in contact with plastics.

Liquid-phase sintered materials:

Tungsten-base alloys with binding elements such as nickel, iron, copper and silver and their alloys are commercial products, the systematic development of which will lead to the improvement of their properties. Principally, however, it is to be expected,that new alloys based on refractory metals can be developed by using classical foundry techniques, in the light of the growing knowledge of the influence of alloying elements on properties.

Coatings and composites.

New processing techniques make it possible, to an increasing degree, to combine the favourable properties of the refractory metals with those of other metals. Spraying techniques and other coating processes have already led to new commercially utilized products. The field of composite materials, especially fibre-reinforced materials using refractory metals as high-strength fibres, is in full development.

4.1.5.8 Appendix

While the above sections have been restricted to refractory metals with a melting point above 2000°C,it is of some interest to consider the high temperature possibilities of some other metals, viz chromium, vanadium, titanium and zirconium which have melting points below 2000°C.

Chromium:
Much research work has been done in investigating the possible use of chromium and its alloys for high-temperature applications. The relatively high melting point (about 1875°C), good oxidation resistance and low density (7.2 g/cm^3) make chromium a possibility for use at high temperatures. It has also good high-temperature strength and creep resistance. On the negative side are its poor low-temperature ductility and poor thermal-shock resistance, but the most serious drawback to the use of chromium-base alloys is the ready absorption of nitrogen with resulting embrittlement.

Vanadium:
Vanadium has a few attractive properties for high-temperature applications, e.g. its relatively high melting point (1900°C) and its low density (6.1 g/cm^3) combined with relatively high strength at intermediate temperatures up to 500°C only. Some vanadium alloys have good high-temperature strength but the use of the metal and its alloys for high-temperature work is limited by the low melting point (675°C) of its oxide V_2O_5. Attempts to raise this melting point by alloying have not been successful.

Titanium and Zirconium:
The melting points of titanium and zirconium are relatively low (1670°C and 1850°C respectively. The possibility of using titanium or zirconium at high temperatures is completely vitiated by the high reactivity of these metals when heated in air or oxygen, e.g. zirconium absorbs oxygen as low as 180°C and rapidly at 450°C. The protective film formed at lower temperatures dissolves in the metal at 450°C with resulting embrittlement. Titanium oxidises rapidly at 600°C and its use at temperatures much in excess of 400-500°C would depend upon the development of a suitable coating.

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4.1.6 Platinum-Group Metals

4.1.6.1 Ranges of Composition of the Major Groups

The platinum-group metals all have relatively high melting points, they do not tarnish or scale when heated in air to temperatures above 800 - 1000 °C and they lose weight only slowly (through volatilisation of their oxides) when heated in air at temperatures up to their melting points. Their limitations (apart from their cost) as materials of construction nearly all stem from the ease with which they alloy with other metals with which they may come in contact, with consequent degradation of their mechanical and corrosion-resistant characteristics.
The platinum metals and the alloys most commonly used for high-temperature service are listed in Table 4.1.6/1.

		Density g/cm^3	Melting Point °C (IPTS - 68)	Principal High-Temperature Applications
Pure Metals				
Heavy Group	Platinum	21.45	1772	Glass melting, furnace heating elements, thermocouples.
	Iridium	22.65	2447	Crucibles for crystal growing spark-plug elements.
	Osmium	22.61	3050	None
Light Group	Palladium	12.02	1554	Catalyst
	Rhodium	12.41	1963	Furnace-heating elements, crucibles for crystal growing
	Ruthenium	12.45	2310	None
Alloys	Platinum- 5% rhodium			
	Platinum- 10% rhodium			The most widely used alloy for high-temperature work. Furnace-heating elements, glass-fibre production, catalyst gauzes for the oxidation of ammonia.
	Platinum- 13% rhodium			Thermocouple alloy
	Platinum- 20% rhodium			Furnace-heating elements and thermo couples.
	Platinum- 30% rhodium			Furnace-heating elements and thermocouples.
	Platinum- 10% iridium			Thermocouple alloy
	Platinum- 10% ruthenium			
	Platinum- 10% rhodium - 30 or 40% palladium			A cheaper substitute alloy for temperatures not above 1250 °C.

Table 4.1.6/1 Properties and Applications of Platinum-group Metals and their Alloys.

In addition to the materials listed in Table 4.1.6/1, dispersion-strengthened materials are now available:
Dispersion-strengthened platinum (with about 0.1 wt-% (0.5 volume-%) of zirconia or thoria).
Dispersion-strengthened platinum 10% rhodium (with zirconia or thoria).
Finally, platinum coatings applied by electrodeposition from aqueous solutions or from a molten salt bath and followed by a pack-aluminising treatment are in course of development for protecting high-temperature alloy turbine blades from attack by sulphur compounds.

4.1.6.2 Availability and Cost

The outputs of primary platinum metals from the Western world in 1973 were approximately as follows:-
Total platinum metals -80.000 kg. Of this, about 62% was platinum, 25% palladium, and 13% was comprised of the other four metals.
The USSR probably produced approximately the same amounts. In the Western world there are two main sources of the platinum metals:

1. The platinum-containing ultra-basic deposits comprising the Merensky reef in the Transvaal, S.Africa.
2. The nickel-copper deposits in the Sudbury district of Canada.

In the operation of the nickel-copper deposits at Sudbury, the platinum metals are a by-product; their output is thus geared to the nickel production. At the present time the platinum metals derived from the Sudbury activities comprise about one third of the output of the Western world. The South African deposits, on the other hand, are worked first and foremost for their platinum metals; nickel, copper and cobalt being by-products. They comprise, moreover, the world's greatest potential source of platinum metals for the foreseeable future. The Rustenburg mines alone extend for thirty kilometers along the Merensky reef which is part of the Bushveld Igneous Complex. The reef is very extensive and its outcrops have been traced for 120 - 130 km along each of its eastern and western limbs, separated by 240 km or more.
In 1971 reserves of economically exploitable platinum were estimated to exceed 6 million kg and it was estimated that these could be recovered within 30 years. The reserves thus appear to be sufficient to provide platinum to the Western world at the current rate for well over 100 years. More recently, the U.S. geological survey have estimated reserves as 10 million kg and resources as 20 - 38 million kg.
It should be borne in mind moreover that beside the primary metals, a very large proportion of the platinum metals employed annually are recovered for re-use. Recovery is usually highly efficient and the high value of scrap ensures that every effort is made to segregate and preserve it for treatment. There is thus a continued increase in the amounts of the platinum metals in circulation.
Costs of the metals from the major producers fluctuate less than those of most non-ferrous metals, as illustrated by the average figures for the last 25 years given in Table 4.1.6/2.

	U.S. dollars / kg.					
	Pt	Pd	Rh	Ir	Os	Ru
Jan 1976	5140	2570	9650	16.100	6430	1930
Average 1973	4820	2480	7140	7140	6430	1900
„ 1970	4180	1160	6750	4820	6430	1770
„ 1965	2890	965	5145	2730	6120	1770
„ 1951	2990	772	4020	6430	6430	2990

Table 4.1.6/2 Average costs of Platinum-group Metals since 1951.

4.1.6.3 Forms available

Platinum and palladium and their industrial alloys are nearly always produced in the form of wrought sheet, bar, rod or wire. The maximum weight of the ingot (usually cast) from which these are formed seldom exceeds 22.5 kg; larger ingots could probably be produced if the demand arose. Ingots have also been made by powder metallurgy and subsequently consolidated by hot forging or rolling; all the platinum metals are produced in the first place in the form of powder.

Finished castings are not normally produced; but small parts have been cast experimentally by centrifugal casting. At present there is no demand for these but there are no technical reasons why they should not be produced if the demand arose.

Rhodium is produced as hot-formed sheet, rod and wire of all sizes.

Iridium also is produced as hot-formed sheet, rod and wire; but wire is seldom produced in sizes smaller than about 0.025 mm diameter.

Ruthenium is available as hot-rolled sheet; and in the form of small spheres made by melting or by powder metallurgy for tipping fountain pen nibs.

Osmium is available only as powder or small melted ingots.

4.1.6.4 Workability and Machinability

Workability

Platinum can be readily worked hot or cold. For hot-working it is commonly heated in air to 1000 - 1200°C; and afterwards is preferably overhauled and then pickled to remove surface contamination such as iron which may have been picked up from the forging anvils or rolls. During cold working the response of platinum may be described as loosely similar to that of copper, though it does not harden quite as rapidly. The hardness of annealed platinum is about 45 - 55 HV and this increases to about 105 after 60% reduction and to about 120 after 80% reduction.

Palladium deforms rather less readily than platinum but otherwise closely resembles it in its response to hot (at 1000 - 1200°C)or cold working. If quenched from above about 850°C after hot working its surfaces remain bright. If cooled slowly in air a dark coloured tarnish film forms on the surface.

Cast rhodium cannot be cold-worked, but above 1300°C the metal is malleable and after the columnar cast structure has been broken down by forging can be hot-rolled or swaged. It must be quenched from above 1400°C if it is to be retained free from tarnish. After hot-working it can be further reduced by cold-rolling, swageing, or wire-drawing but frequent annealing (at about 1000°C and usually in hydrogen) is necessary.

Iridium, either cast or as powder-metallurgy compacts, can be hot-forged like rhodium but with greater difficulty. Ductility is improved and the possibility of cracking is greatly reduced if the metal is first sheathed in platinum or nickel. The coatings can subsequently be removed by pickling in aqua regia or (for nickel) in hydrochloric acid. Afterwards, further reduction by rolling, swaging, or wire drawing can be carried out at about 700°C to 1000°C. Very little reduction by cold working is, however, possible. Iridium to which a fibrous structure and a measure of ductility has been imparted by working is embrittled if it is recrystallised by heating to above about 1000°C.

Ruthenium can be hot forged only by small amounts and with very great difficulty at high temperatures (above 1500°C). The operation is facilitated by prior cladding with platinum, nickel, or stainless steel and can then be carried out below 1500°C.

Osmium is completely unworkable.

The alloys of platinum with up to about 40% of rhodium, 30% of iridium, or 10% of ruthenium, which comprise those of chief industrial use, can all be worked by the same general methods as are used for platinum, making allowance for their greater stiffness and hardness. In general, they need to be quenched to prevent tarnishing by the oxide films of the alloying metals.

Machinability

Platinum, palladium and their chief industrial alloys may all be machined using carbon or high-speed alloy steels or by cemented carbides. They cannot, however, be machined by diamond-tipped tools. Reaction between platinum metals and diamond causes rapid wear and blunting of the diamond cutting edges.

4.1.6.5 Joining

The platinum metals and alloys can all be readily joined by fusion welding, using hydrogen torch, plasma torch, or arc-welding methods. They can be resistance welded or spot welded. No flux is necessary or desirable. In general, welding is a straightforward operation with few problems. Palladium is perhaps the most difficult to handle by gas welding since hydrogen may be absorbed and then may react with oxygen - especially if any impurities are present. Argon shielding is beneficial here. All the metals and alloys can also be soldered, using gold as a solder.

4.1.6.6 Mechanical Properties - Availability of Data

The mechanical properties of the platinum metals and most of their important alloys at room and elevated temperatures are well summarised in reference (1).
Good reviews are also provided by A.S. Darling (2) and by O. Loebich (3).
The mechanical properties of dispersion-hardened platinum have been described by G.L. Selman et al (4).
The properties of dispersion-hardened platinum-rhodium alloys have recently been published by Selman and Bourne (5).

4.1.6.7 Corrosion Properties - Availability of Data

The resistance of the platinum metals to chemical corrosion by a wide range of reagents is summarised in the Edelmetall-Taschenbuch (1), and in references (6) and (7).
A form of corrosion to which all platinum metals are susceptible when operating in air at high temperatures is oxidation. The loss through formation of volatile oxides is small but may need to be taken into account. An appreciation of the problems involved has recently been published by J.C. Chaston (8) and a discussion of the data, with a full bibliography is also available (2)

4.1.6.8 Physical Properties - Availability of Data

Ample and authoritative data on physical properties are available from many sources. Here again very convenient reference compendia are references (1) and (3).

4.1.6.9 Shortcomings and Outstanding Problems

Apart from cost, the most serious shortcoming of the platinum metals is their susceptibility to contamination. The most troublesome and insidious contaminant is silicon. Traces of silicon are readily reduced by the platinum metals from silica and silica-bearing materials such as refractories if the surroundings become - even momentarily - reducing in character. Even small quantities of platinum-silicide can form intergranular films of low-melting platinum - platinum-silicide eutectic with catastrophic results.
Another shortcoming is the ease with which other metals diffuse through platinum. This severely limits the effectiveness of platinum sheaths or coatings from acting to protect underlying metals from oxidation. For instance, platinum coatings have been found ineffective in protecting nickel-base alloy turbine blades from sulphur attack; though as mentioned elsewhere, coatings of intermetallic platinum compounds have recently been developed and show much promise.
In glass-melting equipment, such items as platinum-sheathed molybdenum stirrers have suffered in the past through alloying between the two metals; means of using refractory diffusion

barrier layers are, however, being developed.

4.1.6.10 Current Research

The chief centres of research in Europe on the properties of the platinum metals are:

1. Forschunginstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd, near Stuttgart. This institute, formerly under the direction of Prof. Dr. Phil. Ernst Raub and now of his son Dr. Ch. Raub is supported partly by contributions from the industry and partly by the State. It is particularly concerned with more fundamental problems.
2. The research laboratories of the main platinum producers including those of
   Johnson Matthey & Co. Ltd., Sonning Common, Berkshire, England.
   Engelhard Industries Ltd., London, England.
   International Nickel Ltd., Birmingham, England.
   Degussa, Frankfurt am Main, Germany.

Current research that has been published includes work on improved coatings of platinum intermetallic compounds to protect nickel-chromium base alloys from sulphur attack at high temperatures, the development of dispersion-strengthened platinum-base alloys for high-temperature applications, and investigations on techniques for joining dispersion-hardened platinum-base materials without local softening.
Other research activities are concerned with the development of platinum catalyst units for controlling the composition of exhausts from motor car engines and of palladium alloy membranes for hydrogen-diffusion cells.

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4.2 CERAMICS

By ceramic materials we mean all inorganic non-metallic solids which are characterised by covalent and ionic bonding. Historically, the ceramic industries grew by progressive extension of simple activities such as firing clays or oxide powders to transform them into hard solids.

A particular impetus to progress in the ceramics field has been the ever-increasing demand for materials to contain gases, burning fuels, molten metals, glasses, etc., and other high-temperature materials under progressively more arduous conditions. More recently further impetus has come from the aerospace, nuclear, and electronics fields where a need for even more demanding and sophisticated property combinations has had to be fulfilled. In some way, ceramic technology can be considered to have "come of age" very recently as a result of these new stimuli, and can now offer a very wide range of fabrication techniques and property combinations suitable for new areas of application in transport, energy conversion, pollution control, etc.

4.2.1 Ranges of Compositions of Major Groups

The more important commercial ceramic materials can be divided into groups according to their chemical composition.

4.2.1.1 Oxides

The oxides often have a higher melting temperature than the metal from which they are derived but are usually less refractory than the corresponding nitrides and carbides. The cheapness and availability of oxides, as well as their stability when heated in air or an oxidising environment, accounts for their widespread use in high-temperature processes. In fact for the purposes of the present report they are often too cheap, since they constitute traditional tonnage refractories in many cases: e.g. fire bricks, alumina, silica and dolomite bricks, etc. Further steady progress can be expected in the performance of such materials, but this will best be carried out by suppliers and users with a large degree of experience and investment in the field.

The concept of special oxide ceramics suggests rather more expensive high-performance ceramics such as recrystallised alumina, stabilised zirconia, etc. It is in this area that application of new scientific knowledge can perhaps first be expected to show positive results.

Single oxides.

The major single oxides of interest for high temperature applications include alumina, magnesia, zirconia and beryllia. Alumina is very strong compared to most of the other oxides. This fact, along with economic considerations, seem certain to ensure the continued dominance of alumina in a wide range of industrial applications e.g. thermocouple sheaths, furnace supports, crucibles, etc. Zirconia is often preferred at high temperatures where alumina starts to lose strength, e.g.

> 1300°C. The other uses of zirconia can be explained by peculiar chemical requirements, such as reactivity of alumina with various environments, or the need for high-temperature electrical conductivity. Beryllia is extremely toxic, and so is seldom used. Magnesia is weaker than alumina but may be preferred where its higher chemical stability is important, e.g. handling reactive molten metals, special gases etc.

All the simple oxide ceramics except silica have high thermal expansion coefficients. Thus failures in high-temperature use are often linked to thermal shock or thermal stress. However, this limitation is fundamental and improved thermal-shock resistance normally corresponds to increased strength.

Urania and thoria are dense, expensive and radioactive and are therefore seldom used. Silica finds some use as vitreous silica which has high strength up to 1000°C and a very low expansion coefficient. However, for sintered crystallised silica, the mechanical weakening caused by phase transformations limits its use as a high strength ceramic. Chromic oxide, Cr_2O_3, and stannic oxide, SnO_2, are limited in use by vaporisation problems and high cost.

Most commercial single oxide ceramics, such as alumina, magnesia and zirconia, do in fact contain significant amounts of other oxides which may be present as accidental impurities, as a sintering aid to facilitate fabrication, or as a stabilising entity (e.g. the prevention of excessive grain growth in certain commercial aluminas, (MgO, TiO_2) and the stabilisation of the high-temperature cubic phase of zirconia (CaO, Y_2O_3)).

The effects of impurities and residual porosity on high-temperature properties such as creep strength and electrical and thermal conductivity are difficult to summarise briefly.

Oxides which have been under-estimated and under-used in the past include the rare-earth oxides. The price of these materials is much lower than is generally appreciated, e.g. $ 8 per kilogram for ceria and lanthana, and should continue to fall relative to other oxides as the rare-earth industry gathers momentum. Similarly strontium oxide, SrO, has only recently been produced industrially at low prices and merits further study.

Mixed oxides.

The effect of mixing two or more oxides together is almost always to decrease the melting point as compared to the mean of the pure oxides. Nevertheless, for reasons of improved performance, fabrication or economics, the use of mixed oxide ceramics is often worthwhile. Many mixed oxides are found in a reasonably pure form as natural minerals, e.g. $ZrO_2.SiO_2$ - zircon, $3Al_2O_3.2SiO_2$ - mullite, $CaOSiO_2$ - wollastonite.

A very important property of these materials, the thermal-shock resistance, is inversely proportional to the thermal expansion coefficient. At 300°C four mixed oxides have low values for their expansion coefficients; they are mullite $3Al_2O_3.2SiO_2$, zircon $ZrO_2.SiO_2$, cordierite $2MgO.2Al_2O_3.5SiO_2$, and tialite α-Al$_2$O$_3$.TiO$_2$. The strength of magnesia spinel MgO.Al$_2$O$_3$ is found to be outstanding as compared to other mixed oxides at room temperature and approaches half that of alumina. Mullite and zircon show reasonable strength which, combined with their low expansion coefficient, renders them more useful in general than magnesia spinel.

Cordierite, 2MgO.2Al$_2$O$_3$.5SiO$_2$, is also known as a sintered ceramic, but is more widely known as a glass ceramic with highly desirable properties and is discussed in detail below.

Tialite would be an extremely desirable sintered ceramic for heat exchangers, etc., if the problem of weakening due to phase transformations around 1000°C could be avoided. Promising work on compositon modifications to avoid this problem has recently been reported (1).

Some mixed oxides, such as chrome magnesite, are used as tonnage refractories for lining oxygen steelmaking vessels, etc.

Special mixed oxide refractories, such as zirconia-alumina-silica mixtures, are made by fusion casting, and find widespread application in the glass melting and metallurgical industries. This area of ceramic technology has problems not unfamiliar to specialists involved in the casting of metals, and could perhaps benefit from further research: firstly to resolve these problems, and secondly to suggest how the technology may be expanded for use on other special ceramics and refractories.

Glass ceramics.

Commercially important glass ceramics contain lithium aluminosilicate phases such as β-spodumene, LiAlSi$_4$O$_{12}$, or magnesium aluminosilicates such as cordierite, 2MgO.2Al$_2$O$_3$.5SiO$_2$. The change in dimensions on crystallisation is small and predictable, so that better control over the finished shape is obtained. The lack of porosity, the high surface smoothness and the fineness of the crystals obtained give high strength materials: for example, cordierite glass ceramics show bend strengths of 500 N/mm^2. The low thermal expansion coefficient of these materials ensures high resistance to thermal shock. Their resistance to creep deformation at temperatures above 1000°C is not high in the case of glass ceramics based on lithium aluminosilicates, but is significant for those based on the magnesium aluminosilicates. The detailed creep behaviour is extremely sensitive to the presence of impurities and the details of the heat treatment cycle (2). Work continues in this area although it seems unlikely that materials superior to silicon nitride or silicon carbide will be produced for use at temperatures above 1100°C.

4.2.1.2 Nitride Ceramics

Nitrides are clearly less common and more difficult to synthesise and fabricate than oxides, but their somewhat higher temperature limits and the unusual properties of a few of these phases have raised a certain amount of scientific and industrial interest. The resistance to oxidation of nitrides is, as expected, much less than that of the oxides, and in fact the three nitrides discussed in detail below owe their oxidation resistance to the other element in the compound. This oxidises to form a more or less stable oxide layer, thereby slowing down further oxygen penetration.

Boron nitride, BN, in the stable hexagonal phase should not be confused with General Electric's high-pressure high-hardness cubic modification. The hexagonal form has an unusual combination of properties: like graphite it is of low hardness, high anisotropy, low average elastic modulus and is easily machined.

Aluminium nitride, AlN, is stronger than boron nitride but this is only true of material approaching theoretical density. Recent work (3) has shown how high density can be obtained by a sintering process, thereby avoiding the extra cost of hot pressing. It consists of adding small quantities of nickel, cobalt or iron powders to the AlN powder.

Silicon nitride, Si_3N_4, was for a long time considered an interesting but badly characterised and awkward ceramic material. It was badly characterised in that the crystal structure was difficult to pin down and the transformation between the α and β modifications not understood.

Reaction-bonded silicon nitride usually contains residual silicon, and hot-pressed silicon nitride contains either magnesia or yttria as an aid to densification which tend to form glassy silicate phases at the grain boundaries.

In 1972 it was reported that β-silicon nitride could be synthesised with a large proportion (up to 60%) of alumina in solid solution. The general name for these materials is 'sialon'. Solid solutions containing magnesia, lithia, beryllia or lanthana are also known and under investigation.

4.2.1.3 Carbide Ceramics

From the point of view of solid refractory bodies, silicon carbide, SiC, is by far the most important of the carbides. However, other useful ceramics have been made from boron carbide, B_4C, and chromium carbide, Cr_7C_3, respectively by sintering or hot pressing. Uses for these materials include crucibles, abrasion-resistant shapes, and nuclear shields in the case of boron carbide. The oxidation resistance of most carbides is much less than that of silicon carbide, and it is this weakness which has discouraged further development of carbide ceramics.

The composition of silicon carbide bodies depends upon the details of the fabrication process. At least six methods of fabrication are known. The impurities present in each case include; a silicate phase in clay-bonded bricks, silicon nitride in the material produced in the nitriding-bonding process, residual silicon or graphite in self-bonded materials, alumina and other densification aids in hot-pressed materials, and finally boron in the material made by pressure-less sintering of fine powders.

4.2.1.4 Boride Ceramics

Borides possess some metallic properties and show surprisingly good oxidation resistance up to temperatures within the range 1200 - 1400°C. However, full use of their high strength at high temperature can only be obtained in protective atmospheres.
Although some carbides and borides decompose, most of them show sufficient lack of volatility that they can be used as refractory materials in vacuum up to 2500°C. Fabrication methods include sintering, hot pressing and chemical vapour deposition. Often the boride bodies made by powder-metallurgy techniques show a mixture of boride phases.

The commercially significant borides include zirconium diboride, ZrB_2, and titanium diboride, TiB_2. Dense bodies of these materials can, so far, only be made by hot pressing or chemical vapour deposition, consequently components of these materials are limited in shape and are also expensive.

4.2.1.5 Silicides and other industrially important Ceramics

The oxidation resistance of dense refractory-metal silicides is good, being outstanding in the case of molybdenum disilicide up to 1700°C. Decreasing oxidation resistance has been observed in approximately the following order: $MoSi_2$, WSi_2, $TiSi_2$, VSi_2, $ZrSi_2$, $ThSi_2$, $NbSi_2$, $TaSi_2$, $CrSi_2$ (5). It is believed that the relative volatility of MoO_3 aids in the formation of a stable protective layer on molybdenum disilicide bodies.

Molybdenum disilicide finds widespread use as electric heating elements for use up to 1800°C in air. Kanthal, Superkanthal and Mosilit are some of the trade names. Sulphide and halide ceramic bodies have been prepared. For example, several rare-earth sulphides were examined for compatibility with molten uranium or plutonium. Such materials are, however, not yet commercial in the strict sense of the term.

4.2.1.6 Graphite and Carbon

Graphite and carbons with a wide range of properties can be prepared from various carbon sources (solids, liquids and gases). This variation is to a great extent the result of variation in the carbon crystallite size and orientation, which are obtained by controlling the carbonization itself and by selecting a suitable organic precursor. Carbon technology distinguishes between two major routes of carbonization:

- the low-temperature route, which is mostly applied to solids and liquids and
- the high-temperature route where a gas is cracked.

On the low-temperature route, precursors such as petroleum or pitch are carbonized to highly oriented coke used for the manufacture of graphite electrodes or to produce isotropic fine-grain nuclear graphites. The difference of the properties is obtained by controlling an important phase of the liquid-phase pyrolysis, the so-called mesophase. Using as starting material thermosetting resins, disordered carbons are obtained, commonly called glassy carbons or vitreous carbons, which are impermeable to gases and liquids. The strength is higher than for electrode graphite. Its oxidation rate in air is lower because of its very small surface area and its high purity. Applying appropriate heat treatment the same precursors can be used to produce molecular sieve carbons tailored for size distributions.

Among the carbons produced via the high-temperature route, the area of pyrolytic carbons has made the most progress. Pyrolytic carbons are obtained by the pyrolysis of gases and are deposited on various substrates or in the form of massive shapes. The range of properties and its isotropy is very wide, e.g. the density can range from about 1.4 gm/cm^3 up to almost the theoretical density of the graphite crystal of 2.25 gm/cm^3, consequently controlling the other properties, e.g. strength.

Carbons find a wide field of application from nuclear fuel-particle coating to retain fission products at high temperatures, to the area of biomaterials where they are some of the best materials available.

4.2.1.7 Ceramic fibres

Ceramic fibres form a very important group of materials. It is worthwhile discussing the less expensive fibres here in a separate section in view of the similarities in their methods of production and their applications.

Apart from the natural crystotile ceramic fibres, some of the earliest ceramic fibres were obtained accidently by blowing a jet of air onto molten slag. Based on this, products such as slag-wool and "kaowool" derived from molten clay were produced cheaply and in large quantities. These materials being partially vitreous have a tendency to devitrify and degrade above 1000°C. They do however find widespread use as insulation materials up to this limiting temperature. Average aluminosilicate fibre diameters of 3 micrometers and fibre lengths between 1cm and 25 cm are obtained by this kind of technology (6).

Improved aluminosilicate fibres containing chromic oxide have been developed and are now commercially the limiting stable temperature of use in this case approaches 1400°C. Oxidising and reducing atmospheres pose no problem for these materials.

Silica fibres have a useful maximum temperature of approximately 1200°C and are readily available in textile form.

New ceramic fibres announced in the last two years include ICI's "Saffil" fibres (7) which are essentially pure alumina and zirconia. The fabrication process is not yet published. The fibres are purer, more refractory and more uniform in diameter than aluminosilicate fibres. Continuous use temperatures of 1400°C are claimed for the alumina fibre and 1600°C for the zirconia fibre.

Cheaper carbon fibres derived from pitch are now commercially available and should find uses in high-temperature systems.

The market for ceramic fibres has shown substantial growth and is likely to continue to do so in view of the lightness, flexibility and cheapness of the materials available.

4.2.2 Availability of raw materials and costs.

Oxide-based ceramics are usually derived from raw materials extracted directly from the earth's crust and subjected to comminution and chemical purification processes. They are, therefore, usually widely distributed geographically and supply problems do not exist except in isolated cases, e.g. chromic oxide, major reserves being in Rhodesia, and zircon, reserves in China and Brazil. General information on prices, availability and geographical distribution can be obtained for example in the form of "Roskill Reports on Metals and Minerals" from Roskill Information Services, London.

Mixed oxide ceramics are usually cheaper than single oxide ceramics, e.g. stabilised zirconia is approximately 30 times more expensive than zircon sand, $ZrO_2.SiO_2$.

Nitride, carbide, boride, etc. ceramics usually require metal or semi-metal powders (e.g. Si,Al,B,Ti) as starting materials. Therefore, distribution and resource problems do not exist to the same extent. The prices are in fact much more dependent upon the chemical industry. Prices increase sharply as the purity and reproducibility of these powders increase. Figures quoted also vary markedly with the quantity of material purchased.

The raw materials for the high strength ceramics silicon nitride and silicon carbide are relatively inexpensive compared to those used in superalloys. Price differentials of between ten and thirty times have been quoted, depending upon the particular composition of the superalloy considered. Estimates of the cost of high-temperature ceramic components when produced in large quantities are very difficult to make at the present time due to the rapid developments occurring in fabrication technology.

4.2.3 Forms available

Figure 4.2/1 relates the kinds of ceramics outlined in Section 4.2.1 to the fabrication processes which can, at the present time, be used for each of them. The kinds of shape limitations which exist for each fabrication process are listed in turn. More comprehensive data relating to dimensional limits of components, as well as the temperatures, pressures and production rate appropriate to each material/process combination are not readily available. In some cases, however, they can be obtained through contact with manufacturers and a thorough literature search. The advantages and disadvantages of the various processes can be listed briefly as follows:
Sintering close to theoretical density is usually possible with oxides but often poses problems for non-oxide ceramics. For example, great excitement was generated by the recent discoveries that β-Si_3N_4-Al_2O_3 solid solutions can be sintered and also that fine powders of silicon carbide doped with boron can be sintered. These developments open up the possibility of manufacturing high-strength silicon nitride and silicon carbide ceramic bodies cheaply. Traditional shaping techniques such as slip casting, cold pressing, extrusion, etc. can be used.

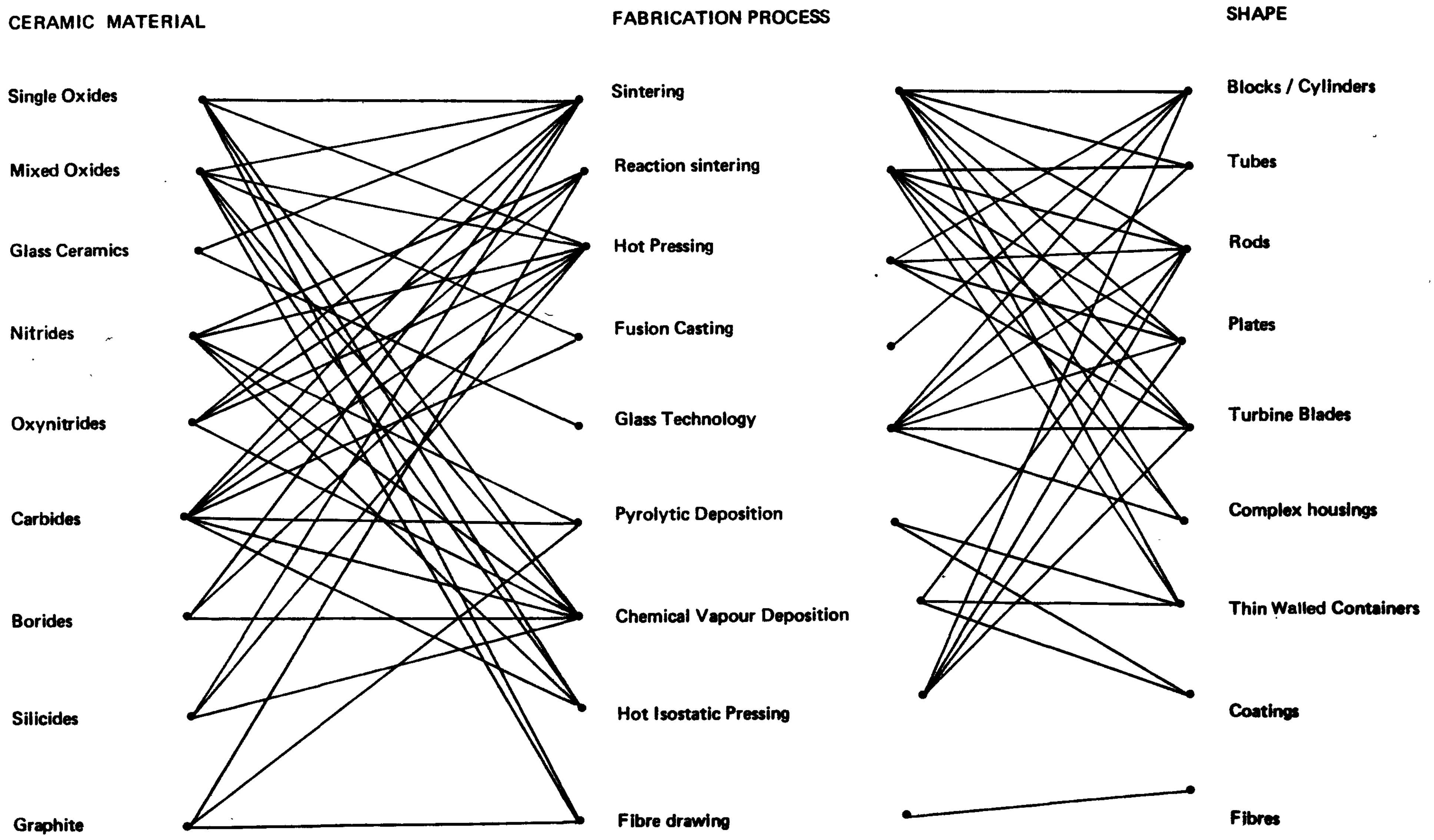

Fig. 4.2/1 Availability of Shapes of Ceramic Materials.

The disadvantages of the sintering process include slowness, poor surface finish and the difficulty of obtaining accurate dimensions. For alumina bodies, for example, a 15-20% volume shrinkage occurs. This shrinkage can only be predicted accurately enough to give dimensional tolerance of ± 2% or ± 200μm whichever is the greater. Component size limitations depend markedly on the composition. For alumina, for example, difficulties are experienced in firing solid cylinders greater than 20 cm outer diameter x 20 cm long. Additions are used to prevent excessive grain growth during the firing of certain oxide ceramics.

Reaction sintering is applicable to some commercial non-oxide ceramics such as silicon nitride and silicon carbide. The major advantages include machinability of the pre-reacted shape and negligible dimensional change during reaction (in the case of the silicon to silicon nitride process for example). The exothermic nature of the reactions usually means that uniformity of properties within a body is not obtained. If the process is tried on components with very thick sections (e.g. > 5 cm for Si_3N_4) then fusion of the silicon in the central region can result, with consequent deterioration in properties.

Hot pressing requires large capital investment and is a difficult, discontinuous process. Die wear is an universal problem for hot-pressing processes. The resulting materials tend, therefore, to be very expensive compared to the sintered equivalent. The process is also limited to simple shapes and usually to rather modest dimensions. Norton in the U.S.A. are however equipped to produce large flat sheets of hot-pressed ceramic. The advantages of the process include its relatively high speed and also the high density, and therefore high strength, of the resulting product. Densification aids may still be necessary during the hot pressing of some ceramics, e.g. MgO or Y_2O_3 in Si_3N_4, Al_2O_3 in SiC, etc.

Fusion casting is only known commercially for some special mixed-oxide refractories. It has also been mentioned in connection with carbide and carbonitride components for the production of components to withstand very high temperatures for rocketry, etc. The main disadvantages are the extremely high temperatures necessary to fuse the materials (arc furnaces are usually used). The casting of these materials also poses special problems akin to those found in a metallurgical foundry but accentuated by the high temperature. The elimination of cracks due to thermal stresses which occur during cooling is a major consideration. Very dense refractory blocks offering the advantage of long furnace life are however obtained.

Glass technology is in general very rapid and highly automated. It is therefore ideal for producing large numbers of relatively inexpensive components. The number of crystallisible oxide glasses which also show good high-temperature strength properties is very limited.

Pyrolytic deposition is the formation of layers by the decomposition of a carbon-containing compound. The process is well known within the nuclear industry and can produce very strong dense layers of silicon carbide or carbon. It is also used in producing silicon carbide rods or fibres by continuous deposition on to tungsten substrates. Anisotropy of the properties of layers so produced is generally obtained. The technique is slow and rather expensive.

Chemical vapour deposition is applicable to nearly all ceramic materials. The various processes of CVD all involve the controlled precipitation of a solid from its vapour phase through a thermally activated chemical reaction. The method is flexible and thin layers can be obtained quite rapidly. Obtaining uniform layers on large or complex components can present problems.

Hot isostatic pressing is a relatively recent development and involves heavy capital investment. It can, however, be used to ensure the absence of residual porosity in components made by other fabrication techniques. 200 kg batches of components having complex shapes can be treated at one time.

Fibre drawing can be either continuous or discontinuous. In the latter case the product is usually used in matt form for filters, insulation panels, etc. The continuous fibres and the textile products which can be made from them tend to be more expensive. Carbon fibres are a well publicised example of a ceramic fibre material which is expensive due to the very sophisticated processing technology. The newer oxide fibres are also made by sophisticated chemical technology and so are also rather expensive.

4.2.4 Workability and Machinability

The equivalent in ceramics technology of the forging, rolling and extrusion processes for metals are not available except for some prefired 'green' compacts. Most high-temperature ceramics are also materials of high hardness. Consequently, the machining and polishing of these materials in the as-fired state poses problems.

Diamond grinding of the hot-pressed or sintered components is widely practised where high accuracy of the finished dimensions is required. This is obviously a very expensive finishing process. It is for this reason that every effort is made to ensure a high quality surface finish and dimensional accuracy during the primary manufacturing processes.

Reaction sintering of silicon to silicon nitride does have the advantage of allowing the preform to be machined close to the final dimensions while still relatively soft (i.e. silicon metal instead of Si_3N_4).

Laser machining of ceramics is being seriously evaluated for cutting and drilling operations. High tolerances can be obtained but the technology is, as yet, very expensive.

For electrically-conducting ceramics such as the carbides and borides spark machining is a possibility. The tool wear and the finish on the resulting surfaces do, however, pose problems. Ceramics which can be machined by normal metal working tools are known. They include graphite, hexagonal boron nitride and a new mica-based glass ceramic developed by Corning.

These materials have in common the presence of plate-like crystals of very low shear strength.

4.2.5 Joining

Traditional ceramics, e.g. bricks and tiles, are joined by either simple 'juxtaposition' or some form of mortar. In the electronics industry the problems associated with metallising alumina ceramics, making glass-to-metal or glass-to-ceramic seals have been solved using a variety of techniques. However, high-strength ceramics for use in complex high-temperature engines and plant will entail even more demanding requirements.

Mechanical joints such as dovetail joints are one range of possibilities which either have been or are being tested. The avoidance of localised stress build-up is the major problem. Flexible interface materials within the joint, such as ceramic fibre mats, porous metals and thin metal sheets, are currently being evaluated (8) for a spin test involving a gas-turbine wheel with a superalloy disc and hot-pressed silicon nitride blades. Other mechanical coupling techniques for joining ceramic turbine rotor materials to metallic shafts include curvic coupling, conical mounts and taper coupling.

An alternative approach (9) to joining both silicon nitride and silicon carbide components uses complex brazing alloys of silicon/chromium or silicon/titanium with additions of up to 10% of either nickel or germanium. They rely for their success on reacting with the free silicon present in both silicon carbide and silicon nitride.

The transfer of the technology of glass-to-metal and glass-to-ceramic (e.g. Al_2O_3) seals to high-temperature ceramic materials such as silicon carbide and silicon nitride will require extensive development work. The difficult problem of finding glazes for silicon nitride has now been solved. It should therefore be possible to develop refractory crystallisable solders to join these ceramics to each other or to superalloys. Multiple layers which provide expansion-coefficient gradients will be needed in some cases to minimise the risk of failure due to mismatch stresses.

4.2.6 Mechanical properties of ceramics - Availability of data.

The data on the properties of ceramics from various sources, often show a large difference due to the fact that the influence of the fabrication technology on the microstructure is not yet fully understood. However, complications of general data, including both mechanical and physical properties of ceramics, are available (23) A revision of this book has just been announced which will be much more comprehensive and will comprise several volumes entitled "Engineering Property Data on Selected Ceramics". The first volume on "Nitrides" is now available from the Metals and Ceramics Information Centre, Columbus, Ohio. Subsequent volumes will be devoted to borides, carbides, oxides, silicides and sulphides.

Information on the short-time ambient and high-temperature strengths of some of the more common high-strength ceramics can be obtained from published articles and manufacturers' data. The latter, however, usually quote average strengths and only recently have Weibull moduli describing the strength distribution been included. The recent call (10) for strength-probability- time data plots where static fatigue effects are taken into account has yet to be followed up by the manufacturers. It is hoped that eventually proof testing will enable guaranteed minimum service life to be quoted for high-temperature ceramic components. Data on long-term strength, i.e. creep and static fatigue are now available (11) for a range of high-temperature ceramics including silicon nitride, silicon carbide and Sialons. Fig. 4.2/2 illustrates the bend strength of selected materials in relation to temperature.

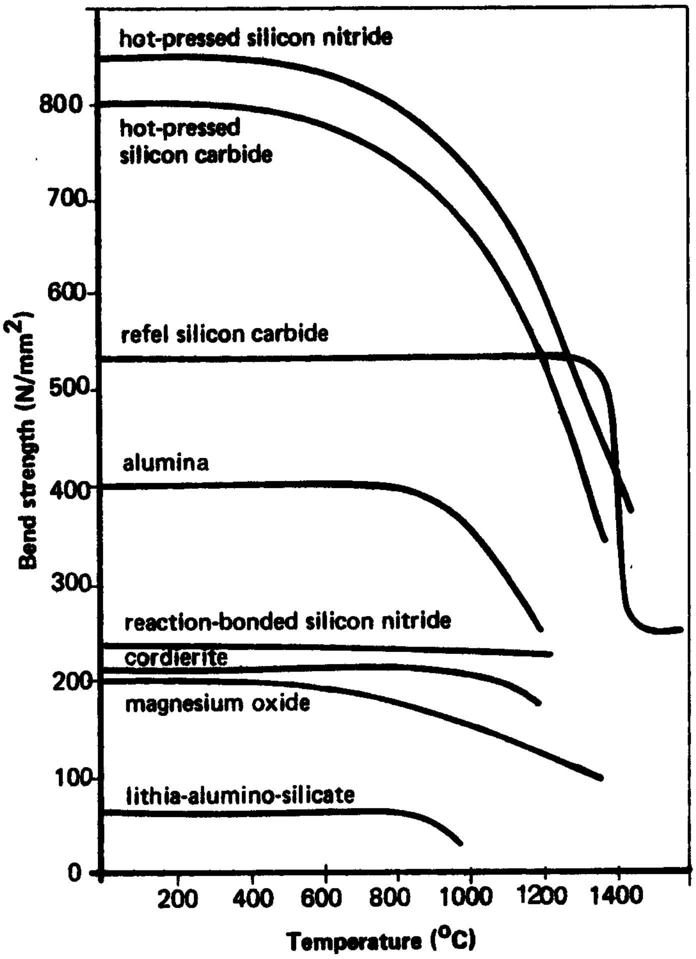

Fig. 4.2/2 *Temperature dependence of bend strength for selected engineering ceramics*

Data on impact and thermal-shock resistance are available in scattered publications and also from manufacturers' data in some cases.

Impact strength of ceramics is very low compared with that of metallic materials but the improvement which results from fibre reinforcement is very significant.

The thermal-shock resistance of ceramics is generally poor and calculations of a thermal-shock parameter,

$$R = \frac{\sigma_{max} K}{\alpha \; G}$$

where R is the thermal-shock resistance in units of temperature,
σ max the strength,
α the thermal expansion coefficient,
G the elastic modulus,
K the thermal conductivity,
from the basic physical properties have been published (17). The relatively poor performance of the oxides at high temperatures is emphasised.

Data on fatigue strength under both high- and low-cycle conditions are very scarce for high-strength ceramics. Similarly wear resistance data under representative operating conditions are very limited.

A very valuable survey of the mechanical properties of silicon and silicon nitride ceramics was published (18) in 1975 covering 171 references. The areas where further testing is required can be estimated from this review article.

Well indexed abstracts of publications in the general area of mechanical properties of both metallic and non-metallic materials are now available in a new series entitled "Mechanical Properties" (29).

4.2.7 Corrosion properties - availability of data

An acceptable level of corrosion resistance for high-temperature materials has been somewhat arbitrarily defined (19) as a weight increase of 0.2 mg cm^{-2}h^{-1}. Graphite and many metals show a decrease in weight on oxidation. Pyrolytic graphite for example loses approximately 200 mg cm^{-2}h^{-1} at 1200^{o}C. Even the best superalloys show inadequate oxidation resistance above about 1150^{o}C. Ceramics such as silicon nitride and silicon carbide show adequate resistance up to much higher temperatures 1300-1600^{o}C), the exact oxidation kinetics depending on composition and microstructure. Sialon materials show distinct advantages over silicon nitride in terms of oxidation resistance. Oxides clearly do not, in general, suffer from corrosion problems when used in oxidising environments. Oxidation of borides, nitrides other than silicon nitride and carbides other than silicon carbide do, however, pose problems when heated to high temperatures in air. Detailed information on their maximum use temperatures is to be found in published articles in some cases. The use of molybdenum disilicide as heating elements is partly due to its very good oxidation resistance up to 1650^{o}C. Other silicides are much less stable in air. When considering the stability of ceramics in non-oxidising atmospheres at high temperatures the data are in general less adequate. For the oxides, alumina appears stable in most gases except fluorine. The formation of lattice vacancies after prolonged firing in hydrogen occurs in both alumina and magnesia. Zirconia, however, tends to form carbides, nitrides or hydrides, when in contact with carbon, nitrogen and hydrogen respectively at high temperatures. Very little is published concerning the stability in such environments of nitrides, borides, carbides and silicides. The effects of sulphur and alkali-salt containing environments are also largely unknown at the present time.

The chemical reactions occurring between molten metals, molten salts and molten glasses on the one hand, and high-temperature ceramics on the other, are known in some cases. The reactive metals such as uranium, titanium, zirconium, the rare earths, etc. are very difficult to handle and require highly inert crucible materials. Rare-earth oxides, rare-earth sulphides, some borides, etc. have therefore been examined to resolve these problems. The high commercial importance of the steel industry has encouraged the development of special oxide or carbide ceramics for nozzles, thermocouple sheaths, etc.. Preliminary results (20) from molten-salt studies indicate that hot-pressed silicon nitride and silicon carbide are dissolved at 1000-1200°C by alkali melts of Na_2SO_4 and Na_2CO_3. The attack by NaCl and V_2O_5 is slight.

The National Physical Laboratory in the U.K. now offers a service whereby the thermodynamic stability of phases which could occur in any unknown compatibility situation is calculated or estimated, and an attempt is made to predict the kind of reaction which is feasible on thermodynamic grounds. Further details can be obtained from Dr. C.P. Jones, National Physical Laboratory, Teddington Middlesex, U.K.

Insight into many corrosion phenomena can be obtained through thermochemical data (heats of formation, etc.), phase diagram and diffusion data. Essential data sources in these respective areas include references 25, 26 and 27.

4.2.8 Physical properties - availability of data

Physical parameters such as density and melting points are in general well catalogued for most ceramic materials. Other properties such as the electrical and thermal conductivities are often known for established industrial ceramics such as alumina and zirconia, but are less well known for the newer and more esoteric materials.

Thermophysical property data for most commercial high-temperature materials are tabulated in reference 28.

Electrical properties of both insulating and conducting ceramics at temperatures within the range 1500-2500°C are of particular interest for MHD generators. Compilations of data in this area exist but a recurrent problem is the stability of the insulators and conductors to chemical degradation in the environments typical of MHD ducts.

4.2.9 Shortcomings and outstanding problems

Although ceramics with high rupture strength, creep strength and high oxidation resistance are already available, the problems associated with brittle materials namely brittle fracture, thermal shock and static fatigue remain a serious drawback. At the present time it would appear that two approaches to overcoming these problems are possible. The first involves developing special ceramic matrix composites which would overcome the above limitations. The second approach is to accept the inherent brittle nature of ceramics, but to have techniques for characterisation and design which are sufficiently sophisticated to allow highly reliable structures to be built. Substantial progress has been made in both these directions. For example, some idea of the extremely rigorous material property characterisation which is necessary to give reliable service over long periods is now becoming known. However the step from theoretical design data to the construction of engineering prototypes will no doubt present new unexpected problems. The complete lack of plasticity of these materials means that components and structures tend to be very "unforgiving" if slight errors are made in dimensions or surface tolerances; this, in combination with the thermal stresses which occur in most systems and the almost inevitable impact during construction, or from dust or larger particles during operation, will in many cases determine the service life of the system. Consequently extensive long-range testing of high-temperature systems incorporating ceramic components will be required by design engineers, before the necessary confidence in ceramics is established for the newer more demanding applications. The techniques of non-destructive testing and proof testing which are currently being developed will be very important in providing the necessary detailed information.

Very limited data are available on the critical stress intensity factor K_{IC} as a function of temperature and test environment. This parameter is an essential starting point for fracture mechanics calculations. The prediction of static fatigue effects requires data on the subcritical stress intensity factor as a function of crack growth rate. Finally the applicability of Weibull statistics to the fracture of complex components subject to multiaxial stress systems needs further confirmation.

The fabrication of ceramic matrix composites has been reported by various workers (13) (15). There is no doubt that improvements in impact and thermal-shock resistance can be obtained by, for example, incorporating metal fibres into a ceramic matrix. However, the results of multiple impacts and thermal shocks are not discussed in detail. Similarly the study of the oxidation resistance and other high-temperature properties of such materials after repeated subcritical impacts needs extensive work.

A very important area where little systematic work has been reported is the joining of ceramic components either to other ceramics or to high-temperature alloys.

Mechanical cyclic fatigue data are extremely limited for high-temperature ceramics. Further work is necessary in this area before rotating and vibrating machinery incorporating ceramics can be built in large numbers.

The machining to final shape of high-precision ceramic components involves two problems, namely, the cost of the operation if diamond tools are used, and also the creation of serious surface flaws during the machining operation. The annealing out of the defects and the application of surface coatings are possible methods of minimising the influence of such defects.

Many of the mechanisms which lead to the deterioration of ceramics depend upon the nature of the grain boundaries. Some examples include creep, corrosion, fatigue and static fatigue. Detailed understanding of these processes depends therefore on knowledge of the distribution of impurities, diffusivities and the general kinetics of grain-boundary phenomena. This information is only just beginning to be assembled.

4.2.10 Current research

Significant progress in the understanding and application of ceramic materials has in the recent past been due mainly to the nuclear and aerospace industries. At the present time the results of a large programme on ceramics in the U.S.A. are becoming available. The work was sponsored by the Advanced Research Projects Agency of the U.S. Defense Department with a total buget of the order of 12 million dollars. The aim of the programme (11) was to construct prototype ceramic gas turbines operating at both ends of the power spectrum, i.e. a 30 MW industrial turbine to be constructed and tested by Westinghouse, and a turbine suitable for a small vehicle, coordinated by Ford. Both have a target 200 hours operation at 1375°C (2500°F).

Support programmes to further materials development characterisation and testing are underway in many universities and industrial laboratories in the U.S.A.

In Europe smaller programmes along similar lines have been, or are being, financed by government agencies and large companies such as MTU in Germany, Fiat in Italy, Leyland in the U.K., etc. The current state of the art of the fabrication and use of silicon nitride and silicon carbide has been recently reviewed (22).

European research groups active in the areas of fracture mechanics and testing of ceramics and materials fabrication and development are in some cases leaders in their respective fields.

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4.3 CERMETS

4.3.1 Ranges of compositions of major groups

Most papers on cermets start with a definition demonstrating that the choice of the term "cermets" is unfortunate. On the one hand the term is very general, relating to all composites made up of ceramics and metals, on the other hand it is only used in practice for a certain type of ceramic-metal combination, viz: metal-matrix dispersion composites such as the nuclear fuel cermet UO_2-stainless steel. All definitions vary between these two extrêmes; that of the ASTM committee is of the more general type: "A hetrogeneous combination of metal(s) or alloy(s) with one or more ceramic phases in which the latter constitutes approximately fifteen to eighty-five per cent by volume and in which there is relatively little solubility between metallic and ceramic phases at the preparation temperature." The volume fraction limit is to exclude dispersion-hardenend metals, and ceramics with a metal-dispersed phase, such as the cutting-tool material Al_2O_3-(Mo, Ni,Co). Other definitions try to eliminate hard metals by defining the ceramic phase in cermets as a compound with predominantly non-metallic (localized) bonds. This definition, however, contradicts the original task of cermet development.

The general uncertainty of what should be included has caused the term "cermet" to be replaced, usually by a combination of the term 'composites' with a specifying addition like 'ceramic-matrix dispersion composites' or 'metal-matrix fibre composites'. There are only a few exceptions where the name 'cermet' is still actually used: nuclear fuels (UO_2-W, UAl_2-Al, PuO_2-Fe, etc.), cathode materials in thermionic generators (UO_2-Mo, Bo_2CaWo_3-W), thermocouple sheaths (ZrO_2-Mo), etc. Taking these types of material into consideration, a very specific and limited definition of cermets can be derived:

> "Cermets are powder-metallurgically prepared metal-matrix composites with isolated or interconnected **ceramic phase(s)** of spherical or irregular shape and of above-micron size"

This definition does not include the following types of composite:

(i) Dispersion- or precipitation-strengthened metals or alloys (TD-Ni, Al_2O_3-W, Al_2O_3-Cu, Fe_2C_3-Fe, SAP, etc.)

(ii) Ceramic-fibre-reinforced metals or alloys (artificial or eutectic)

(iii) Ceramics with metal dispersions (cutting tool materials based on alumina)

(iv) Metal-fibre-containing ceramics (artifical and eutectic)

(v) Other ceramic-matrix composites (glass-wire)

A very thorough bibliography on cermets of all types has been prepared by A. Jesse, Bibliography on cermets (1945-1971) A. Jesse, KFK Karlsruhe report 1958 (May 72) and includes a list of all cermet combinations which have been investigated.

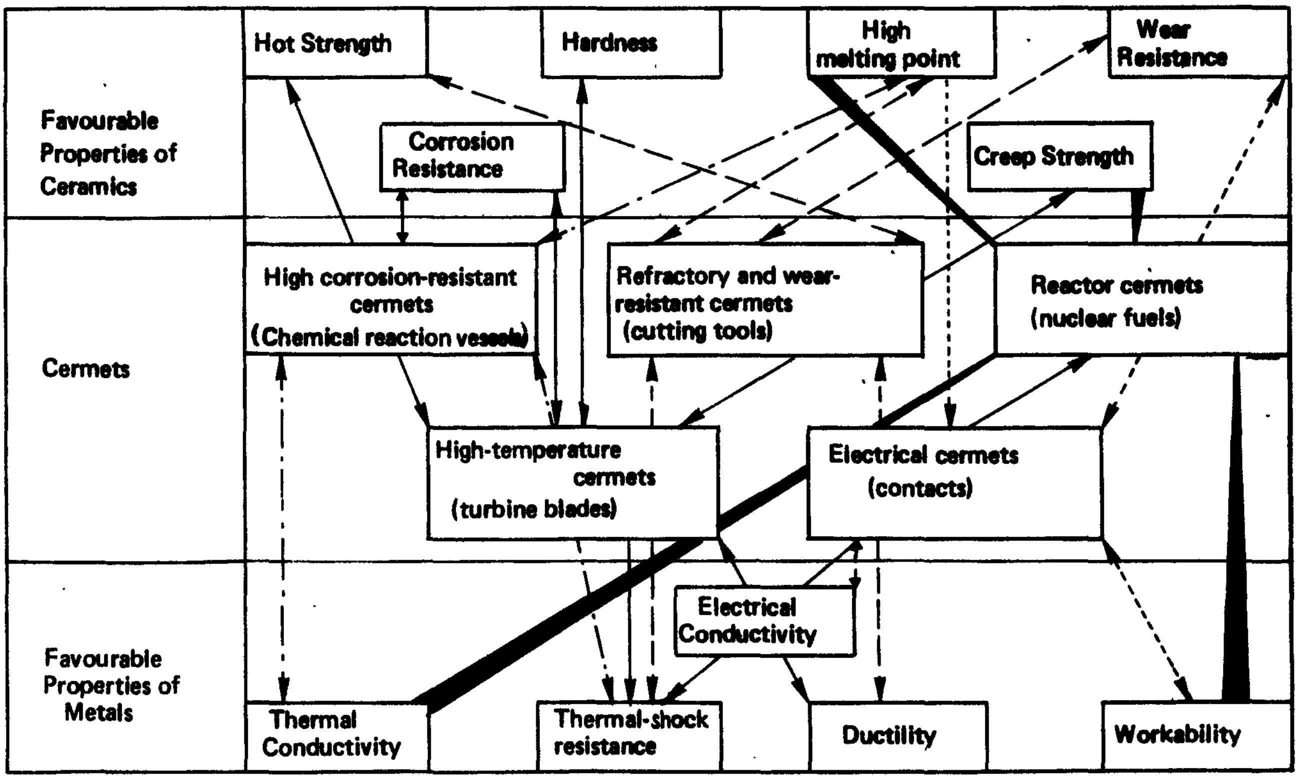

Fig. 4.3/1 Property Combinations in Cermets (2).

Cermets were originally developed to combine the typical favourable properties of both phases. This is demonstrated in Fig. 4.3/1. For instance, in electrical cermets the electrical conductivity, thermal-shock resistance and workability of metals is combined with the wear resistance and high melting point of ceramics. For the present purpose, the high-temperature cermets seek to combine the ductility and thermal-shock-resistance of metals with the hot-corrosion resistance, hardness and creep strength of ceramics.

A grouping of cermets that is in accordance with the given definition is presented in Table 4.3/1 with some examples of applications and typical materials combinations. The cemented carbides are separated with a dashed line from the other cermets because the term 'cemented carbides' is related to the material (carbide cermet), and not to a property or application; cemented carbides can, therefore, also fall into the other cermet groups. Those groupings which are of major relevance to the present survey of high-temperature materials are groups 1,2,5 and 11.

Grouping	Application Examples	Typical Cermet Combinations	Vol.-% Ceramic
1 Cemented Carbides	cutting tools, dies drills	WC-Co, (TiC, MoC_2) - Ni	60 - 90
	jet blades	TiC-Mo (W, Co)	40 - 80
	Wankel-seals	TiC-Fe	
2 Reactor Cermets	nuclear fuels control rods	UO_2-(U,Mo,W,Fe), PuO_2-Fe, U_3O_8-Al, UAl_2-Al B_4C-Al	35 - 95
3 Friction and Anti-friction Materials	bearings	BN-W, Bronze-Graphite, Fe-Graphite, Fe-Fe_2O_3	5 - 25
	brake linings	Fe-(SiO_2), Fe-(Graphite + SiO_2), Fe-(Graph. + Al_2O_3)	5-20
4 Wear Resistant Materials	cutting tools seals	TiC-Fe	30 - 40
5 Corrosion Resistant Materials	thermocouple protect.	ZrO_2-Mo, Al_2O_3-Mo, Cr_2O_3-Cr, Al_2O_3 W	25 - 40
	crucibles	Al_2O_3-Fe	15
	acid-resist parts	Al_2O_3-(Si,Fe)	
6 Electrical Materials	contacts spark plug points	Graphite-Cu (Sn,Pb), CdO-Ag, BeO-Cu	1 - 20
7 Electronic Cermets	emitter cathodes	UO_2-Mo Ba_2CaWo_6-W	80 - 98
8 Magnetic Materials	mass cores	Oxide-Fe (Fe, Ni, Mo-alloy)	
9 Coatings	welding electrodes	Oxides-Fe	10 - 30
10 Pyrotectic Materials	ignition pellets	Fe_2O_3-Al, BaO_2-(Al,Mg), ThO_2-Ca	
11 High-Temp. Cermets	turbine blades	Al_2O_3-Cr, TiC-Ni	20 - 80

Table 4.3/1 *Cermets.*

4.3.2 Availability of raw materials and costs

Cermets are normally prepared by the producer of the finished part. Using metals, alloys and ceramics from normal sources. The availability and prices of the constituents are therefore the same as given in the appropriate chapters for "metals" and "ceramics".

4.3.3 Forms available

Cermets are typically made by powder-metallurgical methods; this implies in most cases mixing (combination) of the powder components, cold compacting and sintering of compacts. However, all other P/M techniques are applicable, such as hot-pressing, extruding, slip casting, hot and cold isostatic pressing, etc.

There are some cermet-typical P/M processes. The use of metal-coated ceramic particles leads to a homogeneous dispersion of the ceramic phase in the metal matrix. Coatings can be applied for instance, by agglomeration, vapour deposition, or electroless plating of the metal phase onto the ceramic particles. Another cermet P/M technique is the infiltration of a ceramic skeleton with the metal phase. This results in homogeneous and dense parts; however, good wetting of the phases is an essential requirement. Preforms of cermets are usually not available.

4.3.4 Workability and machinability

All working processes applicable to the matrix metal can be applied to the cermet as long as the amount of metal phase is high enough (∿50 %) and the ceramic phase is dispersed and not interconnected. With increasing volume fraction of the ceramic phase increasing forces and temperatures must be used to work cermets.

Sheets are usually manufactured by rolling, and rods by extruding or round hammering. Often cladding of the cermets by the matrix metal is applied to enhance working processes.

Final shaping also depends on the composition, e.g., when hard ceramics are involved, diamond-tool shaping (grinding) may be necessary.

4.3.5 Joining

Joining techniques for cermets are the same as for metals. In cases of high ceramic content, the characteristic metallizing processes referred to in Chapter 4.2 can be applied to enhance the joining to metals.

A typical method to improve joints of cermets to either ceramic or metal parts is to stepwise change the cermet composition, i.e. the metal fraction is increased toward a metal part and vice-versa.

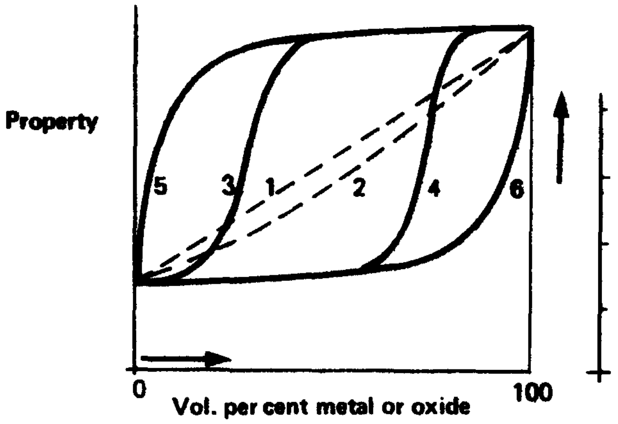

Fig. 4.3/2 Property changes of cermets with composition (3).

4.3.6 Mechanical, physical and corrosion properties

The properties of cermets depend on so many parameters that only a general trend can be given here. Fig. 4.3/2 shows the way properties may vary with composition. Density and Young's modulus follow curve 1, and in case of bad phase bonding curve 2. A hysteresis-type dependency (curves 3 and 4) is usually obtained for conductivity, strength, toughness, and thermal-shock resistance, and curves 5 or 6 are typical for corrosion resistance, wear, hardness and weldability.

The strength dependence of UO_2-steel cermets on the volume fraction of UO_2 is given in Fig. 4.3/3 to demonstrate the strong influence of the processing technique.

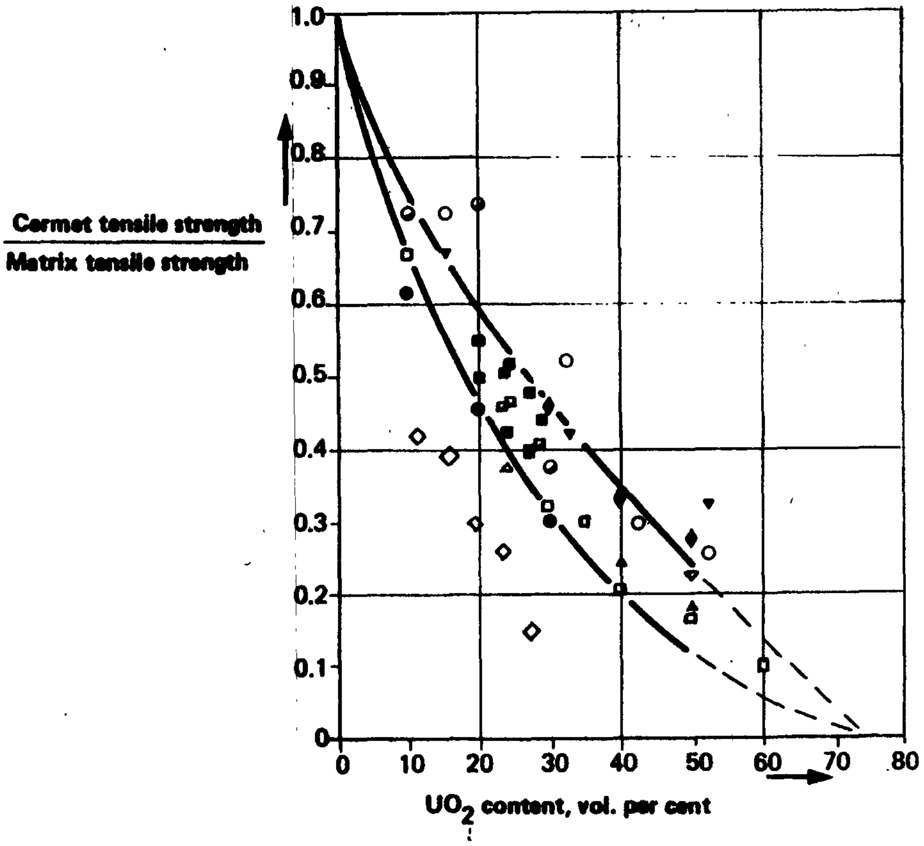

Fig. 4.3/3 *The relative tensile strength of different UO_2-stainless steel cermets as a function of the UO_2 concentration. Symbols indicate different processing techniques (3).*

4.3.7 Shortcomings and outstanding problems

Cermets for high-temperature structural applications have generally not been sucessful, mainly because of the following reasons:

(i) Oxidation resistance of the cermet is controlled by the metal phase

(ii) Phase bonding is usually bad; this cuts down most properties considerably.

4.3.8 Current research

Research activities in the high-temperature cermet field are now confined to reactor and energy-conversion materials.

Research on other metal-ceramic combinations for high-temperature application is mainly directed towards directional composites and ceramic-matrix dispersion composites (see 'composites').

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4.4 COMPOSITES

4.4.1 Introduction

Historically, the motivation for the development of high-temperature composite materials has come from the requirements of the gas-turbine industry. The advantages derived from increasing the turbine-blade-material operating temperature have stimulated alloy development over the last three decades, resulting in an increase of about 10K per year. Current growth curves (see Fig. 6/2) suggest that future improvement by the further development of conventional "superalloys" is limited. The fibre/lamellar composite materials represent one of the more promising alternatives for future development in this field.

The maintenance of high strength in a high-temperature alloy requires a stable microstructure of fine dispersed phases which prevent dislocation motion. The stability of these phases is essentially described by a mechanism due to Thomson and Freundlich in which the solubility of a particle varies as a function of its radius, surface energy and temperature. In real terms this means that large particles grow at the expense of smaller ones because of the difference in surface energy, i.e. lower for larger particles. Seybolt (1) has shown that for a particle of initial diameter d_o and diameter d after time t, Wagner's analysis (2) can be applied so that

$$d^3 = d_o^3 + Kt$$

where the constant K depends on diffusion rate, solubility, surface energy and initial particle-size distribution. The diffusion rate depends on diffusibility and particle separation.

If particles are to be stable then clearly the surface energy has to be low, i.e. oxides, carbides etc., and the diffusion coefficient and solubility should be as low as possible. This mechanism of strengthening depends on dislocation blocking. For sustained strength at temperature it is more appropriate to consider using a high volume fraction of particles whose theoretical shear strength is much greater than that of the metal matrix, so that the particles themselves directly carry the load up to their fracture strength, this being the maximum possible limit. Cottrell (3) was the first to point out that for a metallic matrix this can be achieved using fibrous particles. In this case, matrix strain imparts a shear stress to the adjacent fibre which is thereby loaded. If the fibres are short (discontinuous), further matrix strain may result in flow round the fibre ends giving rise to substantial matrix hardening. Where fibres are very long (continuous) matrix strain may result either in fracture along the fibre matrix interface or continued fibre loading until fibre or composite fracture occurs. By suitable selection of matrix and fibre materials a combination of properties may therefore be achieved in which the contribution of the individual phases is optimised.

This definition of a composite material is somewhat narrow in that it is limited to high volume fractions of a second phase, which is fibrous in nature. For the purposes of this brief discussion on composites for high-temperature applications consideration will only be given to these materials, although it should be recognised that there are many more widely used low-temperature composites such as tinplate, coated bearing alloys, etc. (4).

The recent advent of high-strength, low-density fibres such as boron and carbon has led to a great deal of attention being given to the use of composites in the design of aerospace structures, owing to their high specific properties. Such applications have been mainly limited to low temperatures (no greater than 250°C), for reasons which will be discussed later, and efforts to develop fibres for high-temperature components have been concentrated mainly on controlled phase transformations, such as eutectic reactions in which the fibre is formed in-situ.

Before entering into details of these recent and current developments an analysis of the theory behind composite materials will help to ascertain the objectives of such development programmes, which ultimately have to provide a designer with a proven reliable material from which he can make a component.

4.4.2 Theoretical background

The concept of a fibre composite is not only a conventional matrix-strengthening one. Rather it relies on the reinforcement of a weak matrix by strong fibres, with the load being transferred via the matrix to the fibres. Optimum properties are obtained when certain conditions are fulfilled by both matrix and fibres (5): the fibres should have high strength and elastic modulus; they should be either continuous or have high aspect ratios; they should possess undamaged surfaces and be present in high volume fraction, being aligned in the direction of maximum stress. In contrast, the matrix should act as a bond and as a separation layer for the fibres, as well as providing a protective layer for the fibre surface. The stresses are uniformly distributed through matrix ductility. This is an important point and is difficult to achieve in practice, particularly for discontinuous fibres which have free ends within the matrix. The ability of the metallic matrix to work-harden is a further factor which helps to increase the composite strength. Continuous composites may also be considered as either "conventional" composites where comparatively thick wires, ∿200μm diameter, are entrained within a metallic matrix by liquid-metal infiltration or solid-state sintering, or as "in-situ" composites, fibre diameter ∿1μm derived by the directional solidification of eutectic alloys. The function of the matrix varies according to the fibre type i.e. continuous or discontinuous.

In continuous fibre composites the ultimate composite strength σ_c has been considered to be the sum of the contributions of the individual phases, expressed simply in the so-called "rule of mixtures":

$$\sigma_c = \sigma_f V_f + \sigma_m(1 - V_f)$$

where the subscripts "f", "m" refer to the fibre and matrix phases respectively, and V_f is the volume fraction of the fibres. This equation implies an absence of fibre/matrix interaction, and satisfactorily describes results obtained from conventional composites (6). However the model fails to account for the sensitivity of the creep strength of eutectic composites to the scale of the microstructure, which has been observed by several authors (7,8).
Clearly with these very fine microstructures some degree of phase interaction must be considered. Discontinuous fibres have free ends within the composite volume and the matrix can not only transfer stress by virtue of shear stresses at the matrix-fibre interface but also considerably work harden by flow round the fibre ends. In contrast therefore to continuous fibres, the steady-state stress varies along the length of discontinuous fibres. For a critical fibre length (l_c) the strain in the fibres can be considered to be the same as the matrix. This critical value is directly proportional to fibre strength, diameter, and inversely proportional to matrix shear strain, and provided all fibres exceed this value, the composite strength can again be described by the rule of mixtures.

4.4.3 Component characteristics

Typical matrix materials include plastics, ceramics and metals but only metals provide the best combination for properties for a composite which has to function at high temperatures. Metals not only give surface protection to the fibres but they also prevent mechanical damage and can give the required resistance to atmospheric attack. As a further advantage there are a variety of methods available for manufacturing metallic matrix composites, which are discussed in the next section.

Fibres cover various types of reinforcing agent, e.g. wires, filaments, whiskers and intermetallic lamellae or rods formed by eutectic reactions, and all of these are potential candidates for metallic matrices (Table 4.4/1).
Wires include molybdenum and tungsten with the disadvantage of high density, beryllium (which is very expensive) stainless and plain-carbon steels. Amongst the filaments both boron and silicon carbide are of great interest because of their low density and hence high specific strength and stiffness. Such filaments can be prepared by vapour-phase deposition onto an ultra-fine-diameter wire substrate such as tungsten or glass, but suffer from a very high cost penalty even compared to carbon fibres. Whiskers, with their fine diameters (less than 1μm) have very small values of the critical length and hence can be used as discontinuous fibres. Their main advantage, however, lies in their very high strength which arises from their single-crystal nature and approaches the theoretical strength. Unfortunately they are difficult to produce and handle and new cheap processing techniques are essential if the large volumes required for composites are to be manufactured economically.

Fibre Type	Specific (ρ) Gravity	Youngs Modulus (E) GNm^{-2}	Tensile Strength (σ) GNm^{-2}	$\frac{E}{\rho}$ (GNm^{-2})	σ/ρ (GNm^{-2})
Whiskers					
Graphite	2.2	686	19.6	312	8.9
Alumina	4.0	532	15.4	124	3.85
Silicon Nitride	3.1	385	14.0	124	3.50
Beryllium Oxide	3.0	357	7.0	119.0	1.75
Metallic Wires					
Carbon Steel	7.9	210	4.2	26.5	0.53
Stainless Steel	7.9	210	2.1	26.5	0.26
Tungsten	19.3	350	3.9	18.1	0.20
Molybdenum	10.3	343	2.1	33.3	0.20
Non-Metallic Filaments					
Kevlar	1.47	140	2.8	95.2	1.9
Carbon	1.9	240/450	2.6/1.8	126/236	1.36/0.95
Boron	2.6	413	3.17	159	1.22
E-Glass	2.54	70	1.70	27.5	0.67

Table 4.4/1 *Room-Temperature mechanical Properties of some potentially useful Fibres for Metallic-Matrix Composites.*

Typical materials include alumina (sapphire) and the carbides of both boron and silicon.
The intermetallic eutectic phases produced by controlled solidification have either rod-like or lamellar-like morphologies depending on a variety of factors and seem to hold out significant promise for high-temperature applications. The reinforcing phases include tantalum carbide, nickel aluminide, nickel niobide,etc., these being incorporated principally in nickel or cobalt matrices.

4.4.4 Composite fabrication

The selection of a particular combination of fibre and matrix implies a specific production route so that the fibres can be incorporated into the matrix without undergoing damage. Since a good bond is required between fibre and matrix, this implies that the fibres should be wetted by the matrix. It is also important that there is no chemical alteration of the interface, which can lower the fibre strength. This feature is a necessary pre requisite for practical composites.

Fabrication routes can be classified in a variety of ways although, as with all classification methods, there is a degree of overlap between the different classes or even a combination of two different classes in a sequential operation. With this simple proviso in mind three different types of process can be defined, viz. diffusion, liquid-phase and deposition. These are listed in Table 4.4/2 and further details can be found in the published literature (9).

A. **Diffusion Control**

1. Pressing and sintering of powdered matrix and bare or coated fibres
2. Pressing (often followed by sintering) of coated fibres
3. Pressing of bare fibres between thin foils of matrix metal (powdered matrix can be used in conjunction with the foils)

B. **Liquid-Phase Control**

1. Infiltration of liquid matrix metal between fibres
2. Pressing of a mixture of powdered matrix and fibres at a temperature above the melting or solidus temperature of the matrix e.g. liquid-phase sintering.
3. Unidirectional solidification of eutectic alloy

C. **Deposition Control**

1. Electrodeposition of matrix around prearranged fibres (plus pressing)
2. Plasma- or flame-spraying of matrix around prearranged fibres (plus pressing)
3. Vacuum deposition of matrix around fibres to form thin-film composites

Table 4.4/2 A classification of the Fabrication Routes for Fibre-reinforced Metallic-Matrix Composites.

Each route has its own inherent benefits and deficiencies (10) e.g. electro-deposition techniques are only suitable for pure metals; flame-spraying requires subsequent diffusion bonding of the layers to form a monolithic matrix; sintering can be carried out in both the solid state and by liquid phases, but long times at high temperatures and pressures are often required, which tend to make for high costs; liquid-phase infiltration of fibre bundles is direct and can be a very satisfactory method if carried out rapidly so as to avoid fibre attack by the liquid phase.

In-situ production of the fibres offers the outstanding advantage of near perfect bonding between fibre and matrix because of the low interfacial surface energy and both liquid- and solid-state routes can be used with success. Directional solidification of eutectics has been developed both in Europe and the USA with particularly spectacular results being claimed by Bibring (11) for tantalum carbide fibres in cobalt- and nickel-base matrices and by United Technology Corporation, USA for the Ni_3Nb-Ni_3Al system (12). Such techniques are attractive because of their directness and ability to form complex shapes, but their present principal disadvantages underline the need to make advances in this area. The potential of such materials justifies these continuing efforts.

4.4.5 Discussion

With such a wide variety of potential materials from which composites can be, and indeed have been, fabricated, the questions which have to be answered are: why are so few practical materials in use as components; do the reasons underlying this small number of materials justify further effort; are there any inherent draw backs to metallic-matrix composites for high-temperature applications ?

The use of glass fibres to reinforce polymeric matrices is widely known and few people will not have come into physical contact with these materials. Carbon fibres and new organic fibres based on polyaramides, e.g. Kevlar, are now being used in place of glass fibres and improved properties are being obtained. The use of such fibres in metallic matrices has been strictly limited to applications at ambient temperatures or within 500°C of ambient, because of the results of early experiments on carbon fibres which showed that they underwent structural degradation when heated in contact with metals such as nickel and cobalt, which are the basis of existing superalloys. Silicon-carbide-coated boron fibres in aluminium alloys can be used to make compressor blades in turbine engines, which can involve exposure up to 300°C, and success has been claimed in early development programmes in the USA.

For temperatures above 900-1000°C there are very few fibres available which are stable in oxidation-resistant matrices during processing and service, and even fewer which have the requisite strength and stiffness. In any one matrix the stability is controlled by fibre size and chemical potential of the fibre with respect to the matrix. Fine-diameter fibres with their high specific surface area will obviously react more rapidly than large fibres, e.g. silicon carbide whiskers have been shown to interact with nickel at 900°C and filamentary materials suffer from the same drawback. Of the ceramic whisker and filamentary materials, only alumina seems to be stable at temperature and to have the requisite mechanical characteristics. It can thus be considered as a prime candidate fibre material, despite its high cost and the essential but difficult processing technology required to make it in sufficiently large quantities. Heavy refractory metals such as tungsten, molybdenum, and tantalum can be cold drawn into wire form and retain their strength to high temperatures (1100°C). Of these tantalum is expensive, molybdenum can form low-melting-point eutectics with nickel and cobalt, and tungsten is particularly heavy. Despite this limitation, tungsten wires have been incorporated into cast nickel-base superalloys giving a 90°C improvement in performance temperature at equivalent stress levels compared with the matrix alloy alone (13). The specific mechanical properties (σ/ρ and E/ρ) must be taken into account in assessing such a composite. The other promising composite materials for high-temperature applications are all based on in-situ formation of the reinforcing phase by a eutectic or eutectoid reaction in a temperature gradient. The load-bearing phase can either be an intermetallic compound or a carbide, and its morphology can vary from fibrous to lamellar. Such composites are very attractive engineering materials since in principle the matrix composition can be designed so as to have good impact and fatigue properties plus oxidation resistance, which is essential at high temperatures. This latter requirement is of such importance that coatings are currently applied to ensure that any possible reduction in matrix resistance does not lead to catastrophic oxidative failure.

4.4.6 Critique of available materials

Provided that all the criteria relating to whisker or fibre alignment, matrix integrity and whisker perfection (i.e. whiskers remaining undamaged during processing) are satisfied then composite performance is dependent on matrix-fibre bonding. For metal-ceramic composites such as nickel/alumina-fibres, bonds can be of either chemical or mechanical origin with the latter being readily attainable because of the differences in thermal coefficients of expansion between the two phases which allow the metal to grip the ceramic fibre. Although such a bond is adequate at low temperature, it is less efficient with increasing temperature as the difference in expansion coefficient diminishes. A stable chemical bond is thus required for high temperatures, and in principle this can be provided by reactions to form a second phase. For example nickel and aluminium oxide can react to form a spinel phase, with a bond strength of 70 MN m^{-2}. This is approximately equal to the shear strength required for full theoretical reinforcement to be obtained for fibres which have a high aspect ratio, e.g. 100. However the interphase bonding of these composites appears to be very sensitive to thermal expansion differences between the phases. The increase in matrix strength due to fibre reinforcement, which can be up to 75% at room temperature, is reduced to 10% at high temperatures. This results from an apparently total lack of adhesion between fibre and matrix as a result of disruption of the chemical bond during a single thermal cycle. Thus breakdown is a consequence of differences in expansion coefficient setting up interfacial stresses in the bond zone, and it seems to be an inherent difficulty with all ceramic-fibre/metallic-matrix systems. Furthermore the existence of chemical reaction which produces the necessary bond implies that reaction will continue if long-term exposure at temperature is envisaged and that fibres will eventually be destroyed (14). This pessimistic conclusion is, unfortunately, a very reasonable statement not only of the present state of the art, but also of any future possibilities. It thus seems that composites based on ceramic fibres are not viable for high-temperature applications because of fundamental limitations imposed by the physics and chemistry of the materials.

Cast composites containing refractory-metal wires have been prepared and assessed, and provided interaction is avoided during pouring of the liquid metal or alloy, very substantial reinforcement can be obtained at temperatures around 1100°C using either tungsten-rhenium or molybdenum wires (the latter being protected by a tungsten coating). The advantage is best expressed in terms of temperature increase for a given stress level and Glenny (10) has shown that a 20% volume fraction of molybdenum wires in a conventional nickel-base superalloy (IN 100) gives an 80 deg. C advantage. The main drawback to these composites lies in the weight penalty resulting from the high density of the wires and design considerations will decide their future.

Controlled eutectic microstructures were first shown to behave as classical reinforced composites as recently as 1965 and development since that date has concentrated on several aspects of these novel materials: new reinforcing phases; higher volume fraction of the reinforcing phase; oxidation resistant matrices; fast processing rates; production of components of complex shape; stability at high temperatures and in temperature gradients and during thermal cycling (15). Because of the temperature requirements, suitable alloys have to be selected from systems combining elements such as nickel, cobalt or iron (with the possibility that chromium and the precious metals could also be suitable matrices) or with intermetallic and covalent compounds with high hardnesses, and melting points greater than those of their constituent elements.

As the mechanical properties of eutectic composites are dependent on the properties and volume fraction of the reinforcing phase it is important to know how any given alloy system will behave. If the surface energy of two eutectic phases is isotropic then it can be kept to a minimum if rods form for volume fractions below 32% and if lamellae form above 32%. It is preferable in terms of reinforcing efficiency to have a rod-like phase but, since it tends to form at low volume fractions, lamellar composites will usually be stronger. Furthermore lamellar composites have greater thermal stability than the rod composites.

Aligned microstructures containing either rods or lamellae without any primary phases can be produced at steady-state growth conditions by plane-front solidification at a velocity V with a temperature gradient G across the liquid-solid interface. This solidification mode can break down if the gradient is too small, if the freezing rate is too fast or if impurities, C_o, segregate to the interface, and the aligned structures are then replaced by cellular structures known as colonies. This relationship can be expressed as an equation:

$$\frac{G}{V} = K \frac{C_o}{D}$$

where K is a constant in which factors such as liquidus slope, partition coefficient, etc. are included. For well aligned composites to form, the ratio G/V has to exceed a critical value and if impurities are present then higher values of G/V are required. Typical values cited by Lemkey (15) are:

for a Ni-Al-Nb system with a low impurity level, aligned micro structures formed for $G = 7\ K\ mm^{-1}$ at a velocity V of 6×10^{-1}; for a Co-Cr-C system using standard grade (i.e. higher impurity levels) alloying elements the G/V ratio was $250\ K\ sec\ mm^{-2}$ (compared with $1166\ K\ sec\ mm^{-2}$ for the previously cited alloy). This is an important point since in practical terms the rates of production of eutectic composites will be somewhat limited unless very pure and hence expensive alloying elements are used or very steep (and possible unattainable) temperature gradients are produced. Recent developments have shown that coupled growth of off-eutectic compositions can lead to aligned microstructures although the solidification conditions are very stringent.

Already substantial increases in the values of G have been achieved by the use of liquid metals to cool the solidifying metal rather than simply using circulating air, and this has now enabled more complex compositions to be considered in the search for viable chemical and mechanical properties. Since the service requirements of this type of alloy are demanding more complex alloys, compositions involving multi-component, multi-variant growth have to be considered. Success with so-called pseudo-binary eutectic alloys has been reported by Lemkey (15) typified by a structure of Ni_3Nb lamellae in a nickel-chromium matrix strengthened by Ni_3Al precipitates, and by carbides in both nickel and cobalt alloy matrices. Mechanical property measurements at high temperatures (1100°C) have shown that such alloys are superior to the best conventional superalloys (Mar M200), which have also been directionally solidified in order to align the grains in an anisotropic manner. As previously pointed out, although lamellar eutectics show composite behaviour their tensile properties cannot be fully explained using the rule of mixtures. The effect of lamellar spacing has to be taken into account, since increasing the solidification rate can reduce the inter-lamellar spacing, resulting in increasing the tensile strength of the composite without changing either the volume fraction of the phases or their individual strength properties.

There are however drawbacks to these composites even though their potential is recognised, and three areas of difficulty have been identified: economic production at rapid growth rates; microstructural stability during thermal cycling and in temperature gradients; surface stability with respect to oxidation and hot corrosion. The facility for inclusion of alloying elements in order to optimise desirable properties is also reduced by the crystallographic spatial requirements of the eutectic structure.

Isothermal stability of eutectic composites is controlled by defects in the individual rods or lamellae which arise from growth variations. The presence of faults tends to encourage a growth process similar to that described in the opening paragraph of this section, where Ostwald ripening was shown to be the process controlling particle stability. The stability of eutectic structures in a temperature gradient has particular importance in their application as gas-turbine blade materials. Modern turbine blades and nozzle guide vanes are internally cooled and during service may experience a temperature gradient across the aerofoil wall section of up to 300 deg.C mm^{-1}. Migration of the secondary (reinforcing) phases by thermal diffusion through the temperature gradient can lead to a coarsening of the structure and a consequent loss of strength. This is a problem requiring further research investigation if design limits are to be established for these materials.

Thermal cycling is a process to which many materials are subject and is of particular relevance to eutectic composites. Initial results have shown that some fibre eutectic structures suffer rapid degradation when thermally cycled, e.g. the stress-rupture life of a particular carbide-reinforced alloy was reduced from 100 hours to 8 hours after only 200 cycles. Lamellar structures do not appear to be subject to this degradation mechanism.

4.4.7 Conclusions

There are very few metallic-matrix composites available for high-temperature applications. The reasons for this lack have been analysed in this article and essentially they are related to problems of microstructural stability at high temperature. Viable systems with potential for development appear to be limited to high-strength metallic filaments in conventional superalloy matrices or the eutectic systems which can produce phases with fibrous or lamellar morphologies in metallic matrices by means of controlled-solidification techniques.

Future research should concentrate on these materials, with particular attention being paid to structural stability and improved processing control. As experience with such composites grows and reproducible data are obtained, attention can then be given to the production of specifications for structural designs which will be acceptable to the engineer. This is a task which requires vision, courage and financial commitment but the potential gains will make this effort worthwhile.

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4.5 COATINGS

4.5.1 Introduction

The particular shortcomings of a high-strength high-temperature material with respect to resistance to the corrosive action of the environment may sometimes be overcome - or the life of the component considerably improved - by the application of a surface coating of a corrosion protective material. There are many possible techniques for the generation of such coatings, including roll bonding, weld deposition, metal spraying (flame or plasma), electroplating, electrophoresis, ion plating, sputtering, vapour deposition and pack diffusion. The process used in any application tends to be specially developed for the particular substrate and operational environment, and a comprehensive treatment of the subject would need to be lengthy and detailed. Perhaps most attention in recent years in the high-temperature field has been devoted to coatings for the stator and rotor blades of aircraft-type gas turbines, and the present section is restricted to developments in this field.

Gas turbines operate with a wide range of fuels, from natural gas and high-sulphur diesel fuel to the highly refined aero kerosene, but always have a high air-to-fuel ratio, so the combustion gases are highly oxidising with flame temperatures in the order of 2000°C. These gases are then fed through successive rows of guide vanes and rotor blades, depending on the number of stages required to drive the compressor, and finally expelled through a nozzle as jet thrust, or used to drive a power turbine.

The turbine blade section converts the thermal energy supplied by the combustion into work (mechanical energy) and therefore must withstand the full potential of the hot gases from the combustor. The role of a protective coating is to maintain the integrity of these blades and their guide vanes over extended periods.

Blades for advanced engines are now air cooled and almost invariably cast; this allows the incorporation of intricate cooling passages to maximise the air-metal interaction and lower the metal temperatures by 200 - 250°C.

The first-stage nozzle guide vane is the hottest component in the turbine section, with temperatures ranging from 900-1150°C. It is normally arranged to have a low design stress, to ease the task of resisting the combination of severe thermal stress and high-temperature corrosion. In comparison the turbine rotor blade has a high creep stress imposed by the centrifugal force field and in addition has to withstand stresses resulting from thermal cycling and mechanical fatigue, although at somewhat lower temperatures 800 - 1050°C. Second-stage vanes and blades operate in a temperature regime 100°C below this and may also be coated, dependent on the particular conditions of service and the superalloys involved. The lower temperatures are typical of long-life industrialised aero engines and the upper temperatures represent conditions in military aero engines, with a more limited life.

Conditions in advanced aero engines are now so demanding in terms of power/weight ratio and life, that the limits of material properties are pushed as hard as possible.

In the case of turbine blades this consists of mating coatings and advanced superalloys, so that the materials system becomes a viable entity for component application. This tailoring of materials is a continuing process, because the materials in a gas turbine operate in an environment of dynamic change; i.e. higher temperatures and longer life, and the aim is the highest quality, reliability and cost effectiveness.

The varied roles of gas-turbine engines also affect the choice of coating. In high-altitude aero service, with highly refined fuels and a pure air supply, corrosion is primarily of an oxidation type, whereas in a marine service role the combination of a low quality diesel fuel and the ingestion of sea salt even in minute quantities, causes a very severe form of hot corrosion. In V/STOL aircraft a severe cyclic service is demanded and in this instance thermal fatigue is the major problem.

The ideal coating must satisfy the following criteria:

(i) it must provide satisfactory erosion and hot-corrosion protection,

(ii) it must be able to accommodate thermal changes and the creep strain of the substrate,

(iii) it must not degrade the mechanical properties of the substrate,

(iv) it must have diffusional stability.

4.5.2 Main Types of Coating

Investigations have established that coating alloys forming alumina scales offer the best protection in the high-gas-velocity conditions of gas-turbine engines.

Two main types of coating for application to nickel-base superalloys have evolved to meet these requirements; i.e. pack aluminide and overlay.

Pack Aluminide

Although there are many methods of forming aluminide coatings, the pack process is the most widely accepted, because of its low cost and reliability.

In this process the superalloy becomes coated with an aluminium-rich surface layer at elevated temperature by vapour-phase transfer in a powder pack. A complex aluminide based on the compound NiAl is formed with a composition comprising essentially Ni-Co-Cr with 20 - 40 wt. % aluminium.

There are several established variants of the process:

a) chromium-enriched aluminides with improved hot-corrosion performance,

b) tantalum and chromium, or platinum-modified aluminides with improved stability and oxidation/hot-corrosion performance.

Overlay

The inherent restrictions of the aluminising process, prevent the fine compositional and structural control needed for the attainment of the ideal coating. In order to overcome this situation, overlay coatings have been widely investigated and the most satisfactory outcome has been obtained using the physical vapour-deposition route. This process enables a coating alloy of pre-defined properties to be added to the surface.

Coatings deposited by this process are limited by vapour pressure considerations and are normally nickel- or cobalt-base alloys with high contents of chromium and aluminium, but with the aluminium content restricted to 5-15 wt. % to maintain the ductility and with a small yttrium addition to improve the cyclic oxidation performance. They are normally multi-phase alloys consisting of a ductile matrix, e.g. chromium-rich cobalt-chromium gamma phase, with a high volume fraction of a more brittle phase e.g. beta CoAl.

The following table outlines the capital involvement, availability and relative cost of the more important coatings applied to aircraft-type gas-turbine blades.

Process	Availability	Relative Cost
Pack aluminising	Widely used coating with lowest unit cost. Equipment can be installed at moderate capital cost, enabling facilities to be available throughout the world.	1
Chromium- or chromium-tantalum-modified aluminising	Equipment similar to that for pack aluminising. Process available in Europe and America.	2-3
Platinum-modified aluminising	Equipment similar to that for pack aluminising, plus facilities for platinum electroplating. Process available in Europe and America.	3-5
Vapour-deposited overlay coatings	Sophisticated vacuum equipment and analytical control facilities required, therefore very high plant cost. Production capability available only in America.	7-10

4.5.3 Mechanical and Physical Properties

Although having an impressive high-temperature protective capability, aluminide coatings exhibit low ductility up to the beta-phase (NiAl) brittle/ductile transition temperature. They have therefore, a limited ability to resist the repeated high-strain low-cycle fatigue conditions imposed on them by 'take-off' and 'landing' thermal transients in service. The resulting crack failure of the coating reduces the mechanical integrity of the blade, as well as the protectiveness of the coating.

In contrast, the comparatively steady-state conditions of cruise flight are in the ductile temperature range of aluminide coatings where the ability to accommodate the creep strain is excellent and, provided the coating-process heat cycle is not damaging to the superalloy structure, then the long-term creep properties are virtually unaffected by coating.

The exception to this is when pack-aluminide coatings are applied to thin-wall tubular blades; then a significant part of the total cross section is converted to the coating layer and this must be allowed for in terms of the changed creep properties in the initial design and particularly in recoat procedures.

Coatings of the overlay type do not lead to a reduction in cross section of the unaffected substrate, but the thicker coating layers introduce additional centrifugal loads. Again these must be allowed for in design and in recoat procedures, but such coatings may more readily be tailored precisely to meet special performance requirements, when the high coating cost can be justified. This situation may be found in advanced military high-performance gas turbines, where high-strain thermal fatigue is a dominant feature; or where turbines are operating in particularly aggressive environments and corrosion is the life-limiting feature.

The physical property of most concern in the technology of protective coating is thermal expansion. It is important that the expansion mismatch between coating and substrate is minimised, to avoid differential stresses, which would otherwise adversely affect thermal-fatigue performance.

4.5.4 Corrosion and Erosion Properties

In oxidising service conditions, the protective alumina film is continuously, but relatively slowly, subjected to a damage and repair sequence. However, in more severe conditions of service,traces of salt enter with the intake air, react with the sulphur in the fuel and deposit sulphates which prevent the restoration of the protective alumina film. This allows a catastrophic loss of aluminium and chromium, resulting in a greatly reduced coating life.

Research has established that the essential need to combat oxidation is a high aluminium reserve in the coating to enable repair of the alumina film over extended periods. For optimum resistance to sodium-sulphate corrosion an adequate reservoir of chromium in the aluminide coating is also essential to counteract that being continuously lost to the salt layer. This has led to the development of aluminising for oxidising environments, and the duplex chromium-enriched aluminising process for optimum protection against hot sulphur corrosion.

Erosion by unburnt carbon particles can occur and accelerate corrosion by damaging the protective scales, and much effort is directed towards improved burner design to ensure that this effect is minimised.

A more difficult problem is the development of coatings to resist the erosive action of ingested dust, e.g. quartz. This is a particular problem with land-based turbines sited in dusty terrains.

Although aluminide coatings are hard at ambient temperatures, they are not so at elevated temperatures, and some turbine operators have found benefit from the inclusion of alumina particles in aluminide coatings to counteract this problem. However, despite its importance this aspect of coating wear has not attracted much research effort.

Coatings of the overlay type offer the capability of optimising corrosion performance but the compositions available are limited at the present time to these applicable by the vacuum evaporation process i.e. Ni-Cr-Al-Y and Co-Cr-Al-Y.

At the higher service temperatures, interdiffusion with the substrate becomes a major factor in the life of coatings and special modified aluminide coatings have been developed to meet these demands.

In the Ta-Cr-Al process developed by ONERA tantalum is used as a precoating to an aluminising treatment. The mechanism of the action of the tantalum is not clearly established but it seems probable that the more slowly diffusing species tantalum and chromium form a layer containing about 50 wt. % of the refractory elements, which acts as a diffusion barrier between the substrate and the NiAl coating.

Another promising development is a platinum-modified aluminide. In this process a platinum layer is first applied by electroplating and is then followed by a conventional aluminising treatment. A marked improvement in coating stability is obtained, which, in laboratory tests, leads to a three-fold improvement in coating life.

4.5.5 Shortcomings and Direction of Future Research

1. In the present vapour-deposition process for 'overlay' coating it is difficult to avoid occasional features such as spits from the evaporant pool and columnar growth defects. Unfortunately their presence is difficult to detect and causes degradation of the coating properties.

   Process development is required, either to modify or to provide an alternative technique, which can reliably give a dense coating, with the required fine equiaxed structure.

2. As new coatings extend the life of turbine blading, a corrosion problem may arise in the normally uncoated internal cooling passages. It is important that an internal coating process be developed to deal with this situation.

3. Suitable overlay coating alloys are available for oxidation and moderate hot corrosion service; however there is a requirement, for a research programme to identify coatings providing protection in:
   (a) salt-laden environments
   (b) sand-erosion conditions.

4. It is known that the deterioration of coatings by spalling of the protective scale can be markedly improved by the addition of yttrium, but this element is expensive and

difficult to incorporate into aluminide coatings. A research programme with a mechanistic approach is required to determine if there are other elements or combinations of elements that are equally, or even more, effective and can more readily be incorporated into aluminide coatings.

5. In the broader field of high-temperature technology applications will continue to arise in which specific corrosion problems can most readily be solved by the development of coatings appropriate to the substrate and the operational environment. The knowledge and experience generated by the aero-space industry will be helpful in dealing with such problems.

5. CURRENT HIGH-TEMPERATURE MATERIALS RESEARCH AND DEVELOPMENT

5.1 INTRODUCTION

The object of this section is to give a general picture of current research and development activities on high-temperature materials based on an analysis of known programmes being carried out in Europe, the U.S.A. and other areas. By its very breadth of scope and wealth of detail the topic is difficult to review in a comprehensive manner, without carrying out a detailed survey of all the relevant programmes. This review is therefore written around a general framework which has been developed so as to indicate in an orderly manner the research topics which appear to be receiving major attention. It is not intended to be comprehensive; rather it is indicative of the general themes which can be detected both in Europe and America. The information upon which this review is based has been obtained by several methods, viz. published literature; review papers; conferences; discussions, etc. but it must be emphasised that in a subject which is so sensitive from the industrial and defence standpoints, the element of personal contact is most important. As a final introductory point it must be remembered that most current research activities are a result of decisions taken some time ago, because of the time lag between perception of a need, definition and execution of the necessary programme. In this sense much of the current activity is already rooted in history and perhaps is no longer relevant to tomorrow's needs. The recognition that the driving force for past, present and future developments is not a unique and singular factor but a continuously changing entity will be of assistance in grasping the reasons for investigating the properties, manufacture and behaviour of high-temperature materials.

5.2 BACKGROUND

The major reason for the continued effort to introduce new high-temperature materials is to increase the input temperature of a process so as to improve overall thermodynamic efficiency. Additionally, however, other factors are becoming of increasing importance such as component safety and reliability, reduced maintenance, longer service life, and the functioning of components in unusual environments which are both aggressive and little understood. As an illustration of this the increasing necessity to use impure fuels in engines requires a knowledge of material behaviour in atmospheres which cannot be reproduced in the laboratory; similar considerations apply to the use of nuclear process heat with helium as a working fluid which contains very low concentrations of impurity gases.

It is thus important to distinguish the various applications of high-temperature materials from each other and to define the design constraints which ultimately define the materials needs. It is now widely recognised, for example, that the development of the aircraft jet engine has been a dominant force in the high-temperature materials field, stimulating the development of the initial nickel-base blading alloys from nickel-chromium heater-element materials, and currently of such novel materials as metallic matrix composites and directionally-solidified eutectic alloys.

The major applications of high-temperature materials have been dealt with in Section 3 of this book. The most extreme temperatures and environments are encountered in aircraft gas-turbine engines as higher thrust/weight ratios and efficiencies are sought. Electricity generating stations are more concerned with component reliability and it is then reasonable to sacrifice some absolute thermodynamic efficiency so that mechanical and corrosion problems are less important and a guaranteed longer maintenance-free period can be obtained. This point is all the more relevant for nuclear power where the basic reason for investing in the plant is the cheapness of the fuel, but repair times can be an order of magnitude longer than with conventional plant because of irradiation hazards and the need for very high safety standards. Reliability is an essential requisite of such plant.

Several objectives can thus be defined in current research in the light of the different envisaged technological applications.

5.3 A BASIC FRAMEWORK

A basic framework for analysing this topic is to consider materials research in terms of materials "for-service" and materials "in-service". A brief word of explanation of these concepts will help to clarify this matter.

The early efforts to produce materials with increasing performance as measured either by stress-bearing capacity at a given temperature or environmental resistance at a given temperature, were made to allow higher operating temperatures to be used. This type of research activity is defined as for-service, i.e. a design goal is specified and materials are sought and developed to meet these specifications.

As conditions under which high-temperature materials functioned were better understood it became evident that factors such as reliability, long maintenance-free operating periods, complex stress interactions and non-destructive in-service assessment techniques had to be investigated, and all such activities can be grouped under the banner of materials in-service.

These two groupings are clearly not mutually exclusive and there will be a degree of overlap between them but, by adopting these concepts, it should prove easier to make a sensible analysis of a major proportion of the current research and development programmes.

Amplifying this theme, the essence of the development of materials for service is the design of a specific microstructure and specification of a material composition. Non-availability of a suitable material leads to definition of a research objective. The tendency now is to concentrate on materials processing routes as a means to achieve a specific microstructure in a component, with an improved utilisation of material being obtained as a direct consequence. Typical examples can be found in the extensive programmes developing directional-solidification techniques for turbine blades, first of all using standard cast alloy compositions, and secondly using eutectic compositions so that fibre-reinforced composites can be developed in-situ.

The approach to 'in-service' research and development varies according to the application but a major force in promoting such efforts is the desire to have longer component life in complex-stress situations, whilst resisting the attack of atmospheres which can lead to a reduction in load-bearing capacity. This requirement has catalysed many research programmes some of which will be discussed later, but it is worth noting such topics as: structural stability in isothermal conditions, in a temperature gradient, and during thermal cycling; the interaction of creep and fatigue; predictive techniques for assessing microstructural and phase stability; corrosion in sulphur and halide-bearing atmospheres and the development of coatings to resist such attack and ensure surface stability; the study of wear processes and the development of abrasion-resistant surfaces,etc. This latter category demands a very close link between the laboratory investigator and the design and production engineers if success is to be obtained within a reasonable time-scale and programmes of work investigating this general area tend to be based on a multi-disciplinary approach.

5.4 NATIONAL AND INTERNATIONAL GROUPINGS

Co-operation and collaboration are not only desirable but indeed essential in such an important technology, and a few words on some of the national and international groups active in the field are appropriate. Since 1973 when the so-called energy crisis was first widely recognised there has been an increasing tendency to group together research projects under the general umbrella of energy or energy-related research. An excellent example can be found in the U.S.A. where E.R.D.A. has been created, and it is anticipated that this will take-over from N.A.S.A. as one of the major funding agencies for high-temperature research. E.P.R.I. (Electric Power Research Institute) in U.S.A. is carrying out studies on all forms of electrical power generation, and as part of their general programme, materials needs for future power systems are being considered, as well as current problems such as temper embrittlement of steels and assessment of component safety by acoustic emission techniques.

The petrochemical and gas-turbine industries consume a high proportion of high-temperature materials and efforts to solve the problems presented by these applications tend to have very different structural characteristics, e.g. the petrochemical industry is much more independent financially and invests its own money, whilst gas turbines receive significant government support, either directly through national research establishments or indirectly via companies which have engine procurement orders from national governments. A notable recent example of international cooperation has been the COST 50 programme, which is a European concerted action on materials for gas turbines, grouping more then sixty research projects aimed at solving immediate problems and at defining basic parameters of importance for future applications. A discussion of some of these topics appears later. Typical informal groupings which have been created recently to examine future possible fields of application for high-temperature materials include the nuclear steelmaking club, which is looking at the use of nuclear process heat for steelmaking processes; an international group for looking at the boiler side of power generation; study groups for coal gasification research in the UK, West Germany, Poland and Japan; and several groups for studying nuclear power problems and exchanging information, based both on national government agencies and on companies.

5.5 CURRENT RESEARCH PROGRAMMES

The basis for this analysis is the application to which the various materials will be put and, where appropriate, national interests in a specific area will be pointed out. This inevitably results in some repetition of information given in earlier sections of this White Book.

5.5.1 Gas turbines

This technological area,more fully dealt with in Section 3.6., has provided most of the driving force for the development of new and improved high-temperature materials and the two basic alloy types of interest for operation above 800°C are nickel-base and cobalt-base. In order to fix the relative importance of these materials with respect to other applications it is worth noting that nickel for high-temperature applications only consumes about 15% of total nickel production (more than 50% is used for stainless steels and plating) although the final value of a component made from a nickel-base alloy may be extremely high compared to the materials content.

Early gas-turbine engines used carbide-hardened chromium-nickel stainless steels and, as more efficient engines were required for aircraft, these were quickly replaced by the precipitation-hardened nickel-base alloys (with high creep resistance) pioneered and typified by the alloys of the Nimonic series. Continued material improvements have led to an average annual increase in operating temperature of 10 K over 35 year period; whilst the cooling of turbine components enables them to function in gas temperatures well in excess of the alloy melting point (1).

Materials for gas turbines not only must possess a high rupture strength at high temperatures, they must be ductile at room temperature, and have good environmental resistance to oxidation and hot corrosion. Finally they must be capable of being economically formed into complex shapes. Initial developments led to wrought alloys being widely used but improved casting techniques and powder metallurgy methods are now being introduced. As compositions become more complex, the effect of heat-treatment and of trace elements is being thoroughly investigated by alloy producers and users. Of particular importance is the stability of alloy phases as a function of temperature and time, and their effect on creep resistance and ductility. The formation of new brittle phases during use can lead to embrittlment and dramatic component failure, and current research on the use of a phase-computation technique (Phacomp) for assessing the tendency of an alloy to form these phases, has shown that 'safe' alloys can be designed in this way. The deleterious effect of trace elements (less than 100 ppm) has been shown to be related to grain-boundary effects, and research on the exact mechanism is being carried out in Europe and the U.S.A. using sophisticated instruments for analysing very small volumes or areas of alloys. The development of refining techniques and careful selection procedures for raw materials have both been used to overcome these problems.

It must be noted that gas-turbine technologists, who largely determine the direction of materials research programmes recognise that the traditional metallurgical approach no longer has major development potential, and that increasing design sophistication leads to a need for more complex and costly development programmes (2). More attention is therefore given to processing developments, making the best use of currently available materials.

Processing developments being made in Europe and the U.S.A. have concerned themselves with: control of grain size either by hot-working or by controlled solidification; dispersion-strengthening using a high-energy attrition process; in-situ fibre composites formed by controlled solidification of eutectic alloys, etc. The reasons for such developments are varied but a predominant and common characteristic is to obtain a higher operating temperature with assured reliability. One current development, initiated in the U.S.A., has used the superplastic flow properties of a fine-grained stable structure to make components such as discs out of materials which are normally so strong as to render their forming a difficult, if not impossible, task. An added benefit is a considerable saving in material. Controlled solidification of conventional materials is a further illustration of the emphasis being placed on materials processing; by this technique grain boundaries which are normal to the stress axis can be reduced or eliminated, thus giving better creep properties. European engine makers are known to be looking at this process.

An advantageous combination of some of the merits of precipitation hardening with those of dispersion hardening is obtained by the process termed mechanical alloying. This is achieved using an attrition process, and, by incorporating stable inert oxide phases into the metallic matrix, very strong high-temperature alloys have been developed. Although first developed in the U.S.A. this process is now being further investigated in England and in Switzerland.

The use of eutectic alloy compositions to make blades from in-situ fibre composites has received a great deal of attention in recent years in France, West Germany, Switzerland, England and the U.S.A., using both nickel- and cobalt-base alloys. Problems being investigated include oxidation-resistant compositions; phase stability in a variety of thermal conditions; and processing parameters to ensure the economic production of regular reproducible structures.

In both Europe and the the U.S.A. there is an overall decrease in research and development activity compared with the 1960's. Economic pressures have led to the recognition that alloy development programmes require a disproportionate effort to obtain any specified benefit, and this explains why materials processing research is assuming a more dominant role, along with efforts to obtain closer compositional control and hence a more accurate assessment of long-term in-service behaviour based on better specification. Attention is being paid in the U.S.A. to the possible economic benefits of various developments. Typical amongst such projects is a study of the effects of reducing the materials input weight and its impact on the associated metal-removal processes. This is known as 'near-shape processing' and is exemplified by investment casting of single-piece components (as a substitute for multi-piece assemblage) and by the increasing interest in powder forging and hot isostatic compaction to form final shapes. Government agency funding mainly for defence purposes is aiding the execution of this work in the U.S.A.

A change in development emphasis occurs when materials for marine or land-based engines are considered, especially in view of the market growth prospects for pumping engines in energy exploration and exploitation, power generation units, etc. Reliability, long service life free of maintenance, and the aggressive corrosive environment arising from non-distillate fuels or a contaminated atmosphere have led to concerted efforts to improve surface stability without unduly impairing strength. Current programmes examining fundamental mechanisms are in progress in U.K., Norway, Holland and France, and studies of protective coatings, their formation and performance are being made in France, U.K. and Switzerland. Evaluation and rig testing of materials and components is in progress in U.K., Switzerland and West Germany. It is particularly important that improvements be made to the hot-corrosion resistance of nickel-base alloys in view of their wide-spread use and a recently introduced casting alloy, with increased chromium content, IN939, is a step in this direction. Cobalt-base alloys which are widely recognised as having good hot corrosion resistance (mainly as a result of their generally higher chromium content compared with nickel-base alloys) are the subject of research projects in the U.S.A. concerned with computerised processing control to reduce costs; the improvement of hot-corrosion resistance and powder metallurgy forming technology. Evaluation of cobalt-base alloys is being carried out in France, U.K. and Switzerland.

The topics covered by the COST 50 programme on gas-turbine materials give a good indication of the relative emphases which are placed on new materials, materials processing and in-service assessment. The topics may be divided into two groups: immediate problems encountered in current practice and research for future applications.

Three subjects in the first group, viz. hot corrosion, stability and fatigue, were identified as being of prime importance and these led to investigations into the basic phenomena of hot corrosion; a comparison of hot-corrosion tests (which vary very widely); new coatings for components; metallurgical stability at temperature and under load; and high-temperature fatigue, particularly cycling of stress and temperature, and microstructural effects.

In the second group, the fabrication of superalloys by powder metallurgy routes was selected as a subject with potential, and this is a European reflection of a prior American realisation.

The COST 50 exercise is of particular relevance to collaborative efforts on a European scale because although it has established only modest objectives the project has led to much closer contacts between interested parties and has shown that gas-turbine materials are of special significance, meriting a free exchange of ideas and information. If nuclear process heat is to become a European concerted action then there are good grounds for anticipating a similar successful collaboration between materials suppliers, design engineers, plant constructors and national governments.

The replacement of metallic components by ceramics has long been envisaged as a major step forward in improving gas-turbine efficiencies by virtue of the higher operating temperatures to which ceramic components can be subjected, their high specific strength, their corrosion resistance and inherently low cost. Silicon carbide and silicon nitride have been identified as having outstanding properties based on work carried out in the U.K. and in the U.S.A. The basic problem, however, is the difficulty of designing components in brittle materials for operation under load, and it can be fairly claimed that if designs were available present materials could be used.

A major programme on ceramic gas-turbine engines is at present underway in the U.S.A. There are two objectives: one is for an all-ceramic automobile engine with a 200-hour life at 1370°C; the second is for an electric-power turbine using ceramic vanes operating at 1370°C in a 30 MW power-generating machine. An announcement has also been made recently that the behaviou of a ceramic marine gas-turbine engine will be studied as a follow-up to the above project. Ceramic bearings are also being studied in the U.S.A. and in some circumstances have been shown to be superior to metallic bearings.

Another promising avenue being studied in the U.S.A. and in the U.K. is the possibility of partially substituting nitrogen by oxygen, and silicon by aluminium, in silicon nitride, to produce a so-called sialon. It is claimed that the sialons have better all-round properties than silicon nitride and are easier to fabricate by conventional hot-pressing techniques.

In comparison with the cost of metallic alloy projects the above projects are very cheap but the long-term potential is enormous, since metallic components are now approaching their absolute limit and a quantum jump in efficiency will be possible with ceramic materials. There is a clear need here for a long-term, forward-looking European effort.

To summarise this section: the current emphasis is on cost/benefit analyses for materials development projects, with the main practical work being aimed at process development to reduce costs and improve materials utilisation. Longer-term goals which are being examined in current research projects include novel composite materials and ceramic engines.

5.5.2 Power-plant applications

The basic point with respect to current research activities on materials for this economically important technology is the fact that few if any, of the components in conventional fossil-fuel-fired plant are exposed to temperatures in excess of 800°C. Materials for the fabrication of superheaters and steam pipes have a maximum 100000-hour-life with a stress-rupture value of 50 MNm^{-2} at 700°C, and envisaged service temperatures do not exceed 675°C, even though adequate oxidation resistance is available for 700°C operation (3). Typically an austenitic steel of the Esshete 1250 type with 15% Cr has replaced the 316 stainless grades which can only function satisfactorily up to 600°C. Materials developments in this field are almost exclusively the preserve of steel-makers, with assessments being made in conjunction with plant construction companies and the electrical utilities. An interesting current development is the possibility of using duplex structures in which an inner strength-bearing material, e.g. alloy 800 or Esshete 1250, is clad with an outer layer of high chromium content (50%), so that super-heater tubes can be made with improved corrosion resistance to sulphur- and vanadium-containing atmospheres for oil-fired boilers, and to chlorides for coal-fired boilers. The U.K. has been particularly active in studying these problems and it is now widely recognised that liquid sulphate attack at temperature in the range 640 to 700°C is particularly deleterious. Materials solutions are being sought to this problem and, even though the new materials cost up to three times the conventional steels, the benefit gained is a ten-fold improvement in life.

Nuclear power generators which operate at higher temperatures fall rather more readily into our definition of high-temperature plant. The AGR (Advanced Gas-Cooled Reactor) has an outlet temperature of 650°C (compared with a light-water reactor outlet temperature of about 325°C) and the HTR (High Temperature Reactor), whose coolant can be used either as a source of heat to drive chemical processes or as a working fluid for a direct-cycle turbine, can have an outlet temperature of 1000°C or more. The materials problems wiht AGR's are answered by the use of conventional alloys which operate close to their practical limit at present, but HTR's will require new materials or improved purity helium as a coolant if they are to function above 800°C; the subject is dealt with more fully in Section 3.7.

When considering research programmes on materials for reactors for power generation two points have to be remembered. Firstly, safe continuous operation is essential in view of the high cost of down-time (of the order of U.S. $ 300.000/day), and secondly the lengthy overhaul time for a nuclear reactor compared with conventional plant. The aim, therefore, of much of the current work is reduce the accent on materials requirements by operating at lower temperatures, thereby reducing the effects of both mechanical stresses and environmental attack. Although thermodynamic efficiency is reduced, improved component reliability is obtained and overall economy is raised.

In contrast to power generation, the use of a nuclear reactor for process heat demands the highest possible outlet temperature for adequate efficiency.

There are thus two aspects to materials research for nuclear heat: component reliability for power generation and maximum component temperatures for process technology. The Dragon reactor has successfully worked for many thousands of hours, whilst in the U.S.A. and Germany similar reactors have been satisfactorily running for extensive time periods. There are however very serious materials problems remaining, particularly with respect to service lives of up to 30 years. The helium coolant is slightly impure and is thus in a condition in which it can attack components containing aluminium, titanium, chromium, silicon, etc. The behaviour of the iron-nickel-base alloy 800 in this environment has been and is being, particularly well studied in the U.S.A. and in Europe. One result of these investigations has been the realisation that the elements giving strength via intermetallic compounds (γ') are attacked, and strength is thus lost. In consequence solid-solution strengthening, or even dispersion strengthening, is needed if adequate strength is to be maintained. The movement in alloy specifications from 1% chromium steels for oil-fired stations, to 9% chromium for AGR/fast reactor components, and to nickel-base alloys for the HTR, may well be partially reversed for process-heat applications and it is not ruled out that refractory-metal alloys may find a role to play in this technology.

Current research on nuclear process-heat applications appears to be related to steelmaking, steam reforming and coal gasification, with interests evident in Japan, West Germany, Poland and the U.S.A. The U.K. appears to have little current effort underway and past experiences in this field, in which the U.K. has made significant research and engineering investment, does not lead to optimism about the immediate future of this technology. The problems with heat exchangers, fission product penetration, and a lack of suitable alloys, seem to be at the root of this attitude. A major programme is now underway in West Germany. Nuclear heat transferred by helium is to be used for a steam reformer, and initial design studies at present being carried out suggest that reactor coolant temperatures of 900 - 950°C may be sufficiently high for the envisaged chemical process to be viable. There are obviously very significant problems related to efficiency and safety which have to be answered. A need for the study of carburisation reactions at high temperatures is apparent.

As an area of future activity it seems clear that nuclear process heat will increase in importance and the study of materials behaviour in unusual environments will form a vital part of such developments.

The use of geothermal sources to provide energy, either as dry steam or as liquids with a high salt content, is being investigated in the U.S.A. Materials which can resist both the erosive and corrosive attack of such fluids are not readily available, and research into the mechanisms by which materials such as ceramics and refractory metals deteriorate is essential, since initial results show a short life time for components in conventional turbines driven from these sources. A project investigating geothermal energy sources has just been initiated in the U.K. and materials problems will figure largely in this study.

5.5.3 Chemical technology

This field of application is dealt with in Section 3.2. The upper temperature limit quoted by codes of practice for components used in the chemical industry is about 800°C but recent process developments, such as the steam reforming of hydro-carbons and thermal cracking of feed-stock to produce ethylene, have led to increased demands for more resistant materials. Steels have thus been replaced by iron-nickel-chromium alloys. Research programmes tend to be executed by the chemical plant users in conjunction with alloy suppliers. The aim of such studies is to qualify a given material for a given environment. Typical investigations cover component life (and its prediction) under creep conditions, with particular reference to weld failures. Creep is aggravated or complicated by thermal cycling or by very steep temperature gradients across the wall thickness of a component. Since assessing fitness for purpose, i.e. fulfilling a design requirement, is needed before specifying any one alloy, much of the research tends to be concerned with simple rig testing or creep testing of components. The exact details of research programmes in this field are neither widely nor readily available and it is not possible to discuss them further. However, current developments in this field are influenced by the increased price of the feedstock since 1973, which is leading the chemical industry to use higher temperatures for their processes. This means that there is a continuing move to replace stainless steel by nickel-base alloys, as the corrosion problems become more severe. This in turn means that the alloy producers are having to provide further data on their alloys to qualify them in these new high-temperature situations. As an illustation of this a recent investigation into alloy 800 has shown that, by close control of the composition and tightening of the specification, improved creep strength can be obtained, which can thus lead either to thinner-walled units or higher operating temperatures. Although this approach may seem mundane and pedestrian, the benefits are well worth the effort, since greater efficiency is obtained.

Research into more efficient use of coal is being carried out so that probable shortfalls in the supply of oil and natural gas can be forestalled. Coal liquifaction and gasification are the principal solutions proposed, and these involve materials problems which it will be essential to solve if such processes are to be made available on a commercial scale. Coal gasification methods can be classified according to their energy content, with the lowest value being used for electrical power generation, and the highest as a direct replacement for natural gas. The Lurgi process has worked successfully to produce lower-energy-content fuels, but it suffers from the drawback that it cannot readily be scaled up. By increasing plant size and reaction pressure it is believed that better and cheaper gasification can be achieved, but materials problems arise in the reactor vessel where the coal reacts with oxygen and steam at 14 MNm^{-2} and 1000°C to produce methane and other minor by-products. The aggressive environment, thermal stresses and the production of hydrogen will require some composite-type structure, in which a metallic alloy will be faced with a ceramic insulator. The assembly of such reaction vessels, which will be far larger than nuclear reactor pressure vessels, will ultimately be by welding techniques using proven non-destructive methods for testing the integrity of the vessel prior to service. The first steps to find solutions to these problems have been taken in Europe and in the U.S.A. The motion of a high-pressure hot gas stream containing abrasive particles against the surface of metallic components presents a situation to which there are no ready answers in terms of materials. This is clearly an area deserving research effort. The same problem, combined with a hot corrosive atmosphere containing sulphur, is also encountered in coal-liquifaction processes, and coatings will be demanded by designers if plant life is to be satisfactory. The most commonly used erosion-resistant alloys, e.g. Stellites and cobalt-tungsten-carbide composites, tend to corrode in such an environment and new materials are needed.

Although it is difficult to obtain specific details of research work in progress, serious consideration is being given to extracting the energy content of organic waste which mainly occurs in the refuse produced by our consumer society (a recent American estimate (5) suggests a figure of approximately 7% of the fuel needs for electric power supply could be met from such a source). This type of process leads to an unusual form of corrosion of the container vessel by the liquid slags formed during incineration of the refuse.

It should be noted that the economic structure differences between the petrochemical industry and the public utilities providing power, lead to different relationship between the materials and component supplier, and the end-users. These are reflected in their research and development activities and in the availability of information in their programmes.

5.6 Conclusions

The current problems presented by high-temperature applications are dominated by the needs of the gas turbine, power generation and petrochemical industries, with particular emphasis on the first member of this group since it operates at the higher end of the temperature range and makes the major use of superalloys. Nevertheless it must be borne in mind that for the materials-producing industries the less spectacular applications using solid-solution or carbide-hardened alloys, rather than superalloys are of similar economic importance. Research and development cannot realistically be separated into two categories when the objectives of most of the programmes are so clearly stated, i.e. they are goal oriented. Nevertheless the current programmes tend to be concentrating on processing developments rather than on new materials, and the economic use of materials has become a key factor in deciding on the details of individual development projects. Corrosion problems at high temperature and methods of alleviating them are increasingly figuring in research efforts, whilst the performance in-service under complex stresses of conventional materials is of necessity being studied in parallel with environmental exposure projects. The problems facing high-temperature materials for nuclear power generation and nuclear process-heat applications are daunting, with the latter topic demanding a major step forward in high-temperature technology. For this application the available evidence on materials performance does not lead to great optimism that the problems will readily be solved, and the sheer scale of operation and the service-life requirements will demand very heavy investment in research development and testing before full-scale plant can be constructed.

An overall picture of the scope of current research activities in Europe is difficult to formulate since on many topics the work is funded by private industry itself and is not publicised. Even if the topic is known, the extent of financial support and the man-power involved is rarely available. However, Tables 5/1 and 5/2 attempt to indicate the types of investigation known to be in progress; in Table 5/1 they are categorised in regard to the industries to which the work is directed, and in Table 5/2 in respect of the types of material involved. It is clear from Table 5/1 that almost all topics are being studied in connection with gas turbines, and many of them also in connection with nuclear reactors or the chemical or power industries. Relatively little work is directly aimed at applications in the fields of electrical heating, metal processing, glass and ceramics processing or combustion engines, and only specific assessment of materials is in progress in relation to magneto hydrodynamics and hydrogen production. Table 5/2 indicates that all the major types of material are receiving attention, with nickel- and cobalt-base superalloys being covered on most topics. Austenitic steels and nickel-base solid-solution alloys are also widely studied, the main omissions being in the more advanced production techniques, which would not be expected to offer benefit at an economic level to these materials.

Research Topic		**Chemical Technology and Conventional Power Generation**	**Electrical Heating Metals, Glass and Ceramics Processing**	**Gas Turbines**	**Nuclear Reactors**	**MHD and Hydrogen Production**
Composition :	Wrought	X	X	X	X	
	Cast	X		X		
Production Process :	Single Crystal			X		
	Directional Solidification			X		
	Dispersion hardening			X		
	Powder metallurgy			X		
	Composites, etc.	X		X		
Technology :	Joining	X				
	Thermo-mechanical work			X		
Mechanical Properties :	Creep	X		X	X	
	Fatigue	X		X	X	
	Environmental effects	X		X	X	
Corrosion :	Data	X	X	X	X	X
	Mechanisms	X		X	X	
	Protection		X	X		
Structure :	Stability			X	X	
	Radiation effects				X	
Design and Control :	N.D.T.			X		
	Design practice	X		X	X	
	Fracture mechanics			X		

Table 5/1 *Current European Fields of Research on High-Temperature Materials in relation to Industrial Applications.*

Research Topic	Austenitic Steels	Nickel-base Solid-Solutions	Nickel-base Superalloys	Cobalt-base Superalloys	Refractory Metals	Platinum Metals	Ceramics and Cermets
Composition : Wrought	X	X	X	X	X	X	X
Cast	X	X	X	X	X		
Production Process: Single crystal			X	X			
Directional Solidification			X	X			
Dispersion hardening	X	X	X		X	X	
Powder metallurgy			X	X	X	X	
Composites etc.			X	X			X
Technology: Joining	X	X	X	X	X	X	X
Thermo-mechanical work			X				
Mechanical Properties: Creep	X	X	X	X	X	X	X
Fatigue	X	X	X				X
Environmental effects	X	X	X	X			
Corrosion: Data	X	X	X	X	X	X	
Mechanisms	X	X	X	X	X		
Protection			X	X	X		
Structure : Stability	X	X	X		X		
Radiation effects	X	X	X				
Design and Control: N.D.T.	X	X	X				X
Design practice	X	X					X
Fracture mechanics	X	X	X				X

Table 5/2 Current European Fields of Research on High-Temperature Materials in relation to Material Type.

Due to the inability to obtain comprehensive information on current projects, it has not been considered appropriate to attempt to assess the degree of attention being paid to the different research topics.

The need for reference materials in the general field of high-temperatures materials was identified by a survey conducted in 1971 by the C.E.C., and this has recently been followed by a more comprehensive enquiry embracing scientific and industrial organizations, among which figure Europe's most important producers and users of high-temperature materials and relevant research laboratories. The results of this survey are given in Appendix Table M.

Reference materials with certified composition and/or purity are mostly needed for the calibration and checking of analytical methods such as element analysis, emission spectrography, X-ray absorption and fluorescence and gas analysis. There is also a considerable demand for reference materials for more sophisticated methods, such as quantitative analysis by microprobe, X-ray diffraction, and for activation analysis.

85% of the currently used reference materials with certified composition and purity are obtained from public and private suppliers, which indicates that a certain market has already developed. The range of available solid-form certified reference materials, however, does not meet the entire demand for composition ranges and, in particular, defined impurity levels, of nickel, nickel-cobalt and titanium alloys.

On the other hand, the situation with regard to reference materials with certified physical and/or technological properties is quite different. For these a high demand exists, but they are not so readily available. The origin of about one third of such reference materials is from an organisation's own production or is not even known. The demand centres on mechanical properties (hardness, dilatation, strength, reference defects, etc.); thermal and thermodynamical properties (thermal conductivity, etc.); and physical and/or technological properties (corrosion resistance, density, porosity, etc.).

It is mainly for this reason, that the consulted organizations are highly interested in co-ordinated European collaboration - to which most of them, moreover, can actually contribute by participation in the preparation of reference materials.

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6. FUTURE HIGH-TEMPERATURE MATERIALS RESEARCH AND DEVELOPMENT

6.1 OBJECTIVES

The foregoing sections have shown that the technology of high-temperature materals is, in general, well advanced. On the basis of long experience coupled with well-directed research and development, the materials currently in practical use in industry are giving reasonably satisfactory service. Nevertheless failures in service do occur from time to time and limited life, as a consequence of progressive deterioration of the materials, is commonly accepted. There is thus clear scope for the introduction of improvements, both on the level of properties obtainable to enable new engineering concepts or more advanced designs to be exploited, and in the reliability of existing materials and constructional processes to enable the trouble-free life of current plant to be extended.

It appears that the general experience of operators of high-temperature plant is that service failures are rarely due to creep or stress-rupture; this indicates that the basic requirement of creep strength at the operating temperature is fully appreciated by designers, and that the design codes to which plant is built are adequate. If creep or stress-rupture failures do occur in practice, they are almost invariably due to abnormal temperature excursions. Failures or inadequate performance of components operating at elevated temperatures can usually be assigned to one of three main causes:

i) Corrosion.
ii) Thermal fatigue or thermal shock.
iii) Mechanical fatigue.

Interaction of these three factors may well occur, corrosion for example, frequently providing a nucleus for the start of mechanical or thermal fatigue cracking. In many cases, particularly in the chemical or process industries, failure by any of these mechanisms may be associated with welded joints.

Whereas the corrosion behaviour is characteristic of the material and its environment, and does not depend to any appreciable degree on the particular form of the component involved, the thermal and mechanical fatigue properties are, to a large extent, a function of the shape and size of the component as well as of the inherent properties of the material itself. In order fully to study the conditions under which such failures occur, it is therefore necessary to supplement the testing of small specimens of materials with larger-scale tests of actual or simulated components under realistic conditions of temperature, stress and environment.

At the present time, the forefront of research and development on high-temperature materials is directed to the discovery of new or improved materials capable of operation at increased temperatures under high stresses, or to provide increased resistance to corrosion in specific environments. Such work is largely in the experienced hands of the material producers or direct users and it is not to be expected that others could usefully contribute without installing a comprehensive system for the production and processing of experimental materials, and spending a long period gaining experience of the appropriate production technology. Such action would, in any case, be in competition with existing facilities.

The intensive study of the behaviour of existing high-temperature materials under operating conditions, with a view to modifying the materials themselves, their processing or their conditions of service to give improved performance, is potentionally quite as rewarding as the development of new materials. The users of large plant are, however, primarily concerned with the maintenance of operation using established materials and procedures, while the material producers themselves do not have the economic incentive to develop modifications which will only replace an existing product. This field of activity therefore tends to be neglected in favour of the scientifically and technologically more exciting area referred to above, and it is suggested that it is worthy of increased attention.

The broad pattern of a study of this nature would be as follows:

1. Study and identification of failure modes.
2. Study of material properties and behaviour on laboratory-scale simple specimens.
3. Testing of components or simulated assemblies in prototype rigs.

The recommendations made in section 6.3. conform to this pattern.

6.2 POTENTIAL OF DIFFERENT HIGH-TEMPERATURE MATERIALS

Progress in the development of high-temperature materials, as with other areas of technology, tends to follow a so-called "envelope curve" giving a more or less regular increase in desired characteristics. Such a curve is made up of a series of individual life-cycle curves covering successive technological systems which fulfil a certain function.
In the case of high-temperature materials, the individual curves each represent a family of materials or a technique, which initially provides a rapid gain before slowing down and eventually being overtaken by a new curve representing a new development, even before the full potentiality of the initial curve has been realized. Figure 6/1 shows such a curve for gas-turbine materials, in which the criterion is the temperature for a given stress-rupture life. This suggests that, for this particular application, nickel alloys in the conventional wrought or cast forms have almost reached their full potential; the same applies to iron- and cobalt-base alloys. Prospects for directionally-solidified eutectics and ceramics are now being exploited by appropriate experts and

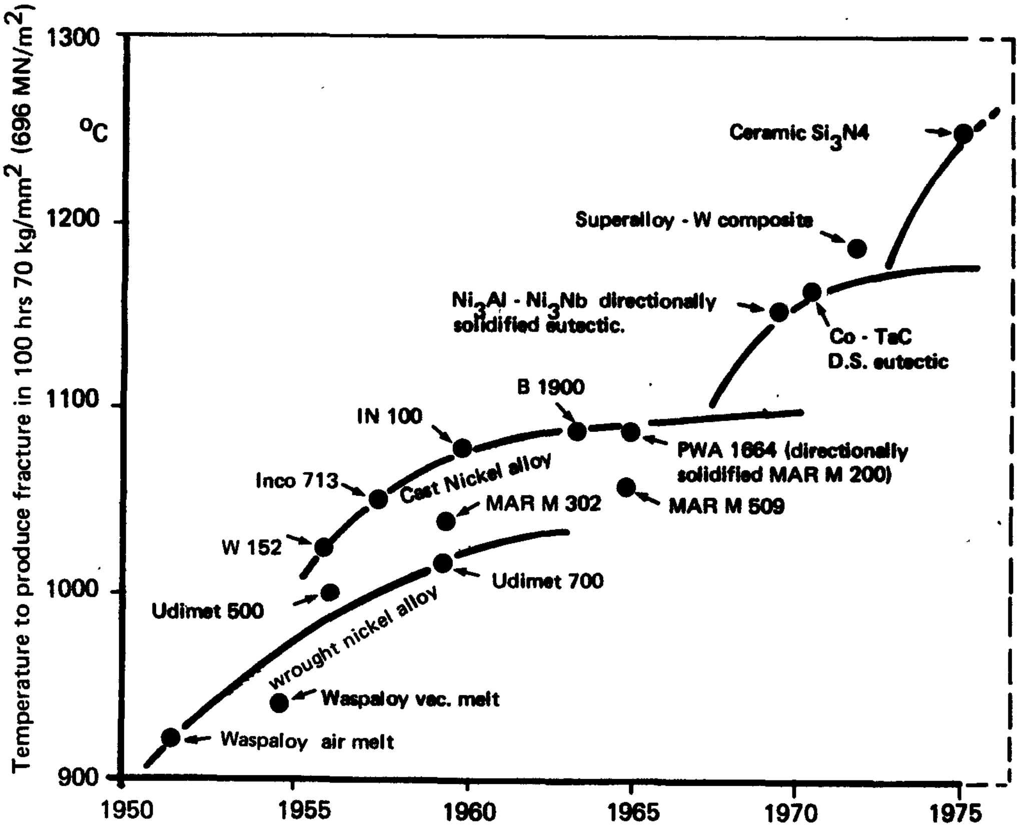

Fig. 6/1 *Progress in High-Temperature Turbine Materials.*

it is most unlikely that a newcomer to the field could catch up before the potentialities of the techniques were essentially exhausted. In the absence of entirely new concepts, which may arise at any time in a largely unplanned manner when creative workers pay attention to any field of technology, it therefore appears unlikely that significant further advance in gas-turbine blade materials is to be expected. However, one possibiliy not apparently yet explored to any extent, is a combination of the two latest elements in the curve of Figure 6/1 , i.e. directionally-grown ceramic or ceramic-metal eutectics.

The above comments on potential of nickel, iron and cobalt alloys do not apply to applications other than to gas turbines, because the criteria of acceptability, including economic factors, are then different. The envelope curve for a different application would be formed of entirely different individual curves so that, for example, the potentiality of nickel-iron based alloys for reformer tubes may still be far from exhausted. The development of appropriate envelope curves requires first the establishment of a clearly-defined parameter based on the known limits to performance of existing materials, which in turn requires a clear understanding of the common modes of failure in service. The parameter may well take the form of an expression including terms for a number of basic mechanical, physical or chemical properties of the material.

With the establishment of an appropriate service parameter for a different application, it should be possible to compile an envelope curve and to assess the suitability for that particular application of alternative materials.To enable the parameters to be determined for all candidate materials, the compilation of a data store covering all basic properties of materials would be desirable.

It is suggested, therefore, that the following steps should be taken as a contribution to the selection of suitable materials for high-temperature service:

1. Study and identification of failure modes for specific applications.
2. Establishment of parameter representing serviceability, and the generation of an envelope cruve.
3. Compilation of property data bank for established alloys.
4. Selection of candidate materials on basis of service parameter.
5. Testing of components in prototype rigs.

It will be noted that items 1 and 5 above duplicate items 1 and 3 of the suggestions listed in Section 6.1.

6.3 RECOMMENDATIONS FOR ACTION

On the basis of the arguments presented above and of the information on different industries and classes of material given in Sections 3 and 4 of this White Book, and also of the picture of current European activity outlined in Section 5, it is suggested that work is required under three broad classifications - first work of a general nature embracing all types of material and applicable to a wide range of uses; second, work of a specific nature aimed at the study of selected aspects of the behaviour of iron-nickel-cobalt base alloys - the proposed topics are all of relevance to a number of different industrial applications; and third, similar specific topics of study of advanced ceramic materials, again of general applicability. At the present time, no specific action is thought to be necessary in regard to the refractory metals or to metals of the platinum group, with the exception of compilation of data, since the applications of these materials are in restricted fields for which research and development activities are generally adequately provided by established suppliers of these materials in collaboration with current or potential users.

6.3.1 General topics

i) Study of failure modes in high-temperature applications

The failure of components in high-temperature service is generally due to one or more of the three factors given in Section 6.1., viz. corrosion, thermal fatigue or thermal shock, or mechanical fatigue; creep or stress-rupture failures are not common since they are adequately guarded against in design and hence may only arise when operational control of the plant is faulty, or perhaps when specific corrosive agents present in the environment have an unexpected effect on the high-temperature properties of the material. Up to the present, the mechanism of many such failures has not been understood because of the difficulty of correlating the conditions experienced by the failed component in service with those obtained in the laboratory under simplified conditions. To systematically analyse these mechanisms, it is necessary to make careful intercomparisons between service failures and failures of samples exposed under controlled laboratory conditions of stress, temperature and environment. Particular attention needs to be paid to the influence of trace amounts of contaminants in the atmosphere.

Failures must be examined using all conventional metallographic techniques, supported by the more recent physical techniques such as ion microscopy and Auger spectroscopy for the examination of fracture surfaces. Particular attention will need to be paid to the possible intergranular penetration of contaminating elements. The laboratory facilities for the reproduction of failures will need to embrace a wide variety of gaseous atmospheres, with and without additional contamination by liquid or solid salt mixtures (simulating fuel ashes, etc..). Stress systems must range from steady stresses producing simple creep deformation to high- and low-frequency cyclic stresses,with or without superimposed steady stresses, to produce fatigue failures. In this project, it is not anticipated that thermal stresses need to be simulated by temperature differences. It is anticipated that failure studies of this type will enable the critical mechanisms for typical applications to be identified, and a parameter involving selected basic properties of a material to be established as representative of the merit of that material for that use.

ii) Compilation of property data bank

For the comparison of different candidate materials for a particular application, and for design purposes, it is necessary to have available all the relevant mechanical, physical and chemical properties. For well-established materials, many of these are already available from suppliers and users, but only in few cases are all the data available at one place, and, in particular, the scatter of properties to be expected is not commonly known.

It would provide a very useful service to the whole engineering community if a central data bank could be initiated and maintained, the input being collected from all available sources. When necessary, determinations of properties by specialist organizations should be undertaken to complete the available data.

iii) Reference materials.

The need for the extension of the availability of reference materials in high-temperature technology has been established by the outcome of the B.C.R. survey (Appendix Table M). The preparation and authentication of such materials could, with advantage, be carried out in co-operation with the body undertaking the compilation of the central data bank.

iv) Component testing rig.

The development of any new device, material or constructional method requires a number of progressive experimental steps:

(1) Basic tests of material, e.g. tensile, creep, fatigue, etc.
(2) Tests of material in appropriate form, i.e. bar, sheet, tube, castings.
(3) Tests of joints and assemblies, i.e. welds, bolts, rivets, joints in dissimilar materials.
(4) Tests of components or assemblies under simulated service conditions, i.e. start-up, shut-down, change of conditions life testing.

(1) and (2) are covered by what are normally described as laboratory tests, but (3) and (4) require special test rigs to accomodate a wide range of shape and size of assembly. Such test rigs are usually specially designed to meet the immediate requirements, but nevertheless some aspects of a test facility may permit a more universally applicable rig to be installed, which, in addition to its use in connection with new developments, would also be applicable to the improvement of existing materials and techniques of construction as outlined in Section 6.1.

A universal type of high-temperature mechanical testing rig requires facilities for a range of stresses to be applied to the part or assembly under test. The applied stresses should be capable of selection from amongst the following:

i) Static: Steady stresses produce creep deformation and eventually fracture. They may be tensile, compressive, torsional or multiaxial, and rig facilities should enable appropriate choice to be made.

(ii)	Fatigue:	Fluctuating stresses lead to fatigue failures. Facilities are required for component or assembly testing under a wide range of frequencies and with superimposed steady and cyclic stresses, i.e. including non-zero mean stress.
(iii)	Impact:	Impulsive stresses may lead to sudden fracture, particularly after some creep or fatigue damage has been generated or structural changes (embrittlement) have taken place. Facilities for impact testing of components at elevated temperatures are required.
(iv)	Friction and wear:	Relative movements of the parts of an assembly may lead to wear, fretting or welding. Test facilities are required to accomodate continuous sliding to measure friction and wear, and reciprocating motion of varying amplitude to assess fretting and seizure. Control of loading between the parts is necessary.

All the above stress conditions should be applicable with the part under test maintained at the required temperature in the appropriate atmospheric environment, as regards composition and pressure; additionally it should be possible to vary the temperature according to a controlled programme.

A special form of multiaxial test facility closely reproducing service conditions involves tube bursting under internal pressure. In this case the atmospheres inside and outside the tube should be independently variable. The size of tubes to be accomodated should range from that appropriate for drawn tubes of boilers and heat exchangers to that for cast tubes of chemical plant, e.g. reformers. As well as constant pressure under isothermal conditions, cycling of pressure and temperature should be allowed for. In order to simulate service conditions, the internal and external media should be variable and the rates of flow controllable, so that appropriate temperature gradients through the tube walls could be maintained or varied according to a planned schedule.

No attempt is made at present to assign limits of temperature, load and environment to the proposed rig facilities; a much more careful survey of engineering requirements would be necessary for this to be done.

6.3.2 Iron, nickel and cobalt alloys

Four areas of study are recommended in relation to these materials, each covering topics of basic importance to the understanding of the behaviour of materials in high-temperature service.

(i) Size effect in relation to mechanical properties.

The strength of materials is conventionally measured in terms of the mean stress which can be sustained by a small sample.

In the case of high-temperature testing, reaction with the environment may be taken place and particularly with long-time creep or fatigue tests, this may seriously affect the measured strength by:

a) General corrosion causing a reduction of load-bearing section,
b) Grain-boundary corrosion giving a wedge effect, or
c) Inward diffusion of deleterious elements along grain boundaries influencing creep mechanisms, cavitation, etc.

Previous work has revealed a size effect in nickel-base alloys when creep testing has been carried out in air, and the effect was correlated with grain size of the alloy. However, the operating mechanisms were not identified. An investigation is proposed in which selected alloys of interest to the aircraft and stationary gas-turbine industries are studied in a range of relevant atmospheres, including burnt fuels with different levels of sulphur, halides and fuel ashes, as well as HTR helium, and possibly also vacuum. Creep tests will be carried out at different temperatures and stresses, on samples of different sizes. The tested samples will be examined by normal metallography and by specialized physical techniques including ion microscopy and Auger spectroscopy. In some cases, the use of radioactive tracers in the environment will be considered.

(ii) Corrosion.

a) High-temperature stress-corrosion studies.

The corrosive attack of materials in service is of such importance in high-temperature technology that a broad study of the operating phenomena is justified. Most corrosion studies are currently made on unstressed samples and it is therefore important to establish the extent to which corrosion mechanisms and rates are influenced by steady or cyclic stresses. A systematic exploration of this field can be made in environmental creep or fatigue testing equipment, the rates of attack being monitored by weight change measurements and by measurements of the depth of penetration by microscopy. The materials to be studied should initially be those of interest in industrial gas turbines and in chemical plant, while the atmospheres should be air, sulphurizing and carburizing, with temperatures in the range 800 - 1000°C. The effects of solid and liquid deposits, such as fuel ashes, etc. would also need to be studied. Tests will need to be scheduled to continue for up to 10 000 hours. The major factor in the control of hot corrosion rates is the formation of an adherent and coherent coating of corrosion product, and the effectiveness of this depends on its mechanical and thermal properties in relation to those of the underlying metal. The interpretation of the results of stressed corrosion tests will involve an understanding of these properties, particularly the elastic moduli and thermal expansion characteristics of both alloy and scale.

At a later stage when the experimental technique has been established and initial results understood, the behaviour of protective coatings under stressed conditions should be studied.

b) Effect of rare-earth elements and oxides on scaling.

It is known on empirical grounds that small additions to an alloy of certain reactive metals or their oxides can produce a very marked effect on the coherence and adherence of chromium-containing oxide scales. The effect has been used for over 40 years in connection with electrically-heated resistance materials and more recently has been shown to be beneficial in stainless steel fuel cans in advanced gas-cooled nuclear reactors. Prominent among the effective elements are calcium, zirconium and the rare-earth metals. The benefits of such additions are not confined to improved scale adherence, since it is found that a continuous chromium oxide scale forms at lower chromium contents and grows more slowly than in untreated alloys, and the temperature dependence of the oxidation rate is reduced. The effective addition may be made as the metal to the alloy, as a dispersed oxide or even as an initial surface coating of oxide.

Although a number of mechanisms have been proposed to explain the effect, none has been established as valid. A satisfactory understanding would permit the effect to be more efficiently exploited.

A study of the phenomenon is proposed covering the following aspects:

Comparison of effectiveness of different elements.
Determination of optimum technique of introduction.
Applicability to different alloys involving both chromium- and aluminium-containing protective scales.
Effectiveness in different corrosive environments.
Range of temperature of effectiveness.

The techniques of study should be thermogravimetric under both isothermal and temperature-cycling conditions, allied to constitutional studies of the scales formed, and to metallographic measurements of the depth of penetration of corrosion effects.

c) High-chromium nickel-base alloys.

The petrochemical industry has conventionally used iron-nickel-chromium alloys containing about 20% chromium for applications at temperatures around 1000°C, but with increasingly severe conditions of temperature and environment alloys with about 50% chromium have been introduced. The simple binary 50 Ni-50 Cr alloy has poor strength and is brittle, but improved alloys containing small proportions of niobium and/or zirconium give improvement in both strength and ductility. A study of their scaling and corrosion resisting characteristics in different environments, coupled with an assessment of the rare-earth effect (see above) would form a basis for the extension of their serviceability in this important field.

Commercially available samples of the alloys should be examined in terms of constitution and morphology of the scale formed in different environments and temperatures, and the kinetics of the corrosion processes determined.

iii) Diffusion of interstitial elements in nickel-iron-chromium alloys.

The mechanical properties of high-temperature alloys operating in a corrosive environment are influenced by the reactions at the surface and by the diffusion of the reacting elements within the alloy. In some cases the diffusing element is picked up from the environment and in others, it may be removed from the alloy by the environment, for example, carburization or decarburization. Two interstitial elements, viz. carbon and hydrogen, are of particular important to the behaviour of iron-nickel-chromium alloys in high-temperature service, and these alloys are of practical significance in a variety of industries including metallurgical, chemical, petrochemical and nuclear power.

It is proposed that a study of the diffusion process should be made to establish the kinetics and to analyse the operating mechanisms. Bulk diffusion and grain boundary diffusion of the interstitials must be differentiated as they can differ by 2 or 3 orders of magnitude, and account must be taken of the formation of separate phases by the diffusing species in reaction with the major constituents, as well as with minor addition elements such as titanium, niobium and aluminium. The diffusion of the interstitial elements through any initially-formed oxide scale would also be studied.

The techniques of study should involve metallography, microprobe analysis, chemical analysis and radioactive tracers.

iv) High-temperature behaviour of welded joints.

Although the inherent high-temperature properties of materials may be well characterized by tests on simple specimens, their behaviour in service is frequently determined by the properties of welded joints, and it is rarely that these are available in a realistic form. A weld commonly involves component parts of complex shape which may not be amenable to post-weld heat treatment, so that the joint when put into service may embrace regions with different thermal histories, different compositions (since consumables such as filler wires and electrodes may not match the parent material) and residual internal stresses.

A comprehensive study should be undertaken of the creep, fatigue and thermal fatigue properties of welded joints covering the following variables in a systematic fashion:

Nature and condition of parent metal.
Welding technique i.e. metallic arc, inert gas tungsten arc, etc.
Composition and form of consumables.
Post-weld heat treatment.
Effects of service environment.
Joints between dissimilar metals.

Initial work should be carried out on simple laboratory-scale test specimens cut from welded plate, or in the condition of undressed welds, but further assessment would necessitate tests on prototype components in the type of larger-scale testing rig outlined in section 6.3.1 item (iv).

6.3.3 Ceramics

In comparison with metals, all ceramic materials are characterized by three major shortcomings which inhibit their use in stress-carrying high-temperature applications. These are brittleness, poor thermal shock resistance and the variability of properties due to the presence of surface and internal flaws. These shortcomings have received a good deal of attention and some progress in combatting them has been achieved, but nevertheless the advanced ceramic materials, typified by silicon nitride, silicon carbide and the "sialons" (materials formed by the partial nitriding of sintered mixtures of silica and alumina) still suffer from these characteristic failings. The basic development of silicon nitride and silicon carbide, so far as the effects of composition on properties are concerned,has been carried close to the expected limit, but practical applications are nevertheless few because of the failings mentioned. Action in this area should therefore be aimed at possible methods of overcoming these failings or avoiding their consequences by modified design philosophies. The following lines of study are proposed:

i) Surface treatments.

The flaws which spread under the influence of stress to form cracks, which, in turn lead to eventual fracture, include the very important surface flaws. It is therefore probable that surface treatments could be devised to reduce the number or the magnitude of such flaws, or to modify their character so that they do not develop under stress. Possibilities which should be explored include the following:

Generation of a surface layer under compressive stress (akin to toughened glass).
High-melting-point glazes.
Plasma-sprayed coatings.
Metallic layers, chemically deposited or evaporated.

An effective coating or treated layer would need to be unaffected by the service temperature or by corrosion by the environment, and to have physical characteristics, particularly thermal expansion coefficient,appropriate to the substrate. The effectiveness of a treatment should be assessed primarily by mechanical tests on a statistical basis, but the influence of reflective coatings on thermal shock resistance should be determined.

ii) Study of fracture statistics and mechanisms at normal and elevated temperatures.

The short-time strength of ceramics at normal temperature is controlled by the initiation of fracture from existing flaws. For a given material and size of specimen the strength is inversely related to the dimensions of the largest flaw. The considerable variation in measured strength of brittle materials due to the range of effective flaw sizes can be expressed statistically using the empirical procedures due to

Weibull. These have mainly been applied to simple 3- or 4-point bending strengths determined on constant-section test specimens, but have also been extended so that the results are applicable to specimens of different size and geometry. However the more generalized application of strength statistics to specimens or components of complex shapes subjected to multiaxial stress systems at normal and elevated temperatures would increase the confidence of engineers in their practical application.

The time-dependent strength of brittle ceramics is normally described in terms of the "static fatigue strength", which represents the constant uniform stress which will produce fracture in a given time, i.e. the equivalent, in metallurgical parlance, of the stress-rupture strength. The mechanisms operating to produce time-dependent fractures are crack growth of sub-critical-size flaws under the influence of stress, and the accelerating effect of corrosion from the environment. These are specific to the material and the environment under consideration, and detailed study of the kinetics and mechanisms for advanced ceramics under different conditions of temperature and environment would aid in the understanding of their fields of practical applicability. Most static fatigue testing has been limited to relatively short periods of time (less than 10^5 sec $\sim$ 27 hours) and it is important, particularly at higher temperatures when thermally activated processes such as diffusion are so much accelerated, to determine the properties over much longer periods - more akin to those used in creep and stress-rupture testing in metallurgy.

There is, therefore, a need for a comprehensive programme of "static fatigue" testing of advanced ceramics in different environments and at different temperatures, and analysis of the results both in terms of empirical statistics and of operating mechanisms.

iii) Application of non-destructive testing to failure statistics

In the light of the accepted dependence of the strength of ceramics on the presence of flaws, it is apparent that the effective minimum strength could be increased by the elimination of the larger flaws. This could be achieved by improvements in processing procedures or by identification and rejection of components containing them. For this purpose improved N.D.T. procedures are necessary. The critical flaws have sizes in the range 1-50 μm and are related to the grain size or pore size of the ceramic. Scanning or microscopic techniques aimed at the detection and location of individual flaws seem to hold little prospect of success, but greater possibilities exist with those techniques based on the effect of flaws on bulk properties such as mechanical damping. Proof testing has been used to eliminate specimens containing large flaws, but this may lead to extension of sub-critical flaws in borderline specimens without producing failure, and thus making them more susceptible to subsequent failure in service. One possibility worthy of study is the combination of proof testing, with monitoring of crack extension, perhaps by such methods as acoustic emission, so that specimens suffering crack extension without immediate failure could also be rejected.

iv) Joining of ceramic parts and of ceramics to metals

The development of reliable methods of making joints between similar and dissimilar ceramic materials, and between ceramics and metals, would widen considerably the opportunities for their engineering application, similar to the benefits obtained from the development of welding techniques for metals. The use of glasses for fused joints is restricted to lower-temperature regions of an assembly, but some form of high-temperature reaction bond, using pre-placed reagents, would possibly enable the refractory nature of the parts to be maintained. The brittle characteristics of the ceramics make it particularly necessary to ensure that close match of thermal expansion coefficients of the mating parts and the joint material is maintained.

There is a considerable existing technology relating to glass-to-metal joints and to brazed joints between certain ceramics and metals, but such assemblies are usually designed for service at only moderate temperatures. The situation with regard to advanced ceramics and the operation of joints at elevated temperatures demands further research.

APPENDICES

TABLE A NOMENCLATURE

Activity

A thermodynamic term describing the effective concentration of a species as modified by its relative affinity for the other constituents of the system.

Anti-phase boundary (A.P.B.)

The boundary between independent regions in an ordered crystal where the repeat patterns of atoms are out of step with one another.

Aspect ratio

The ratio of the longest dimension of an elongated micro-structural feature to the smaller dimension at right angles, e.g. **Grain aspect ratio (G.A.R.)**

Atomisation

The dispersion of a molten metal stream into droplets by jets of gas or liquid, the solidified droplets being collected as metal powder.

Austenite (austenitic)

A solid solution of one or more elements in **face-centred-cubic (f.c.c.)** iron, nickel or cobalt, often referred to as γ-phase.

Bucket

The aerofoil shaped component (usually called a "**blade**" in aircraft engines) on to which the hot gases impinge to produce rotary motion in a gas turbine.

Burner can

The component of a gas turbine in which fuel is combusted to provide hot gases to power the engine. Also called **combustion chamber.**

Burner rig

Apparatus which provides a simulated gas-turbine environment for assessing the hot-corrosion resistance of high-temperature alloys.

Catastrophic oxidation

The rapid oxidation that occurs in certain alloys when the protective oxide layer breaks down and bare metal, depleted in protective elements such as chromium or aluminium, is exposed to oxidizing gases.

Cermet

A body consisting of ceramic particles bonded with a metal.

Closed dies

Forging or forming dies designed to restrict the lateral flow of metal within the die set.

Composite

A heterogeneous body usually containing particles, fibres or sheets which confer additional properties, such as improved high-temperature strength, to the matrix.

Cracking

A process used to reduce the molecular weight of hydro-carbons by breaking molecular bonds by thermal or catalytic methods.

Creep

Time dependent strain occurring under stress.

Creep-rupture

Same as **Stress rupture.**

Die casting

A casting process where molten metal is forced into the cavity of a metal mould. (also refers to a casting made in above process.)

Diffusion bonding

A method of joining metals by applying heat and pressure to induce recrystallisation across the interface without producing a molten phase.

Directional solidification (D.S.)

Solidification of molten metal under a directional temperature gradient such that feed metal is always available for the portion that is solidifying.

Disc

A disc-shaped component of a gas turbine, mounted centrally on an axial shaft, to the circumference of which the buckets (blades) are attached.

Dislocation

A linear defect in the structure of a crystal; when dislocations are moved through a crystal under an external stress they produce a change of shape of the crystal.

Dispersion hardening

An alloy strengthening mechanism resulting either directly (at moderate temperatures) or indirectly (at high temperatures) from the presence of a fine dispersion usually of oxide in the alloy matrix.

Drop forging

Forging with a hammer falling under gravity, such that the period of contact with the material is very short.

Ductile-brittle transition temperature (DBTT)

The temperature, either above or below room temperature, at which certain alloys exhibit a sudden change from ductile to brittle behaviour when deformed in a given manner.

Electron beam

A method of directing a controlled stream of electrons at a metal to produce localised heating, as in **electron-beam melting (EBM) or electron-beam welding (EBW).**

Eutectic

An isothermal reversible reaction in which a liquid alloy forms two or more intimately mixed solid phases on cooling. Also refers to the alloy composition which undergoes the above reaction and to the resulting microstructure which forms.

Eutectoid

A term similar to 'eutectic', in which a solid solution (rather than a liquid solution) forms two or more intimately mixed phases on cooling.

Extrusion

A process of forcing material through a shaped die orifice to produce an article with the desired cross-sectional outline.

Fatigue

A failure mode in which cracks are initiated and propagated under the action of a repeated, or fluctuating stress, the maximum value of which is below the tensile strength of the material. In thermal fatigue, the cyclic stresses are produced by fluctuations in temperature.

Ferrite (ferritic)

A solid solution of one or more elements in **body-centred-cubic (b.c.c.)** iron, often referred to as α-phase.

Flame Spraying

A method of applying metallic coatings inwhich a wire or powder feed is melted in a high-temperature gas flame and molten droplets are blown against the workpiece.

Free Energy of Formation (ΔF, ΔG)

A thermodynamic measure of the stability of a compound relative to its constituent elements, a larger negative number indicating greater stability.

Gamma prime (γ')

An intermetallic compound, $Ni_3(Ti,Al)$, that acts as a precipitation-strengthening agent in many nickel-base superalloys.

Gatorising

A patented process for precision forming superalloy components, such as turbine discs, from blanks using the alloy in a superplastic condition.

Green compact

A powder-metallurgical term describing a powder body in the pressed but unsintered condition.

Header

A pipe, conduit, or chamber which distributes fluid to a series of smaller pipes or conduits.

Hoop stress

Circumferential stress in a vessel having axial symmetry, c.f. the stress within a hoop of a wooden barrel.

Hot corrosion

A term used to describe the type of surface attack suffered by alloy components in hot oxidizing atmospheres containing impurities such as sulphur, sodium, vanadium, chloride, etc.

Hot salt corrosion (HSC)

This occurs when conditions favour the deposition of salt films on turbine components.

Hot isostatic pressing (H.I.P.)

A process, frequently used for the consolidation of powders in which a hot gas transmission medium applies pressure equally in all directions.

Hubbing

An operation in which a shaped tool is pressed into a metal blank to produce a shaped cavity, such as a die impression for a metal mould.

Induction melting (I.M.)

Melting in a furnace in which an alternating current in a primary coil surrounding the charge develops heat within the charge by electromagnetic induction (frequently performed under vacuum, V.I.M.).

Intermetallic compound

An intermediate phase in an alloy system, having a narrow range of homogeneity and relatively simple stoichiometric proportions, in which the nature of atomic bonding can vary from metallic to ionic.

Internal oxidation

Formation of isolated oxide particles beneath a metal surface by preferential reaction of certain alloy constituents with inwardly-diffusing oxygen atoms.

Investment casting

A process of casting metal into a mould produced by surrounding an expendable pattern made of, for example, wax, with a refractory slurry. After setting of the refractory at room temperature, the wax is removed by melting.

Laser-pellet concept

Inertially confined system in which fuel pellets are heated to ignition by laser beams, using a pulsed mode of laser operation.

Liquidus

The point on an equilibrium phase diagram representing the temperature at which a given composition begins to freeze on cooling or finishes melting on heating.

Lithium aluminium silicate (L.A.S.)

A commercially important glass ceramic phase (spodumene).

Magnesium aluminium silicate (M.A.S.)

A commercially important glass ceramic phase (cordierite).

Martensite

Usually a metastable phase in iron alloys formed by the shear transformation of austenite on cooling. The distorted iron structure is characterised by an acicular or needle-like microstructure.

Mechanical alloying

A powder metallurgical technique involving dry, high-energy grinding of powder constituents to produce alloyed or composite particles, frequently used to prepare oxide dispersion-strengthened superalloys

Mirror concept

Magnetically confined plasma system, mostly using open-ended geometry, operating in a steady state mode.

Mismatch

A small error in registry between the similarly oriented lattice planes of a **coherent precipitate and an** alloy matrix. With an **incoherent precipitate,** the mismatch is so large that no special orientation relation exists.

Non-destructive testing (NDT)

Inspection or testing by methods that do not destroy the part to determine its suitability for use.

Nozzle guide vane (NGV)

A stationary component of a gas turbine that directs the hot gases from the burner can onto the buckets (blades).

Open dies

Forging or forming dies in which there is little or no restriction to lateral flow of metal.

Order-disorder

The ability of the atoms in many alloy phases to occupy specific sites in the lattice, rather than being randomly distributed.

Oxide dispersion strengthening (O.D.S.)

Strengthening of an alloy by the incorporation of a dispersion of inert oxide particles.

Overlay coating

A coating formed by the deposition of a layer of protective metal or alloy upon a component surface by techniques such as plating, spraying or sputtering.

Pack Coating (or diffusion coating).

A protective coating produced by heating a component in a powder 'pack' so that protective elements such as chromium or aluminium diffuse into the alloy surface.

Pigtail

A flexible small-bore pipe through which hot gas passes between header and reaction tube in a reforming process.

Plasma

A highly ionised gas which may be produced by an electric arc and used as a very intensive heat source in plasma spraying, **plasma arc welding (P.A.W.), melting (P.A.M.)**, and **refining (P.A.R.).**

Precipitation hardening

Hardening caused by the precipitation of a constituent from a supersaturated solid solution.

Precision casting

A process (such as investment casting) for producing castings of reproducible accurate dimensions.

Press forging

Forging between dies in a press, over an extended period of time relative to drop forging.

Proof stress

The stress that will cause a specified small permanent set in a material, for example, 0.2% plastic strain.

Pyrolysis

Thermal decomposition of a material without producing combustion.

Reaction sintering

Densification of a heated porous compact which is accompanied by reaction between the constituents themselves or with the sintering atmosphere.

Refining

Purifying crude or impure metals, by methods such as **Electroslag refining (ESR), Vacuum arc refining (VAR)**, or **Plasma arc refining (PAR).**

Reforming

The thermal or catalytic conversion of petroleum naphtha into more volatile products of higher octane number.

Relaxation

Reduction of stress either at constant strain or by creep.

Remelt stock

A term used to describe standard-size pre-alloyed ingots for subsequent remelting into cast components

Rotating electrode process (REP);

A process for producing high-purity metal powder in which molten droplets are flung from a rotating electrode.

Semi-conductor

An electrical conductor whose resistivity at room temperature is in the range of 10^{-9} - 10^{-2}ohm.cm and in which the conductivity increases with increasing temperature over some temperature range.

Sigma Phase (σ)

A hard, brittle intermetallic phase occurring in many binary and ternary alloys of the transition elements; the sigma phase in the iron-chromium system is commonly encountered in high-temperature alloys.

Slip casting

A process in which a powder slurry is poured into an absorbent mould, from which the green 'casting' may be subsequently removed, dried and sintered.

Solid solution

A single solid homogeneous crystalline phase containing two or more chemical species.

Solidus

The point on an equilibrium phase diagram representing the temperature at which a given composition finishes freezing on cooling or begins to melt on heating.

Spalling

The cracking and flaking of particles from a surface.

Stacking-fault

A planar defect in a crystal which results when the atomic stacking sequence is incorrect; stacking faults form most readily in deformed metals having a low, rather than high, **Stacking fault energy (SFE)**

Stainless steel

An iron-base alloy containing chromium and exhibiting corrosion resistance together with a useful degree of strength at moderate temperature.

The classification in Table C is based primarily on the prevailing structure; "ferritic", containing little or no nickel; austenitic with around 10 wt% nickel; up to 35 wt% nickel in the "high nickel class". The 'precipitation hardening' class contains alloys with ageing additions, such as copper and molybdenum.

Static fatigue

Failure of brittle materials held for an extended time under a constant load, resulting from crack propagation due to environmental attack.

Stress intensity factor, K_{Ic}

A parameter which measures the resistance of a material to fracture in the presence of a notch, crack or flaw.

Stress rupture

Failure which occurs in tension under constant load and temperature, under conditions which cause deformation by creep.

Substructure

Structural features, such as are formed by a large number of dislocations, which occur on a scale smaller than the grain size of a material.

Superalloy

A nickel-, cobalt-, or iron-base alloy developed for high temperature service where high stresses are encountered and where high surface stability is frequently required.

The division of the superalloy classification in Table C relates to the severity of operating conditions for which the alloys are designed. Thus 'high-nickel superalloys', relying primarily on solid-solution strengthening, have a lower temperature capability than "nickel-base superalloys" which primarily employ precipitation hardening and have more substantial refractory metal additions.

Superplasticity

A dramatic increase in degree of deformability exhibited by certain alloys having a stable fine grain structure when slowly deformed at an elevated temperature.

Thermo-mechanical processing (TMP)

A sequence of mechanical working operations and intermediate heat treatments designed to improve high-temperature strength properties in certain superalloys.

Theta-pinch concept

Magnetically confined system, open or closed geometry, operating in a pulsed mode.

Tokamak concept

System with toroidal (closed) magnetic confinement scheme, operating in a quasi-steady-state mode.

Topologically close-packed (T.C.P.)

The description given to intermediate phases (such as σ, μ, Laves, etc.) often encountered in superalloy compositions, in which layers of close-packed atoms are displaced from one another by sandwiched larger atoms.

Ultimate tensile strength (U.T.S.)

The maximum conventional stress that a material can withstand.

Void

A point defect in the structure of a crystal where either one or several lattice sites are unoccupied by atoms.

Weibull statistics

A technique for the analysis of the strengths of brittle materials based on the weakest link concept of failure at the most severe flaw in the sample. Values of the Weibull modulus range from about 5, for ceramics with highly variable strengths, up to 30 for very consistent ceramics.

Work hardening

An increase in hardness and strength caused by plastic deformation at temperatures lower than the recrystallisation range.

Yield point

The first stress in certain materials, usually less than the maximum attainable stress, at which an increase in strain occurs without an increase in stress; sometimes there may be a decrease in stress after yielding.

TABLE B MATERIAL PROPERTIES PRIMARILY RELEVANT TO THE USE OF METALLIC MATERIALS IN HEAT-TRANSFER SYSTEMS.

1\. physical properties
1.1 modulus of elasticity E_{static} & $E_{dynamic}$
1.2 Poisson's ratio
1.3 lin. mean coefficient of thermal expansion
1.4 thermal conductivity
1.5 specific heat
1.6 density

2\. structural stability
2.1 chemical composition
2.2 structural composition
2.3 influence of heat treatment

3\. short-time mechanical properties
- $\sigma_{0,2}$ -, σ_1-limit
- tensile strength
- uniform elongation
- rupture elongation + reduction of area
- σ/ε diagram
- notch impact strength, lateral expansion

3.1 as function of temperature
3.1.1 as received condition (normal operation)
3.1.1.1 influence of product form
3.1.1.2 heat to heat variations
3.1.1.3 influence of heat treatment
3.1.2 after loading
3.1.2.1 thermal stress
3.1.2.2 thermal & mechanical stress
3.2 for emergency conditions
3.2.1 influence of strain rates
3.2.2 influence of extreme conditions

4\. long-term properties
4.1 stress rupture & creep behaviour
4.1.1 rupture strength
4.1.2 stress rupture ductility
4.1.3 stress for x % strain
4.1.4 transition secondary/tertiary creep range
4.1.5 extrapolation feasibility for service life
4.1.6 effect of form, composition and initial heat treatment
4.1.7 influence of short-time loading
4.1.8 evaluation of remaining life time

4.2 fatigue behaviour
4.2.1 high-cycle fatigue
4.2.2 low-cycle fatigue
4.2.2.1 temperature dependence
4.2.2.2 hardening behaviour
4.2.3 interaction creep-fatigue
4.3 relaxation behaviour
4.3.1 influence of stress level
4.3.2 influence of hold time

5. fracture mechanics
5.1 cyclic fracture behaviour
5.2 monotonic fracture behaviour

6. effect of environmental conditions
6.1 reactor coolant influence
6.1.1 corrosive influences
6.1.1.1 general corrosion
6.1.1.2 substitutional corrosion
6.1.1.3 interstitial corrosion
6.1.2 influence on mechanical properties
6.1.2.1 physical reactor coolant influence
6.1.2.2 as selective corroding medium
- values to be determined see points 3, 4, 5

6.2 steam corrosion behaviour
6.2.1 oxidation stability
6.2.2 ripple formation
6.2.3 stress corrosion under normal conditions
6.3 corrosion behaviour under particular operational condition
6.3.1 stress corrosion in case of steam generator leakage
6.3.2 interaction reactor coolant-H_2O
6.3.3 corrosion sensitivity during cleaning process and plant shut down
6.4 tribological properties
6.4.1 self weldability
6.4.2 wear resistance against mechanical friction
6.4.3 influence of operational surface changes

7. workability
7.1 forming
7.1.1 rolling and forging
7.1.2 machining
7.1.3 casting
7.2 commercial availability of material
7.2.1 product forms & international availability
7.2.2 product dimensions
7.3 ease of joining
7.3.1 weldability
7.3.1.1 welding procedures
7.3.1.2 filler materials
7.3.1.3 heat treatment

7.3.2 solderability
7.3.2.1 filler materials
7.3.2.2 heat treatment
7.3.3 repair ability
7.3.3.1 before operation
7.3.3.2 after operation
7.3.4 special fabrication procedures

8. testability
8.1 material adequacy for non-destructive testing
8.2 meeting certain requirements

9. specifications and codes
9.1 within European Community
9.2 outside Community

10. international experience
10.1 available material data
10.2 production procedures
10.3 operational experience

11. costs
11.1 material costs
11.2 production costs
11.3 development costs
11.3.1 generation of material data
11.3.2 qualification

12. time limit for qualification

13. concept - related parameters

TABLE C COMPOSITIONS OF IRON-, NICKEL- AND COBALT-BASE ALLOYS.

Table C lists, by classified composition, iron-, nickel- and cobalt-base alloys. The alloys are identified by reference to their commercial names, with AFNOR and Luftfahrt-Werkstoff number designations being given in certain cases.

The column headed "Company Identification" refers to an organisation closely connected with the particular alloy, whether as a producer, developer or patent holder.

A small letter 'm' in the composition columns refers to the maximum level allowed for a particular element.

The alloys are listed alphabetically, and those with a purely numerical designation follow at the end of the alphabetical compilation in each group.
Alloys marked with ♦ are considered to be advanced experimental materials.

Alloy Base	Alloy Classification	Alloy Designation	Alloy Composition															Cast or Wrought	Company Identification	Alternative Designations	
			Fe	Ni	Co	Cr	W	Mo	Nb	Ti	Al	B	Zr	Si	Mn	C	Other			AFNOR	Werkstoff
Fe	Ferritic Stainless Steels	FV 535	Bal	0.5	6	10.5	-	0.75	0.3	-	-	0.008	-	-	-	0.85		W	Firth Vickers, U.K.		
		FV448	Bal	0.75	-	11	-	0.7	0.4	-	-	-	-	0.5	0.8	0.1	0.05N	W	Firth Vickers, U.K.		
		Greek Ascoloy	Bal	2.0	-	13	3.0	-	-	-	-	-	-	0.3	0.4	0.12		W	Vanadium Alloys, U.S.		
		H.46	Bal	0.6	-	11.5	-	0.65	0.25	-	-	-	-	0.4	0.6	0.16	0.3V	W	Jessop-Saville, U.K.	Z18CDVNb11	1.4914
		H.53V	Bal	0.55	6.5	10.6	-	0.8	0.4	-	-	-	-	-	-	0.08		W	„ „ „	Z10CKD10	1.4911
		Jethete M152	Bal	2.5	-	12	-	1.75	-	-	-	-	-	0.2	0.7	0.1	0.3N	W	United Steel Companies U.K.	Z12CND12	
		MF2	Bal	-	-	12	-	-	-	-	1.1	-	-	0.4	0.2	0.04		W	Allegheny Ludlum, U.S.		
		Kanthal A1	Bal	-	2.0	23	-	-	-	-	5.5	-	-	-	-	0.06		W	Kanthal AB, S.		
		Kanthal D	Bal	-	2.0	22	-	-	-	-	5.7	-	-	-	-	0.1		W	„ „ „		
		410	Bal	-	-	12.5	-	-	-	-	-	-	-	1.0m	1.0m	0.15m		W	------		
		422	Bal	0.7	-	12	1.0	1.0	-	-	-	-	-	0.36	0.65	0.22	0.25V	W	Crucible, U.S.		
	Precipitation Hardening Stainless Steels	AFC - 77	Bal	-	13	14.5	-	5.0	-	-	-	-	-	-	-	0.15	0.4V	W	Crucible, U.S.		
		AM 350	Bal	4.25	-	16.5	-	2.75	-	-	-	-	-	0.4	1.0	0.1	0.1N	W	Allegheny Ludlum, U.S.		
		AM 355	Bal	4.25	-	15.5	-	2.75	-	-	-	-	-	0.4	1.0	0.15	0.1N	W	„ „ „		
		Illium P	Bal	8.0	-	28	-	2.0	-	-	-	-	-	-	-	0.25	3.5Cu	W	-------		
		17-4 PH	Bal	4.25	-	16	-	-	Nb + Ta 0.27	-	-	-	-	0.6	0.28	0.04	3.3Cu	W	Armco, U.S.		
	Austenitic Stainless Steels	304	Bal	9.0	-	19	-	-	-	-	-	-	-	1.0m	2.0m	0.08m		W	-------		
		321	Bal	10.5	-	18	-	-	-	5×C	-	-	-	1.0m	2.0m	0.08m		W	-------		
		347	Bal	11	-	18	-	-	Nb+ Ta 10×C	-	-	-	-	1.0m	2.0m	0.08m		W	-------		
	High Ni Austenitic Stainless Steels	HK - 40	Bal	21.2	-	25.1	-	-	-	-	-	-	-	1.35	0.6	0.44	0.045N	C	Alloy Casting Inst., U.S.		
		HN	Bal	25	-	21	-	0.05m	-	-	-	-	-	2.0m	2.0m	0.35		C	„ „ „ „		
		Thermalloy 52	Bal	24	2.0	22	1.2	-	0.8	-	-	-	-	-	-	0.4		W	Abex Corp., U.S.		
		35Ni 20Cr (Chromax)	Bal	35.5	-	19.5	-	-	-	-	-	-	-	2.0	1.0m	0.15m		W	------- (Driver Harris, U.S.)		
		310	Bal	20.5	-	25	-	-	-	-	-	-	-	1.5m	2.0m	0.25m		W	-------		
		332	Bal	32	-	21.5	-	-	-	-	-	-	-	0.5	1.0	0.04		W	-------		

Alloy Base	Alloy Classification	Alloy Designation	Alloy Composition															Cast or Wrought	Company Identification	Alternative Designations	
			Fe	Ni	Co	Cr	W	Mo	Nb	Ti	Al	B	Zr	Si	Mn	C	Other			AFNOR	Werkstoff
Fe	High Mn Alloys	CMN	Bal	15	-	25	-	-	-	-	-	-	-	-	12	0.65	0.45N	W	Crucible, U.S.		
		16-5-6	Bal	15	-	16	-	6.0	-	-	-	-	-	0.5	7.5	0.07m	0.35N	W	Timken, U.S.		
		22-4-9	Bal	3.5	-	20.5	-	-	-	-	-	-	-	0.15	8.5	0.55	0.4N	W	Armco, U.S.		
	High Fe Super-Alloys	A-286 (Tinidur)	Bal	26	-	15	-	1.25	-	2.15	0.2	0.003	-	0.4	1.4	0.05	0.03V	W	Fried Krupp, D.	Z06NCT25	1.4944
		CG-27	Bal	38	-	13	-	5.5	0.6	2.5	1.5	0.01	-	0.1	0.1	0.05		W	Crucible and General Electric, U.S.		
		CRM 6D	Bal	5.0	-	22	1.0	1.0	1.0	-	-	0.003	-	0.5	5.0	1.05		C	Chrysler Corp., U.S.		
		Discaloy	Bal	26	-	13.5	-	2.75	-	1.75	0.1	-	-	0.8	0.9	0.04		W	Westinghouse, U.S.		
		Incoloy 800	Bal	32	-	20.5	-	-	-	-	-	-	-	0.35	0.75	0.04	0.3Cu	W	Henry Wiggin, U.K.		
		Incoloy 802	Bal	32.5	-	21	-	-	-	0.75	0.58	-	-	0.38	0.75	0.35		W	" " "		
		Incoloy 901	Bal	42.7	-	13.5	-	6.2	-	2.5	0.25	-	-	0.4	0.45	0.05		W	" " "	Z8NCDT42	2.4662
		N 155 (Multimet)	Bal	20	20	21	2.5	3.0	1.0	-	-	-	-	0.5	1.5	0.15	0.15N	W	Union Carbide, U.S. (Cabot Corp., U.S.)	Z12CNKDW20	1.4974
		V-57	Bal	27	-	14.8	-	1.25	-	3.0	0.25	0.01	-	0.75m	0.35m	0.08m	0.5Vm	W	Allegheny Ludlum, U.S.		
		16-25-6	Bal	25	-	16	-	6.0	-	-	-	-	-	0.7	1.35	0.08m	0.15N	W	Timken, U.S.		
		Crown Max.	Bal	11	-	23	3.1	-	-	-	-	-	-	1.6	-	0.14		C	Firth Vickers, U.K.		
	Fe-base Super-Alloys	MA 956E ♦	Bal	-	-	20	-	-	-	0.5	4.5	-	-	-	-	-	$0.5Y_2O_3$	W	Henry Wiggin, U.K.		
		15-4-1 ♦	Bal	-	-	15	-	-	-	-	4.0	-	-	-	-	-	1Y	C	General Electric, U.S.		

Alloy Base	Alloy Classification	Alloy Designation	Alloy Composition															Cast or Wrought	Company Identification	Alternative Designations	
			Fe	Ni	Co	Cr	W	Mo	Nb	Ti	Al	B	Zr	Si	Mn	C	Other			AFNOR	Werkstoff
Ni	High Ni Super-Alloys	Brightray B	25	Bal	-	16	-	-	-	-	-	-	-	-	-	0.1	0.2Cu	W	Henry Wiggin, U.K.		
		Brightray S	1.0	Bal	-	20	-	-	-	0.4	-	-	-	-	-	0.1		W	″ ″ ″		
		Chronite	10	Bal	-	13.5	-	-	-	-	1.0	-	-	0.4	1.0	-		C	Chronite, U.K.		
		D-979	27	Bal	-	15.0	4.0	4.0	-	3.0	1.0	0.01	-	-	-	0.05		W	Allegheny Ludlum, U.S.		
		Hastelloy B	5.0	Bal	2.5m	0.6	-	28	-	-	-	-	-	0.7	0.8	0.10		C	Cabot Corp., U.S.		
		Hastelloy S	1.0	Bal	-	15.5	-	14.5	-	-	0.2	0.009	-	-	-	0.02m	0.02La	W	″ ″ ″		
		Hastelloy X (Nimonic PE 13)	18.5	Bal	1.5	21.8	0.6	9.0	-	-	-	-	-	0.5	0.5	0.1		W	″ ″ ″ (Henry Wiggin, U.K.)	NC22FeD	
		Inconel 600	7.2	Bal	-	15.8	-	-	-	-	-	-	-	0.2	0.2	0.04	0.25Cu	W	Henry Wiggin, U.K.		
		Inconel 601	14.1	Bal	-	23	-	-	-	-	1.35	-	-	0.25	0.5	0.05	0.5Cu	W	″ ″ ″		
		Inconel 617	-	Bal	12.5	22	-	9.0	-	-	1.0	-	-	-	-	0.07		W	″ ″ ″		
		Inconel 625	3.0	Bal	-	22	-	9.0	3.6	-	-	-	-	0.2	0.3	0.05	0.1Cu	W	″ ″ ″		
		Inconel 700	0.7	Bal	28.5	15.0	-	3.75	-	2.2	3.0		-	0.3	0.1	0.12	0.05Cu	W	″ ″ ″		
		Inconel 706	40	Bal	-	16	-	-	Nb+ Ta 2.9	1.75	0.2	-	-	0.18	0.18	0.03		W	″ ″ ″		
		Inconel 718	18	Bal	-	19	-	3.0	5.0	0.8	0.6	-	-	0.2	0.2	0.04	0.1Cu	W	″ ″ ″	NC19FeNb	2.4668
		Inconel X-750	6.75	Bal	-	15	-	-	0.85	2.5	0.8	-	-	0.3	0.7	0.04	0.05Cu	W	″ ″ ″	NC15FeT(Nb)	
		NA-22H	Bal	48	-	27	6.0	-	-	-	-	-	-	1.0	1.3	0.5		C	Blaw-Knox, U.S.		
		Nichrome (60Ni 16Cr)	Bal	60	-	15	-	-	-	-	-	-	-	1.4	1.0m	0.04		W	Driver Harris, U.S.		
		Nichrome V (80Ni 20Cr)	-	79	-	20	-	-	-	-	-	-	-	1.4	-	0.04		W	″ ″ ″		
		T.D. Ni (D.S. Ni)	-	Bal	-	-	-	-	-	-	-	-	-	-	-	-	(5) 2.0ThO$_2$	W	Fansteel, U.S. (Sherritt Gordon, Can.)		
		T.D. Ni Cr◆ (D.S. Ni Cr)	-	Bal	-	20	-	-	-	-	-	-	-	-	-	-	(5) 2.0ThO$_2$	W	Fansteel, U.S. (Sherritt Gordon, Can.)		
		T.D. Ni Cr Al◆	-	Bal	-	16	-	-	-	-	4.0	-	-	-	-	-	(5) 2.0ThO$_2$	W	Fansteel, U.S.		
		WAZ 16	-	Bal	-	-	16	2.0	2.0	-	7.0	-	0.5	-	-	0.2		C	N.A.S.A., U.S.		
		WAZ 20	-	Bal	-	-	18.5	-	-	-	6.2	-	1.5	-	-	0.15		C	″ ″″″		
		50Cr 50Ni	1.0m	Bal	-	50	-	-	-	-	-	-	-	1.0m	0.3m	0.1m		C	-------		
		60Cr 40Ni	1.0m	Bal	-	60	-	-	-	-	-	-	-	1.0m	0.3m	0.1m		C	-------		
		8077	-	Bal	-	16	-	-	-	-	4.0	-	-	-	-	-	1.5Y$_2$O$_3$	W	Cabot Corp., U.S.		
		RA 333	18	Bal	3	25	3	3	-	-	-	-	-	-	-	0.05		W			

Alloy Base	Alloy Classification	Alloy Designation	Alloy Composition															Cast or Wrought	Company Identification	Alternative Designations	
			Fe	Ni	Co	Cr	W	Mo	Nb	Ti	Al	B	Zr	Si	Mn	C	Other			AFNOR	Werkstoff
Ni	Ni-base Super-Alloys	AF2-1DA	0.5m	Bal	10	12	6.0	3.0	-	3.0	4.6	0.015	0.10	0.1m	0.1m	0.35	1.5Ta	W	Universal Cyclops, U.S.		
		Astroloy	-	Bal	15	15	-	5.25	-	3.5	4.4	0.03	-	-	-	0.06		W	------		
		B1900	0.35m	Bal	10	8.0	0.1m	6.0	0.1m	1.0	6.0	0.015	0.08	0.25m	0.2m	0.1		C	Pratt and Whitney, U.S.		
		C242	1.0m	Bal	10	20.5	-	10.5	-	0.3	0.2	-	-	0.3	0.3	0.3		C	Rolls Royce (1971), U.K.		
		C263	0.7m	Bal	20	20	-	5.9	-	2.15	0.45	0.001m	0.02	0.4m	0.4	0.06		W,C	" " "	NCK20D	
		C1023	0.5m	Bal	10	15.5	0.2m	8.5	0.25m	3.6	4.2	0.0006	-	0.2m	0.2m	0.16		C	" " "		
		G64	-	Bal	-	11.0	4.0	3.0	2.0	-	6.0	0.25	-	0.5	0.4	0.13		C	Jessop-Saville, U.K.		
		G81	0.5	Bal	18	19.5	-	-	-	2.3	1.3	+	-	-	-	0.05		W	" " "		
		G83	-	Bal	10	10	-	10	-	3.0	2.0	+	+	0.5m	0.5m	0.1		W	" " "		
		GMR 235D	4.5	Bal	-	15.5	-	5.0	-	2.5	3.5	0.05	-	0.3m	0.1m	0.15		C	General Motors, U.S.		
		IN 100	-	Bal	15	10	-	3.0	-	4.75	5.5	0.015	0.05	-	-	0.15	1.0V	C	International Nickel, U.K.	NK15CAT	
		IN 587	-	Bal	20	28.5	-	-	0.7	2.3	1.2	0.003	0.05	-	-	0.05		W	" " "		
		IN 597	-	Bal	20	24.5	-	1.5	1.0	3.0	1.5	0.012	0.05	-	-	0.5		C	" " "		
		IN 738	0.5m	Bal	8.5	16	2.6	1.8	0.9	3.4	3.4	0.01	0.10	-	-	0.17	1.8Ta	C	" " "		
		IN 792	-	Bal	9.0	12.7	3.9	2.0	-	4.2	3.2	0.02	0.10	-	-	0.21	0.8Hf optional 3.9Ta	C	" " "		
		IN 939 ◆	-	Bal	19	22.5	2.0	-	1.0	3.7	1.4	0.01	0.10	-	-	0.15	1.4Ta				
		M21 (PD 21)	0.5m	Bal	1.0	5.8	10.5	2.0	1.5	0.5m	6.0	0.02	0.12	-	-	0.1		C	" " "		
		M 22	1.0m	Bal	-	5.7	11	2.0	-	-	6.3	-	0.6	-	-	0.13		C	" " "		
		M-252	-	Bal	10	19	-	10	-	2.6	1.0	0.005	-	0.5m	0.5m	0.15		W	General Electric, U.S.		
		MAR-M-002	1.0	Bal	10	9.0	-	10	-	1.5	5.5	0.015	0.05	-	-	0.15	1.5Hf 2.5Ta	C	Martin Marietta Corp., U.S.		
		MAR-M-004	-	Bal	-	12	-	4.5	2.0	0.6	5.9	0.01	0.1	-	-	0.05	1.3Hf		" " " "		
		MAR-M-200	-	Bal	10	9.0	12.5	-	1.0	2.0	5.0	0.015	0.05	-	-	0.15		C	" " " "		
		MAR-M-211	-	Bal	10	9.0	5.5	2.5	2.7	2.0	5.0	0.015	0.05	-	-	0.15		C	" " " "		
		MAR-M-246	0.15	Bal	10	9.0	10	2.5	-	1.5	5.5	0.015	0.05	0.05	0.1	0.15	1.5Ta	C	" " " "		
		MAR-M-421◆	1.0m	Bal	10	15.5	3.0	1.75	1.75	1.75	4.25	0.015	0.05	0.2m	0.2m	0.15		C	" " " "		
		MAR-M-432◆	-	Bal	20	15.5	3.0	-	2.0	4.3	2.8	0.015	0.05	-	-	0.15	2.0Ta	C	" " " "		
		MA-753	-	Bal	-	20	-	-	-	2.5	1.5	0.007	0.07	-	-	0.05	1.3Y_2O_3	W	Henry Wiggin, U.K.		
		MA-754E◆	-	Bal	-	20	-	-	-	0.5	0.3	-	-	-	-	-	0.6Y_2O_3	W	" " "		
		Nimocast PE 10	3.0	Bal	2.0m	20	2.6	6.0	6.7	-	-	-	-	0.25	0.3	0.25		C	" " "		
		Nimonic 75	5.0m	Bal	-	19.5	-	-	-	0.4	-	-	-	1.0m	1.0m	0.1m		W	" " "	NC20T	2.4630
		Nimonic 80A	3.0m	Bal	2.0m	19.5	-	-	-	2.5	1.4	0.008m	0.015	1.0m	1.0m	0.1m		W	" " "	NC20Ta	2.4631
		Nimonic 90	1.5m	Bal	18	19.5	-	-	-	2.4	1.5	0.02m	0.15m	1.0m	1.0m	0.13m		W	" " "	NC20KTA$_t$	2.4632
		Nimonic 105	1.0m	Bal	20	14.5	-	5.0	-	1.2	4.7	0.007	0.15m	1.0m	1.0m	0.12		W	" " "	NKCD20AT$_v$	2.4634
		C 130	-	Bal	-	21.5	-	9.8	-	2.5	0.7	-	-	-	-	0.1	-	C			
		IN 586	-	Bal	-	25	-	10	-	-	-	-	-	-	-	0.05	0.03Ce	W	Henry Wiggin, U.K.		

Alloy Base	Alloy Classification	Alloy Designation	Alloy Composition														Cast or Wrought	Company Identification	Alternative Designations	
			Fe	Ni	Co	Cr	W	Mo	Nb	Ti	Al	B	Zr	Si	Mn	C	Other			AFNOR	Werkstoff
Ni	Ni-base Super-Alloys	Nimonic 115	1.0m	Bal	14.2	15.0	-	4.0	-	4.0	5.0	0.018	0.15m	1.0m	1.0m	0.15		W	Henry Wiggin, U.K.	NCK15ATD	2.4636
		Nimonic PE 11	Bal	39	1.0m	18	-	5.25	-	2.3	0.8	0.001m	0.05m	0.5m	0.2m	0.06		W	" " "	Z8NCD38	
		Nimonic PK 33	1.0m	Bal	14.0	18.0	-	7.0	-	2.2	2.1	0.005m	0.06m	0.5m	0.5m	0.07m		W	" " "	NC19KDu/v	2.4665
		Nimonic PE 16	Bal	43.5	2.0m	16.5	-	3.3	-	1.2	1.2	0.003m	0.04m	0.3m	0.2m	0.06		W	" " "	NW11AC	
		René 41	-	Bal	11	19	-	10	-	3.1	1.5	0.01m	-	-	-	0.09		W	Teledyne Allvac, U.S.		
		René 77(1)	1.0m	Bal	18,5	15	-	5.2	-	3.5	4.25	0.05m	-	-	-	0.15m		W	General Electric, U.S.		
		René 80◆	-	Bal	9.5	14	4.0	4.0	-	5.0	3.0	0.015	0.03	-	-	0.17		W	" " "		
		René 85◆	-	Bal	15	9.3	5.35	3.25	-	3.25	5.25	0.015	0.03	-	-	0.27		W	" " "		
		René 95◆	-	Bal	8.0	14	3.5	3.5	3.5	2.5	3.5	0.01	0.05	-	-	0.15		W	" " "		
		TAZ 8B◆(2)	-	Bal	5.0	6.0	4.0	4.0	1.5	-	6.0	0.004	1.0	-	-	0.125	8.0Ta	C	N.A.S.A., U.S.		
		TRW VI A◆	-	Bal	7.5	6.0	5.8	2.0	0.5	1.0	5.4	0.02	0.13	-	-	0.13	9.0Ta 0.5Re 0.43Hf	C	TRW, U.S.		
		Udimet 500	4.0m	Bal	18	19	-	4.0	-	2.9	2.9	0.005	-	-	-	0.08		W	Special Metals Inc., U.S.	NCK20DAT	
		Udimet 700(3)	1.0m	Bal	18.5	15	-	5.2	-	3 5	4.25	0.05m	-	-	-	0.15m		W	" " "		
		Udimet 710◆	0.5m	Bal	15	18	1.5	3.0	-	5.0	2.5	0.02	-	0.2m	0.1m	0.07		W	" " "		
		Waspaloy A(4)	2.0m	Bal	13.5	19 5	-	4.3	-	3.0	1.4	0.006	0.09	0.5m	0.5m	0.07	0.03Sm 0.1Cum	C	Pratt and Whitney, U.S.	NC20KDTA	
		713C	-	Bal	-	12.5	-	4.2	2.0	0.8	6.1	0.012	0.10	-	-	0.12		C	International Nickel, U.S.	NC13AD	2.4670
		713 LC	-	Bal	-	12	-	4.5	2.0	0.6	5.9	0.01	0.10	-	-	0.05		C	" " "		

1. René 77 has the same composition as Udimet 700, but certain elements are controlled to prevent sigma phase formation.
2. Directionally Solidified.
3. Very similar to Astroloy.
4. Very similar to Waspaloy B, but heat treatment procedure differs.
5 2 Vol. percent ThO_2

\- Added.

Alloy Base	Alloy Classification	Alloy Designation	Alloy Composition															Cast or Wrought	Company Identification	Alternative Designations	
			Fe	Ni	Co	Cr	W	Mo	Nb	Ti	Al	B	Zr	Si	Mn	C	Other			AFNOR	Werkstoff
Co	**Co-base Super-Alloys**	AiResist 213◆	-	-	Bal	19	4.7	-	-	-	3.5	-	0.15	-	-	0.18	6.5Ta 0.1Y	W	AiResearch, Carrett Corp., U.S.	.	
		AiResist 215◆	-	-	Bal	19	4.5	-	-	-	4.3	-	0.13	-	-	0.35	7.5Ta 0.17Y	C	" " "		
		FSX 414	2m	10.5	Bal	29.5	7	-	-	-	- -	0.012	-	1m	1m	0.25		C	General Electric, U.S.		
		FSX 418	2m	10.5	Bal	29.5	7	-	-	-	-	0.012	-	1m	1m	0.25	0.15Y	C	" "		
		Haynes 151	-	-	Bal	20	12.7	-	-	-	-	0.05	-	1m	1m	0.50		C	Cabot Corp., U.S.		
		Haynes 188	1.5	22	Bal	25.5	15.0	-	-	-	-	-	-	0.2	0.75	0.08	0.08La	W	" "		
		HS 21	1.0	3	Bal	27	-	5	-	-	-	-	-	0.6	0.6	0.25		C	" "	KCN22W	
		J 1570	2.0	28	Bal	20	7.0	-	-	4.0	-	-	-	-	-	0.2			General Electric U.S.		
		J 1650	-	27	Bal	20	12.0	-	-	3.8	-	0.02	-	-	-	0.2	2.0Ta		" "		
		L 605	-	10	Bal	20	15	-	-	-	-	-	-	0.5	1.5	0.1		W	Crucible Steel, U.S.	KC20WN	2.4964
		(HS 25)																			
		(WF 11(																			
		LDA 204◆	-	10.5	Bal	25.5	7.5	-	-	-	-	-	-	-	-	0.8	4Ta	C	Avco Lycoming, U.S.		
		MAR-M-302	-	-	Bal	21.5	10.0	-	-	-	-	0.005	0.20	0.2	0.1	0.85	9Ta	C	Martin Marietta Corp. U.S.	KC22WTa	
		MAR-M-322	-	-	Bal	21.5	9.0	-	-	0.75	-	-	2.0	0.10	0.10	1.0	4.5Ta	C	" "		
		MAR-M-509	1.0	10	Bal	21.5	7.0	-	-	0.2	-	0.1m	0.5	0.1m	0.1m	0.6	3.5Ta	C	" "	KC24NWTa	
		MAR-M-905◆	-	20	Bal	20	-	-	-	0.5	-	-	0.1	-	-	0.05		W	" "		
		MAR-M-918	0.5m	20	Bal	20	-	-	-	-	-	-	0.1	0.2m	0.2m	0.05	7.5Ta	W	" "		
		MP 35N◆	-	35	35	20	-	10	-	-	-	-	-	-	-	-	-	W	Latrobe Steel Co., U.S.		
		(Multiphase)																			
		S 816	3.0	20	Bal	20	4.0	4.0	4.0	-	-	-	-	0.4	1.20	0.38		W	Allegheny Ludlum, U.S.		
		Thermalloy A1	-	1.0	Bal	31.0	13.0	2.0	-	-	-	-	-	-	-	2.25		C	Abex Corp., U.S.		
		UMCO 50	21	-	Bal	28	-	-	-	-	-	-	-	0.7	0.6	0.12m		W	Union Miniere, B.		
		W1 52	2.0	1m	Bal	21	11	-	20	-	-	-	-	0.5m	0.5m	0.45		C	Tungsten Institute, U.S.		
		X 40	1.5	10	Bal	22	7.5	-	-	-	-	-	-	0.5	0.5	0.5		C	General Electric, U.S.	KC25NW	
		(HS 31)																			
		X 45	2m	10.5	Bal	25.5	7.0	-	-	-	-	0.01	-	-	1m	0.25		C	" " "		

TABLE D *TRADE NAMES AND DESIGNATIONS OF IRON-, NICKEL- AND COBALT-BASE ALLOYS*

The Table lists in alphabetical order some of the trade names and designations used for iron-, nickel- and cobalt-base materials.

Designations, which therefore refer to one specific alloy (e.g. A-286) are marked with an asterisk (*). Trade names proper (e.g. Nimonic) appear only once, although there may be many alloys in a given series.

When seeking to indentify the composition of a particular alloy from the trade name, the user of Table D is referred either to Table C (for the more common alloys) or to a reference cited in the bibliography (Table L) (for the less well known materials).

For alloys with perhaps an unfamiliar commercial name (e.g. Pyromet 80A) it is useful to remember that the composition of the alloy is very often indicated by the designation following the trade name. Thus Pyromet 80A would be equivalent to Nimonic 80A.

The column headed "Company Identification" in Table D refers to an organisation closely connected with the particular trade name or designation whether as a producer, alloy developer or patent holder.

Users of Table D should note that purely numerical designations (e.g. 713C) follow at the end of the alphabetical compilation.

Trade Name designation	Well-known in Europe?	Reference		Company Identification	Country
		Table	Biblio-graphy		
A 286*	Yes	C		Fried Krupp	D
AF 183*	Yes	C		Allegheny Ludlum	U.S
AF 2-1DA*	Yes	C		Cyclops Corporation	U.S
AFC - 77*	Yes	C		Crucible Inc.	U.S.
AiResist	Yes	C		Garrett Corporation	U.S.
Alkrothal	No		1	Kanthal Corporation	U.S.
Allegheny	No		1	Allegheny Ludlum	U.S.
Allegheny Stainless Steel	No		1	,, ,,	U.S.
Allvac	No		1	Teledyne Allvac	U.S
Almar	No		1	Allegheny Ludlum	U.S.
Altemp	No		1	,, ,,	U.S.
AM	Yes	C	1	,, ,,	U.S
AMSCO	No		1	Cannon-Muskegon	U.S
ARMCO	Yes	C	1	Armco Steel Corporation	U.S.
Astroloy	Yes	C		Wyman-Gordon Co Whittaker Corporation	 U S
ATG	Yes		2	Creusot Loire	F
ATGM	Yes			Creusot-Loire	F
ATGW	Yes			Creusot-Loire	F
ATS	Yes		2	Rheinstahl Giesserei AG	D
ATV	Yes		2	Creusot Loire	F
ATVS	Yes		2	,, ,,	F
Austenal	No		1	Howmet Corporation	U.S
B-1900*	Yes	C		Pratt and Whitney	U.S.
B-1910*	No		1	,, ,,	U.S.
Boron Stainless	No		1	Jessop Steel Co	U.S.
BVT	Yes			Fried Krupp	D
BX	No		167	......	U.S.S R.
Brightray	Yes	C		Henry Wiggin	U.K
C-10*	No		1	H K Porter Co Inc	U.S
C-16*	No		1	Teledyne Ohiocast	U.S.
C20Nb3*	No		1	H.K. Porter Co Inc	U.S.
C-207*	No	H		General Electric/U.S.A.F.	U.S.
C-242*	Yes	C		Rolls Royce (1971) Ltd.	U.K
C-263*	Yes	C		,, ,,	U.K.
C-1023*	Yes	C		,, ,,	U.K
C1 - 41*	No	H		General Electric/U.S.A F	U S

Trade Name designation	Well-known in Europe?	Reference		Company Identification	Country
		Table	Biblio-graphy		
CA	No		1	......	U.S.
CAF	No		1	......	U.S.
CAPI	No		1	Certified Alloy Products Inc.	U.S.
Carpenter	No		1	Carpenter Technology Corp.	U.S.
CB-30*	No		1	......	U.S.
CC-50*	No		1	......	U.S.
CD-4MC*	No		1	Eastern Company	U.S.
CD-4MCu*	No		1	......	U.S.
CE-30*	No		1	......	U.S.
CF	No		1	......	U.S.
CG	No		1	......	U.S.
CG-27*	Yes	C		Crucible Steel/General Electric	U.S.
CH	No		1	......	U.S.
Chatillon 3538*	No		2	Usines Saint-Jacques	F
Chromax*	Yes	C		Driver-Harris	U.S.
Chrome	Yes	H		Bendix Corp.	U.S.
Chromel	Yes		1	Hoskins Mfg. Co.	U.S.
Chromic	No			H.K. Porter Co. Inc.	U.S.
Chronite*	Yes	C		Chronite	U.K.
CK-20*	No		1	......	U.S.
CMN*	Yes	C		Crucible Steel	U.S.
CN	No		1	......	U.S.
Croloy	No		1	Babcock and Wilcox	U.S.
CRM*	Yes	C	2	Chrysler Corp.	U.S.
Chromadur*	Yes		2	Fried Krupp	D
Crucible	No		1	Crucible Inc.	U.S.
CT	No		1	......	U.S.
Custom	No		1	Carpenter Technology Corp.	U.S.
CW-12M*	No		1	......	U.S.
CY-40*	No		1	......	U.S.
CZ-100*	No		1	......	U.S.
D979*	Yes	C		Allegheny Ludlum	U.S.
Discaloy*	Yes	C		Westinghouse	U.S.
D.S. Nickel*	Yes	C		Sherritt Gordon	CAN
Duraloy	No		1	The Duraloy Co.	U.S.

Trade Name designation	Well-known in Europe?	Reference		Company Identification	Country
		Table	Biblio-graphy		
Alloy E*	Yes	H		Dept. of Supply	AUS.
Eastern Alloy	No		1	Eastern Stainless Steel Co.	U.S.
E-Brite 26-1*	No		1	------	U.S.
Elgiloy*	No		1	Elgiloy Co.	U.S.
EME*	No		2	------	U.S.
Escalloy 20*	No		1	Eastern Stainless Steel Co.	U.S.
ESCO	No		1	Esco Corp.	U.S.
EZ Head*	No		1	U.S. Steel Corp.	U.S.
FA	No		1	Cooper Alloy Corp.	U.S.
FS 85*	No		167	Fansteel	U.S.
FSX	Yes	C		General Electric	U.S.
FV	Yes	C	167	Firth Vickers	U.K.
G	Yes	C	2	Jessop-Saville	U.K.
Gannaloy*	No		1	Baldwin-Lima-Hamilton Corp.	U.S.
GE-B-129*	No		2	General Electric	U.S.
Glidden 830*	No		1	SCM Corporation	U.S.
GMR	Yes	C		General Motors Corp.	U.S.
Greek Ascoloy*	Yes	C		------	U.S.
Alloy H*	Yes	H		Dept. of Supply	AUS.
H.	Yes	C	2	Jessop-Saville	U.K.
HA-(see Haynes Alloy)	Yes		B		U.S.
HA*	No		1	------	U.S.
HAB*	No		1	------	U.S.
Harper 600 Mod*	No		1	ITT Harper Inc.	U.S.
Hastelloy	Yes	C		Cabot Corp.	U.S.
Haynes Alloy	Yes	C		Cabot Corp.	U.S.
Haynes Stellite	Yes	C		Cabot Corp.	U.S.
HB-100*	No		1	------	U.S.
HC*	No		1	------	U.S.
HC-30*	No		1	------	U.S.
HD*	No		1	------	U.S.
HD-40*	No		1	------	U.S.
HE	No		1	------	U.S.
Hecla	Yes		2	Hadfields	U.K.
HF*	No		1	------	U.S.
HH	No		1	-----	U.S.
HI	No		1	-----	U.S.
HK	Yes	C	1	-----	U.S.
HL	No		1	-----	U.S.
HN	Yes	C	1	-----	U.S.
HNM*	No		2	Crucible Steel	U.S.
Hoskins	No		1	Hoskins Mfg. Co.	U.S.
Howmet	No		1	Howmet Corp.	U.S.
HP-40*	No		1	Duraloy Co.	U.S.
HR Crown Max*	Yes		2	Firth Vickers	U.K.
HS (see Haynes Stellite)	Yes	C			
HT	No		1	-----	U.S.
HTX	No		2	Crucible Inc.	U.S.
HU	No		1	-----	U.S.
HW	No		1	-----	U.S.
HX	No		1	-----	U.S.
I-336*	No		2	-----	U.S.
I-700* (1)	No		1	Teledyne Allvac	U.S.
I-1360*	No		2	General Electric	U.S.
Illium	Yes	C	2	Stainless Foundry and Eng. Inc.	U.S.
IM-15*	No	H		Westinghouse/N.A.S.A.	U.S.
IN	Yes	C	1	International Nickel	U.K.
Incoloy	Yes	C		Henry Wiggin Huntington Alloy Products	U.K. U.S.
Inconel	Yes	C		Henry Wiggin Huntington Alloy Products	U.K. U.S.
Alloy J*	Yes	H		Dept. of Supply	AUS.
J -	Yes	C		General Electric	U.S.
J 1500	No		1	------	U.S.
Jal Head	No		1	Jones and Laughlin Steel Corp.	U.S.
Jethete	Yes	C	2	United Steel Companies Ltd.	U.K.
JS-700*	No		1	Jessop Steel Co.	U.S.
Kanthal	Yes	C		Kanthal A B.	S
KNC 3*	No		1	Cooper Alloy Corp.	U.S.

Trade Name designation	Well-known in Europe?	Reference		Company Identification	Country
		Table	Bibliography		
Kromarc	No		1	......	U.S.
K42B*	No		2	Westinghouse	U.S.
(L)	No		1	Lebanon Steel Foundry	U.S.
L-605*	Yes	C		Crucible Steel	U.S.
Lapelloy	No		1	Timken Co.	U.S.
LCI.B* -	Yes		64	Union Carbide (U.K.)	U.K.
LC2* -	Yes		64	" "	U.K.
LDA 204*	No	C		Avco Lycoming	U.S.
Lescalloy	No		1	Latrobe Steel Co.	U.S.
Linco*	No		1	" "	U.S.
LWI* -	Yes		64	Union Carbide (U.K)	U.K.
M21*	Yes	C		International Nickel	U.K.
M22*	Yes	C		" "	U.K.
M-	Yes	C	1, 2	General Electric	U.S.
MA	Yes	C		Henry Wiggin Huntington Alloy Products	U.K. U.S
MAR-M	Yes	C	1	Martin Marietta Corp	U.S.
Marwedur*	Yes		2	Mannesmann	D
Metco -	Yes		64	Metco Ltd.	U.K.
Metcoloy -	Yes		64	" "	U.K.
Midvac 57*	No		1	Midvale-Heppenstall Co.	U.S.
MF 2*	No	C	163	Allegheny Ludlum	U.S.
MM	No		1	Martin Marietta Corp.	U.S.
Moly Ascoloy* (see Jethete M152)		C			
MP 35 N*	Yes	C		Latrobe Steel Co.	U.S.
MTS -	No		2	....	D
Multimet* (see N-155)	Yes	C		Cabot Corporation	U.S.
Multiphase* (see MP35N)					
N	No		1	Eastern Co.	U.S.
N-12M*	No		1	......	U.S.
N-155*	Yes	C		......	U.S.
NA-22H*	Yes	C		Blaw Knox	U.S.
Nichrome*	Yes	C		Driver-Harris Co.	U.S.
Nichrome	Yes	C	1	" "	U.S.
Nickelvac	No		1	Teledyne Allvac	U.S.
Nicral	Yes			Creusot-Loire	F
Nicrfe*	No		1	The Shenango Co.	U.S.
Nicrmo*	No		1	" "	U.S.
Nicrofer	Yes			Vereinigte Deutsche Metallwerke AG	D
Nicrotung*	No		1	Westinghouse	U.S.
Nimocast	Yes	C	55	Henry Wiggin	U.K.
Nimonic	Yes	C	55	Henry Wiggin	U.K.
Nivco*	No		1	Westinghouse	U.S.
Noxis 4*	Yes		2	Aubert and Duval	F
NS 190*	No		2	.....	F
Ohioloy	No		1	Teledyne Ohiocast	U.S.
OR-1*	No		163	Allegheny Ludlum	U.S.
Oneral	Yes		2	O.N.E.R.A.	F
PER	Yes		2	Aubert and Duval	F
PH-55A*	No		1	Cooper Alloy Corp.	U.S.
Pyromet	Yes	C	1	Carpenter Technology Corp.	U.S.
Q	No		1	Quaker Alloy Casting Co.	U.S.
R - (see René)	Yes	C		.....	
R-235* (2) (Hastelloy)					
RA 333*	No		1	Wallace-Murray Corp.	U.S.
Refractaloy	No		1	Westinghouse	U.S.
René 41*	Yes	C		Teledyne Allvac	U.S.
René	Yes	C	1, 2	General Electric	U.S.
RGT	Yes			Röchling Burbach	D
S-590*	No		1	Carpenter Technology Corp.	U.S.
S-816*	Yes	C		Allegheny Ludlum	U.S.
Sandvik	Yes		1	Sandvik	S.
Sanicro	Yes		1	"	S.
SEL	No		1	.....	U.S.
Simalloy 5616*	No		1	Wallace Murray Corp.	U.S.
Sirius	No		1	.....	F
SM200* (seee MAR-M200)	Yes	C			
SPIN	No		1	Centrifugal Products Inc.	U.S.
Stainless	No		1	U.S. Steel Corp.	U.S.
Stellite	Yes		64	Deloro Stellite (U.K.)	U.K.

Trade Name designation	Well-known in Europe?	Reference		Company Identification	Country
		Table	Bibliography		
Stellundum +	Yes		64	Deloro Stellite (U.K.)	U.K.
Supertherm*	No		1	Abex Corp.	U.S.
TAZ	Yes	C	2	N.A.S.A.	U.S.
T.D. Ni*	Yes	C		Fansteel Metallurgical Corp.	U.S.
T.D. NiCr*	Yes	C		″ ″	U.S.
Tenelon*	No		1	U.S. Steel Corp.	U.S.
Thermalloy	Yes	C	1	Abex Corp.	U.S.
Thetaloy*	No		2	Pratt and Whitney	U.S.
Thermon	Yes			Thyssen Edelstahlwerke	D
Tinidur* (see A286)	Yes	C		Fried Krupp	D
Tophet	No		1	Wilbur B. Driver Co.	U.S.
TPA*	No		1	Carpenter Technology	U.S.
TRW	Yes	C	1	TRW Metals Div.	U.S.
Tribomet +	Yes		64	Bristol Aerojet	U.K.
Tuf-Wear	No		1	Oklahoma Steel Castings Co.	U.S.
Turbaloy 13*	Yes		2	General Electric	U.S.
UCAR	Yes			Union Carbide	U.S.
Udimet	Yes	C	1	Special Metals Inc.	U.S.
UMCO	Yes	C	1	------	B
Uniloy	No		1	Universal Cyclops	U.S.
Unimar	No		1	″ ″	U.S.
Unitemp.	Yes	C	1, 2	″ ″	U.S.
USAmet*	No		1	Elgiloy	U.S.
USS	No		1	U.S. Steel Corp. .	U.S.
V-57*	Yes	C		Allegheny Ludlum	U.S.
Vaccumtherm	Yes			Stahlwerke Südwestfalen	D
Vitallium*	No		2	Howmet	U.S.
W-545*	No		2	Westinghouse	U.S.
Waspaloy*	Yes	C		Pratt and Whitney	U.S.
Waukesha	No		1	Waukesha Foundry Co.	U.S.
WAZ	Yes	C		N.A.S.A.	U.S.
WBD	No		1	Wilbur B., Driver Co.	U.S.
WF 100D*	Yes		2	Fried Krupp	D
WI 52*	Yes	C		Tungsten Institute	U.S.
X20T2*	Yes		2	Aubert and Duval	F
X-40*	Yes	C		General Electric	U.S.
X-45*	Yes	C		″ ″	U.S.
X-50*	No		2	″ ″	U.S.
X-63*	No		2	″ ″	U.S.
X-750*	Yes	C		International Nickel	U.S.
XSH*	Yes		2	Aubert and Duval	F
15-4-1*	Yes	C		General Electric	U.S.
16-15-6*	Yes	C		Timken	U.S.
16-25-6*	Yes	C		″	U.S.
17-14 CuMo*	No		1	Armco	U.S.
19-9	Yes		1	Universal Cyclops	U.S.
22-4-9	Yes	C		Armco Steel Corporation	U.S.
22-6-9	Yes		1	″ ″ ″	U.S.
35Ni 20Cr	Yes	C		------	
35Ni 30Cr	Yes		1	-------	
50Cr 50Ni	Yes	C		------	
60Ni 16Cr	Yes	C		------	
60Cr 40Ni	Yes	C		------	
70Ni 30Cr	Yes		1	------	
80Ni 20Cr	Yes	C		------	
713C	Yes	C		International Nickel	U.S.
8077	Yes	C		Cabot Corp.	U.S.

NOTES

1. Same as Inconel Alloy 700
2. Similar to GMR235
+ Coating materials.

TABLE E SPECIFICATIONS AND DESIGNATIONS OF HIGH-TEMPERATURE ALLOYS

The Table lists European and U.S. specifications and designations of a number of common iron-, nickel- and cobalt-base alloys.

For each alloy, only one particular standard is given under each national category, although in some instances there may be more than one. However, reference to the particular standard quoted will enable other applicable standards to be quickly identified.

Various standards offices from whom further information on particular alloy specifications may be obtained are included in Table K.

The following notations are used in Table E:

A.E.C.M.A.	*Association Européenne des Constructeurs de Materiel Aerospatiale.*
A.F.N.O.R.	*Association Française de Normalisation (F).*
DIN	*Deutscher-Normenausschuss (D).*
A.M.S.	*Aerospace Material Specification (issued by the Society of Automotive Engineers) (U.S)*
A.S.T.M.	*American Society of Testing and Materials (U.S.).*
W.D.L.	*Luftfahrt-Werkstoff Number (D.).*

In addition to the British Standards Yearbook and the A.S.T.M. Index, the information sources listed as references 1, 55, 57 and 254 in the bibliography (Table L) were used.

Alloy	A.E.C.M.A. (recommendations)	AFNOR (designations)	British Standards Aerospace	DIN	Royal Swedish Air Board Specifications	United States Specifications		W.D.L. (specifications)
						AMS	ASTM	
A 286	Fe-PA 92 - HT	Z06NCT25	HR 251	X 5 NiCrTi 26 15		5525	A638-70	1.4944
D 979						5509		
GMR 235							A567-66	
Hastelloy C						5389	A567-66	
Hastelloy X	Ni-P 93-HT	NC22FeD	HR 6	NiCr22Fe18Mo	MH.03	5536	A567-66	
Haynes 188		KCN22W				5608		
HS 21						5385	A567-66	
IN 100	Ni-C 104 - HT	NK15CAT	HC 204			5397		
Incoloy 901	Fe-PA 99-HT	Z8NCDT42	HR 53	NiCr15MoTi	MH.16	5660		2.4662
Inconel 718	Ni-P 100 - HT	NC19FeNb		NiCr19NbMo	MH.06	5383	A637-70	2.4668
Inconel X-750		NC15FeT(Nb)			MH.04	5582		
L-605	Co-P 92 - HT	KC20WN	HR 240	CoCr20W15Ni		5537		2.4964
(HS 25)								
(WF 11)								
M-252						5756	A637-70	
(J 1500)								
MAR-M-302		KC22WTa						
N-155	Fe-PA 91-HT	Z12CNKDW20		X12CrCoNi2120		5532	A639-70	1.4974
Nimonic 75	Ni-P 91 - HT	NC20T	HR 5	NiCr 20 Ti	MH.05			2.4630
Nimonic 80A	Ni-P 95 - HT	NC20TA	2HR 1	NiCr 20 TiAl	MH.07		A637-70	2.4631
Nimonic 90	Ni-P 96 - HT	NC20KTA$_t$	2HR 202	NiCr20Co18Ti	MH.10			2.4632
Nimonic 105	Ni-P 61 - HT	NKCD20AT$_v$	HR 3	NiCoCr15MoAlTi	MH.14			2.4634
Nimonic 115	Ni-P 102 - HT	NCK15ATD	HR 4	NiCoCr15MoAlTi				2.4636
Nimonic 263	Ni-P 105 - HT	NCK20D	HR 10					
Nimonic PE16		NW11AC	HR 207	X8NiCrMoTiAl4316				
Nimonic PK33		NC19KD$_{u/v}$		NiCr 18Co14MoTiAl				2.4665
Nimonic PK50		NC20K14				5544		
Nimocast PE10	Ni-C 103 - HT	NC20Nb	HC 202					
René 41						5545		
S-816		KCN20DNbW		CoCr 20Ni 20W		5534	A639-70	
713C	Ni-C 98 - HT	NC13AD	HC 203	G-NiCr 13 Al 6MoNb	MH 31	5391	A567-66	2.4670
Udimet 500		NCK20DAT				5384	A567-66	
Udimet 700		NK20CDAT						
Waspaloy		NC20KDTA		Ni Cr 20 CoMo		5544	A637-70	
X40		KC25NW	HC 301			5382	A567-66	
(HS 31)								

TABLE F MAJOR PRODUCERS OF IRON-, NICKEL- AND COBALT-BASE ALLOYS

Table F lists producers of primary alloy products (in the form of remelt stock, wrought stock, powder) and secondary components (in the form of castings, forgings or high-temperature coatings). The mark "X" in the matrix indicates that the product is believed to be commercially available; an entry has not been made in cases where the product is either used internally by the firm or is employed on a developmental scale.

The listing attempts to give a broad cross-section of different classes of producers and (as is particularly evident for the USA) does not pretend to be exhaustive.

The classification of the "alloy base" is that used in Table C, and indicates the element present in greatest proportion by weight. "Wrought stock" includes bar, strip, wire and blanks or preforms for subsequent forging.

MAJOR MATERIALS PRODUCERS I

Country	Company	Alloy base			Alloy form			Component form		
		Fe	Ni	Co	Remelt Stock	Wrought Stock	Powder	Castings	Forgings	Coatings
Belgium	Fabrique Nationale Herstal S.A. Herstal	X	X	X				X	X	
	Floridienne S.A. - N.V., Brussels	X	X	X			X			
Denmark	Helsingor Vaerft A/S, Helsingor	X	X					X	X	
	Marx & Jeppesen A/S	X	X					X		
France	Aubert et Duval, Neuilly-sur-Seine	X	X	X	X	X		X	X	
	Creusot-Loire, Paris	X	X	X	X	X	X	X	X	X
	Microfusion S.A., Gennevilliers		X	X				X		
	SNECMA, Evry		X	X				X	X	
	Ugine Aciers (PUK Group), Ugine	X	X		X	X		X		
W. Germany	Deloro Stellite, Koblenz	X	X	X			X	X		X
	Korver & Nehring GmbH, Krefeld		X	X				X		
	Fried. Krupp Hüttenwerk AG, Bochum	X	X			X	X		X	
	Mannesmann AG, Dusseldorf	X				X				
	Rheinstahl Giesserei AG., Bochum	X	X	X				X		
	Schmidt & Clemens GmbH, Uberengelskirchen	X						X	X	
	Stahlwerke Rochling-Burbach GmbH, Volklingen/Saar	X	X	X	X	X			X	
	Stahlwerke Sudwestfalen AG., Siegen	X	X	X	X	X			X	
	Thyssen Edelstahlwerke AG., Krefeld	X	X		X	X				X
	Vereinigte Deutsche Metallwerke AG., Werdohl/Westf.	X	X			X		X	X	
Ireland										
Italy	Acciaierie E Ferriere Lombarde Falck, Milan	X				X				
	Breda Siderurgica SpA, Milan	X				X			X	
	Dalmine SpA, Milan	X				X				
	FIAS sas, Gorla Minore	X	X			X				
	Fiat SpA, Turin	X	X	X				X	X	

MAJOR MATERIALS PRODUCERS I

Country	Company	Alloy base			Alloy form			Component form		
		Fe	Ni	Co	Remelt Stock	Wrought Stock	Powder	Castings	Forgings	Coatings
Italy continued	IMPEASrl, Milan		X			X				
	Italsida Spa, Genoa	X				X			X	
	Terni, Rome.	X	X						X	
Luxembourg	ARBED S.A., Luxembourg	X	X			X		X	X	
Netherlands	Cirex B.V., Almelo	X	X	X				X		
	Elbar B.V., Arcen		X	X						X
	Nederlandsche Nikkel Mij B.V., Amsterdam		X			X	X	X		
U.K.	Bristol Aerojet Limited, Weston-super-Mare		X	X						X
	British Steel Corporation (B.S.C. Sheffield Division), Stocksbridge	X	X			X				
	B.S.A. Metal Powders, Birmingham	X	X	X			X			
	British Driver Harris Co Ltd., Stockport		X			X				
	Cameron Iron Works, Livingston, Scotland	X	X						X	
	Deloro Stellite (U.K.) Ltd., Swindon	X	X	X			X	X		X
	Deritend Precision Castings Ltd., Droitwich	X	X	X				X		
	Doncasters Monk Bridge Ltd., Leeds	X	X						X	
	Firth Brown Limited, Sheffield	X	X			X			X	
	Henry Wiggin & Co. Ltd., Hereford	X	X		X	X	X			
	High Duty Alloys Ltd., Redditch	X	X						X	
	Howmet Misco Division, Exeter	X	X	X	X	X		X		
	Joseph Lucas (Industries) Ltd., Birmingham		X	X						X
	Metco Ltd., Chobham, Surrey	X	X	X						X
	Omes-Faulkners Ltd., Colnbrook	X	X						X	
	Ross & Catherall Ltd., Sheffield	X	X		X			X		
	Union Carbide Corporation, Glossop	X	X	X	X	X		X		X
	G.L. Willan Ltd., Rotherham	X	X		X			X		

MAJOR MATERIALS PRODUCERS I

Country	Company	Alloy base			Alloy form			Component form		
		Fe	Ni	Co	Remelt Stock	Wrought Stock	Powder	Castings	Forgings	Coatings
U.S.A.	Avco Lycoming Division, Stratford, Conn.	X	X	X					X	
	Cabot Corporation, Kokomo, Ind.	X	X	X		X	X	X	X	X
	Cannon - Muskegon Corp., Muskegon, Mi.	X	X	X	X					
	Carpenter Technology Corp., Reading, Pa	X	X			X				
	Driver Harris Company, Harrison, N.J.		X			X				
	General Electric Co., Schenectady, N.Y.	X	X	X				X	X	X
	Huntington Alloys, Huntington, Virginia	X	X		X	X				
	Howmet Metal Products Division, Plymouth, Mi	X	X	X	X	X		X		
	Kelsey Hayes Co., Philadelphia, Pa.	X	X	X			X			
	Latrobe Steel Company, Latrobe, Pa.	X	X	X		X				
	Martin-Marietta Corp., Baltimore		X	X				X		
	Metallurgical International Inc., Tintern Falls, N.J.	X	X	X			X			
	Nuclear Metals Incl., Concord., Mass.	X	X	X			X			
	Special Metals Corporation, New Hartfort, N.Y.	X	X	X	X	X	X			
	United Technologies Corp., East Hartford, Conn.	X	X	X				X	X	X
Others (Austria)	Vereinigte Edelstahlwerke A.G. (VEW), Kapfenberg, Ternitz, and Judenburg	X	X	X		X		X	X	
(Canada)	Sherritt Gordon Mines Ltd., Fort Saskatchewan, Alberta		X	X		X	X			
(Sweden)	AB Bofors, Bofors	X	X			X			X	
	Bulten-Kanthal AB, Hallstahammar	X	X	X		X		X		
	Deloro Stellite, Trolhatten	X	X	X			X	X		X
	Sandvik A.B., Sanviken	X	X			X				

TABLE G MAJOR PRODUCERS OF REFRACTORY METALS, PLATINUM-GROUP METALS, CERAMICS AND COMPOSITES

This Table lists major producers of refractory materials in the whole range of forms from powders, through wrought products to finished components.

The class of "ceramics" refers to advanced ceramics for structural applications, namely B_4C, BN, SiC, Si_3Ni_4, Mo_2Si. LAS and MAS. The listing does not include producers of graphite or carbon products, silica or refractory oxides, insulating fibres, refractory bricks or refractory powders.

There is only one entry in the "composite" class, because dispersion-strengthened products have been treated elsewhere (Tables C and H) as alloys rather than composites. Also producers of cemented carbides have been excluded, although these form a large class of materials whose high-temperature properties are important e.g. metal cutting tools.

MAJOR MATERIALS PRODUCERS II

Country	Company	Refractory Metals					Pt Metals	Ceramics	Composites
		Cr	Mo	Nb	Ta	W			
Belgium	Johnson Matthey & Pauwels, S.A , Brussels						X		
	Metallurgie Hoboken-Overpelt N.V. - S.A., Hoboken			X	X		X		
	Société Belge des Produits Refractaires "Belref" S.A., Saint-Ghislain							SiC	
Denmark									
France	Ateliers Partiot, Paris							B_4C	
	Caplain St. André, Paris						X		
	Cime Bocuze, Lyons		X						
	Compagnie des Metaux Précieux, Paris						X		
	Comptoir Lyon-Allemand-Louyot, Paris						X		
	Ugine Carbone (PUK Group), Grenoble					X			
Germany	Annawerk GmbH, Rodental							Si_3N_4	
	Cesiwid Elektrowarme GmbH, Erlangen							SiC, $MoSi_2$	
	Degussa, Frankfurt				X		X	Si_3N_4	
	Gesellschaft fur Elektrometallurgie mbH, Dusseldorf	X							
	W.C. Heraeus GmbH, Hanau			X	X		X		
	Rosenthal AG							Si_3N_4	
	Hermann C. Starck, Dusseldorf		X	X	X	X	X		
Ireland									
Italy	Metalli Preziosi SpA, Milan						X		
Luxembourg									
Netherlands	Dryfhout & Zoon Edelmetaalbedrijven NV, Amsterdam						X		
	N V Kawecki - Billiton Metaalindustrie Arnhem			X	X			X	

MAJOR MATERIALS PRODUCERS II

Country	Company	Refractory Metals					Pt Metals	Ceramics	Composites
		Cr	Mo	Nb	Ta	W			
U.K.	Advanced Materials Engineering Ltd., Gateshead							Si_3N_4	
	Associated Engineering Developments, Rugby.							Si_3N_4	
	Borax Consolidated Limited, London							B_4C, BN	
	British Nuclear Fuels Ltd., Warrington							SiC	
	Carborumdum Co. Ltd, St Helens							SiC	
	Engelhard Industries Ltd., Sutton, Surrey						X		
	Johnson Matthey Metals Ltd., London						X		
	London & Scandinavian Metallurgical Co. Ltd., London.	X				X			
	Morganite Electroheat Ltd., Perth							SiC	
	Murex Ltd., Rainham	X	X		X	X			
Others (Austria)	Metallwerk Plansee A.G., Reutte, Tyrol		X		X	X			
(Sweden)	Bulten-Kanthal AB, Hallstahammer							$MoSi_2$	
	AB Ferrolegeringar, Trollhätten	X	X						
(U.S.A.)	Amax Specialty Metals Corporation, Cleveland, Ohio		X			X			
	Cerodyne Inc. Santa Ana, California							B_4C, SiC Si_3N_4	
	Corning Glass International, New York							LAS MAS	
	Duramic Products Inc., Palisades Park, N.J.							BN, SiC Si_3N_4	
	Engelhard Industries, Murrayhill, N.J.						X		
	Fansteel Inc., Chicago			X	X	X			
	Kawecki Berylco Industries Inc., New York			X	X				
	Matthey Bishop Inc., Worcester, Mass.						X		
	Norton International Inc., Worcester, Mass.							SiC Si_3N_4	
	Sintercast, Division, West Nyack, N.Y.								Ferro-TiC

TABLE H TRADE NAMES, DESIGNATIONS, COMPOSITIONS AND STANDARDS OF REFRACTORY MATERIALS.

The table gives details of refractory metals, platinum-group metals, and their alloys, ceramics and composites, for which producers were given in Table G.
As in Table D, specific alloy designations are marked with an asterisk (*). "Company Identification" may refer to either a developer or a producer of the alloy.

Trade Name, Designation	Composition		Company Identification	Relevant Standard
	base	other (wt%)		
Alloy E*	Cr	2 Ta, 0.5 Si, 0.1 Ti	Dept. of Supply (AUS)	-
Alloy H*	Cr	2 Ta, 0.5 Si, 0.5 R.E.	,,	-
Alloy J*	Cr	2 Ta, 0.5 Si	,,	-
C 207*	Cr	7.5 W, 0.8 Zr, 0.2 Ti 0.1 C, 0.15 Y	General Electric (USAF)	-
Cl-41*	Cr	7.1 Mo, 2 Ta, 0.09 C, 0.1 (Y - La)	General Electric (NASA)	-
IM - 15*	Cr	1.7 Ta, 0.1 B, 0.1 Y	Westinghouse (NASA)	-
Chrome-30*	Cr	6 MgO, 0.5 Ti	Bendix (U.S. Navy)	-
Chrome-90*	Cr	3 MgO, 2.5V, 0.5 Si	,,	-
Chrome-90S*	Cr	3 MgO, 2.5 V, 1 Si, 0.5 Ti, 2 Ta, 0.5 C	,,	-
	Mo	-	-	AMS 7800
-	Mo	30 W	-	-
-	Mo	0.5 Ti	-	AMS 7813
TZM*	Mo	0.025 C, 0.48 Ti, 0.09 Zr	-	-
TZC*	Mo	0.14 C, 1.25 Ti, 0.12 Zr	-	-
Climelt, CMX	-	-	Amax (U.S.)	-
-	Nb	-	-	AMS 7850
SU 31*	Nb	17.0 W, 2.5 Hf	-	-
-	Ta		-	AMS 7849 ASTM B364
-	Ta	10 W	-	AMS 7848
-	W		-	AMS 7899
GE 125*	W	25 Rh	General Electric (U.S.)	-

Trade Name, Designation	Composition		Company Identification	Relevant Standard
	base	other (wt%)		
-	Pt	-	-	-
-	Pt	5 Rh	-	-
-	Pt	10 Rh	-	-
-	Pt	13 Rh	-	-
-	Pt	20 Rh	-	-
-	Pt	30 Rh	-	-
-	Pt	10 Ir	-	-
-	Pt	10 Ru	-	-
-	Pt	10 Rh, 40 Pd	-	-
ZGS	Pt	0.1 ZrO_2	Johnson Matthey (U.K.)	-
ZGS	Pt	10 Rh, 0.1 ZrO_2	,,	-
Carborid	B_4C	(hot pressed)	Ateliers Partiot (F)	-
Crusilite	SiC	(heating elements)	Morganite Electroheat (UK)	-
KT	SiC	(self bonded)	Carborundum Co. (UK)	-
NC, Crystar	SiC	(recrystallised, self bonded)	Norton (US)	-
Refel	SiC	(self bonded)	British Nuclear Fuels (UK)	-
SG Glowbar	SiC	(heating elements)	Carborumdum Co (UK)	-
Silit	SiC	(heating elements)	Cesiwid Elektrowärme (D)	-
NC	Si_3N_4	(hot pressed)	Norton (US)	-
Mosilit	$MoSi_2$	(heating elements)	Cesiwid Elektrowarme (D)	-
Cercor	LAS	-	Corning Glass (US)	-
Ferro TiC HT - 6*	TiC	infiltrated Ni-base alloy	Sintercast (US)	-

TABLE J MAJOR MATERIALS USERS

The Table gives examples of major users of all the high-temperature materials in various areas of applications. The listing is for the E.E.C. countries with a few important additions. The U.S.A. has been excluded; many major American users are also involved in materials production and examples will be found in Table F.

MAJOR MATERIALS USERS

Country	Company	Field of Activity					
		Gas Turbines	Petrochemicals	Heating and metallurgical processing	Glass an ceramics processing	Nuclear power	Internal combustion
Belgium	ACEC S.A., Charleroi	X				X	X
	Cockerill, Seraing	X		X			X
	Fabrique Nationale Herstal S.A., Herstal	X				X	
	Glaverbel S.A., Brussels				X		
	Petrofina S.A., Brussels		X				
Denmark	Aalborg Vaerft A/S, Aalborg			X			
	A/S Burmeister and Wains-Motor OG Maskinfabrik AF 1971, Copenhagen						X
	Dansk Esso A/S, Copenhagen		X				
	Gulf Oil A/S, Copenhagen		X				
	Helsingor Vaerft A/S, Helsingor	X				X	X
	Kastrup OG Holmegaards Glasvaerker A/S, Copenhagen				X		
France	Aerospatiale (SNIAS), Paris	X					
	Alsthom, Paris	X					X
	Antar Petroles de l'Atlantique, Paris		X				
	Avions M. Dassault, Paris	X					
	Boussois-Souchon-Neuvesel (BSN), Paris				X		
	Chantiers de l'Atlantique, Paris	X					X
	Citroen S.A., Paris						X
	Creusot-Loire, Paris	X		X		X	X
	Electricite de France, Paris					X	
	Framatome, Courbevoie					X	
	Hispano Suiza, Bois Colombes	X					X
	MATRA, Velizy	X					
	Pechiney-Ugine Kuhlmann, Paris		X	X			
	Peugeot Automobiles S.A., Paris						X
	Regie Nationale des Usines Renault, Boulogne-Billancourt						X

MAJOR MATERIALS USERS

Country	Company	Field of Activity					
		Gas Turbines	Petrochemicals	Heating and metallurgical processing	Glass an ceramics processing	Nuclear power	Internal combustion
France continued	Rhone-Poulenc, Paris		X				
	St. Gobain Industries, Neuilly-sur Seine				X		
	SNECMA, Paris	X					
	Société Nationale des Pétroles d'Aquitaine, Courbevoie		X				
	Sociétés Nouvelles des Aciers de Pompey, Neuilly-sur-Seine			X			
	Turbomeca, Bordes	X					
W. Germany	AEG Kanis Turbinenfabrik GmbH, Nürnberg	X					
	Badische Anilin & Soda Fabrik AG. (BASF)		X				
	Bayer AG		X				
	Bayerische Motoren Werke AG (BMW), Munich						X
	Brown Boveri & Cie AG., Mannheim	X				X	
	Daimler Benz AG., Stuttgart	X					X
	Demag AG., Duisberg		X	X			
	Gerresheimer Glas AG., Düsseldorf				X		
	Gutehoffnungshütte Sterkrade AG., Oberhausen	X					
	Hoechst		X				
	Klöckner-Humboldt-Deutz AG., Cologne	X					X
	Fried. Krupp GmbH, Essen	X		X		X	
	Maschinenfabrik Augsburg - Nürnberg AG. (MAN), Augsburg	X		X			X
	Messerschmitt-Bölkow-Blohm GmbH, Munich	X					X
	Motoren und Turbinen-Union, Munich	X					X
	Rosenthal A.G., Selb				X		
	Vereinigte Glaswerke, Aachen				X		
	A.G. Versuchsreaktor AVR GmbH, Düsseldorf					X	
	Volkswagenwerke A.G., Wolfsberg	X					X
Ireland	Electricity Supply Board (ESB), Dublin	X					

MAJOR MATERIALS USERS

Country	Company	Field of Activity					
		Gas Turbines	Petrochemicals	Heating and metallurgical processing	Glass an ceramics processing	Nuclear power	Internal combustion
Italy	Alfa Romeo SpA, Milan	X					X
	Anic SpA, Palermo		X				
	Breda, Milan	X		X			X
	Fiat SpA, Turin	X				X	X
	Franco Tosi SpA, Milan	X					
	Grandi Motori Trieste, Trieste	X					X
	Innocenti Meccanica SpA, Milan			X			
	Italiana Vetro Siv, Vasto				X		
	Montedison SpA, Milan		X				
	Nuovo Pignone, Florence	X					
	Rinaldo Piaggio, Finale Ligure	X					
Luxembourg	ARBED S.A., Luxembourg			X			
	S.A. Métallurgique et Minière de Rodange - Athus, Rodange			X			
Netherlands	Amst. Droogdok Mij NV, Amsterdam	X					
	Fokker - VFW BV.	X					
	Hoogovens, Ijmuiden			X			
	Philips NV, Eindhoven			X			X
	Royal Dutch/Shell		X				
	Schelde BV, Flushing	X				X	X
	Thomassen Holland BV, De Steeg	X					
	Unilever NV, Rotterdam		X				
	Van Doornes Automobielfabrieken (DAF), Eindhoven						X
	Verenigde Machinenfabrieken NV (VMF), Amsterdam	X		X			X

MAJOR MATERIALS USERS

Country	Company	Field of Activity					
		Gas Turbines	Petrochemicals	Heating and metallurgical processing	Glass an ceramics processing	Nuclear power	Internal combustion
U.K.	Babcock & Wilcox, London			X		X	
	Birlec Ltd., Walsall			X			
	British Aircraft Corporation, Bristol and Weybridge	X					
	British Leyland Motor Corporation Ltd., London	X					X
	British Nuclear Design and Construction Ltd., Leicester					X	
	British Petroleum Company Ltd., (BP), London		X				
	Burmah Oil Company Ltd., Glasgow		X				
	Davy International Limited, London			X			
	General Electric Company Ltd., (GEC) London	X				X	
	Imperial Chemical Industries Ltd., (ICI), Billingham		X				
	Lucas Industries Ltd., Birmingham	X					
	Pilkington Brothers Ltd., St. Helens				X		
	Rolls Royce (1971) Ltd., London	X					
	Ruston Gas Turbines Ltd., Lincoln	X					
	Whessoe Limited, Darlington			X		X	
Others (Sweden)	Allmana Svenska Elektriska AB (ASES), Vasteras			X			
	AB Nohab, Trollhattan	X					X
	Saab-Scania AB, Linkoping					X	X
	Stal-Laval Turbin AB, Finspong	X					
	AB Volvo Gothenburg	X					X
(Switzerland)	Brown Boveri & Cie AG., Baden	X				X	
	Sulzer Brothers AG., Winterthur	X				X	X

TABLE K RESEARCH ORGANISATIONS, ADVISORY BODIES, INFORMATION OFFICES AND STANDARDS OFFICES.

The Table lists the major organisations in the E.E.C. countries and the U.S.A., with a few other important additions.

Commercial industrial research laboratories have been excluded; most of the major producers and users maintain their own research laboratories, which can frequently be approached as sources of technical information.

University research departments have also been excluded.

Country	Organisation	Research Organisation	Advisory Body	Information Office	Standards Office
Belgium	Belgian National Specification, Brussels				X
	Centre d'étude de l'énergie nucléaire (CEN), Mol	X			
	Centre de Recherches Métallurgiques (CRM), Liège	X			
	Fonds National de la Recherche Scientifique (FNRS), Brussels		X		
	Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture (IRSIA), Brussels		X		
Denmark	Danish Council for Scientific and Industrial Research, Copenhagen		X		
	Danish Standards Association, Hellerup				X
France	Association Européenne des Constructeurs de Matériel Aerospatial (AECMA), Paris				X
	Association Francaise de Normalisation (AFNOR), Paris				X
	Association Nationale de la Recherche Technique (ANRT), Paris		X		
	Association Technique pour la Turbine à Gaz (ATTAG), Paris		X		
	CEA Saclay, Grenoble, Cadarache, Fontenay-aux-Roses	X			
	Centre National de la Recherche Scientifique (CNRS), Paris		X		
	Centre de Recherche sur la Physique des Hautes Temperatures - CNRS, Orleans	X			
	Institut de Recherches de la Siderugie (IRSID), Saint-Germain-en-Laye	X			
	Institut de Soudure, Paris	X			
	Office National d'Etudes et de Recherches Aerospatiales (ONERA), Chatillon	X			
W Germany	Battelle - Institut eV, Frankfurt	X			
	Deutsche Forschungs - und Versuchsanstalt für Luft- und Raumfahrt (DFVLR) Porz-Wahn	X			
	Deutscher Normenausschuss (DNA), Cologne				X
	Deutscher Verband fur Schweisstechnik (DVS), Dusseldorf	X			
	Fraunhofer Gesellschaft zur Forderung der Angewandten Forschung, Munich	X			
	Kernforschungszentrum Karlsruhe, IMF, Karlsruhe	X			
	KFA Julich, Julich	X			
	Max Plank Institut fur Metallforschung, Stuttgart	X			
	Zentralstelle fur Luft und Raumfahrtdokumentation und Information (ZLDI), Munich			X	

Country	Organisation	Research Organisation	Advisory Body	Information Office	Standards Office
Ireland	Institute for Industrial Research and Standards, Dublin	X	X	X	X
	National Science Council, Dublin		X		
Italy	Centro Informazioni Studi Esperienze (CISE), Milan	X		X	
	Centro Sperimentale Metallurgico SpA, Rome	X		X	
	Consiglio Nazionale delle Richerche (CNR), Rome		X		
	Ente Nazionale Italiano di Unificazione, Milan				X
	Instituto Italiano della Saldatura, Genoa	X		X	X
	Joint Research Centre, Ispra	X (EEC)			
	Laboratorio per la Technologia dei Materiali Metallici Non Tradizionali (LTM) Milan	X			
Luxembourg					
Netherlands	Centrale Organisatie TNO, The Hague	X	X		
	European Space Research and Technology Centre (ESTEC), Noordwijk	X (European)			
	Metaalinstituut TNO, Delft	X			
	Nationaal Lucht- en Ruimtevaart-Laboratorium (NLR), Amsterdam	X			
	Nederlands Instituut voor Lastechniek, The Hague	X			
	Nederlands Normalisatie Instituut, Rijswijk				X
	Joint Research Centre, Petten	X (EEC)			
U.K.	Admiralty Materials Laboratory (AML), Poole	X			
	Atomic Energy Research Establishment (AERE), Harwell	X			
	Berkeley Nuclear Laboratories, Berkeley	X			
	British Ceramics Research Association, Stoke-on-Trent	X			
	British Investment Casters Technical Association (BICTA), Sheffield			X	
	British Standards Institution, London				X
	Central Electricity Research Laboratories (CERL), Leatherhead	X			

Country	Organisation	Research Organisation	Advisory Body	Information Office	Standards Office
U.K. (continued)	Defence Research Information Centre, Orpington			X	
	Fulmer Research Institute Limited, Stoke Poges	X			
	International Research & Development Co. Ltd., Newcastle-upon-Tyne	X			
	National Engineering Laboratory (NEL), Glasgow	X			
	National Gas Turbine Establishment(NGTE), Pyestock	X			
	National Physical Laboratory (NPL), London	X			
	Royal Aircraft Establishment (RAE), Farnborough	X			
	Society of British Aerospace Companies Ltd., London		X		
	Welding Institute, Abington	X			
U.S.A.	American Iron & Steel Institue (AISI), New York				X
	American Society for Testing of Materials (ASTM), Philadelphia				X
	Battelle Columbus Laboratories, Columbus, Ohio	X		X	
	National Aeronautics & Space Administration (NASA), Washington, D.C.	X	X	X	
	National Materials Advisory Board, Washington, D.C.		X		
	Society of Automotive Engineers (SAE), New York		X	X	X
	Wright Patterson AFB, Ohio	X			
Others (Canada)	Chalk River Nuclear Laboratories, Chalk River, Ontario	X			
	National Aeronautical Establishment, Ottawa	X			
(Norway)	Central Institute for Industrial Research , Oslo	X			
(Switzerland)	Battelle - Geneva Research Centre, Geneva	X			

TABLE L BIBLIOGRAPHY

The items in the bibliography are divided into the following categories:

- *Data Compilations*
- *Books*
- *Conference Proceedings*
- *Review Papers*
- *Commercial Literature*
- *Journals*

Items in the "Review Papers" section are so grouped that those dealing with similar topics (e.g. oxidation and corrosion: ceramics and refractory metals) are listed together.

The list of journal titles omits the more well-known publications and includes some of those of more general relevance to the field of high-temperature materials.

Category	No.	Publication
Data Compilations	1	Simmons, W.F., and Gunia, B., Compilation and Index of Trade Names, Specifications and Producers of Stainless Alloys and Superalloys, A.S.T.M. Data Series DS 45A, October, 1972.
	2	Simmons, W.F. and Metzger, M.C., Compilation of Chemical Compositions and Rupture Strengths of Super-Strength Alloys, A.S.T.M. Data Series DS 9d, October, 1967.
	3	- , Information Sources on the Ceramics Industry, UNIDO Guide to Information Sources, No. 17, 1975.
	4	Smith, M.F., Superalloys - A Bibliography with Abstracts, N.T.I.S.,/ PS - 75/179, October, 1974.
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	55	Betteridge, W. and Heslop, J., (ed.), The Nimonic Alloys, 2nd Edition, Edward Arnold, London, 1974.
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TABLE M *RESULTS OF A SURVEY ON THE NEED FOR REFERENCE MATERIALS USED AT HIGH TEMPERATURES (HIGHER THAN 700°C)*

1. Introduction

Reference materials (RMs) are defined as any substance or prepared specimen, one or more characteristics of which are determined with a maximum of accuracy and precision. These materials therefore constitute information carriers which can be used for the calibration, checking and testing of measuring instruments or of measuring and analytical procedures and to provide a common basis for uniformity and accuracy of measurements.

Use and need for such RMs were generally assessed by means of a pilot survey in 1971 organized by the Commission of the European Communities. The analysis of the replies to the inquiry was published in the report EUR 4886 (1973) and revealed numerous and various needs for new and improved RMs, among which a considerably high interest and demand was indicated for RMs for high-temperature materials such as refractory metals, refractory and ceramic materials and superalloys, the latter however to a smaller extent.

Since these results became significant in the frame of the High Temperature Materials White Book, the Community Bureau of Reference (BCR) of the Commission of the European Communities launched a specific inquiry into RMs for high-temperature materials. The inquiry, started in March 1976, was addressed to relevant public and private organizations/firms mainly within the European Community. The survey was completed in July 1976 and the general results are summarized in this paper.

2. General Results

2.1 Participants

In total 531 questionnaires were sent out to organizations and firms mainly within the nine countries of the European Community; 110 replies have been received at July 1976, distributed as given in Table M/1.

Country	Number of Questionnaires sent out	Number of Received Replies
Belgium	77	16
Denmark	10	2
France	80	22
F.R. Germany	157	23
Great Britain	89	26
Ireland	6	1
Italy	71	11
Netherlands	33	6
Luxemburg	4	1
Others	4	2
	531	110

Table M/1 : Numbers of questionnaires sent out and of replies received.

2.2 Need for Reference Materials

94 (85 %) of the organizations which answered declared that they use, wish or plan to use RMs (here referred to as "users").

16 (15 %) of the participants declared that they do not use, wish or plan to use RMs (here referred to as "non-users"). However 8 of the non-users were producers and/or suppliers of RMs.

In the user organizations the interest in reference materials is different depending on different types of activity, the following of which were mentioned :

- Quality control	23.3 %
- Applied research	18.8 %
- Production control	17.2 %
- Control of conformity to standards specified by law, regulations, terms of contracts	12.3 %
- Development of analytical methods	9.4 %
- Development of methods of measurements or tests	8.7 %
- Other types of activity	10.3 %
	100.0 %

2.3 Origin and field of application of RMs

The users indicated the origin and the field of application of their RMs as given in Table M/2.

Table M/2: Origin of RMs

Origin	Field of Application	
	Analytical Chemistry.	Measurements of Phys. or Technological Properties
National or Private Bodies	83 %	66 %
Own Production	15 %	20 %
Not yet known	2 %	14 %
	100 %	100 %

2.4 Requirements for new and improved Reference Materials

2.4.1 General

38 % of the users consider that the actually available RMs meet their criteria of choice.

59 % of the users are only partly or not satisfied with available RMs.

3 % have not answered.

71 % of all participants find it desirable that reference materials on internationally agreed scales should be available, so that comparative measurements could be more readily made in individual laboratories.

2.4.2 RMs with certified composition or purity

35 % of the users think, that the range of actually available RMs of certified composition or purity covers their actual or foreseen needs.

57 % think that this is not, or is only partly, true.

8 % have not replied.

2.4.3 RMs for physical and technological properties

53 % of the users are interested in RMs having certified physical and/or technological properties.

37 % are not interested in such RMs.

10 % have not answered.

2.4.4 Participation in a BCR action

55 % of the participants, i.e. 58 % of the users and 32 % of the non-users, wish to participate in a co-ordinated action by the Commission of the European Communities in the following activities :

- Circular analysis	29 %
- Comparative measurements	23 %
- Perfecting of measurement methods	20 %
- Others	28 %

The organizations which wish to participate in a co-ordinated action indicated the following types of RMs on which they are able to collaborate

- RMs of certified composition or purity	36 %
- Elements and/or ultra-pure compounds	17 %
- RMs with certified technological properties	16 %
- RMs with certified physical or physico-chemical properties	15 %
- Qualitative reference samples	11 %
- Others*	5 %
	100 %

*Among these were mentioned :

- Crack testing
- Eddy-current testing
- RMs for oxygen, hydrogen and nitrogen in metals and

solids
- Electron microprobe homogeneity tests for alloys.

2.4.5 Summary of results

The results are summarized in the Table M/3.

Table M/3: Summary of answers

Requirements in RMs	YES	1) No 2) Partly 3) No opin.	No Reply
The actually available RMs meet the users's criteria of choice:	38%	59% 1) 2)	3%
The range of RMs of certified composition or purity available at present meets the user's actual or foreseen needs:	35%	57% 1) 2)	8%
Interest in RMs having certified physical and/or technological properties (users):	53%	37% 1)	10%
RMs based on internationally agreed scales should be available (participants):	71%	4% 1) 18% 3)	7%
Participation in a co-ordinated action by the Commission of the EC (Participants):	55%	30% 1) 10% 3)	8%

2.5 Critiques of actually available RMs

As shown in section 2.4., 59 % of the users were not or only partly satisfied with the actually available RMs. From this group 76 indications were received which, however, concern generally the demand for new and/or advanced RMs, rather than criticise the quality of existing RMs.
These indications can be summarized as follows:

- Availability	25 %
- Composition range	20 %
- Defined impurity levels	10 %
- Manufacturing criteria*	12 %
- Properties**	17 %
- RMs for Analytical Methods	16 %
	100 %

* Accuracy, stability, cost, etc.

** Mechanical, physical and physicochemical, thermal and thermodynamical properties.

3. Demands for RMs

3.1 General

The survey was set up so that <u>both</u> needs for RMs of certified composition and/or purity, and RMs having certified physical and/or technological properties, could be assessed.

3.2 Demands for RMs with certified composition and/or purity

As stated in paragraph 2.4, 57 % of the users think that the available range of these RMs does not, or only partly, cover their actual or foreseeable needs. From this group 455 indications were received concerning

- the sub-sections of high-temperature materials for which, in general, these types of RMs are most needed.
- the principal analytical methods to be calibrated.

The results are summarized in Table M/4 and illustrated in Fig. M/1.

The analytical methods most frequently mentioned are

- Elemental Analysis (112)
- Emission Spectrography (112)
- X-ray (absorption, fluorescence) (90)

Sub-sections of High-Temperature Materials	Number of replies*	Analytical Methods										Total Number of Indications
		Elemental Analysis	Emission - Spectrography	X-ray (absorption, fluorescence)	Mass - Spectrometry	Microprobe and Ion Analyzer	Gas Analysis	Spectrophotometry	Titrimetry Electrochem. meth.	Activation Analysis	Miscellaneous **	
Ferrous (Steels etc.)	54	37	43	29	5	7	4	3	4	2	6	140
Super Alloys	33	23	26	21	6	5	7	1	1	2	7	99
Refractory Metals	22	14	11	14	1	4	4	--	--	2	7	57
Pure and Prec. Metals	8	6	5	4	2	3	1	--	1	--	5	27
Refract. and Ceramic Mat.	35	22	17	15	3	8	4	1	2	3	7	82
Glasses	9	6	4	4	2	3	1	--	--	2	4	26
Elements / Compounds	8	3	3	1	--	2	1	--	--	--	2	12
Others	6	1	3	2	--	2	2	--	--	2	--	12
Total	175*	112	112	90	19	34	24	5	8	13	38	455
		25%	25%	20%	4%	7%	5 %	1%	2%	3%	8%	100%

* In most of the questionnaires more than one item is mentioned

** Flame spectrophotometry, combustion, X-Ray diffraction, etc.

Table M/4 Demand for RMs of certified composition and/or purity

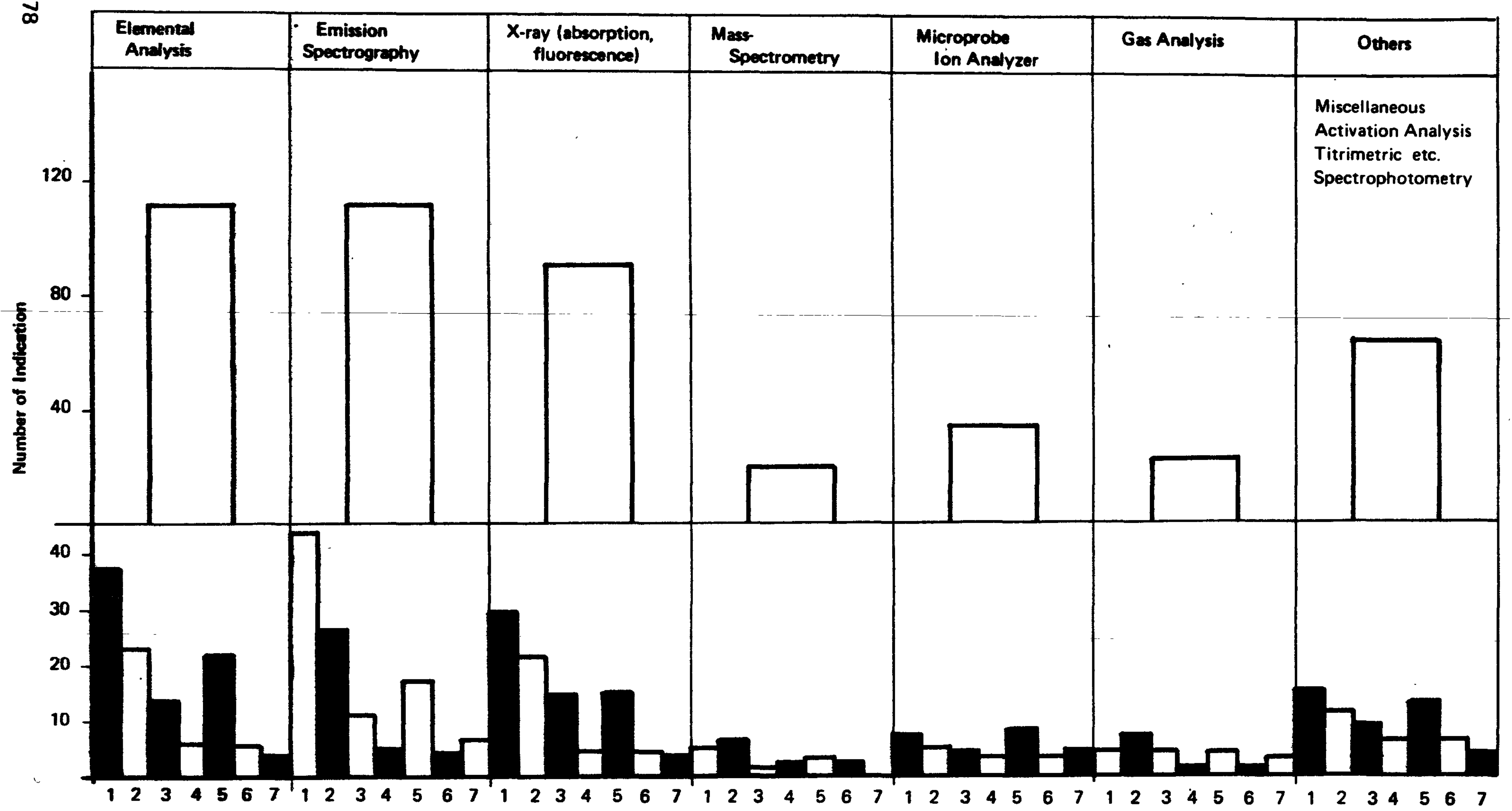


Fig. M/1 *Demand for RM's of certified composition/purity*
Total Number of indications 455

3.3 Demands for RMs with certified physical and/or technological properties

From the users who declared interest in RMs, in total 160 indications on properties relevant to certification were received.

3.3.1 RMs with Mechanical Properties

-	Elasticity	9
-	Hardness	24
-	Dilatation	21
-	Reference defect	9
-	Strength*	13
-	Surface state	1
		77 indications

* (Rupture, creep, high-temperature, fatigue, tensile strength, impact, compression)

3.3.2 RMs with Thermal and Thermodynamic Properties

-	Enthalpy - Heat capacity	8
-	Heat of reaction	6
-	Thermal conductivity	15
-	Thermal radiation	4
-	Diffusion	4
-	Melting point	1
		38 indications

3.3.3 RMs with physical, physicochemical or technological properties

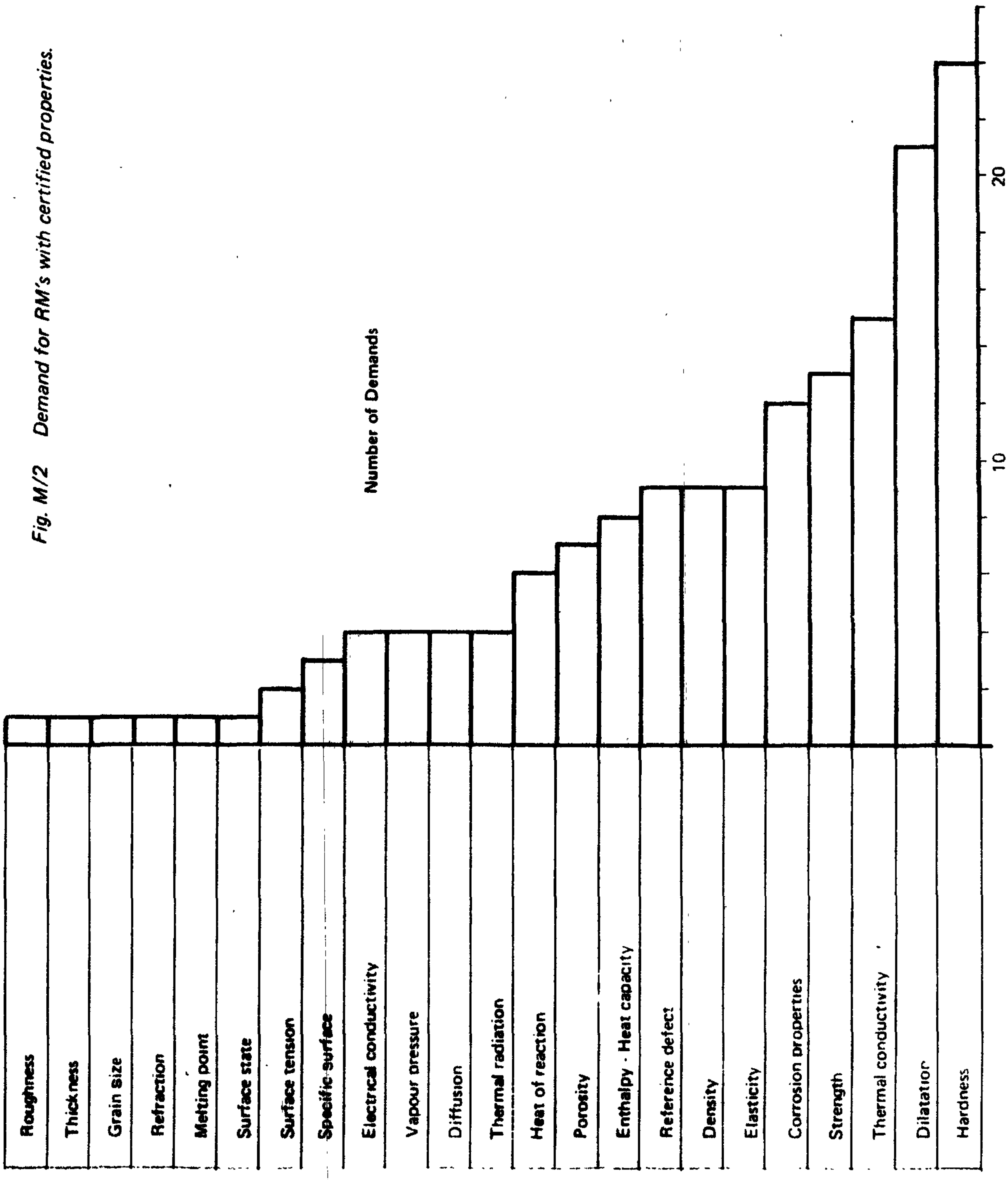
-	Density	9
-	Vapour pressure	4
-	Porosity	7
-	Corrosion properties	12
-	Electrical conductivity	4
-	Surface tension	2
-	Refraction	1
-	Grain Size	1
		40 indications

3.3.4 RMs for Dimensions

-	Specific surface	3
-	Thickness	1
-	Roughness	1
		5 indications

The results are illustrated in Fig. M/2.

Fig. M/2 Demand for RM's with certified properties.



3.4 Demands for RMs for analytical methods

The needs for RMs for the following analytical methods were particularly emphasized

- Spectrography
- Spectrophotometry
- X-ray fluorescence analysis
- Gas analysis
- Reference defect for ultrasonic detection
- Elemental solutions for atomic absorption
- Temperature measurements
- Trace element analysis
- Cerium and rare-earth metals in high-temperature materials
- Defined impurity levels

3.5 Standardized measurement methods

In addition to reference materials there was also a certain interest in standardized measurement methods indicated for the following fields:

- Eddy-current testing
- Sonic testing
- Magnetoscopy
- Radiography
- Temperature measurement
- Measurement of dimensions

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