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High-temperature materials – a general review

G. W. MEETHAM
Rolls-Royce plc, P.O. Box 31, Derby, DE28BJ, UK

Materials that allow operation at high temperature are essential in many industries from material producing and processing to transportation and power generation. After brief comments on typical operating environments, high-temperature aluminium alloys, steels and nickel alloys are discussed, referring to alloy types, characteristics and applications. Future development possibilities are indicated. The engineering ceramics silicon nitride and silicon carbide are discussed with particular emphasis on defect tolerance considerations. The various forms and applications of high-temperature carbon, including carbon–carbon composite, are included and a discussion on "engineered materials" concepts, such as thermal insulators and ablative materials, concludes the review.

1. The need for high-temperature materials

High-temperature technology is of major importance in many industries including primary metal and non-metal production, material processing, chemical engineering, transportation and power generation. For many of these industries the price of fuel is a major component of overall operating costs. Materials that allow operation at high temperature are essential for industrial competitiveness because the efficiency of fuel conversion and use is related to operating temperature. Current operating temperatures in various applications are shown in Fig. 1 together with the melting temperatures of selected materials. Up to ~ 4000 °C more than one material option may exist depending on operational requirements. However, no material is capable of operating above 4000 °C and thermal ablation must be used at these temperatures.

Many industries could benefit from still higher operating temperatures. The temperature of superheater tubes for steam-raising boilers in power plants is currently 560 °C; if this could be increased to 650 °C, efficiency would increase from 35% to 36.5%. This would result in a saving ~ 3.5×10^6 t of coal per year, i.e. 4% of the total coal used in the United Kingdom for power generation [1]. The use of ceramics in diesel engine development in the United States has allowed higher operating temperatures, thus improving efficiency (an increase from 38% to 65% appears possible) and reducing exhaust pollution [2]. Higher temperature operation has a powerful effect on the performance of the gas turbine engine. For example an increase of 150 °C in turbine entry temperature combined with elimination of internal air cooling of turbine components can give an improvement of around 6% in gas generator thermal efficiency [3]. This order of benefit led to the progressive development of nickel superalloys for gas turbine applications and more recently led to the search for materials with higher temperature capability than the superalloys.

2. Operating environment

High-temperature materials operate in environments with a wide spectrum of mechanical and chemical conditions. The temperature may be relatively constant (e.g. in continuously operated heat-treatment furnaces) or subject to severe cycling (e.g. in jet engines where the thin edges of turbine blades can experience temperature changes of more than 1000 °C in seconds). The operating stress can vary from very low stress levels in furnace heating elements, for example, to high combined centrifugal and thermal stresses in a gas turbine disc.

Some measure of inherent oxidation resistance is an essential characteristic of high-temperature materials; however, many applications involve significantly more complex corrosive environments than simple

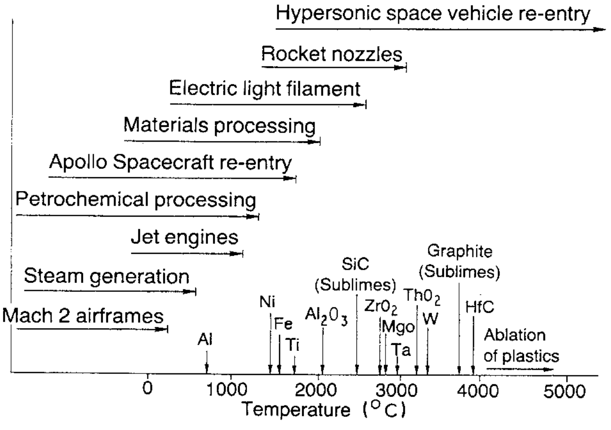

Figure 1 Typical operating temperatures in high-temperature environments.

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TABLE I Temperature capability of high-temperature material systems

Material	Approx. max. use temp., T_u (°C)	$\frac{T_u}{T_m}$	Application
Aluminium (RR350)	300	0.45	Stressed
Low-alloy steel	580	0.37	Stressed
Austenitic steel (A286)	600	0.4	Stressed
Nickel superalloy (MarM002)	1000	0.77	Stressed
Nickel (Brightray H)	1250	0.9	Unstressed
Alumina	1850	0.9	Unstressed
Tungsten	2500	0.74	Unstressed

oxidation. In certain types of coal gasification, the atmosphere may be reducing to some extent; thus alloys that rely on chromium oxide scales for protection do not perform as well as aluminium oxide-forming alloys. Oxidation is further modified by atmospheric and fuel contaminants as in, for example, the use of lower grade fuel such as residual fuel oil, instead of higher fractions such as kerosene, in industrial turbines and boilers. The lower grade fuels contain larger amounts of impurities such as vanadium, sulphur and sodium which accelerate corrosion. Erosion is an important factor in applications such as fluidized-bed coal combustion.

The required life can range from minutes for a rocket motor, through 50 000 to 100 000 h for industrial steam and gas turbines, to more than 20 y for large steam turbine installations.

Operational stress has a major influence on temperature capability, with the limit being 0.7 to 0.9 of the melting temperature, T_m, in unstressed applications and 0.3 to 0.7 T_m in stressed applications (Table I).

On the basis of the T_u / T_m factor, aluminium alloys can be considered as high-temperature alloys. Although they can operate up to 300 °C compared with 580 °C for low-alloy steels, this represents a T_u / T_m factor of 0.45 compared with 0.37 for low alloy steels.

The broad stress–temperature operational regimes of various materials in stressed applications are illustrated in Fig. 2 [4]. The strength is based on the 0.2% proof stress for metals and an appropriate proportion of the flexure strength for ceramics and composites.

Specific strength (Fig. 3) is an important property in materials for rotating machinery. The superior specific strength of titanium relative to steel and nickel superalloys has provided the motivation for its development for aerospace applications. Major progress has been achieved in increasing the temperature capability of titanium alloys. A recent alloy, IMI829, can be used up to 600 °C, some 250 °C higher than the early Ti 6–4 alloy (Fig. 4).

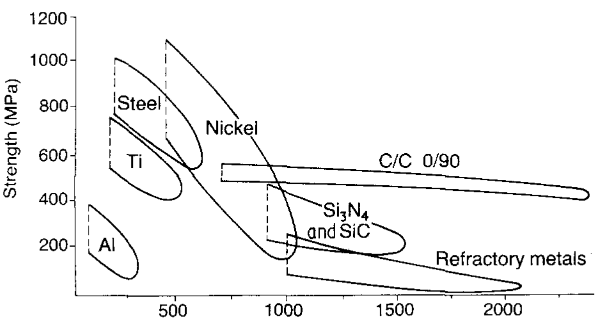

Figure 2 Stress/temperature regimes of high-temperature materials.

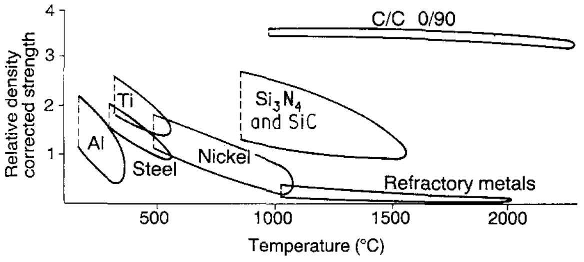

Figure 3 Specific strength comparison of high-temperature alloys.

Despite the fact that the T_u / T_m factor for IMI829 of 0.36 is similar to that for low-alloy steel, titanium alloys are not normally considered as high-temperature materials, and will thus not be discussed here.

The remainder of the review will discuss the various types of high-temperature material, their key characteristics and applications. The chemical compositions of alloys mentioned in the text are given in Table II.

3. Aluminium alloys

The basis for high-temperature aluminium alloys was the discovery of precipitation hardening in Al–Cu alloys. Wrought alloys are based on two systems, Al–Cu–Mg (the 2000 series) and Al–Zn–Mg–Cu (the 7000 series). The latter have the greater response to age hardening but susceptibility to stress corrosion has restricted the use of the strongest alloys in this system. The 2000 series has the higher temperature capability (Fig. 5) with precipitation hardening being augmented with dispersion strengthening with intermetallics in some alloys.

The early emphasis in aircraft construction materials was on maximizing tensile properties. The subsequent need to improve defect tolerance led to a greater importance of properties that govern behaviour in the presence of cracks and other flaws, especially fracture toughness. This has resulted in

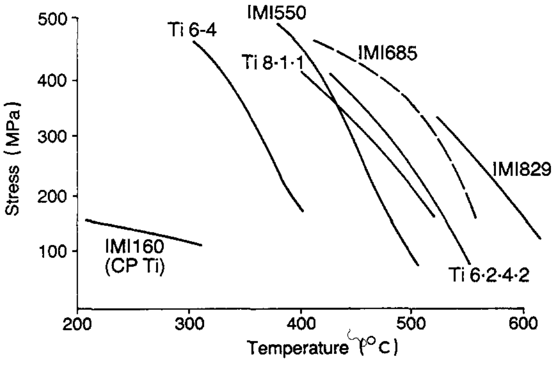

Figure 4 Typical 0.1%/100 h creep strength for various titanium alloys.

TABLE II Chemical composition (wt %)

Alloy	Al	Cu	Mg	Zn	Ni	Ti	Zr	V	Sn	Mo	Si	Nb	Fe	Cr	Co	W	Ta	Hf
7075	Bal.	1.6	2.4	5.5							0.4							
2024	Bal.	4.4	1.5								0.5							
RR350	Bal.	5			1.5	0.2	0.2											
Ti6-4	6					Bal.		4										
IMI829	5.5					Bal.	3		3.5	0.25	0.3	1						
A286	0.2				26	2				1.3			Bal.	15				
FV535					0.6			0.2		0.7		0.3	Bal.	11				
Inconel 600					Bal.								8	15				
Inconel 601	1.5				Bal.									23				
Inco 901	0.2				Bal.	2.8				5.7			36	12				
Nimonic 80A	1.4				Bal.	2.3								20				
IN100	5.5				Bal.	4.7		1		3				10	15			
MarM002	5.5				Bal.	1.5								9	10	10	2.5	1.5

restrictions in iron and silicon content in some alloys (Fig. 6 [5]). High fatigue crack growth rates similarly limited the use of powder alloys which otherwise had attractive mechanical properties.

Al–Si alloys have good casting characteristics but they do not have high temperature capability. Al–Cu alloys are better in this respect and castability problems have been resolved, with the RR 350 alloy being used for compressor casings in jet engines.

Recently, various rapid solidification techniques have been applied to the development of novel alloy compositions containing elements such as iron and chromium with low diffusion coefficients. These techniques include splat cooling, centrifugal atomization and vapour deposition followed by consolidation and mechanical working. Strengthening is achieved by super-saturating the aluminium lattice and incorporating a dispersion of 20 to 30 vol % fine intermetallic particles such as Al_6Fe and Al_7Cr. The creep strain data in Fig. 7 [6] show the potential of this technology to improve temperature capability over conventional alloys.

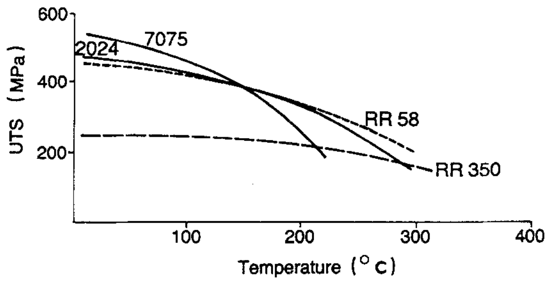

Figure 5 Ultimate tensile strength of aluminium alloys.

4. Steels

There are two basic types of high-temperature steel; ferritic/martensitic and austenitic. Both have high strength and high corrosion-resistant versions.

Low alloy steels solid-solution strengthened by 0.5% Mo have long been used for superheater tubing and other boiler components in steam turbines up to about 480 °C. Cr–Mo and Cr–Mo–V steels (precipitation hardened by V_4C_3) have higher temperature capability and have been used in steam turbine rotors and turbine discs in early jet engines. The subsequent need to increase jet engine component life at the temperatures at which the strongest low-alloy steels were operating led to the development of the high-strength martensitic 12% chromium steels, e.g. FV 535. Materials of this type are still in use for turbine discs in industrial gas turbines. Developments are underway to increase further the temperature capability of these materials in view of the projected benefits of higher temperature operation in power generation.

Ferritic materials such as FeCrAl have been developed specifically for high-temperature oxidation resistance and are used as resistance heating elements in ceramic, glass and metal-processing furnaces. They have low strength at high temperature. The addition

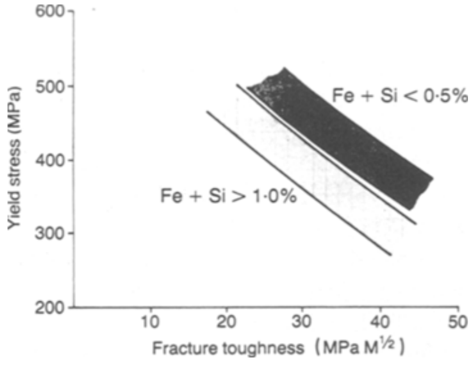

Figure 6 Effect of iron and silicon content on fracture toughness of Al–Cu–Mg alloys.

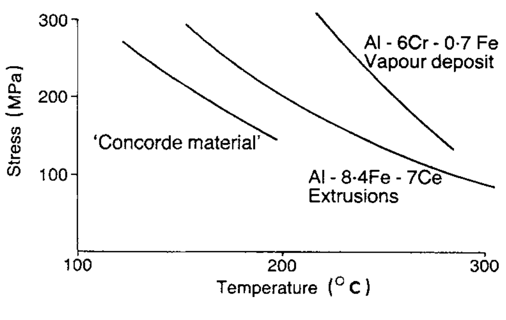

Figure 7 Creep strength (0.2%/100 h) of rapidly solidified aluminium alloys.

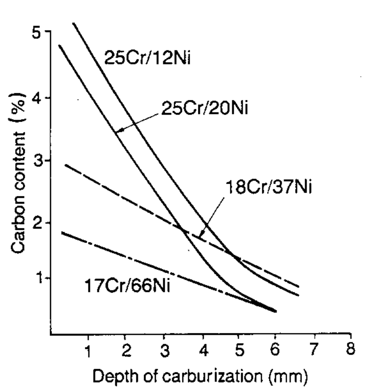

Figure 8 Effect of nickel content on carburizing characteristics after 1000 h at 1100 °C in an atmosphere of 65% N_2, 25% H_2 and 10% CH_4.

of nickel to stabilize the face-centred cubic austenitic structure increases the strength with little effect on oxidation resistance.

Steels with higher chromium and nickel than the 18-8 types are more suitable for high-temperature service because of their superior strength, oxidation and corrosion resistance. Although nickel has little effect on oxidation resistance, it provides a major improvement in corrosion resistance, particularly in relatively low oxidation potential environments where resistance to carburization is required (e.g. in production of ethylene by cracking hydrocarbon–steam mixtures (Fig. 8) [7].

Early high-strength austenitic steels were strengthened by complex carbides. Subsequently, precipitation hardening with a $(FeNi)_3$ Ti precipitate was used in A286. This has significantly higher temperature capability than the martensitic 12% chromium steels (Fig. 9). It was used in early jet engine discs and is still used for turbine discs in industrial gas turbines.

5. Nickel alloys

Nickel–chromium alloys date back to the early 1900s when their high-temperature oxidation resistance was first recognized. The subsequent development of nickel alloys has had two objectives: (1) increased oxidation and corrosion resistance; (2) increase of strength and temperature capability. The latter has been motivated almost entirely by the gas turbine and has been so successful that nickel superalloys can be used in stressed applications up to a greater proportion of their melting temperature than any other alloy system.

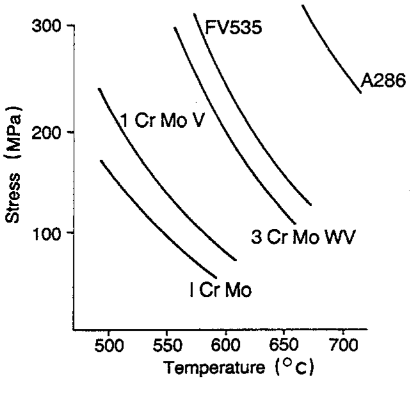

Figure 9 Creep properties (rupture in 1000 h) for various high-temperature steels.

The excellent oxidation resistance of nickel–chromium alloys resulted in their early use in electric resistance heating elements. Subsequently, incorporation of small amounts of reactive elements such as calcium, cerium and silicon has significantly improved the oxidation resistance under cyclic conditions. Since this early work, the development of general corrosion-resistant nickel alloys has resulted in Inconel 600 becoming the traditional alloy for general industrial furnace parts and the stronger and more oxidation resistant Inconel 601 being used in more demanding applications such as solid waste incinerators and ash-handling equipment in power generation.

Nickel superalloys were developed to meet gas turbine requirements in which elevated temperatures are combined with mechanical stress and the need for high surface stability. When they were first introduced, the properties of nickel superalloys were so superior to those of their predecessors that simple alloy development alone was sufficient to meet the design needs, with relatively little contribution from the manufacturing process other than to produce the required shape. Subsequently the alloy compositions became progressively more complex. The alloying additions that may be present are shown in Fig. 10. The height of the major alloying element blocks give an indication of the amount that may be present and their major functions are indicated [8]. Trace elements can have a profound influence on properties and behaviour and beneficial trace elements are cross-hatched, detrimental elements are shaded horizontally.

Subsequent to the alloy composition dominated regime, there was a regime in which both material composition and manufacturing process played important roles. In the 1960s, for example, it was realized that low-cycle fatigue behaviour was limiting the life of gas turbine discs. This led to the use of controlled thermomechanical processing in which the forging and subsequent heat-treatment conditions are selected to produce a predetermined microstructure to enhance particular properties in alloys such as Inco 901. Attempts to develop higher fatigue strength by forging more highly alloyed superalloys achieved little success because increased chemical segregation in the ingot made forging more difficult. This problem led to the introduction of a pre-alloyed powder technology for disc manufacture in the mid 1970s.

The latest regime is dominated by the manufacturing process with material composition being of secondary importance. This is exemplified by directionally solidified and single crystal castings, in which the major property benefits are due to the particular crystal structure produced by the casting process [9].

The combined benefits of alloy composition and manufacturing process on the creep strength of turbine blade alloys are illustrated in Fig. 11 [10].

The oxide scale formed on nickel superalloys depends on alloy composition (Fig. 12) [11]. Early alloys such as Nimonic 80A contained around 20%

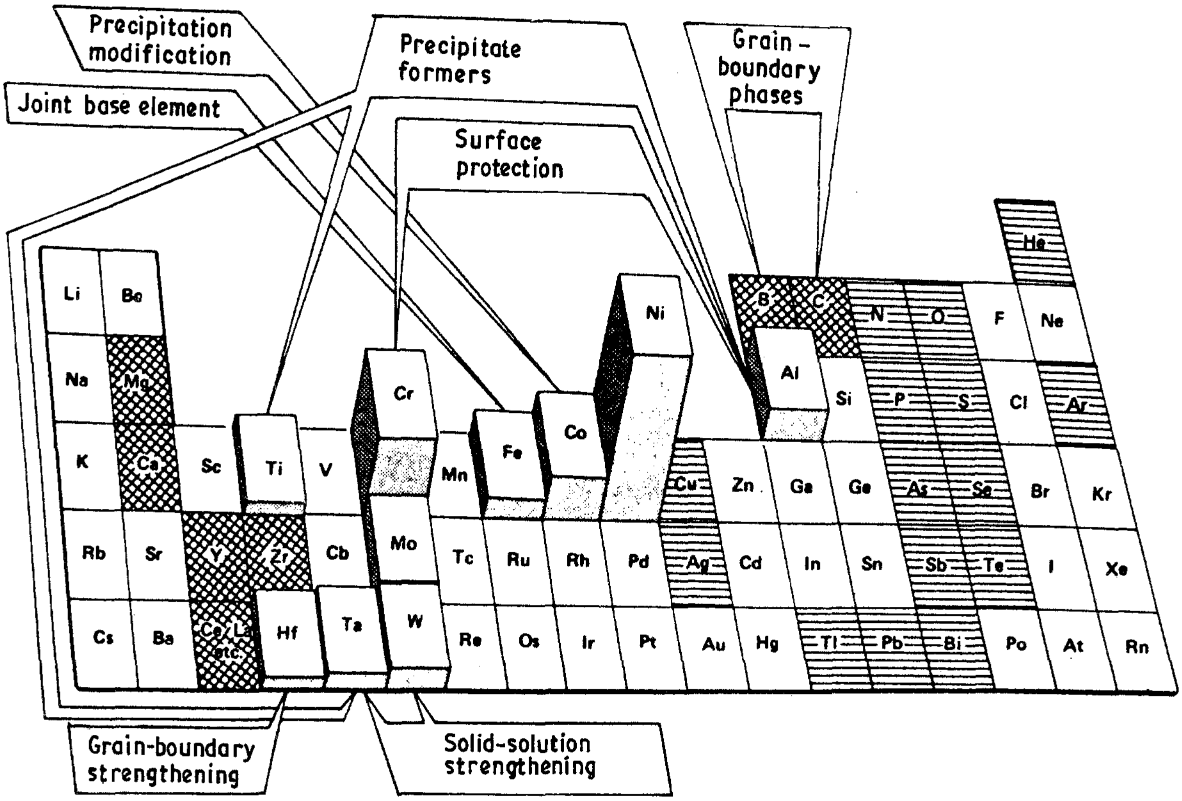

Figure 10 Elements in nickel superalloys and their principal effects.

chromium and relatively low aluminium content. They thus formed Cr_2O_3 predominantly. The subsequent compositional changes necessary to increase creep strength involved, *inter alia*, increase in aluminium and decrease in chromium content. Thus later alloys, such as IN100 and MarM002, formed Al_2O_3 scales. This resulted in improved oxidation resistance but markedly reduced resistance to hot corrosion at intermediate temperatures in environments involving sulphur and sea salt contamination [12]. This has been a major factor in the increased use of corrosion-resistant coatings on nickel superalloy components.

These coatings are either of diffusion or overlay types. Diffusion coatings are applied by pack cementation processes in which the part is surrounded by powdered aluminium material, a halide activator and an inert powder dilutent [13]. Aluminium is transferred to the surface and diffuses into the base material to form nickel aluminide. A typical aluminide coating is 50 µm thick and contains 30% aluminium. Aluminide coats were introduced in the early 1960s and are still used on many components. Improved coatings are, however, required for the highest temperature oxidation and the most severe hot corrosion environments. This need has resulted in the development of improved aluminides and MCrAlY overlay coats. One of the most important modified aluminide coats is platinum aluminide [12]. The incorporation of platinum improved protection by introducing a platinum aluminide phase into the coating microstructure and by stabilizing the nickel aluminide phase. Overlay coats [14] are deposited on the component surface, usually by electron-beam physical vapour deposition or plasma spraying at low pressure or with a protective argon shroud. A wide range of MCrAlY compositions is available in which the base coating element, M, can be nickel, cobalt or iron. Chromium (15% to 30%) and aluminium (6% to

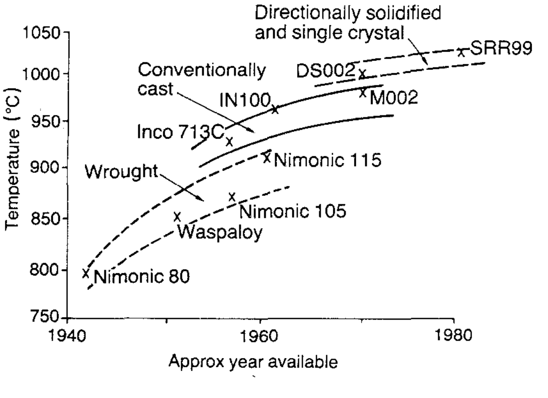

Figure 11 Temperature capability of turbine blade alloys (based on 1000 h creep rupture under a stress of 150 MPa).

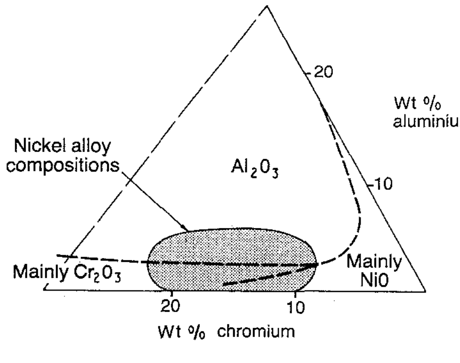

Figure 12 Effect of chromium and aluminium on oxides formed on nickel superalloys.

12%) provide corrosion resistance. Yttrium improves oxide scale adherence. Coating thickness is normally 100 to 150 μm and composition depends on the environment against which protection is required. A CoCrAlY coating with high chromium and low aluminium that forms Cr_2O_3 may be better in hot corrosion conditions, whereas a CoNiCrAlY with high aluminium and low chromium that forms Al_2O_3 may be better against oxidation.

It is crucial that coating performance is predictable and reliable in both environmental and mechanical behaviour. This requires a level of coating and coating/base material interface behaviour understanding comparable with that which has existed for base component materials. In the past this level of understanding has not existed for coatings and current progress must continue in order that coating behaviour is an integral part of the component design process. A likely consequence is a move towards coating application processes which provide a greater degree of microstructural control.

6. Ceramics

The first engineering applications of ceramics involved low stress, moderate- to high-temperature environments in thermal or electric insulation, resistance heating and other applications.

During the last 25 years the use of ceramics in high-temperature applications involving significant tensile stress has increased, largely because of an improved understanding of the relationship of processing, microstructure and properties, and the consequent improved materials and manufacturing technology. Ceramics with better strength and temperature capability are now available. Silicon nitride and silicon carbide have been the subject of major developments in recent years, in view of their relatively good thermal shock resistance and consequent potential for gas turbine applications [15]. Silicon nitride exists in two basic forms: porous and dense. The porous form, reaction-bonded silicon nitride, is produced by controlled nitridation of a silicon powder compact in a nitrogen atmosphere at 1400 °C. It is used in light alloy foundries for pouring spouts, continuous casting dies, etc., and in heat treatment and brazing fixtures. Dense silicon nitride is made by several processes including pressureless sintering, hot pressing and hot isostatic pressing. Oxides such as MgO, Y_2O_3 and Al_2O_3 are incorporated as sintering aids. MgO reacts with SiO_2 to create a low-viscosity grain-boundary glassy phase of limited temperature capability. A more refractory glass is produced by addition of Y_2O_3 with consequent higher temperature capability (Fig. 13).

The programmes to confirm the potential of ceramic components in gas turbines have highlighted the need for improved defect tolerance in stressed applications. This has resulted in the development of various types of ceramic composite. Probably the simplest form of ceramic composite is the *in situ* fibrous microstructure produced by liquid-phase sintering silicon nitride (Fig. 13). Such material has K_{1c} of the order of 7 to 9 MPa $m^{1/2}$ compared with 3 to 5 MPa $m^{1/2}$ for the equiaxed microstructures produced by hot pressing material with lower levels of sintering additive. There has been increasing interest in the last decade in whisker-reinforced ceramics. Sintered Al_2O_3 has a fracture toughness of ~ 2 MPa $m^{1/2}$ and the incorporation of 20 vol % SiC whiskers increases this to 8 MPa $m^{1/2}$. This results in improved tool performance with a further benefit in thermal shock resistance arising from the increased thermal conductivity due to the SiC whiskers. The highest levels of defect tolerance are achieved in continuously reinforced ceramics with work of fracture values of 50 to 100 kJ m^{-2} having been obtained on carbon/carbon and pyrex reinforced with Nicalon fibre. The actual toughness depends on interface control, however (Fig. 14).

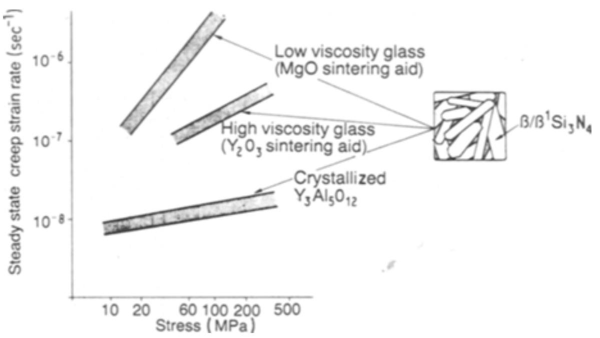

Figure 13 Influence of grain-boundary phases on creep properties of silicon nitride at 1350 °C.

Components in silicon carbide reinforced with Nicalon fibres have already been run in gas turbine engines. Outstanding problems include lack of fibres with the required temperature capability. The non-stoichiometry of Nicalon limits temperature capability to around 1000 °C.

7. Carbon and carbon–carbon composites

Carbon and graphite have long been used in high-temperature applications that require mechanical strength and thermal shock resistance. Their primary use is in resistance and induction-heated furnaces and as electrodes for electric arc furnaces.

Pyrolytic graphite is a highly anisotropic form of graphite with thermal and mechanical properties that

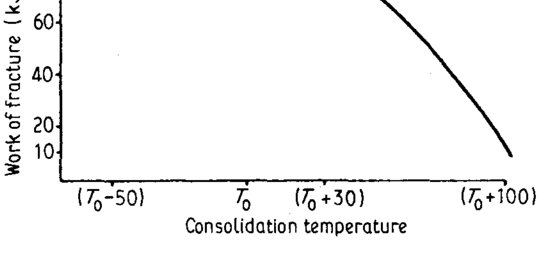

Figure 14 Effect of consolidation temperature on toughness of Nicalon/Pyrex composite.

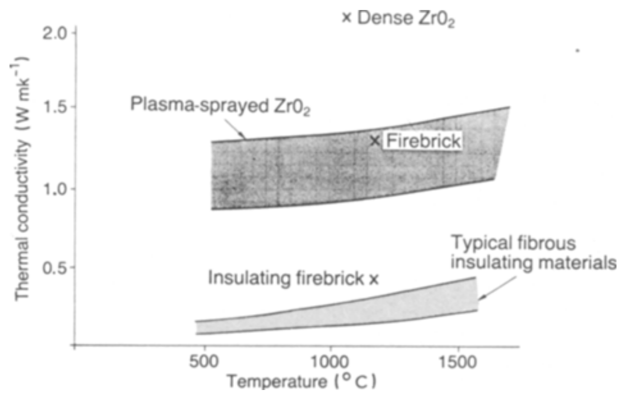

Figure 15 Thermal conductivities of various insulating materials.

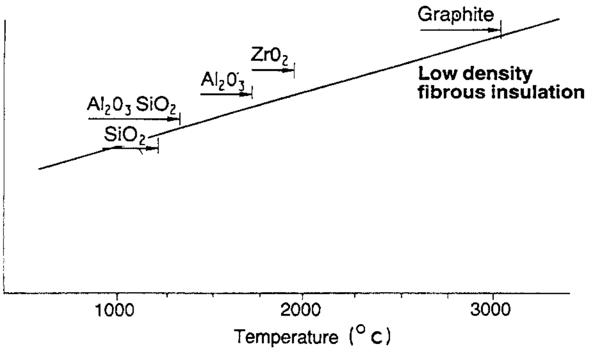

Figure 16 Temperature capability of fibrous insulators.

depend strongly on crystal direction. In the direction perpendicular to the basal plane, pyrolytic graphite has one of the lowest thermal conductivities of all solid insulating materials at high temperature. For this reason, it has been used for rocket nozzle inserts and nose tips in re-entry vehicles. Brittle failure problems were encountered with some of these components and the need for a tougher material was met by carbon–carbon composites.

Although tougher, the composite material is no more resistant to oxidation than monolithic graphite. This is not a major problem in single-mission applications (e.g. rocket nozzles) or when the material experiences only brief exposure to high temperature and design allows a measure of oxygen exclusion (e.g. aircraft brakes). For long-term, high-temperature applications, some forms of oxidation protection is required [17]. In the space shuttle orbiter vehicle where the nose cone and wing leading edges reach temperatures around 1500 °C during re-entry, the carbon–carbon composite is protected with an external coating of silicon carbide. For potential jet engine applications involving a greater degree of thermal cycling and extended dwell times at ~ 1000 °C (in addition to high-temperature excursions > 1500 °C), improved oxidation resistance is required, and techniques such as matrix inhibition are being developed. Glass-forming elements are incorporated in the matrix material so that glass forms as cracks are generated, thereby protecting the base material from further oxidation.

8. Thermal insulating materials

Solid insulators, often containing porosity to reduce thermal conductivity, have been very widely used. Fibrous insulators have thermal conductivity approaching an order of magnitude lower (Fig. 15).

The actual fibre material makes only a minor contribution to the overall thermal conductivity but determines the temperature capability of the insulator (Fig. 16). Fibrous insulating materials are used as hot-face linings in heat-treatment furnaces, where their lower weight and thermal mass compared with conventional refractories result in reduced cycle time and consequent fuel savings. Other applications include combustion chamber and pipeline insulation in the petrochemical industry. Rigidized silica fibre tiles are used on the space shuttle orbiter *Columbia* in which the silica fibre structure supports a glass-coated outer skin that radiates a high proportion of the heat energy back to the atmosphere.

9. Thermal ablative materials

Some environments generate temperatures capable of vaporizing most known engineering materials, e.g. hypersonic re-entry vehicles can approach 8000 °C. Materials with specific characteristics are required to withstand such temperatures by using thermal ablation.

The use of materials as a heat sink is a long established technique that employs the heat content of the material in the solid state. This is typically ~ 10% of the total heat-absorbing capacity of a material, which includes melting and vaporization. Thermal ablation is defined as the consumption of solid material by using its total heat capacity, with an air flow to remove continuously the products formed. Full ablative potential is achieved only if the material is retained at the surface long enough for it to vaporize; uniform surface removal is essential. These requirements led to the concept of a composite material with the ablative component held in place by fibres that are more refractory. Reinforced plastics are excellent ablative materials and have been used in many aerospace applications, including the *Apollo* re-entry shield and *Titan 3C* rocket nozzles [18]. Ablation takes place as illustrated in Fig. 17. The surface temperature increases rapidly because of the low thermal conductivity until thermal degradation starts: the gas produced by the volatile components in the plastic forms a boundary layer on the component and provides some

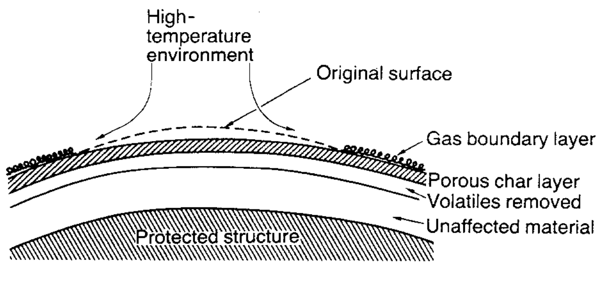

Figure 17 Schematic representation of the ablation process.

insulation: the remaining carbon char is oxidized, sublimed, or eroded.

10. The future

Further improvement in key properties are probable in all of the material types discussed. However, these improvements will not satisfy all of the requirements for high-temperature materials and it is likely that the concept of "engineered materials" will be subject to major development and growth in the future. An "engineered material" can be defined as a multi-material system which has a spectrum of properties not attainable in any one material. Classic examples of "engineered materials" are the fibrous insulation supporting the radiative skin used on the space shuttle orbiter vehicle and the thermal ablative materials.

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