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FIBRE STRENGTHENING OF CERAMICS AND GLASSES
(Background Material)

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Mechanical and Physical Behaviour of Metallic and Ceramic Composites

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Ceramic composites at extremes of performance

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ABSTRACT

This paper is a brief review of some of the factors which may limit the performance of ceramic matrix fibre composites (CMC), particularly the effects of temperature on properties. It outlines the present practical limits on their performance, and current thoughts on the maximum temperatures which are potentially achievable. Ceramic matrix fibre composites are here taken to include glass and glass-ceramic matrices, as well as true ceramic matrices, reinforced with continuous carbon and ceramic fibres; whisker toughened ceramics; and carbon matrix systems such as carbon-carbon composites.

1. INTRODUCTION - THE REQUIREMENT

The main motivation for the development of high strength, high toughness CMC has been the increasing requirement of the aerospace industry for materials capable of operating at high temperatures in aggressive environments with acceptable mechanical properties. The important properties sought are: short-term high strength with low variability; long-term strength, including resistance to creep and fatigue; toughness, including good damage tolerance and impact strength; resistance to thermal shock and cycling; and resistance to abrasion and chemical erosion. These properties need to be retained for acceptable lengths of time under operating conditions, details of which will depend upon the specific applications but include temperatures which can range from below ambient to very high, and atmospheres of air, rarified air and combusting fuel gases. For example, for advanced military aircraft gas turbine engines, materials are sought which can survive operational cycles which could include periods at temperatures in excess of 2000°C (Kirk 1988), and for re-usable space vehicles re-entry temperatures of 1500°C or higher can occur (Barker et al. 1988).

Although other, non-aerospace applications for CMC are emerging, which do not require extreme temperature capability, such as dies and other forming tools, medical implants, and in land transport engines, the main direction of research is towards high temperature capability. It is therefore important to assess continuously what current research is telling us about achievable goals.

2. CURRENTLY AVAILABLE MATERIALS

All of the successful techniques for the manufacture of CMC currently require processing at high temperatures and chemical compatibility and thermal expansion mismatch between fibres and matrix are therefore important. In principle, problems of high temperature reactions between fibres and matrix might be alleviated by interfacial barriers but thermal expansion mismatch presents a more severe problem. Because stresses induced by thermal mismatch as the composite cools can cause the composite to crack and fragment, the fibres and matrices which can be combined successfully are limited. In general a fibre with the same or a higher coefficient of thermal expansion (CTE) than the matrix is preferred, so that the matrix is placed into compression on cooling. Differences in thermal expansion mismatch in the fibre's radial direction can be important in a more subtle way by affecting the strength with which the matrix grips the fibre. This can control the effective fibre-matrix bond strength and the resulting composite toughness (Phillips 1974).

At the present time there are three different generic types of CMC which are furthest developed, characterised by the methods used to incorporate fibres or whiskers into the matrix (Phillips 1987, 1988). These are: continuous fibre reinforced glass-ceramic and glass systems produced by a solid-state, slurry impregnation, route followed by hot-pressing (Sambell et al. 1974); gas phase or liquid phase infiltrated fibre preforms (Naslain 1985, Naslain and Langlais 1985); and hot-pressed whisker toughened ceramics (Wei and Becher 1985). Most of the available information about the high temperature behaviour of CMC has been obtained from these.

Only a limited number of fibres and whiskers capable of operating to temperatures beyond 1000°C are presently available. These include carbon (or graphite) fibres and fibres based on SiC and Al_2O_3, and whiskers of SiC and Si_3N_4. The mechanical properties of these different generic types of material, the advantages and disadvantages of the different fabrication routes, and to some extent the applications of the materials, differ (Phillips 1988).

Highest strengths are achieved by the hot-pressed glass and glass-ceramic matrix systems. These can be fabricated with low matrix porosity and rule of mixtures strength to 60 volume % ($^v/o$) of fibre (Dawson et al. 1987). The relatively low failure strain of the matrix can, however, result in multiple matrix microcracking at stresses well below the ultimate room temperature strength of the strongest of these systems (Phillips et al. 1972). Matrix microcracking can, under some circumstances, precipitate failure, reduce the maximum strength and could also affect fatigue behaviour.

The gas phase and liquid phase fabrication routes are used for materials which include the true ceramic matrix composites and carbon-carbon. These always contain much porosity, typically minimum values of around 10% are the lowest practically achievable. Porosity reduces composite strength and this, coupled with the use of multidirectional fibre preforms results in a lower strength material.

The whisker toughened materials are the easiest to manufacture, most closely resemble monolithic ceramics, and have low porosity, but can only accommodate relatively low volume fractions of reinforcement ($\lesssim 30$ $^v/o$) and benefit from only a modest transfer of whisker strength into the composite.

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3. TEMPERATURE LIMITATIONS

A good starting point for a discussion of the maximum achievable temperature capability of CMC is the assessment by Hillig (1985) who has considered the necessary criteria which must be satisfied for a composite to survive and have useful properties under stress at high temperature in air. Melting (or dissociation) temperature gives an absolute upper bound but other considerations reduce this substantially. These include, as a minimum: stability with respect to volatilisation; low internal chemical reactivity; retention of stiffness; and a creep rate for the fibre < 10^{-7}sec^{-1}. He concluded that only an oxide matrix would have sufficient stability against oxidation to act as a protective matrix or coating and that a non-oxide fibre would be necessary on grounds of stiffness and bonding. He also pointed out that a non-oxide matrix might be suitable with an oxide coating to protect it and that a further barrier between fibres and matrix may be necessary even for an oxide matrix.

Despite his reservations, embodied in the three laws of high temperature chemistry attributed to Searcy that: everything reacts with everything at high temperatures; everything reacts faster at higher temperatures; and the products may be anything; Hillig compiled, calculated and infered enough thermochemical data to conclude that there are a number of oxides, carbides, borides and nitrides, as well as carbon, which might function together to temperatures in the range 1700°C to 2100°C. Of the non-oxides only carbon, Si_3N_4 and SiC are currently available as fibres or whiskers. He also considered briefly the creep stability of whiskers grown with single screw dislocations and, from a consideration of the work required to nucleate dislocation loops, concluded that there is little likelihood that spontaneous nucleation of dislocations will occur and therefore that the whiskers will have considerable resistance to creep. A conclusion which can be drawn from his survey is that SiC whisker reinforced Al_2O_3 is one of the most promising practical systems. The maximum temperature capabilities of the materials considered by Hillig are listed in Table 1 and this list is still the best widely available. Fleischer (1985) has also provided a useful compilation of the relative high temperature capabilities of single phase materials with melting temperatures between 2000°C and 4000°C.

Table 1. Provisional maximum temperature of use (T_u) of some oxides and non-oxides, after Hillig. T_m is melting or dissociation temperature

Oxides		
Material	T_m (K)	T_u (K)
ThO_2	3493	2290
HfO_2	3117	2020
UO_2	3113	2050
MgO_2	3098	1825
ZrO_2	3037	2125
CaO	2882	2015
BeO	2843	1990
SrO	2727	1750
Al_2O_3	2327	1630
Cr_2O_3	2300	1610

Non-Oxides		
Material	T_m (K)	T_u (K)
TaC	4528	2980*
HfC	4163	2915*
NbC	3886	2365
C	3825	2670
ZrC	3803	2660
HfN	3660	2560
TiC	3530	2470
HfB_2	3523	2345
TaN	3360	1855
TaB_2	3310	2315
SiC	3100	2170*

* Calculated on basis of 0.7 T_m as likely maximum temperature determined by creep.

Thermodynamic calculations are useful for carrying out an initial assessment of the suitability of combining two materials into a composite (Knights 1988). Reactions between the two components at high temperature can result in material loss. The importance of this can be assessed by calculating vapour pressures and Hillig has suggested, on the basis of practical experience, that for long-term use the vapour pressure at exposed surfaces should be $\lesssim 10^{-6}$ bar but at internal surfaces might be acceptable up to 0.1 bar. An example of the type of equilibrium thermodynamic calculation that can be carried out is illustrated below (Knights 1988). Silicon carbide is one of the most oxidation resistant carbides but in air environments or combustion gases some protection might be required for a SiC matrix above about 1500-1600°C. If Al_2O_3 is used as a protective coating a variety of reactions will occur beneath the protective alumina film as shown in the example:

		At 2000K
	CO(g)	6×10^{-3}
	SiO(g)	6×10^{-3}
$Al_2O_3 + SiC \rightarrow$	Si	3×10^{-5}
	SiC(g)	5×10^{-11}
	$Al_2O(g)$	4×10^{-3}
	Al(g)	3×10^{-3}
	Total	2×10^{-2} bar

This example shows that internal interactions would limit the protection system to about 2000K on the 0.1 bar criterion. Higher temperature systems would require use of more stable oxides or other protection. Computer codes are available for solving multi-phase, multi-component systems and are well proven (Knights 1988, Erikson 1975). Thermodynamic calculations are invaluable in most situations where interaction with other phases, gaseous or condensed, is possible. They can indicate the most probable chemical degradation mode, give limits to treatment or use temperatures and suggest protective interlayers between phases and external coatings - an invaluable precursor to more expensive experimental work. The thermodynamic data are readily available (Knights 1988, Chase et al. 1985, Kubaschewski and Alcock 1979). There are pitfalls in applying the data in not considering some little known gaseous species or in not considering the correct equilibria. Although thermodynamic calculations are useful at the scoping stage, they only provide information about equilibrium states. For information about the kinetics, and therefore for certainty about the importance of particular reactions, experiments or prior expertise are necessary. Lack of these data are currently a major problem.

The practical systems which currently exist use C fibres, Al_2O_3 fibres, SiC fibres and SiC whiskers. Of these the C fibre and Al_2O_3 fibre systems appear to approach the temperature limits in Table 1 when the behaviour of the fibre is the controlling factor: $\gtrsim$ 2300°C for C and $\sim$ 1300°C for Al_2O_3. However the SiC fibre systems tend to have a much lower temperature capability because of creep of the fibres and fibre structural changes, and the SiC whisker reinforced Al_2O_3 systems do not appear to have significant improvements in creep behaviour over unreinforced Al_2O_3. Another important factor which may limit the temperature capability of SiC fibre reinforced glass-ceramic below the temperature capability of the matrix is the occurrence of matrix microcracking.

4. PROPERTIES OF FIBRES

A more extensive review of the performance of fibres is given elsewhere in these proceedings by Bunsell, however, it is worth summarising here some key facts.

DiCarlo (1985) has published data for CVD SiC fibres showing a dependence of strength on test temperature and heat treatment temperature at temperatures ≥ 1200°C. Room temperature strength was reduced to a half by an exposure of 15 minutes at 1500°C in an inert atmosphere, apparently due to microstructural changes. The strength at temperature in oxygen after 15 minutes exposure was reduced to a half at about 1100°C. These results are better than those from Nicalon SiC fibres. Bunsell (1986) showed that significant creep of Nicalon SiC occurred above 1100°C.

Alumina fibres, such as the α-alumina DuPont FP fibre or the γ-alumina Sumitomo fibre, are also restricted to less than 1200°C because of creep (Bunsell 1986). Recently, DuPont has publicised a new alumina-zirconia fibre, PRD-166, which is substantially stronger than FP alumina and has a better retention of room temperature strength after exposure to high temperature (Romine 1987). High temperature strength and creep properties have not been published and it can be speculated that, if the mechanism of strengthening over the α-alumina fibres is the zirconia martensitic transformation, the higher room temperature strength may not be retained to high temperatures as the efficiency of the martensitic transformation toughening mechanism decreases.

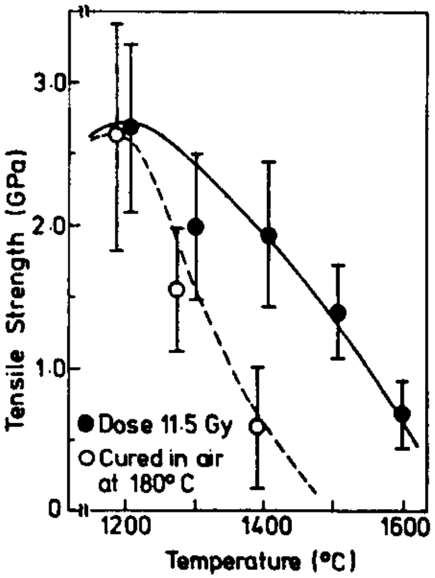
Substantial development work is under way, particularly in the USA, to produce ceramic fibres of higher temperature capabilities (Mah et al. 1987). An interesting approach by Japanese scientists, utilising an intermediate radiation processing stage, has resulted in a significant improvement in polycarbosilane based ceramic fibres (Okamura et al. 1988). Current manufacturing processes involve a thermal oxidation stage at $\sim$ 180°C to cross-link the thermoplastic polymer and prevent it melting during higher temperature processing. By substituting irradiation cross-linking they were able to produce SiC fibres with a low oxygen content. Fibres produced in the standard way lost 50% of their strength at around 1300°C while the radiation processed fibres could be taken to 1500°C, Fig. 1.

Despite current development work, it appears unlikely that, in the near future, substantial improvements in temperature capabilities will be obtained for ceramic fibres and that creep or microstructural changes will restrict long-term use to $\lesssim$ 1400°C.

Carbon fibres can retain their short-term strengths to temperatures in excess of 2500°C provided they are protected from oxidation (Fitzer et al. 1984). They also have good creep resistance (Strife and Sheehan 1988). Currently therefore they are the only reinforcement commercially available which offer the prospect of a temperature capability much above 1500°C.

5. COMPOSITE STRENGTH

A full discussion of CMC mechanical properties would need to take into account the fibre distribution and the stress state and assess whether the property is matrix or fibre dominated. For example a unidirectional composite with a glass matrix under shear stress may be limited by the viscosity of the matrix as temperature increases, while a unidirectional composite under tensile stress may be limited by the fibre behaviour. Such an extensive discussion is not possible here and is restricted to fibre-dominated modes of behaviour.



. 1. The effect of radiation processing on the high temperature strength
SiC fibre (Okamura et al. 1988).

Glass and glass-ceramic composites. The maximum temperature capability
arbon fibre reinforced glass and glass-ceramics in air is determined by
lation of the fibres at around 400°C (Sambell et al. 1974, Prewo and Batt
). The matrix tends to provide only very limited protection for the
es and methods of protecting the surface by glass have not been
essfully pursued. Matrix microcracking under stress would make such
ective methods suspect. In an inert environment strength is retained to
eratures at which the matrix creeps excessively, approximately 1000°C to
°C for glass-ceramics.

maximum temperature capability of glass and glass-ceramic matrix
osites reinforced with Nicalon SiC fibres is defined either by the
erature at which fibres creep or degrade, or the maximum temperature at
h the matrix viscosity is adequately high to maintain a low creep rate.
higher temperature materials are the glass-ceramic matrix systems and for
e the highest temperatures achievable defined by the matrix creep rate or
fibre degradation temperature are very similar, at around 1200°C (Prewo
, Cooper and Chyung 1987).

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The presence of air does not appear to have a very significant effect on the maximum temperature capability of Nicalon SiC/glass-ceramic composites. It can however affect the strength at lower temperatures through a mechanism initiated by matrix microcracking. Optimisation of fabrication of composites of Nicalon SiC fibre in lithium aluminosilicate matrices (SiC/LAS) is not straightforward and several different systems have been produced, apparently differing in heat treatment temperature and the specific composition of LAS. Prewo has described the properties of three systems designated SiC/LAS I, SiC/LAS II and SiC/LAS III (Prewo 1986, 1988). System I has relatively low strength compared with II and III and fractures at a stress lower than the matrix microcracking stress. This system retains its strength to the maximum temperature, Fig. 2. Systems II and III are stronger and display matrix microcracking. When tested in air they both exhibit a significant reduction in strength to a stress level equivalent to the matrix microcracking stress at around 800°C, Fig. 3, and this has been attributed to an embrittlement effect. The strength and toughness of Nicalon SiC/LAS composites are controlled by the production at the interface of a continuous carbon rich layer, due to the excess of carbon in these SiC fibres (Cooper and Chyung 1987). The combination of a matrix microcrack and an oxidising atmosphere appear to embrittle the fibres at these intermediate temperatures, although there is some regain of strength at higher temperatures. Details of the mechanisms are not understood, nor the reason for the regain of strength as temperature increases, but this may be due to suppression of matrix microcracking as temperature increases due to increased plasticity of the matrix.

5.2 Ceramic matrix composites. Fig. 4 shows the variation of short-term strength of SiC/SiC and C/SiC composites with temperature (Heraud 1988). Strength increases with increasing temperature, perhaps due to reduction of thermal stresses, and is again retained to the maximum capability of the fibres. Unlike the glass-ceramic matrix composites, in this case the decrease in strength at intermediate temperature does not occur, presumably due to the differences between the fibre-matrix interfaces of these different materials.

Fig. 5 shows data on a SiC whisker toughened Al_2O_3 system (Tiegs and Becher 1985), indicating that the whiskers have had only a relatively small effect on the maximum temperature limit.

5.3 Carbon-carbon composites. In inert atmospheres strength can be maintained at very high temperatures by C-C composites with short-term retention of strength to > 2500°C (Fitzer 1987) and good resistance to creep (Strife and Sheehan 1988). In oxidising atmospheres significant loss of strength begins at around 500°C, the exact temperature depending on the details of fabrication and degree of graphitisation (Goto et al. 1986). At temperatures < 1200°C oxidation is controlled by chemical rate effects and some catalytic effects; at higher temperatures it is controlled by diffusion of reactive species.

Considerable research is being carried out into oxidation protection (Buckley 1988, Strife and Sheehan 1988). In practice the major problems are not just high temperatures but also thermal cycling which induces cracking and spalling of protective barriers. Strife and Sheehan (1988) have recently summarised the data currently available to the public on oxidation protection. Some features of a protective system are illustrated in Fig. 6. The matrix may contain oxidation inhibitors such as boron, silicon, zirconium and hafnium in the form of non-oxide ceramics. An outer coating is required which will provide a barrier to inward diffusion of oxygen and outward carbon diffusion. The barrier must also possess low volatility to

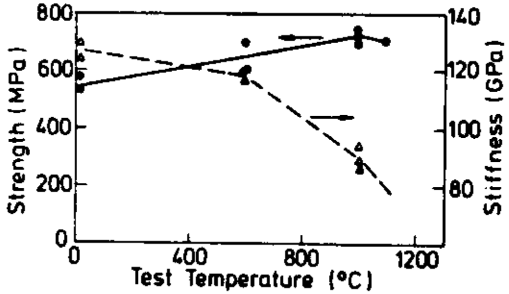

Fig. 2. Flexural strength and stiffness of 0°SiC/LAS (LAS-I) in air as a function of temperature (Prewo 1986).

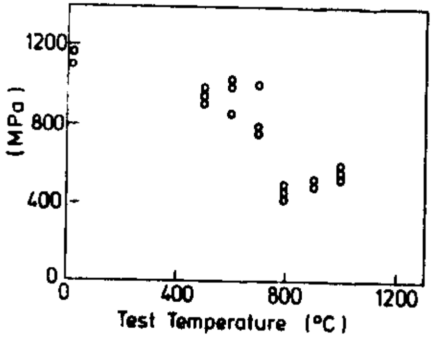

Fig. 3. Flexural strength of 0°SiC/LAS (LAS-II) in air as a function of temperature (Prewo 1986).

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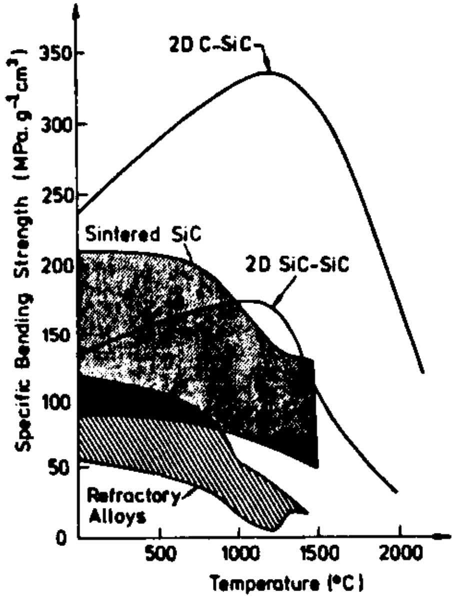

Fig. 4
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Fig. 4 Specific flexural strength of SiC-SiC and C-SiC as a function of temperature (Heraud 1988).

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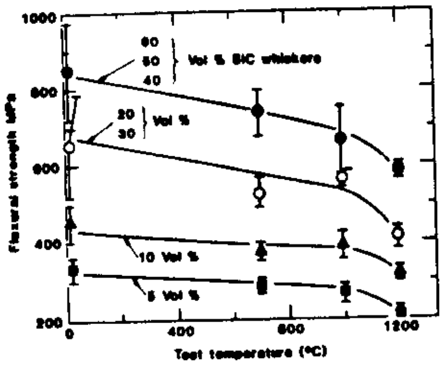
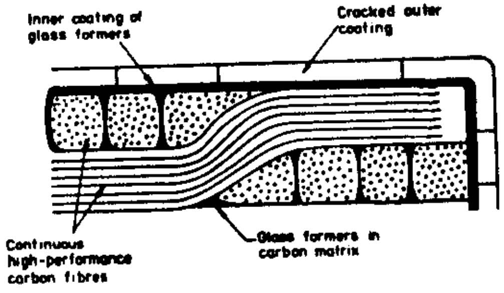


ig. 5. Flexural strength of SiC whisker toughened alumina as functions of mperature and whisker content (Tiegs and Becher 1987).



ig. 6. Schematic representation of a carbon-carbon oxidation-protection ystem (Strife and Sheehan 1988).

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prevent excessive erosion in high velocity gas streams, with good adherence to the substrate. Because of the tendency for the barrier to crack because of thermal mismatch and temperature cycling an inner, glass-forming system is required with appropriate viscosity-temperature characteristics to seal microcracks in the outer barrier. At temperatures up to 1800°C silicon based materials are most suitable as barriers because the kinetics of oxide growth are substantially lower than for aluminium, hafnium and zirconium based ceramics. A practical system currently in use for applications such as the space shuttle uses silicon carbide as the primary oxidation barrier for carbon-carbon leading edges and nose caps. This barrier develops microcracks because of thermal mismatch between the SiC and the C-C. The cracks are impregnated with tetraethylorthosilicates (TEOS) by a process which leaves the cracks sealed with SiO_2. Other low temperature glass- formers are also being developed to enhance the sealing capability of the TEOS system (Buckley 1988). Systems such as this have shown oxidation resistance for hundreds of hours of cycling between room temperature and 1370°C, and for up to 20 hours under stress in high flow-rate burner rig tests at 1540°C (Strife and Sheehan 1988).

For protection above 1800°C very different coating systems are required and development has not yet been pursued successfully to a state where practical systems exist. Oxides such as ZrO_2, HfO_2, Y_2O_3 and ThO_2 have adequate thermal stability for long-term use but have high oxygen permeabilities. Silica has a low oxygen diffusivity and is the best oxide candidate as an oxygen barrier but phase changes on cooling cause a volume contraction and resulting disruption. Iridium has been shown to give excellent protection at 2000°C-2100°C for short times but suffers from excessive erosion due to volatile oxide formation, lack of adherence, relatively high coefficient of thermal expansion, high cost and limited availability.

Strife and Sheehan (1988) suggest a multilayer coating system for > 1800°C consisting of: a refractory oxide as outer layer for erosion protection; a SiO_2 glass inner layer as oxygen barrier and sealant for cracks in the outer layer; a second layer of refractory oxide; followed by an inner layer of refractory carbide to interface with the C-C substrate and provide a carbon diffusion barrier, i.e. refractory oxide/ SiO_2 glass/refractory oxide/refractory carbide.

6. FATIGUE

For fatigue similar considerations apply as for conventional polymer composites but with the additional effects of matrix microcracking and/or environmental attack. Matrix microcracking in particular has been perceived as a potential problem since the early development of glass and glass ceramic matrix systems.

Phillips et al. (1972), Phillips (1982) and Linger (1974) investigated the effects of cycling into the matrix microcrack region on carbon fibre reinforced glasses and found no significant changes in strength after 3 x 10^7 cycles, although there did appear to be an increasing tendency to a reduction in toughness at high cycles, and an increase in the density and penetration of matrix cracking.

Prewo (1987) has made a more extensive study recently of unidirectional and 0°/90° composites of SiC/LAS. His tests at room temperature to 10^5 cycles yielded similar conclusions to Phillips and Linger: fatigue into the microcracked region did not result in a reduction in either fatigue strength or residual strength. At higher temperatures however significant changes did occur and reflected the effects described earlier for static strength. At 600°C and 900°C fatigue or stress-rupture testing above the matrix microcracking stress caused composite fracture with a noticeably embrittled fracture mode. At 600°C effects were particularly severe. Although initial static strengths were high, fatigue or stress rupture tests above the matrix microcracking stress resulted in fatigue strengths, stress rupture strengths and residual strengths equal to the matrix microcracking stress: severe composite degradation took place in air when matrix microcracking occurred. At 900°C the static strengths were much lower, fatigue strengths and stress rupture strengths were similar to the matrix microcracking strength: residual strengths however were much higher. It appears that at 900°C the mechanism of degradation operating at 600°C was effectively stopped, but the mechanisms responsible for this behaviour are not yet understood.

7. IMPACT AND TOUGHNESS

Temperature can have a marked effect on the toughness of some CMC, particularly those based on glass and glass-ceramic systems. These effects arise from differences in thermal mismatch and increasing plasticity of the matrix.

Where the fibre has a different coefficient of thermal expansion than the matrix, the radial mismatch can affect the fibre-matrix bond strength. If the fibre has a higher CTE than the matrix, on cooling from the fabrication temperature the fibre contracts away from the matrix in the radial direction. This can result in a decrease in the strength with which the matrix grips the fibre or even, in principle, the opening up of a gap between fibre and matrix, and thus a reduction in fibre-matrix bond strength. This can cause an increase in toughness through increases in pull-out length and debonding length and a reduction in shear strength. At low temperatures thermal expansion mismatch is at its greatest and can lead to relatively tough material (Phillips 1974). As temperature increases the mismatch decreases and can lead to an increase in bonding and thus increasing tendency to embrittlement (Luh and Evans 1985).

For systems where fibre and matrix are the same this effect does not occur and Fig. 7 containing data showing the variation of K_{IC} with temperature (Heraud 1988), indicates that the toughness of SiC-SiC is unaffected by temperature.

Recent studies of the impact behaviour of model, laminated, glass and glass-ceramic systems, indicated an unexpected effect of delamination (Phillips et al. 1988a). In those experiments $(0,90)_{2s}$ laminates of carbon fibre reinforced borosilicate glass were subjected to impact. At room temperature the specimens fractured in a fibrous manner with no significant delamination. At higher temperatures there was a tendency for the specimens to delaminate on impact. It is unclear why this should occur as the thermal mismatch stresses which might promote delamination should decrease as temperature rises.

One of the principal objectives in the development of ceramic matrix fibre composites has been the search for tough, high temperature materials. Consequently the toughness, damage tolerance and impact resistance of these materials are of particular importance. One aspect of impact, of great practical engineering significance, but which has been largely neglected, is the behaviour of a material when impacted while under stress. Fig. 8 shows the results of such impact tests carried out on two different ceramic matrix fibre composites. The data are here displayed as an impact map, in which impact energy is plotted against applied stress, the solid lines showing the locus of data points for total fracture. It can be seen that impact behaviour is sensitively affected by applied stress. In addition, there is a transition in behaviour as applied stress is increased. At low applied stresses the borosilicate glass composite is superior to the LAS composite, but as stress is increased the LAS system becomes superior. This behaviour was reflected in the morphology of fracture (Phillips et al. 1988b).

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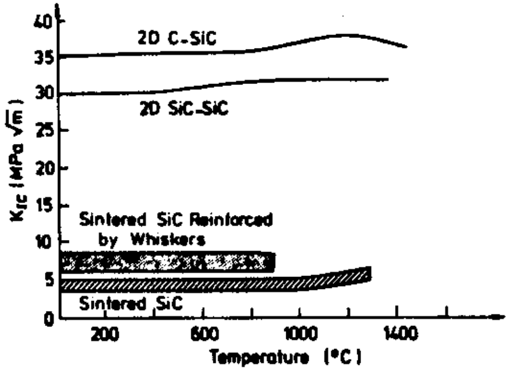


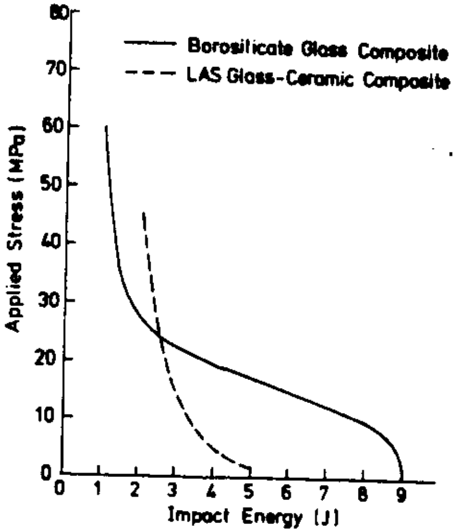
Fig. 7. Fracture toughness (K_{IC}) of SiC-SiC and C-SiC as a function of temperature (Heraud 1988).

8. THE FUTURE

The explosion in research into the development and characterisation of CMC which occurred in the early 80's is now yielding data which are delineating the potential achievements of CMC and potential problems.

The main limitation in the maximum temperature capability of ceramic fibre systems is set at around 1400°C, the temperature limits of the fibres. Carbon fibres offer much higher temperature capability if the oxidation problem can be solved.

It is interesting to speculate on the features of a truly high temperature fibre. Fig. 9 illustrates some possible features. Such a fibre would be expensive but not impossible since CVD techniques are now regularly used to tailor the surface of fibres. For example AVCO market a number of different types of SiC fibres, listed as SCS-2, SCS-6 and SCS-8, which have different ratios of Si:C at their surfaces to suit different potential matrices (Naslain and Langlais 1986).



8. An impact fracture map for two glass/glass-ceramic matrix fibre
osites. The lines indicate the boundary between a total failure
ition and a condition of some residual strength (Phillips et al.
a,b).

interface, and interfacial reactions, of high temperature systems are
important even than for polymer matrix systems and are poorly
rstood. The interaction of matrix microcracking with the interface and
ingress of the gaseous environment is clearly an important topic of
arch.

e search for a true high temperature system, capable of operating at
00°C, it would be naive to seek an open-ended goal, such as "long time at
rature". It is necessary to focus upon a specific set of operating
eters: mean temperature/time; maximum temperature/time; thermal cycling
amme; stress state; and environment, and to develop a system which can
this specific need. The shape of the component might be a critical
r and the time at maximum temperature could define whether a thermal
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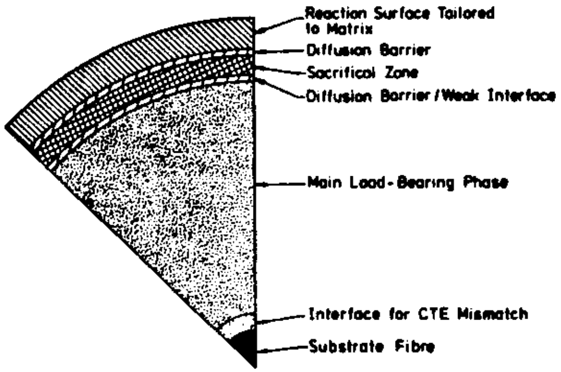

Fig. 9. A conceptual multiphase fibre.

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Mechanical Characterization
Non-destructive Testing
Polymer Matrices

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Volume 2

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HIGH TEMPERATURE FIBRE COMPOSITES

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ABSTRACT

The present state of development, and some of the research requirements, of fibre composites for use under stress in the temperature range 150°C to 2000°C are reviewed briefly. Materials considered include composites with high temperature polymer, metal, glass, glass-ceramic, ceramic and carbon matrices.

INTRODUCTION

The term High Temperature Fibre Composite (HTFC) means different things to different people. To the polymer scientist it might mean a composite which will operate beyond conventional epoxide resin systems, perhaps 150°C and upwards. To the ceramicist it might mean a composite which will survive for a long time under stress at around 1200°C or higher. To people developing metal, glass or glass-ceramic matrix composites it can mean some temperature capability between these extremes. Development of composites with each of these matrices started in the 1960's or earlier, but despite this the present combination of market pull, from new and more demanding applications seeking new or improved materials, and materials push, from new and improved materials seeking advanced applications, make HTFC one of the most rapidly developing, widely researched, technological areas today. They offer the prospects of substantial improvements over conventional, homogeneous materials for some existing applications, and new limits to materials use in terms of high specific strength combined with temperature capability, thus enabling radically new engineering development. The present, main problem for most systems is the development of fabrication techniques - for the more mature systems the development of rapid, low-cost, production processes, while for the newer, innovatory materials, still at the laboratory scale, there are formidable basic fabrication problems before the materials can achieve properties which will make them acceptable for critical engineering applications. In all cases there is a dearth of essential data for performance prediction and design.

This paper reviews the present state of development of fibre composites for load-bearing applications at temperatures above 150°C with the emphasis on the higher temperatures. The reasons for, and the problems inherent in, developing HTFC to a stage where they can be used for highly stressed engineering applications, differ between the different classes of material. Consequently the following sections consider separately polymer, metal, glass and glass-ceramic, and ceramic including carbon matrices, and finally the prospects for ultra high temperature (> 1400°C) composites. A unifying theme is provided by the similarity of the dependence of their mechanical and physical properties on the properties of the constituent fibres and matrices through the basic principles developed for conventional, room temperature, fibre composites. This gives a sound basis for initial predictions of properties. Systems based on short fibres, woven fabrics and continuous, unidirectional fibres are being developed for all the different matrices and in reviewing the subject it is worth remembering that there are two main, rather different, reasons for developing composites. In general, short fibre systems are developed for applications for which the matrix material is broadly suitable but has some shortcomings which the incorporation of fibres can improve, for example by increasing the stiffness or creep resistance of metals or increasing the toughness of ceramics. Continuous fibre systems are developed for applications where the high stiffness and strength of high performance fibres are required and the matrix has the secondary role of providing a load transfer medium suitable for the temperature of the application. Woven reinforcement systems fall somewhere between these two extremes.

The generic types of high performance fibres and whiskers which are currently available are, in ascending order of temperature capability in oxidising atmospheres, aramid, glass, carbon, boron and ceramics such as

SiC, Si_3N_4 and Al_2O_3. The maximum temperatures of use depend on the stress on the fibre and on the way that the fibre strength degradation mechanism is affected by the presence of a matrix during fabrication and in service. Aramid fibres are unlikely candidates for applications requiring prolonged exposure above 150°C. The highest temperature polymer matrices are capable of withstanding prolonged continuous exposure up to ~ 300°C. At the higher temperatures in this range the accelerated attack of environmental water vapour on glass fibres, which on Arrhenius arguments is likely to double in severity with every 10°K-20°K rise in temperature, renders glass fibres suspect. Carbon fibres are thus the most economical, safe reinforcement for high temperature polymers, and the main limitation on these composites is the polymer matrix. Glass matrices and the lower temperature metal matrices, aluminium and magnesium, with typical maximum temperature capabilities of ~ 500°C can be reinforced with carbon fibres to give useful properties to around 400°C-450°C, and with the higher temperature fibres for applications up to the limitation of the matrix. Glass-ceramics are readily available with a temperature capability to around 1000°C and thus approach the temperature limitation even of some ceramic fibres. Ceramic matrices, which are here taken to include carbon, are capable of operating well beyond the maximum temperature of currently available ceramic fibres, which either thermally degrade, oxidise or creep excessively under load, in the temperature range 1000°C-1200°C. Thus, currently, the limitation on the maximum temperature for use in oxidising environments is the limited temperature capability of existing fibres. In non-oxidising atmospheres carbon fibre reinforced carbon and perhaps ceramic matrices potentially give useful properties well in excess of 1200°C, perhaps to 2000°C.

Although this paper is entitled High Temperature Fibre Composites, the different composite systems have properties other than high temperature capability which can make one more appropriate for a lower temperature application than another material. For example: glass and metal matrix composites do not absorb moisture in air and thus desorb less volatiles under vacuum, making them more suitable than polymer matrix composites for some space applications; metal matrix composites are reported to have better tolerance to impact damage and better transverse strength than epoxide matrix composites. Thus it is not necessarily for its high temperature performance that a composite may be selected for a particular application. In the succeeding sections the advantages of the different composites, other than just temperature capability, will be listed and the term High Temperature Fibre Composite is more accurately taken to mean not just high temperature capability but also high temperature fabrication route.

HIGH TEMPERATURE POLYMERS

The main, potential, advantages to be obtained from developing composites based on high temperature polymer systems are:

- The very high specific strengths and stiffnesses which the low densities of polymers (∿ 1 gm.cc^{-1}) can yield.
- Easier, lower temperature fabrication than metal and glass matrix systems.
- Lower cost, more easily replaceable, tooling for their fabrication than metal components.

The main interest is in continuous fibre systems, either of laminated unidirectional plies or made from woven fabrics. The highest, prolonged, operational temperatures are presently achievable with polyimide resins at ∿ 300°C or somewhat higher. Glass fibre systems can have useful long-term properties up to around 200°C but at higher temperatures carbon and the lower cost ceramic fibres are more suitable.

The main interest in high temperature (> 150°C) systems is concentrated in aerospace where high specific properties coupled with elevated temperature capability can command a high financial premium (typically ∿ £100/lb in aircraft engines for example) by enabling weight saving. This is well illustrated by the recent publicising of the development of an air duct for a jet engine, designed to carry by-pass air at 205°C, manufactured out of ceramic and carbon fibre reinforced bismaleimide resin [1]. Compared with metal, the composite component is claimed to have lower tooling and production costs, lower weight and better fatigue resistance. There is also interest in the automotive industry for engine and other under-bonnet applications although generally the temperatures are not as severe nor the economic driving force as strong (typically < £3/lb). Despite this there are developments in valve trains, con-rods, heater fans and other components.

There are several systems with potentially good high temperature properties. Polymers of interest include, among the thermosetting resins: high temperature epoxide resins, such as those based on tetrafunctional epoxides, phenolics, bismaleimides (BMI), polystyryl pyridine (PSP) and polyimides; while thermoplastics include materials such as polyethersulphone (PES), polyetheretherketone (PEEK) and related systems [2,3].

Polyimides were the first high temperature systems to achieve any significant use and their development dates back to the 1960's. Delmonte provides a good review of developments to 1980 [4]. A variety of polyimide systems has been developed. Some of these give the highest temperature capability of available polymers but require carefully controlled, prolonged curing schedules lasting up to 24 hours, and are relatively brittle. Epoxides, phenolics and bismaleimides offer easier fabrication but at the expense of a lower temperature capability. Very approximate maximum temperatures of use are [2]: polyimides 300°C, bismaleimides 250°C, phenolics 250°C and epoxides 180°C, but these temperatures are very dependent on the stressing of the component and the time under stress. A significant problem is that as the temperature capability of thermosetting resin systems is increased, there is a tendency for increased brittleness. The main goals of high temperature thermosetting resin development are the versatility and ease of processability, of conventional epoxide resins, with similar or better strain capability and toughness.

High temperature thermoplastic systems are attractive because they can have much greater toughness and strain capability than thermosets with adequate temperature capability. Other advantages over thermosets include easier, more rapid final fabrication of the component from the pre-preg and the potential to produce complex structures by filament winding or tape laying processes, with fibres lying along non-geodesic paths and along re-entrant surfaces.

ICI have recently publicised [3,5] their development of PEEK-related systems. Figure 1 shows the temperature dependence of some APC (Aromatic Polymer Composites) systems. In particular APC (HTA) has a glass transition temperature (Tg) of 260°C. Leach, Cogswell and Nield [5] have pointed out that the maximum temperature capability of true thermoplastic systems is limited by viscosity-temperature relationships. Too high a

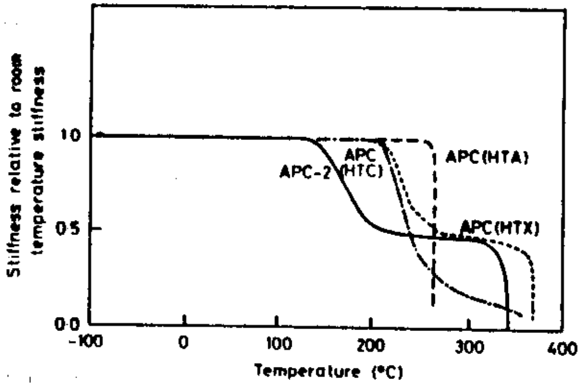


Figure 1. The effect of temperature on the transverse stiffness (relative to the room temperature value) of unidirectional APC carbon fibre composites [5].

viscosity during the impregnation of fibres results in poor wetting, high porosity and a poor composite. Common experience is that the minimum practical processing temperatures for amorphous and partly crystalline thermoplastics are respectively around 150°C and 200°C above Tg, and that the maximum temperature at which most organic linkages become unstable is around 450°C. Consequently, they regard the maximum Tg of a useful thermoplastic system for composites as around 210°C for a crystalline material and 260°C for an amorphous material. Common experience again indicates that the maximum service temperature for a highly stressed composite under conditions where matrix dominated properties, such as transverse tensile or interlaminar shear strengths, are important, is around Tg-30°C [5]. Thus the maximum practical temperature capability of a true thermoplastic system under these conditions is likely to be around 230°C. There is some evidence that the presence of carbon fibres can affect the morphology of crystallisation through strong fibre-matrix interactions [6] and such effects might be exploitable to increase effective service temperatures of thermoplastic systems: another possibility for improving the high temperature properties of these systems after fabrication of the component is to cross-link the polymer, for example by irradiating the component with ionising radiation such as electron beams or gamma radiation, although this would probably add a substantial cost to systems which are already expensive.

A major problem in selecting polymer matrices for particular high temperature applications is the lack of comparative high temperature data. The glass transition and heat distortion temperatures provide a rough guide, particularly for matrix dominated properties, and are easily measured, but there is a need for more high temperature data on, at least, stress relaxation, creep and compression, but eventually also on the other important engineering properties such as fatigue and damage tolerance.

METAL MATRIX COMPOSITES

Research into the reinforcement of metals with ceramics has been underway since the early 60's, the emphasis then being on reinforcement of Ni superalloys, for aeroengine applications, to improve creep rupture [7]. Problems of fibre-matrix compatibility, and the development of alternative engineering solutions to existing problems, diminished interest in metal matrix composites (MMC) until the availability of boron fibres in the late 60's, which stimulated aerospace interest, and the development of lower cost multi-filament silicon carbide and alumina fibres and whiskers in the mid to late 1970's, which excited wider interest in lower-cost industries. Although there remains interest in very expensive materials such as aluminium reinforced with boron fibres, and the large diameter SiC monofilament reinforcement, for advanced military aircraft and space vehicles and structures, there is a considerable drive to introduce lower cost metal matrix composites, based on lower cost fibres, into those and lower cost applications.

The advantages of MMC over competing materials vary, depending upon the application. Compared with unreinforced metals they can have: higher specific strength, higher specific modulus, better high temperature creep resistance. Compared with polymer matrix composites they can have: better transverse strength, toughness and damage tolerance, resistance to environment (particularly radiation), negligible outgassing, high thermal and electrical conductivity, better thermal stability, and higher temperature capability.

Currently interest is focussed primarily on aluminium and magnesium alloys for applications approaching 500°C, and titanium up to around

600°C-700°C. Boron reinforced aluminium has been developed to the greatest level of maturity but is expensive, as is monofilament SiC MMC which is also under development. Lower cost applications are concentrating on SiC and Si_3N_4 whisker reinforcements and SiC multi-filament tow fibres, such as Nicalon and Tyranno fibres, and alumina multi-filament tow materials, such as DuPont FP alumina.

There are potential applications for reinforcement in all the different forms - whisker, fabric and laminated unidirectional plies. Whisker reinforcements offer the potential of castable systems with improved strength and stiffness allowing thinner sections and higher performance. Fabric and short fibre preforms can be infiltrated by pressurised, liquid metal, techniques such as squeeze-casting. Unidirectional tapes of fibre reinforced metal can be consolidated into multi-directional laminates by processes such as diffusion bonding and braze bonding. The liquid metal routes are currently regarded as the only ways of economically manufacturing components for low cost applications, and the diffusion bonding type techniques are primarily of interest for high cost aerospace applications.

The current status of development and existing applications are described in references 8 to 10. The first major use of MMC was in the Space Shuttle in which large numbers of boron-aluminium tubes, some of which were up to almost 3 m long, were used. The most publicised, lower technology application of MMC has been alumina reinforced aluminium employed as part of a Toyota diesel engine piston. Most existing applications of MMC are of boron/aluminium as high cost aircraft components, but the number of lower cost applications is increasing with particular interest from the automotive industry for which MMC may be more attractive than high temperature polymer systems on grounds of cost and ease and rapidity of manufacture. Current and future applications include [7]:

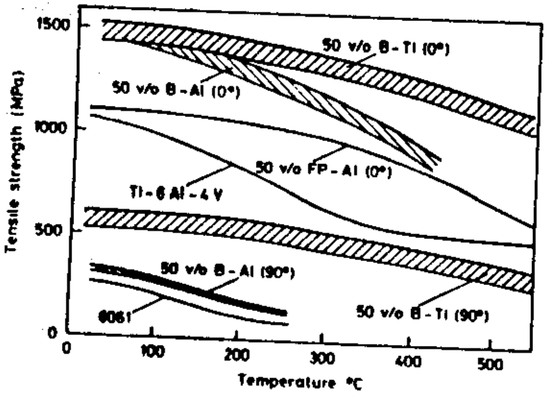
- Satellite and space structures (e.g. deployable antennae, solar panel arrays, laser mirrors, X-ray telescopes).
- Aircraft (e.g. spars, skins, undercarriage components, propellors, compressor blades).
- Missiles (e.g. skins, rocket motors, fins).
- Helicopters (e.g. gear box housings, rotor hubs, skids).

- Inertial guidance platforms (replacement of Be alloys).
- Electronic hardware (e.g. microwave guides, heatsinks, radar antennae).
- Reciprocating engine components (e.g. pistons, conrods, drive shafts).
- Tanks (e.g. armour, tracks, gun barrels).
- Light weight bridging components.
- Deep submersible hulls (e.g. torpedoes, mines, countermeasures).
- Sports equipment (e.g. tennis racquets, skis, bicycle frames, yacht masts).

A good, brief overview of high performance MMC is given by Trumper et al. [7]; Cornie et al. give a more detailed account of processing [11]; and Warren and Andersson discuss the problems of fibre-matrix compatibility with particular reference to SiC fibres [12]. Although a wide variety of fabrication routes has been employed, only liquid metal routes provide composites which can compete economically with conventional materials in applications outside aerospace. Ceramic fibres are very poorly wetted by liquid metals and for conventional casting techniques it is necessary to modify the fibre surface or alloy the metal specifically to improve wetting. Infiltration can be improved by using higher pressure techniques such as squeeze casting. The advantage of this technique is that it does not require the fibres to be coated with graded coatings, an expensive process, and enables hybrid fibre systems to be more easily produced - this can be a considerable advantage and Trumper et al. show an example of a hybrid laminate of layers of boron fibre and low cost alumina fibre in a zinc matrix [7]. Some examples of components produced by the UK MMC Collaborative Programme are shown in Figure 2 [13].

Figure 3 shows some data on the effect of temperature on strength for a number of systems [7]. Compatibility of fibre and matrix, and development of optimum fibre/matrix interface characteristics are key topics for the development of optimum performance. Reaction between fibre and matrix can lead to a brittle interface. Development of cracks, at low strains, at the interface perpendicular to the fibres can produce catastrophic reductions in effective fibre strength, illustrated in Figure 4 [14]. Investigation and optimisation of the interface is an important topic for future research, which will have important

Figure 2. Some examples of MMC sample forms and components produced by the UK Metal Matrix Composites Collaborative Programme [13].



igure 3. The effect of temperature on strength of some fibre reinforced alloys [7].

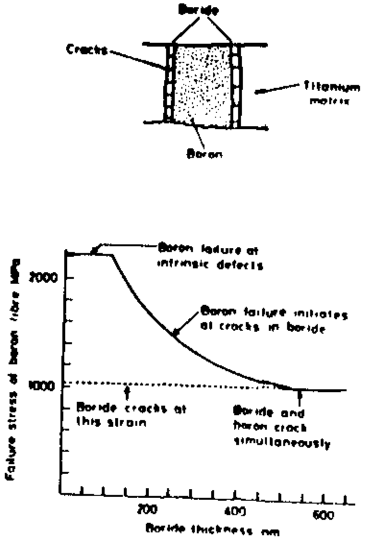


Figure 4. The effect of reaction zone width on the tensile properties of boron fibre reinforced titanium after exposure to elevated temperatures [14,7].

consequences for fabrication. A good basic theoretical understanding of creep and fatigue exists [15] but a better understanding of the effect of prolonged exposure to temperature, with the resulting fibre-matrix reaction, on creep and fatigue processes is needed.

GLASS AND GLASS-CERAMIC MATRICES

Composites consisting of high strength, light weight fibres in glass and glass-ceramic matrices were first developed in the late 1960's [16,17,18]. A detailed review is given by reference 17. Early work concentrated on carbon fibres because of the limited availability and high costs of ceramic fibres although a SiC fibre reinforced glass-ceramic system was also developed, using SiC/tungsten substrate fibres [19]. The mechanical properties of those carbon fibre and SiC fibre reinforced glasses and glass-ceramics were excellent, and compared well with the high performance, carbon fibre/epoxide composites which were under development at the same time. The main disadvantage of the carbon fibre reinforced systems was their lack of resistance to oxidation which prevented their use above about 400°C. The development of ceramic fibres of potentially acceptable costs in the mid to late 1970's, particularly Nicalon SiC, increased interest in these materials particularly, initially, in the USA where Prewo and his co-workers at United Technologies made significant advances [20]. Currently there is much research under way in the USA and the UK, particularly into SiC reinforced glass-ceramics.

Short fibre, woven fibre and laminated unidirectional ply composites have been developed and currently the main interest is in the laminated materials. The advantages of carbon fibre reinforced glasses and glass-ceramics over polymer matrix systems include: improved hydrothermal response and outgassing, lower coefficient of thermal expansion, better radiation resistance and greater hardness. These make them attractive for space applications. They are also capable of operating to higher temperatures than the high temperature polymers and there is a window of opportunity for them between 300°C and perhaps 450°C, although here they have to compete with MMC. Silicon carbide and other ceramic fibre reinforced glass-ceramics offer the potential of operating to at least 900°C and perhaps to 1100°C-1200°C. The main interest in these is for high temperature engine components, where the combination of high specific strength and substantially superior toughness over monolithic ceramics is important.

Although a variety of manufacturing routes have been explored, the most successful is the slurry impregnation route illustrated in Figure 5 [16,21], in which a tow of fibre is drawn through a slurry of glass or glass-ceramic powder in a solution of organic binder and solvent. This results in a handleable tape, consisting of fibres through which are homogeneously distributed powder held in place by the binder. The tape can be stacked in the required sequence, and hot pressed in a process which involves burning off the binder. This requires temperatures and pressures up to around 1200°C and 6 MPa. Selection of fabrication conditions to produce the best properties has required identification of the correct temperatures and pressures such that a fully dense matrix is obtained with little damage to the fibres. In addition, in order to avoid cracking due to thermal mismatch stresses after manufacture, the coefficients of thermal expansion (CTE) of fibres

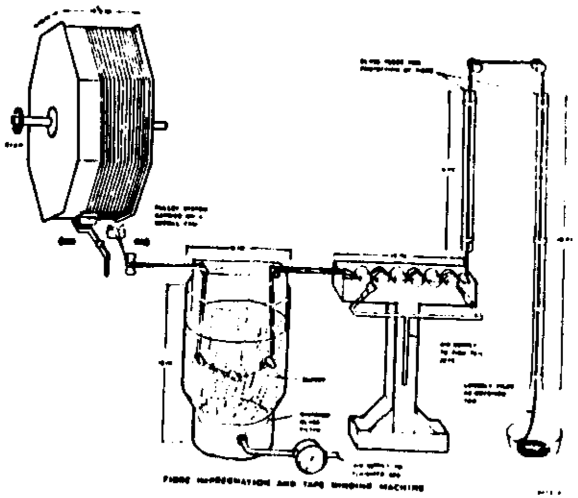


Figure 5. The slurry route for the production of glass matrix composites [16,21].

and matrix must be matched. Accordingly the most successful composites have been produced with low CTE borosilicate glass and glass-ceramics. Details of successful hot pressing routes for carbon fibre systems have been published and materials can now be produced routinely. For SiC fibre/glass-ceramic systems the manufacturing details are less straightforward, particularly where a devitrification stage is required, and development work has been necessary to achieve optimum fibre-matrix bonding [32]. Fine details of the fabrication processes are not generally available.

The bond between fibres and matrix in these systems is particularly important as it can have a very marked effect on the toughness and strength of the composite. This is a topic which is very poorly understood. In carbon fibre composites the bond appears to be predominantly mechanical keying and can be varied by appropriate choice of matrix CTE, as shown in Table 1 [22,23]. In SiC fibre systems some reaction between fibres and matrix is reported and the system is more sensitive to changes in matrix composition, although again changes in bonding can be obtained through control of the CTE [19]. In Al_2O_3 fibre systems very strong bonding between fibres and matrix occurs and results in a brittle composite. Control of the fibre-matrix bond strength is an important area for future research.

Table 1

Effect of bond strength on the shear strength and toughness of carbon fibre reinforced glass and glass-ceramic [23]

	Relaxation Temperature °C	CTE 10^{-6} °C^{-1}	Radial Shrink 10^{-6}m	ilss MPa	WoF k Jm^{-2}
Borosilicate Glass	520	3.5	0.9	59 71	3.1 3.6
Glass-ceramic	1000	2.0	2.4	32 26	4.5 10.3

C fibre CTE $\alpha_r \to \sim 8 \times 10^{-6}$ °C^{-1}
$\alpha_a \to \sim 0$

Figure 6 shows the variation of strength of an early carbon fibre reinforced glass as a function of volume fraction of fibres [24]. Highest strengths tend to be obtained at $V_f \sim 40\%-50\%$ as at higher volume fractions porosity becomes a problem, resulting in lower strengths, Figure 7. Routine achievement of high V_f with low matrix porosity is an important goal for highest specific strengths. Current SiC reinforced borosilicate glasses, containing 47 ^{v}/o of fibres, have flexural strengths of around 1300 MPa, failure strains ~ 1.5%, a work of fracture ~ 50 kJm^{-2}, a candidate fracture toughness of 26 MPa $\sqrt{m}$, and a Weibull modulus of around 20. These properties are retained to 500°C, the temperature at which the matrix softens [25].

An important feature of these composites is that the matrix has a lower strain to failure than the fibres. This can result in the matrix microcracking, as the composite is stressed, at stresses well below the ultimate strength, Figure 8. The stresses at which matrix microcracking occurs are higher than predicted from a simple isostrain model because the presence of fibres suppresses microcracking [24]. An early model of Aveston, Cooper and Kelly (ACK theory) explained the suppression of microcracking by considering the energy balance involved in creating a crack [26]. This model enabled the derivation of a relationship between the strain (or stress) for cracking and material parameters of the form

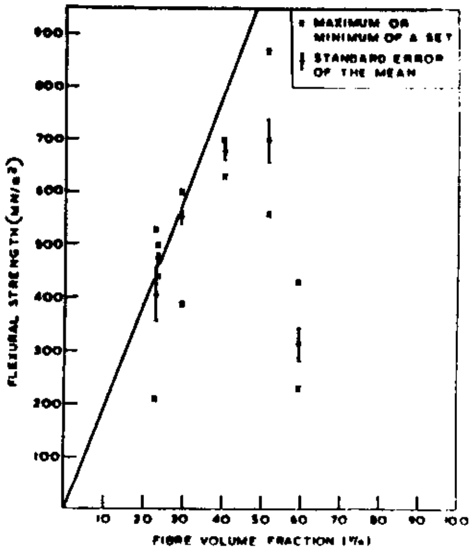


Figure 6. The variation of strength with volume fraction of fibres for a carbon fibre reinforced glass [24].

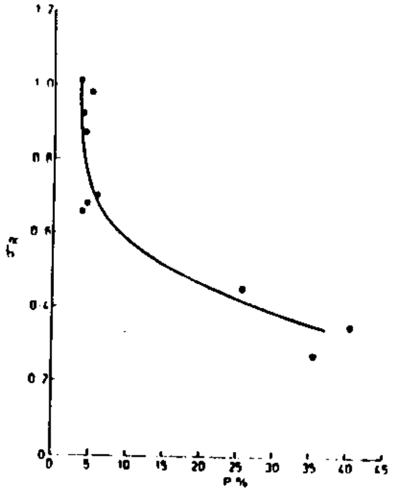


Figure 7. The variation of experimental strength, σ_R, expressed as a fraction of the theoretical strength, with the total porosity, P, for a carbon fibre reinforced glass [21].

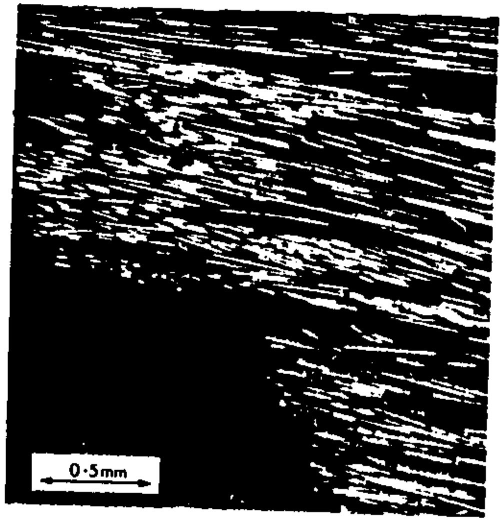


Figure 8. Microcracking developed in a carbon fibre reinforced glass on loading [24].

$$\varepsilon_m = \left(\frac{12\ \gamma_m\ \tau\ E_f\ V_f^2}{E_c\ D_m^2\ V_m\ r}\right)^{1/3}$$

where ε_m is the strain at microcracking; γ_m is fracture energy of matrix; τ is fibre-matrix shear strength; E_c, E_f, E_m are moduli of composite, fibre and matrix; r is fibre radius; and V_f, V_m are volume fraction of fibres and matrices. More recently Marshall, Cox and Evans [27], and McCartney [28] have developed another approach to the problem which provides greater insight into the processes involved in microcrack initiation and growth. Their model predicts a flaw size/failure stress relationship of the form shown in Figure 9. For flaw sizes greater than a critical size, the stress at which matrix microcracking will occur is independent of flaw size and approximates to the ACK value. At lower flaw sizes the stress increases as flaw size decreases. This might have implications for future development. For reasons which are listed below, matrix microcracking could be a limiting factor in the operational use of brittle matrix systems. If flaw size could be reduced below the limiting value defined in the figure, the microcracking stress and strain might be substantially increased. There is interest in protecting these, and other brittle matrix composites, from environmental attack by using coatings. If the coating thickness controls the intrinsic flaw size, thin coatings may be better than thick coatings because they will limit the maximum flaw size.

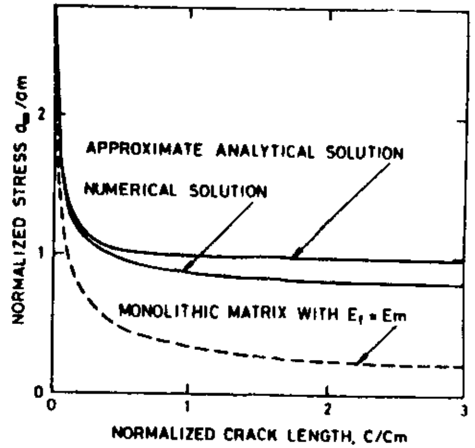


Figure 9. Equilibrium-stress/crack-size functions for a penny shaped matrix crack in a composite and in a monolithic matrix [27].

The extent to which matrix microcracking may limit engineering performance for these composites is not yet understood. Matrix microcracking does not appear to have any significant effect on short-term strength, either static or fatigue [29]. There are concerns, however. During fatigue, matrix microcracking may initiate a network of cracks orthogonal to the original microcracks, by shear, as happens in polymer composites. They might, thus, initiate fatigue failure. They also permit easy paths for environmental attack on the fibres. Finally, there is some indication that they may initiate the premature failure of Nicalon SiC/glass-ceramic composites when held under stress at temperature, by permitting a mechanism of degradation of the fibres which would not otherwise occur, causing significant reductions in the strength of the composite at temperatures as low as 900°C [30,32]. The occurrence, implication and suppression of matrix microcracking is an important area for future research.

One reason for the attraction of these materials is their high toughness compared with monolithic ceramics. Toughness is not a simple, unique property, but is a class of properties all connected by the idea that they are a measure of the amount of work that needs to be done to fracture the material. Compared with monolithic ceramics and glasses the composites have much greater works of fracture, up to several tens kJ m^{-2}, comparable with polymer matrix composites. Linear elastic fracture mechanics is not applicable to these materials and therefore numbers quoted as critical or candidate stress intensity factors are of little value, however the high damage tolerance which these values of work of fracture imply is of value for applications where the components are at risk of damage in service, while under stress [31]. In this context more research is needed into the effects on residual strength of damage under both unstressed and stressed conditions.

The strengths of carbon and ceramic fibre reinforced glasses and glass-ceramics are maintained, or may even increase, with increasing temperature, until temperatures at which either the fibres begin to degrade or the matrix becomes ductile. Carbon fibre reinforced systems are oxidised in air at around 400°C although in a non-oxidising atmosphere they can be used to temperatures at which the matrix softens, typically ~ 500°C for a borosilicate glass or > 900°C for a glass-ceramic. SiC reinforced systems could, in principle, be used to temperatures > 1000°C, above which temperature creep of the fibres becomes a problem [33,34]. However, as already mentioned, there is an indication that the strength of Nicalon SiC fibres in a glass-ceramic matrix can be degraded when under stress at ~ 900°C [30,32]. These fibres are non-stoichiometric and stoichiometric fibres might have better high temperature properties.

CERAMIC MATRIX COMPOSITES

Development of ceramic matrix composites (CMC) started in prehistory with the use of a variety of natural fibres and other additives as tempers [17,35,36]. Significant modern research into the development of ceramic matrix composites started in the late 50's with the work of Tinklepaugh [37] and for a time there was an interest in the reinforcement of ceramics with refractory metal wires. Their high density and disappointing lack of resistance to oxidation at high temperatures

prevented their exploitation. In the late 60's and early 70's systems based on carbon fibres and ceramic whiskers were investigated but the problems of thermal mismatch between carbon fibres and ceramic matrices, the oxidation of carbon fibres and the relatively poor properties of the whisker systems, again prevented their exploitation, although the work demonstrated that very high toughness values could be achieved and this acted as a spur to later development [17]. The development of improved and potentially low cost ceramic fibres and whiskers in the late 1970's, coupled with the search for improved ceramics and high temperature materials, have prompted a massive increase in research into ceramic matrix fibre composites (CMC) in the last few years, and this is probably the most rapidly developing area of research into high temperature composite materials. The main problem in the development of these materials is the high temperatures required for their fabrication, which leads to problems of chemical compatibility between fibres and matrix during processing. Key areas for research include: understanding the high temperature chemistry of potential systems; development of lower temperature fabrication processes; and development of procedures for improving fibre/matrix compatibility, such as the use of fibre coatings.

There are several recent overviews of the subject which provide a useful background to current research [17,18,38,39], although the rate of development is so rapid that they do not contain some of the very recent significant advances, particularly to do with details of the development of whisker toughened materials, and Chemical Vapour Deposited (CVD) and sol-gel impregnated preforms. At present there are several main types of CMC of particular interest including: whisker reinforced ceramics; composites produced by CVD or liquid impregnation of fibre preforms; and hot pressed continuous fibre systems.

The main disadvantage of ceramics is their low toughness which makes them susceptible to damage by thermal and mechanical shock, and also intolerant to flaws introduced during manufacture or in service, which in turn can lead to considerable variability in strength. Increasing the toughness of a ceramic should reduce all of these problems. Consequently there have been two, rather different, broad approaches to the development of CMC. The initial aim was to produce a system which would retain the useful properties of a ceramic, together with substantially improved toughness, to high temperatures: whisker and short fibre reinforced ceramics fall into that category. The subsequent development of ceramic fibres with high strength and stiffness capable of operating to high temperatures prompted the need for compatible high temperature matrices which could produce composites which would enable the fibres to realise their full potential: the continuous fibre systems fall into that category.

Short Fibre and Whisker Reinforcement

It is necessary to differentiate between short fibre and whisker reinforcement. The former typically consist of chopped fibres, e.g. SiC, C, having diameters $\gtrsim$ 8 μm; the latter, e.g. SiC, Si_3N_4, have diameters $\lesssim$ 1 μm. This difference in size has a significant effect on mismatch stresses and toughening mechanisms. Short fibre and whisker reinforced systems are less tolerant to thermal mismatch between fibres and matrix than are continuous, aligned fibre systems, and only a relatively small number of practical systems are possible [40]. Even where thermal cracking does not occur, the strengths of random, short fibre composites are usually lower than those of the unreinforced matrix because of the combination of stress concentrations from the fibres and the residual thermal stresses, although some degree of strengthening can be obtained by aligning the fibres even if this is only partial [17,40]. Substantial increases in toughness, measured as a work of fracture, can be obtained with short fibres, Table 2. Although increases in toughness obtained in this way can be useful, particularly for improving resistance to thermal shock, significant corresponding improvements in strength appear to have been obtained only in one or two systems, consisting of hot pressed whisker reinforced ceramics, Figures 10 and 11 show data for a SiC whisker reinforced Al_2O_3 [41]. A similar material is marketed by the Greenleaf Corporation as a cutting tool and die material, for which its high K_{IC} value compared with unreinforced ceramic is seen as an advantage.

For ambient temperature applications whisker reinforced ceramics have to compete with zirconia toughened ceramics. A major advance in recent years in ceramic science has been the development of zirconia toughened systems. High values of toughness can be obtained at ambient temperatures

Table 2

Typical strength and toughness data for glasses, ceramics and their composites (Z is zirconia)

	Strength MPa	Work of Fracture J m^{-2}	K_{IC} MPa $\sqrt{m}$
Glass	100	2-4	0.5
Alumina	500	40	4
Silicon Carbide	500	40	4
Silicon Nitride	600	100	5
Fully Stabilised Z.	180		2.4
Partially Stabilized Z.	600-800		6-8
Z. Toughened Ceramic	300-800		10
Tetragonal Z. Polyx.	1000-2500		7-12
Whisker Reinforced Si_3N_4	400-800		6-9
Short Fibre Reinforced Glass	50-150	600-800	7
Continuous Fibre Reinforced Ceramic/Glasses	700-1000	10^3-10^4	10-20

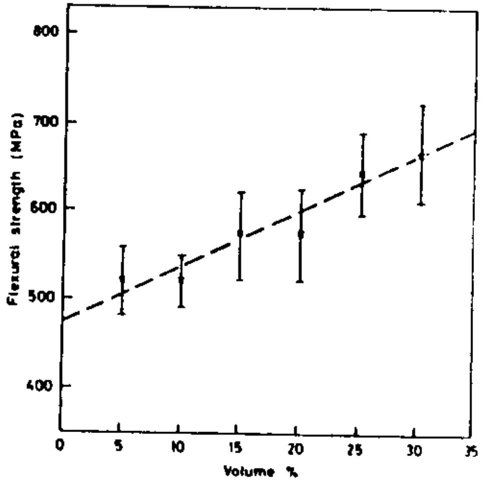


Figure 10. The flexural strength of SiC whisker reinforced alumina [41].

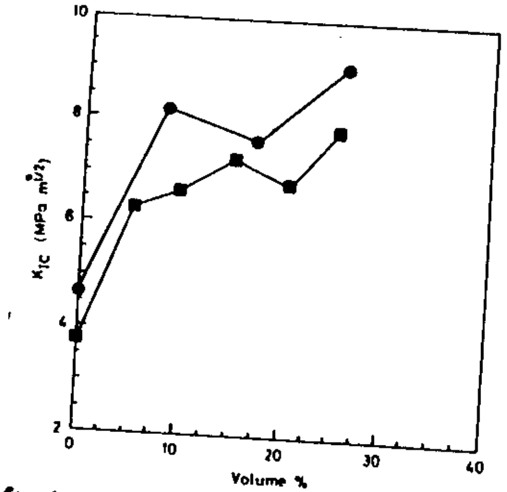


Figure 11. The fracture toughness of SiC whisker reinforced alumina [41].

due to a phase transformation in the high stressed zone near the tip of a crack. However, the driving force for the phase transformation decreases as temperature increases and toughness and strength tend to decrease correspondingly. The toughness of whisker toughened ceramics, expressed as a K_{IC} value, is comparable with that of zirconia toughened ceramics at room temperature. Table 2 shows some comparative values. As temperature is increased the toughness of the whisker reinforced ceramic is unlikely to decrease and the CMC will thus have an advantage over zirconia toughened ceramics at high temperatures. Claussen and Petzow [42] have suggested that whisker and zirconia toughening may be combined and their results indicate that there may be a useful synergistic effect, Table 3.

A good, qualitative understanding exists of toughening mechanisms in whisker toughened ceramics and it is believed that the important mechanisms are those which occur in conventional ceramics, crack pinning and deflection [43]; while in short fibre systems it appears that the dominant mechanisms are similar to those in other composites, fibre pull-out and debonding. This is to be expected as the importance of pull-out, debonding, etc., on theoretical grounds increase as fibre diameter increases.

Table 3

Possible synergistic effects in the use of SiC whiskers to further toughen zirconia toughened alumina (ZTA) [42]

Matrix	Volume % Whisker	K_{IC} MPa $\sqrt{m}$	Strength MPa
Al_2O_3	0	4.7	520
Al_2O_3	20	8.5	650
ZTA	0	6.2	1080
ZTA	20	13.2	700

Gas Phase and Liquid Phase Impregnation

Another important class of CMC is those produced by the infiltration of a fibre preform by gas or liquid to produce a matrix. This can be accomplished by gas phase processing [38], pyrolysis of liquid organometallic precursors [38,44], and possibly by sol-gel processes. A major advantage of these fabrication routes is that they require lower processing temperatures than hot-pressing, and thus reduce problems of chemical compatibility between fibre and matrix during processing. In the gas phase processing route a gaseous precursor is used to deposit the ceramic onto the heated ceramic fibre pre-form substrate, e.g. SiC from CH_3SiCl_3/H_2. This process has been developed to a state of some maturity and is used commercially. It enables complex structures of large size to be produced but is a very slow process requiring days, or even weeks for large components. The liquid organometallic route uses a precursor such as polycarbosilane (to produce SiC) and several impregnation/pyrolysis sequences to achieve maximum impregnation. These techniques yield material with a relatively high matrix porosity, ~ 20-30%, and a consequent relatively low strength, of around a half the flexural strength that would be predicted from the rule of mixtures. Figure 7 showed an empirical relationship between strength and porosity obtained for a hot pressed composite material: the relationship appears to be similar for the CVD materials and may be a general relationship.

Hot-pressed Continuous Fibre Systems

A variety of ceramic matrix composites have been produced by hot-pressing, and the slurry impregnation route described previously for glasses and glass-ceramics can be used for producing pre-preg tape. The advantage of hot-pressing is that a low porosity matrix can be achieved, to provide highest mechanical properties, but at the expense of a high temperature/pressure process which can only produce relatively small components of simple shape. The high temperatures required for hot-pressing also present problems of fibre-matrix chemical reaction.

ULTRA HIGH TEMPERATURE COMPOSITES

Currently the main temperature limitation on ceramic matrix composites is due to the lack of available fibres with good properties above 1000°C-1200°C. Above this temperature range fibre degradation or creep of existing ceramic fibres becomes excessive. At present only carbon fibres provide a higher temperature capability but these require the development of oxidation barriers.

The technology of carbon/carbon composites is well developed and complex structures can be manufactured routinely by infiltration of a fibre preform through gas phase or liquid infiltration/pyrolysis techniques [45,46]. To date their high cost has restricted their use to aerospace and special applications. In inert or reducing atmospheres strength is retained to at least 1600°C, and can be higher at the higher temperatures than at low temperatures, Figure 12 [47]. Their main limitation is their susceptibility to oxidation in air at high temperatures, unprotected composites having poor oxidation resistance at temperatures as low as 500°C [48]. In current applications carbon/carbon composites are subjected to high temperatures in air for only short times, e.g. engine brakes and rocket nozzles. Superalloys for turbine blades are usually protected from oxidation at high temperatures by dense layers of Al_2O_3, SiO_2 or Cr_2O_3 and similar and other processes are being researched for the protection of carbon/carbon. A particularly promising approach appears to be the use of organometallics to deposit ceramic coatings into the surface of the composite in a method akin to the gas and liquid phase techniques described earlier for the production of ceramic matrix composites. For example Naslain and his co-workers [49,50] have deposited SiC and TiC using CH_3SiCl_3/H_2 and $TiCl_4/CH_4/H_2$ to produce composites with much reduced weight change in air at 1500°C-1600°C, although at higher temperatures the resulting oxide layers are not thermodynamically stable in contact with solid carbon and carbides [48].

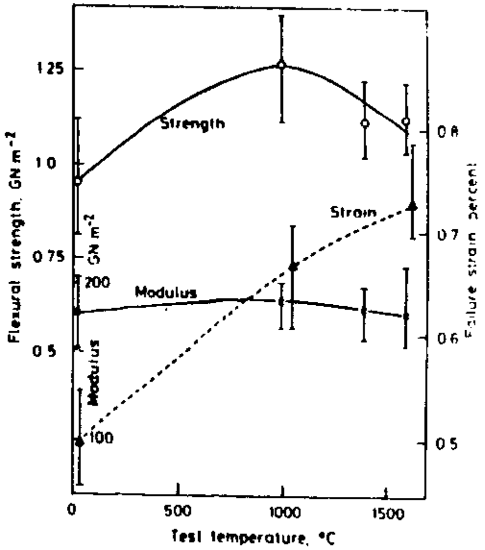


Figure 12. The flexural properties of a carbon-carbon composite as a function of temperature in vacuo [47].

Prospects for ultra high temperature composites, materials which can operate in air for long periods of time at temperatures above 1200°C are determined by the three laws of high temperature chemistry attributed to Searcy [51].

1. Everything reacts with everything at high temperatures.
2. Everything reacts faster at higher temperatures.
3. The products may be anything.

Hillig [51] has assessed the prospects for developing high temperature ceramic composite systems, and Fleischer [52] has considered high temperature single systems. Hillig [51], in an elegant exposition, considered the necessary criteria which must be satisfied for a composite to survive and have useful properties under stress at high temperatures in air. These are, as a minimum: stability with respect to volatilisation; low internal chemical reactivity; retention of stiffness; and a creep rate for the fibre < 10^{-7} sec^{-1}. He further assumed that only an oxide matrix would have sufficient stability against oxidation; a non-oxide fibre would be necessary on grounds of stiffness and bonding; and that the matrix would provide a measure of oxidation protection for the fibre. He also pointed out that a non-oxide matrix might be suitable with an oxide coating to protect it; and that a further barrier between fibres and matrix may be necessary even for an oxide matrix. Although there is a dearth of good quality thermochemical data he was able to compile some, and calculate or infer others, and concluded that there are a number of oxides, carbides, borides and nitrides, as well as carbon, which might function together to temperatures in the range 1700°C to 2100°C. Of the non-oxides only carbon, Si_3N_4 and SiC are currently available as fibres or whiskers. He also considered briefly the creep stability of whiskers grown with single screw dislocations and, from a consideration of the work required to nucleate dislocation loops, concluded that there is little likelihood that spontaneous nucleation of dislocations will occur and therefore that the whiskers will have considerable resistance to creep. A conclusion which can be drawn from his survey, although not explicitly stated, is that SiC whisker reinforced Al_2O_3 is one of the most promising practical systems. It is interesting that such a material already exists.

DISCUSSION

The lack of firm data on the high temperature strength of composites, and particularly on the effects of prolonged exposure to temperature while under stress, is currently a major problem in assessing their limits of performance. However some interesting conclusions can be drawn by calculating the properties that they might have, ideally, on the basis of known performance. Figures 13 and 14 show the specific strengths and stiffnesses (σ/ρ and E/ρ) of a number of typical systems, of C, B, SiC (Nicalon), Al_2O_3 (FP) fibres in polymer, metal and ceramic matrices, calculated on the basis of 60 $^{v}/o$ of unidirectional fibres with reasonable assumptions about the retention of properties to high temperatures. The temperature limitation is based on use, under stress in air. Too much significance should not be given to the absolute values but the trends are a useful indicator to future developments. Several points emerge. It can be seen that achievable specific strengths and stiffnesses decrease markedly as the temperature capability is increased. Although high specific properties are not the only useful criteria, an important goal is to extend the performance of materials beyond the boundary indicated on the figures. Glass and glass-ceramic matrix systems are very competitive with metal matrix systems. The relatively poor properties of the more economical ceramic fibres and the relatively high density of ceramics decrease the specific properties of their composites to relatively low levels, compared with the performance of high performance polymer systems at room temperature.

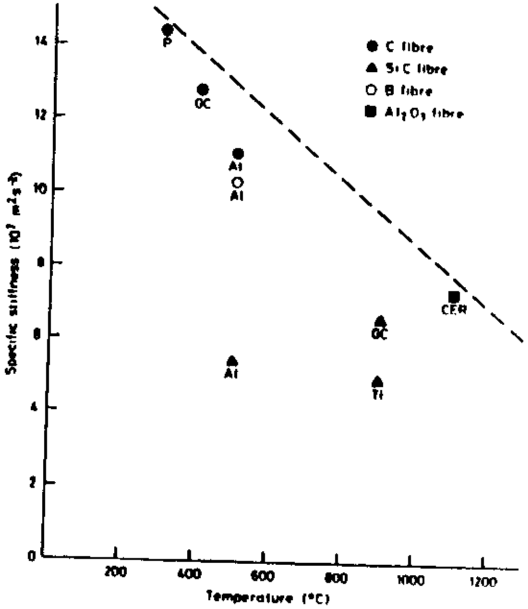


Figure 13. Calculated specific stiffness and approximate maximum temperature limitation of some unidirectional composites. P is Polymer, GC is Glass-ceramic, Al is aluminium, CER is ceramic, Ti is titanium.

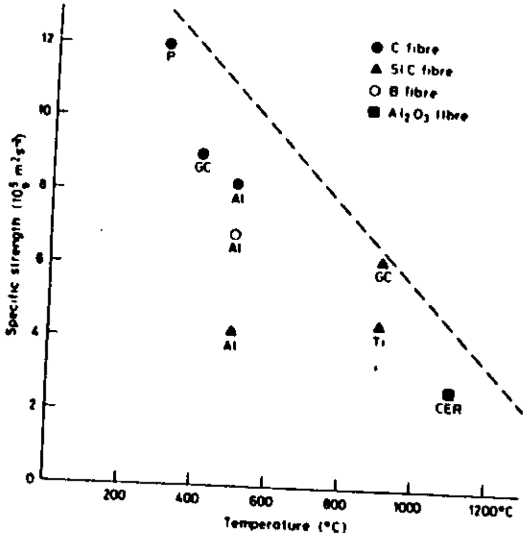


Figure 14. Calculated specific strength and approximate maximum temperature limitation of some unidirectional composites. P is Polymer, GC is Glass-ceramic, Al is aluminium, CER is ceramic, Ti is titanium.

The economic costs of most, if not all, the materials which have been discussed are high and their major potential uses are currently in aerospace and specialised applications. Reduction of cost is an essential goal if the materials are to have wide use outside aerospace. In this context it is worth noting that the fabrication and total costs of glass and glass-ceramic matrix systems may be competitive with the higher temperature polymer systems in the temperature range 250°C-300°C, and have a particularly useful role between 300°C and 500°C, as well as being useful to 900°C.

Consideration of specific strengths and stiffnesses are useful in the early stages of materials development and this has often provided the initial driving force for composite development. However, as the understanding and development of materials proceeds towards maturity, the user's perception of the advantages of a new material often change. The high specific strengths and stiffnesses of composites decrease as multi-directional fibre systems are developed and, as in the case of quasi-isotropic high performance graphite/epoxy composites, are reduced to values close to those of improved conventional materials, such as the Li/Al alloys. However, with a better understanding of the performance of a material, other properties are often then perceived to give it an advantage - as for example, fatigue, damage tolerance and ease of fabrication. In the case of many of the high temperature composites discussed here, we are still at the early stage of understanding their advantages and disadvantages. As research and development proceeds we can expect changes in our perception of their important virtues.

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SILICON CARBIDE FIBRE REINFORCED NITRIDED SILICON NITRIDE COMPOSITES

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ABSTRACT

Silicon carbide (Nicalon)-fibre reinforced silicon nitride composites were fabricated. Test bars were obtained by slip infiltration of fibre bundles with Si and Si_3N_4 powder and subsequently nitrided in nitrogen at 1350°C for three hours. No reaction was seen between fibre and matrix. Bend tests showed a non-brittle fracture with pull-out and fibre debonding resulting in an increased fracture toughness. Fracture surfaces and polished cross-sections were investigated with SEM.

INTRODUCTION

High performance ceramics such as silicon nitride, silicon carbide, zirconia and alumina are materials with high resistance to wear, corrosion and high temperatures. They have found applications in heat engines, as cutting tool tips and in the aerospace industry. Ceramics are, however, brittle materials with low fracture toughness and probabilistic fracture strength determined by an inherent flaw population. In order to increase the fracture toughness and reliability of ceramics, fibre reinforcement has been successfully employed for some fibre/matrix systems. SiC (whisker) /Al_2O_3 [1], SiC (long fibre) / glass-ceramic [2] and SiC (long fibre) / SiC (chemical vapour infiltration) [3] are materials where an increased fracture toughness and reliability has led to a wider use of ceramics. Silicon nitride is perhaps