

Ceramic Matrix Composites

J. Mukerji

Central Glass and Ceramic Research Institute, Jadavpur, Calcutta-700 032

ABSTRACT

The present state of the knowledge of ceramic-matrix composites have been reviewed. The fracture toughness of present structural ceramics are not enough to permit design of high performance machines with ceramic parts. They also fail by catastrophic brittle fracture. It is generally believed that further improvement of fracture toughness is only possible by making composites of ceramics with ceramic fibre, particulate or platelets. Only ceramic-matrix composites capable of working above 1000 °C has been dealt with keeping reinforced plastics and metal-reinforced ceramics outside the purview. The author has discussed the basic mechanisms of toughening and fabrication of composites and the difficulties involved. Properties of available fibres and whiskers have been given. The best results obtained so far have been indicated. The limitations of improvement in properties of ceramic-matrix composites have been discussed.

INTRODUCTION

Ceramics have high melting points and are resistant to oxidation and corrosion. In this respect they are superior to metals. However, they are extremely brittle and prone to thermal shock failure. As a result, they cannot be easily used in structural applications at high temperatures. To overcome these inherent unfavourable properties of ceramics, attempts were made to combine ceramics and metals by making *cermets*. This met with little success.

Silicon nitride was developed in the 1960s. It had outstanding thermal shock resistance and better toughness than conventional ceramics. This was followed by the solid-state densification of *SiC*, a material of excellent thermal shock resistance and capable of retaining its strength at high temperatures. Simultaneously with *SiC* transformation toughened *ZrO₂* of a toughness of around 10 to 15 MPa m^{1/2} came into being. These discoveries kindled interest in the use of ceramics in high performance applications not only to

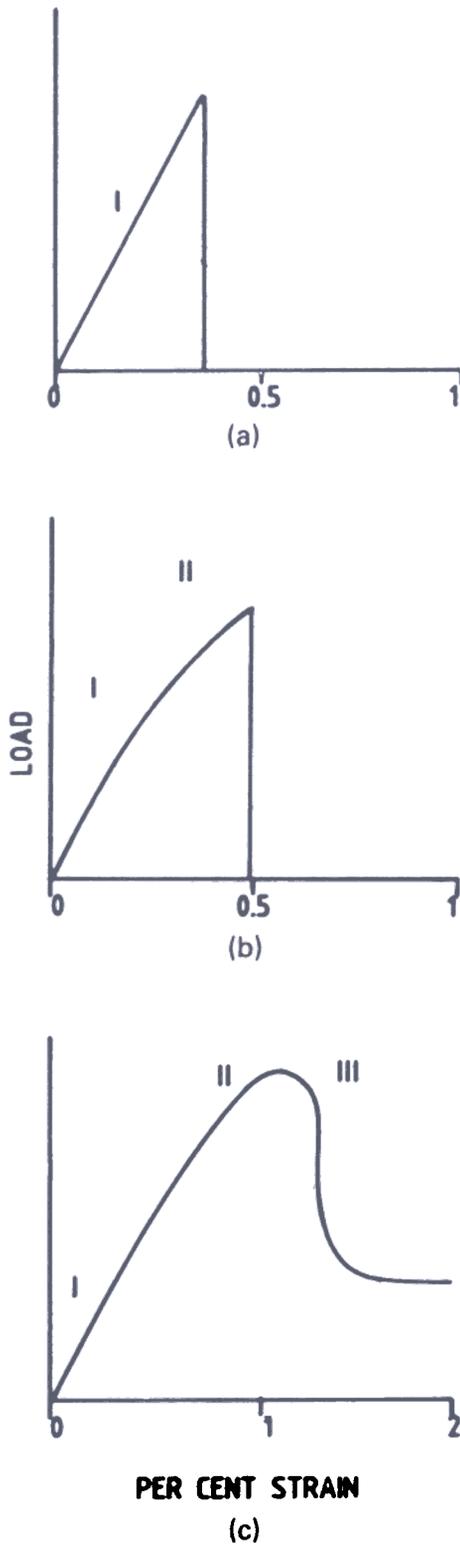
replace costly superalloys but also for use in those areas where even the superalloys did not perform.

Although the toughness of *Si₃N₄* (≈ 5 MPa m^{1/2}) is high compared to other ceramics (≈ 1.5 to 3.5 MPa m^{1/2}), it is still too low for many structural applications. Similarly, the application of *SiC* is toughness-limited (3.4 MPa m^{1/2}). Transformation toughened *ZrO₂* cannot really be called a high temperature material because of poor thermomechanical properties and degradation due to annealing and also low temperature (250 °C) in contact with moisture.

The general opinion is that further improvements in the toughness of these ceramics is possible by making composites with particulates or fibres and should be the future direction of research. This paper discusses the mechanism of toughening composites, their limitations, and problems associated with their fabrication. We shall also concentrate on composites for application at high temperatures and shall not discuss such materials as fibre reinforced plastics (FRPs) or glass.

2. BASIC FRACTURE MECHANICS FOR TOUGHENING

Figure 1 shows the stress-strain behaviour for a brittle material. The slope of the curve in Fig. 1(a)



determines the elastic modulus whereas, the fracture strength (σ) is determined by the fracture toughness (K_{Ic}) and largest flaw in the sample by the Eqn

$$\sigma = YK_{Ic}/c^{1/2} \tag{1}$$

where, Y is a dimensionless factor describing the sample and the stress distribution, and c is the critical crack length.

In a composite (Fig. 1(b)), a slow crack growth occurs (part II) before failure; the nature of crack changes as it grows leading to a reduction in stress intensity at the crack tip. It may be due to crack deflection, fibre pull-out, etc. The third type of behaviour is non-brittle in character in that there is no catastrophic failure (Fig. 1(c)) and is the characteristic of a long fibre composite with a weak fibre-matrix bond. The curve has three regions; the stress proportional to strain (part I), followed by matrix cracking but component sustained by fibre (part II) and ultimately fibre pull-out takes place (part III). Catastrophic failure is prevented in such a composite but the matrix is irreversibly damaged.

2.1. Methods Available for Toughening

Table 1 shows the main mechanisms of toughening for ceramic-matrix composites¹.

Table 1. The main mechanisms of toughening for ceramic matrix composites

Mechanism	Basic requirement	Applicable to
Load transfer from matrix to fibre	$E_f > E_m, E_f/E_m$ at least >2	Fibre-matrix composites
Fibre pull-out	Good fibre-matrix bonding, optimum interfacial shear strength, long pull out length.	Fibre matrix composites
Crack impeding second phase	$(K_{Ic})_{f,p} > (K_{Ic})_m$	Fibres/particulates
Crack deflection	Weak matrix second phase bonding	Fibres/particulates
Prestressing	$\alpha_{f,p} > \alpha_m$, compression on matrix	Fibres/particulates
Microcracking	Thermal expansion mismatch; micro-cracking	particulate composite

Figure 1. Stress-strain curve for brittle fracture and for composites.

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Table 2. Typical properties of ceramics and fibres

Materials	E (Gpa)	Tensile strength (MPa)	Thermal expansion ($^{\circ}\text{C} \times 10^{-6}$) (20-1000 $^{\circ}\text{C}$)	Density
Matrix Ceramics				
Si_3N_4	307	410	2.3	3.2
SiC	400	310	4.8	3.2
Al_2O_3	380	250	8.5	3.9
$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	143	83	5.3	
ZrO_2	17-25	130	7.6	5.6
Borosilicate glass	60	100 (MOR)	3.5	2.3
Fibres				
Carbon	350	1380-2070	0 ^(a) 8 ^(b)	1.9
Boron	440	2800-3400	8.2	2.3
SiC	480	2100	4.8	3.35
Nicalon ^(c)	185	2700		2.55
HPZ ^(d)	150	2200		2.35
Al_2O_3 ($>99\% a$)	380	1400		3.9
$84\text{Al}_2\text{O}_3$ 15SiO_2	224	2300		3.05

a : axial; b : radial; c : $\text{SiC}=65\%$, $\text{C}=15\%$, $\text{SiO}_2=20\%$; d : $\text{Si}=59\%$, $\text{C}=10\%$, $\text{N}=28\%$, $\text{O}=3\%$.

The first method is well developed and is being used for a long time in the fabrication of FRPs and is a common method for metal-matrix composites (MMCs). The requirement is that the fibre should be of higher Young's modulus (E) than the matrix. The composite becomes stronger only when the volume fraction of the fibre exceeds a critical value (V_c) which is approximately equal to the ratio of the tensile strength of the matrix (δ_m) and fibre (δ_f). The improvement of strength of the composite is thus achieved by a V_f higher than the V_c and a high E_f/E_m ratio. This is the case of continuous fibre.

In the case of short fibre the stress is zero at the end and rises along its length giving rise to a shear stress acting on the fibre/matrix interface. This stress increases linearly from the end until it reaches the mean composite strain. The transfer length of the fibre is the length over which the load transfer takes place. The stress on the fibre increases until the transfer length meets at the middle or the fibre fractures. For the fracture to occur the critical aspect ratio is $l_c/d = \delta_f/2\tau$, τ is the shear stress at the interface, d is the diameter of the fibre, l_c is the length, and δ_f is the theoretical fibre strength.

Significant effect can be achieved with high E fibres in low E matrix such as SiC fibre in glass matrix where E_f/E_m is around 5-6. A strength improvement of 3 to 6 times with corresponding improvement in the fracture toughness has been reported. Unfortunately, in the case of advanced ceramics, the E approaches that of the fibre specially at elevated temperatures. Table 2 gives the E of some typical ceramics and common fibres. It may be seen that the E_f/E_m ratio is far from advantageous and the possibility of exploiting the load transfer mechanism is limited.

2.2 Fibre Pull-out

The primary energy absorbing mechanism is the work required to pull the fibres from the matrix. The greater the pull-out length the greater the apparent toughness of the composite. The fracture toughness of the composite (K_c) is related to the fracture toughness of the matrix (K_m), shear stress required to separate the fibre from the matrix (τ), the fibre diameter (D), the volume fraction of the fibre (V_f), the fibre aspect ratio (l_f) and the Young's modulus (E) by the Eqn²

$$K_c = [K_m^2 + (\tau/2)V_fDE(l_f)^2]^{1/2} \quad (2)$$

This relation suggests that large fibres with a high τ are

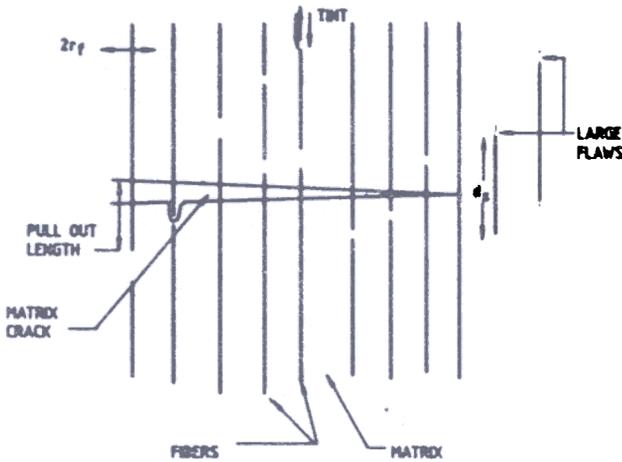


Figure 2. Fibre pull-out during rupture³.

prerequisites for good K_{Ic} with a fibre of a given property. It may be noted that if the τ is too high, fibre failure may occur. Figure 2 shows the fibre pull-out mechanism³. As the crack in the matrix advances the fibres oriented normal to the plane of crack are strained; the maximum stress occurs across the crack aperture with decreasing fibre stress and increasing distance into the matrix. Fibres break depending on the stress required to propagate largest flaw in the fibre and pull-out of the matrix. The distribution of the point of fibre failure and the length of pull-out depend on the size and distribution of the flaws in the fibre. The work of fibre pullout (γ) is given by³:

$$\gamma = \frac{V_f r_f^2 (S_f - S_f^*)^3}{12 \tau^2 d_f}$$

where, $(S_f - S_f^*)$ is the difference between the stress to extend large flaws in the fibre and the strength of the unflawed fibre and d_f is the spacing of flaws in the fibre.

Table 3. Strength and toughness of fibre-glass composites

Fibre type	Glass type	Strength (MPa)	K_{Ic} (MPa m ^{1/2})
Graphite ^(a) (50 v %)	Borosilicate ^(b)	689	22
SiC(65 v %)	Borosilicate	830	18.9

a: hercule HMS fibre, b: 7740 Corning borosilicate, c: nicalon.

The above two mechanisms have been very successfully used for toughening of SiC fibre-glass and graphite fibre-glass composites⁴⁻⁷. Remarkable strength and toughness have been achieved as shown in Table 3. These composites can be used only up to 600 °C.

2.3 Crack Impedement Mechanism

A crack propagating in a matrix containing a second dispersed phase bows^{8,9} between the particles increasing the crack propagation stress (Fig. 3). It has been shown

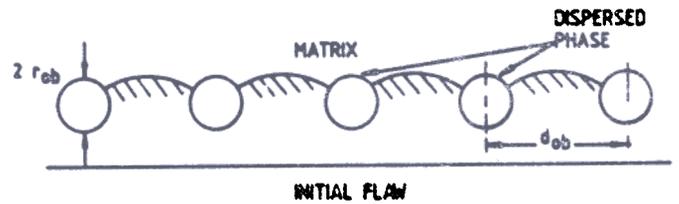


Figure 3. Crack bowing out between particles.

that the stress needed to propagate the crack between particles increases as the ratio of the obstacle spacing to obstacle diameter (r_{ob}/d_{ob}) decreases. This method of toughening is, however, limited by the fact that at higher values of the ratio obstacle penetration occurs and no further increase in toughness and strength are observed (Fig. 4). The effect of particle morphology and of (r_{ob}/d_{ob}) has been shown in Fig. 5.

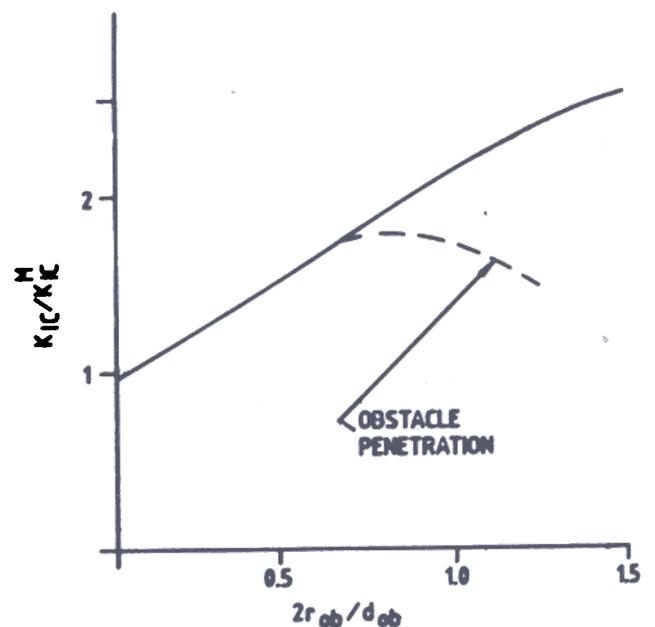
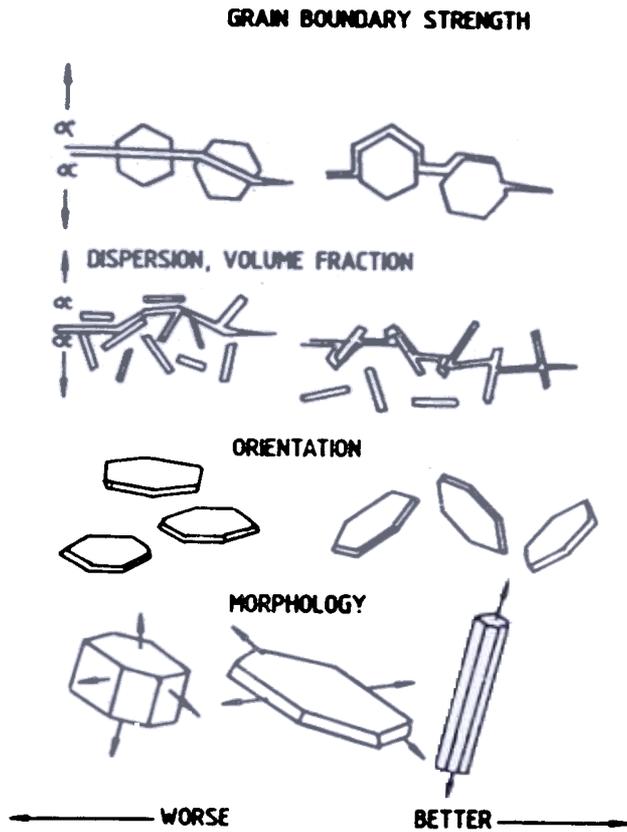
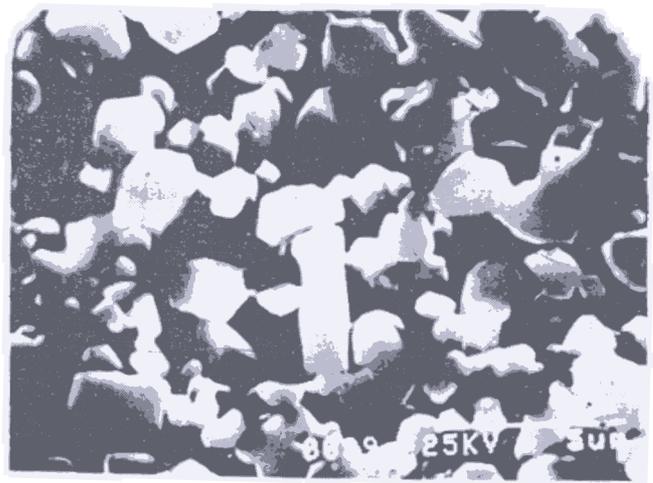


Figure 4. Plot of r_{ob}/d_{ob} and improvement³ in K_{Ic} .



(a)



(b)

Figure 5. Particle morphology and crack deflection (Telle, R. Brook, R.J. & Petzow, G. *J. Hard Materials*, 1991, 2, 79-114).

Figure 6. Microstructure of reaction bonded SiC showing the effect of uniformly distributed small SiC obstacles (a) large SiC obstacles with large matrix area and (b) with small matrix area.

An example of how this principle can bring about toughening may be seen from the two microstructures (Fig. 6) of reaction bonded SiC which may be considered as a composite of α -SiC in an Si matrix. Uniformly distributed fine α -SiC (Fig. 6(b)) with a body diagonal of matrix of 0.57 to 5.72 μm gives a toughness of 4.2 $\text{MPa m}^{1/2}$ as compared to coarse SiC with large matrix area (Fig. 1(a)) with a body diagonal of Si of 57.7 to 142.0 μm having a toughness of 2.84 $\text{MPa m}^{1/2}$ only.

In contrast to fibre matrix composites where the toughening effect is directional, this mechanism with particulate gives a nearly isotropic toughening. Second phase - matrix property mismatch may give rise to tensile or compressive stress around the second phase. In the former case a crack in the matrix may go round the second phase without much particle crack interaction. In the latter case, the matrix crack may be directly dragged into the second phase with maximum matrix-second phase interaction with substantial improvement in toughness. Since the stress field

decreases as $1/r^3$ from the particle-matrix interface, a high density of dispersed second phase favours such a mechanism. The stress may arise from thermal expansion mismatch, phase transformation or from difference of elastic moduli.

Crack deflection will also depend on the particle morphology and aspect ratio¹⁰. The strain energy release rate, G_T for a given volume fraction of a second phase and for a given aspect ratio (I_p) of randomly distributed rod particles have been calculated¹⁰. The results show that the toughening effect saturates at a V_f of 0.2 and I_p of 10 giving an upper limit to strain energy release

rate of the composite to that of the matrix (G_c/G_m) of around 4. Knowing that

$$G_{lc} = K_{lc}^2(1 - \nu^2)/E \quad (4)$$

one can write

$$\frac{(K_{lc})_c}{(K_{lc})_m} = \frac{[(G_c/G_m) [E_c(1 - \nu_m^2)/E_m(1 - \nu_c^2)]^{1/2}}{(4)}$$

where, ν is the Poisson's ratio.

For most ceramic composites, $E_c = E_m = 400$ GPa and $(\nu_c) = (\nu_m) = 0.3$. This gives a value of 2 for the left hand side of the Eqn (5) which implies that the maximum possible improvement will be by a factor of two.

2.4 Internal Compression

Thermal toughening of glass by creating surface compressive stress is well known^{11,12}. Ceramics may also be toughened by thermal quenching although such toughening may be localised to the surface only. This arises due to the differential cooling between the surface and the interior layer of a ceramic. Similarly, when a composite is cooled after preparation, stress develops as a result of constraint imposed by two phases on each other. In case of a fibre-matrix composite the stresses (S) are given by:

$$S_m = (a_f - a_m) E_f V_f E_m \Delta T/E_c \quad (6)$$

$$S_f = -S_m V_m/V_f = (a_m - a_f) E_m V_m E_f \Delta T/E_c \quad (7)$$

In case of particulate composites, assuming spherical particle in an infinite matrix, the hydrostatic stress on the particle (P) and the radial and tangential stress components in a matrix (S_r and S_t) are given by:

$$P = S_r = S_t = -\frac{(a_m - a_p) \Delta T}{[(1 + \nu_m)/2E_m] + [(1 - 2\nu_p)/E_p]} \quad (8)$$

The other symbols have their usual meaning.

The corresponding stress in the matrix is given by

$$S_r = -2S_t = P(r/x)^3 \quad (9)$$

where r is the particle radius and x the radial distance from the particle.

If the second phase has a lower thermal expansion (α) than the matrix (*SiC* fibre- Al_2O_3 matrix, for

example), the second phase will have a compression (axial in case of fibre) and tension in the matrix and vice versa (*SiC* fibre- Si_3N_4 matrix, for example). Similar to application of load in short fibre composite, there is a mismatch interfacial shear stress and falling tensile stress at the end of the fibre. With rigid interfaces the interfacial shear stress may be around 1000 MPa. This may result in debonding on cooling and rupture as often found in pressureless sintered *SiC* platelet- Si_3N_4 composites.

2.5 Microcracking

Microcracking ahead of the crack tip was found to be a reason of toughening of phase transformed zirconia¹³. Such microcracks throughout the matrix may be of less value. Increased toughness may be due to lowering of elastic modulus in the zone of microcrack and due to absorption of strain release energy. Short fibre may cause microcracks at the end faces due to tensile failure, due to shear stress failure in the transfer length or due to mismatch. The reduced stress intensity (K_m) at the crack tip due to microcracking is given by¹⁴:

$$K_m = K' - AvK' - BEa_f h^{1/2} \quad (10)$$

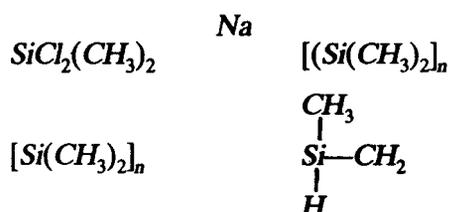
where K' is the stress intensity of the uncracked matrix, ν is a measure of the microcracking density and Av is the toughening effect of the reduction of elastic moduli, A is a coefficient depending on the shape of the zone. The last term contributes to the zone dilation on the toughening, where h is the thickness of the microcracked zone, B is a function of the zone shape and a_f is the fractional dilation.

3. FIBRES FOR MAKING COMPOSITES

Short or continuous fibres for making composites may be derived from oxides or non-oxides. The first inorganic fibre which came into the market in the 1960s was that of carbon which has been successfully used in carbon fibre glass composites. Such fibres are not suitable for use in ceramic matrix composites because of their reaction with oxygen. Another form of carbon fibre made from a precursor of pitch has higher resistance to oxidation¹⁵ and may be suitable for ceramic-matrix composites. Short fibres of small diameter based on alumina¹⁵ and *SiC*^{16,17} were available in 1970s. Another form of the short fibre is the whiskers which are monocrystals having almost theoretical strength¹⁸.

Properties of fibres of interest have been given in Table 2. The fibres made of alumina, mullite and in admixture with other oxides like ZrO_2 retain their strength and stiffness up to 800 °C. At 1000 °C about 25 per cent of the elastic modulus is lost and the fibres creep. The oxide-based fibres seem to be more suitable for MMCs than for ceramic-matrix composites.

The appearance of the SiC-based fibres with high elastic modulus and high temperature strength retentivity kindled interest in ceramic matrix-fibre composites. The starting material for preparation of the fibre is dichlorodimethylsilane which is made to react with Na to form polymethyl silane. The latter is autoclaved at 10 MPa pressure when Si-C bonds are formed giving rise to polycarbosilane which consists of six atoms arranged in a cyclic manner as in beta-SiC. The polycarbosilane is pyrolysed in an inert atmosphere at 1300° C to produce the fibre. The fibre usually contains free C, Si and O.



Whiskers are made mainly by a vapour phase reaction. The formation of Si_3N_4 wool and whiskers during the formation of reaction bonded silicon nitride is well known. The main method for making SiC whiskers may be summarised as follows¹⁰:

- Thermal decomposition or hydrogen reduction of organic Si compounds such as $Si(CH_3)_3Cl$ in the temperature range²⁰ 1100-1500°C,
- CVD process using VLS mechanism²¹,
- Reaction between SiO_2 and C at temperature of 1600-1700°C, and

Table 4. Properties of some selected whiskers

Whisker	Tensile strength (GPa)	E (GPa)	Density
SiC	21	490	3.18
Si_3N_4	14	385	3.18
Al_2O_3	20	450	3.96
B_4C	14	490	2.52

- Supersaturation in molten phase of a Si alloy.

The properties of some of the whiskers are detailed in Table 4

4. PREPARATION OF CERAMIC-MATRIX COMPOSITES

Ceramic matrix-fibre particulate composites are made by normal ceramic fabrication process of mixing, shape formation and consolidation. However, extra precaution is needed in this case specially as regards the volume fraction and appropriate dispersion of the second phase in the matrix. Agglomerated second phase will act as a single particle and leave large area of the matrix without the reinforcing phase. The following precautions have to be taken while preparing CMCs.

- Uniform second phase particle size with oversize removed by sedimentation,
- Breaking up of aggregate by ultrasonic. Short fibres are sometimes badly tangled. This has to be done in a glove box and in an appropriate liquid medium,
- Intimate mixing with matrix powder with good dispersion avoiding particle separation due to density difference, and
- Second phase particles of nonspherical shape like fibres or platelets tend to orient themselves during slipcasting, uniaxial pressing or injection moulding yielding non isotropic properties.

4.1 Consolidation

Consolidation of a composite containing a nonsintering second phase (SiC platelet or fibre in Si_3N_4 , for example) presents special problem. Since the matrix sinters faster, a tensile hoop stress develops which can produce radial cracks giving rise to pore or debonding. The stress can be relieved when viscous flow is possible like in glass matrix composites or when the matrix can creep under a load like that of Al_2O_3 . Sintering of bimodal powder has been analysed²². The inhomogeneous sintering effects are most severe when the ratio of creep relaxation rate of the matrix to that of the densification rate is < 0.1 and is negligible at a value of > 10 . For this reason it is very difficult to obtain theoretically dense product in pressureless sintering of such composites as is shown in the densification curve of Si_3N_4 with TiC particulate

addition²³ (Fig. 7). Similarly, use of 15 v per cent SiC fibre in Al_2O_3 reduces the sintering density of the matrix²⁴ from 96 per cent to 75 per cent at 1500°C. Such composites can therefore be only made in simple shapes by hot-pressing or by increased amount of liquid phase as in Si_3N_4 .

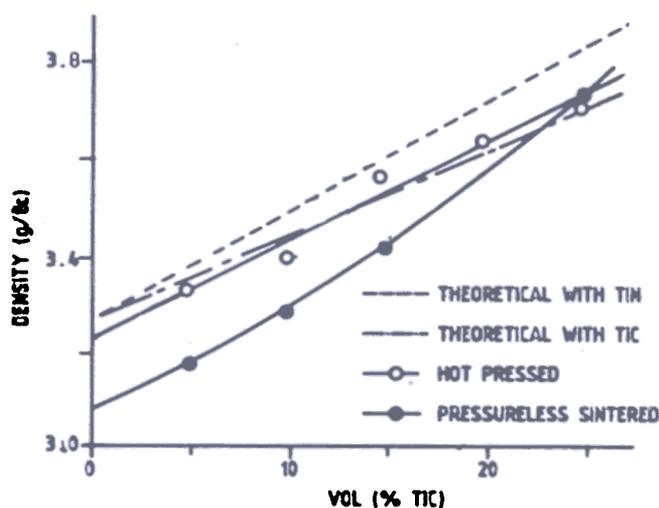


Figure 7. Curve showing density obtained by pressureless and pressure sintering of Si_3N_4 -TiC composites; TiC gets converted²³ into TiN.

4.1.1 Ceramic-matrix composites with continuous fibre

Two- or three-dimensional preforms of woven fibres are infiltrated with the matrix by (i) vapour phase²⁵, (ii) polymer infiltration and pyrolysis²⁶⁻²⁹, (iii) melt infiltration^{30,31}, (iv) sol-gel infiltration^{32,33}, and (v) reaction bonding^{23,34-36}. Some of these processes have the drawback of large matrix area, fibre damage during infiltration and fibre-matrix reaction at high temperature.

5. MECHANICAL PROPERTIES OF COMPOSITES

The improvement in the strength and toughness of glass fibre plastic matrix and ceramic fibre glass or glass ceramics matrix are remarkable^{37,38}. This is due to the large difference in the values of E between the fibre and matrix, and also because they are formed by a viscous flow process. Even the latter cannot be called a true high temperature material as its use may be limited to 600 to 800°C. The reported improvement of toughness in the case of advanced ceramic matrix has been very limited. On the other hand in most cases a lowering of strength has been observed. The mechanical

Table 5. Mechanical property data of composites

Matrix	Second phase	K_{Ic}	Reference
Si_3N_4	SiC_f (20 v%)	10.0	30,31
	$SiC_{p,pf}$ (10 v%)	7-8	32-34
	TiC_p (15-20 v%)	6	23,35
Al_2O_3	SiC_f (20 v%)	8.7	30,31
	TiC_p (20 v%)	6.6	36,37

property data obtained by various authors have been given in Table 5, which also gives an indication of the improvement of toughness achieved. The value given in the table is the highest reported. In some cases little or no improvement in the K_{Ic} value have been observed. It may be attributed to the difference in the processing techniques by different researchers. The improvement of toughness is in most cases associated with a reduction of strength. Considering the K_{Ic} of Si_3N_4 and Al_2O_3 matrices of about 5-6 and 3 respectively, the improvement by compositing is 50 to 100 per cent. However these values are quite low for many structural applications. On the contrary the increase in the value for a glassy matrix ($K_{Ic} = 0.4$) is almost 50 times as shown in Table 2. The best improvement of toughness is obtained for continuous fibre ceramic-matrix composites and may be the most fruitful direction of future research.

Al_2O_3 fibre has been used in ceramic matrix without much success. It has been composited in an MgO matrix by slurry infiltration³⁸ and in SiC matrix by pyrolysis of infiltrated polysilane polymer³⁹. In the former, the strength was very poor and there was no improvement in K_{Ic} . In the latter, a strength of only 121 MPa was recorded which improved to 250 MPa after a coating was applied. The main reasons why alumina fibres have not given expected results are: (i) the fibre reacts with the matrix at high temperature, and (ii) it degrades at high temperature needed for fabrication.

6. DEGRADATION OF THE SECOND PHASE

Degradation of fibres may occur in contact with oxygen or in oxide containing materials. Protective layers of C , BN , SiC , etc have been used with success^{40,41}. Silicon carbide fibre in Si_3N_4 matrix can degrade as the temperature reaches above 1600°C at 0.1 MPa N pressure. If a temperature of 1800°C is needed for liquid phase sintering or hot pressing, it

would be desirable to have a minimum N pressure of over 0.5 MPa to prevent fibre degradation. Similarly, many particulates like TiC are not compatible with Si_3N_4 and convert to TiN , if sintering is done at 0.1 MPa N.

7. OTHER METHODS OF MAKING COMPOSITES

Various other methods of making composites by *in-situ* reaction followed by consolidation have been developed.

Double decomposition reaction: Double decomposition reactions have been used to produce particulate mixtures of oxide and nitride⁴², carbide and carbide⁴³⁻⁴⁵ borides and carbides⁴⁶⁻⁴⁸, carbide and nitride⁴⁹. Although an improvement of the toughness has been observed because of crack impedement and crack bowing to a value of 5-6 MPa m^{1/2} over the matrix toughness of around 3 MPa m^{1/2} the value is clearly low for many structural applications.

Melt infiltration and oxidation/nitridation: A fibre preform may be infiltrated with molten aluminium followed by oxidation of the metal to produce an Al_2O_3-SiC fibre composite^{50,51}. The low temperature used for infiltration prevents damage of the fibre.

8. CONCLUSIONS

The advanced ceramics developed during the last three decades were initially found to have some favourable properties which prompted intensive work for their use as high temperature structural part in process industries and in heat conversion devices. Although high temperature strength retention, stress rupture, and resistance to corrosion were good, they failed by catastrophic brittle fracture. Many such failures were recorded during spin test of turbine rotor⁵². The reason is the low K_{Ic} inherent in the material. The next phase was the improvement of K_{Ic} with 'graceful failure' by making composites with fibre. However as it stands today, the only substantial improvement has been found with continuous or woven fibres. Short fibre/whisker composites have yielded a value of K_{Ic} which is not yet adequate for use in structural applications. On the other hand a nonsintering second phase brings about difficulty in achieving full density with consequent reduction in strengths. Fibres are also difficult to handle due to health hazards. Since the theoretical aspects of improvement of K_{Ic} are now well

developed, it is hoped that continued study in the behaviour of composites for high temperature application will ultimately yield result.

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