JOURNAL OF MATERIALS SCIENCE 26 (1991) 4845–4854

Whisker reinforcement of glass-ceramics

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Silicon carbide whisker reinforcement of anorthite and cordierite glass ceramics has been studied. At 25 vol % whisker loading the flexural strengths increased from 65–103 MPa to 380–410 MPa, the fracture toughnesses increased from 1.0–1.5 MPa $m^{1/2}$ to 5.2–5.5 MPa $m^{1/2}$. The strengths decline to 240–276 MPa at 1200 °C. The reasons for the decrease in strength with temperature are discussed. Whiskers from two different sources with differences in diameters and aspect ratios were evaluated and the effect of the whisker morphology on the composite properties was studied. It was found that larger diameter, higher aspect ratio whiskers result in improved composite performance. The composites were also characterized in terms of their thermal properties, i.e. thermal expansions and thermal conductivities. The thermal expansion coefficient from 25–1000 °C for anorthite-based composite was 4.6×10^{-6} °C^{-1} and that for the cordierite-based composite was 3.62×10^{-6} °C^{-1}. The thermal conductivities at 1000 °C were 3.75 and 4.1 W m^{-1} K^{-1} for cordierite and anorthite composites, respectively.

1. Introduction

Composite materials formed by combining two distinct materials on a macroscopic scale, have found many applications in aerospace, automotive, marine and other industries. Particularly noteworthy are the polymer matrix composites reinforced with glass or graphite fibres. In these composites a low-modulus low-strength polymer matrix is reinforced with high-modulus high-strength fibres to obtain a strong, lightweight high-performance material. The fibres may be continuous, or discontinuous with high aspect ratios. Continuous fibre reinforcement results in higher performance composites than discontinuous fibre reinforcement but making complex shapes with such composites is difficult. Discontinuous fibre-reinforced composites generally are lower strength materials but can be formed into complex shapes by economical processes such as injection moulding.

Polymer matrix composites are limited to applications with upper use temperatures of up to 300 °C. For higher temperature usage, glass and glass-ceramic matrix composites have been proposed [1–5]. The reinforcements used were either graphite fibre or silicon oxycarbide fibre (Nicalon^R). In the last few years silicon carbide whiskers have also been studied as reinforcements for glasses and glass-ceramics [6–8]. Whisker reinforcement of ceramics such as alumina, silicon nitride, etc., has also been studied [9–11]. The advantages of glass-ceramics as matrices are that the composites based on these matrices may be easily processed as a glass and then cerammed to convert the glass matrix to a highly crystalline and refractory glass-ceramic. While the upper use temperature of glass-ceramic matrices is high compared to glass matrix composites, processing of the composites remains relatively simple. Hybrid glass-ceramic matrix composites, where both the continuous fibre (Nicalon) and silicon carbide whiskers have been used as reinforcements, have also been reported [12]. The hybrid composites have substantially improved mechanical properties compared to composites reinforced with only fibres.

Similar to the discontinuous fibre-reinforced polymer composites, whisker-reinforced glass-ceramic composites have several processing advantages if a complex shaped part is required for a given application. Powder processing methods such as sintering, or glass-forming processes may be used with these materials to form complex net-shaped parts economically.

In this paper, work on two refractory glass-ceramic matrix systems reinforced with silicon carbide whiskers is reported. The glass-ceramic systems consist of (1) a calcium–aluminosilicate system with anorthite as the major phase, and (2) a barium–magnesium–aluminosilicate system with cordierite as the major phase. These two systems are refractory and useful to temperatures ⩾ 1200 °C. There is, however, a significant difference in the moduli, the thermal expansions and thermal conductivities of these materials. The influence of these differences on the composite performance has been studied.

2. Materials and processing

As mentioned before, the glass-ceramics used consisted of a calcium–aluminosilicate (CAS) glass ceramic and a barium–magnesium–aluminosilicate [BMAS] glass-ceramic, with anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) and cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) as the predominant crystal phases, respectively.

The whiskers used were from two different sources. The cordierite matrix experiments were done with SC-9 whiskers (Advanced Composite Materials Corporation, Greer, South Carolina, USA, designated W1) and Tokamax whiskers (Tokai Carbon Corporation, Tokyo, Japan, designated W2). The change in whisker source was necessitated because of the unavailability of the SC-9 whiskers from ACMC. Both types of whisker were characterized in terms of their morphology.

The composites were fabricated by first mixing the whiskers and glass powders in isopropanol in a blender and then filtering and drying this mixture. The glass powder–whisker mixture was then hot pressed in graphite dies in a nitrogen atmosphere at 1400–1500 °C.

The fully dense composites obtained were then cut into appropriate specimens to measure mechanical and thermal properties.

The flexural strength and fracture toughness of the specimens was measured in four-point bending with 20 mm load and 40 mm support spans. Fracture toughness was measured with single-edge notch bend technique. This technique has been shown [7] to give a more conservative fracture toughness value than the chevron notch technique for whisker-reinforced glass matrix composites and is easy to use. The composite and matrix moduli were measured by a sonic resonance technique. Thermal conductivity was measured using the laser flash technique developed at Virginia Polytechnic Institute.

3. Results and discussion

3.1. Whisker characterization

The properties of the composites are determined essentially by the type of reinforcement used. The silicon carbide whiskers from the two sources were thus characterized by image analysis with respect to their morphology. Figs 1–3 show the comparison of the diameter distribution, length distribution and aspect ratio distribution, respectively, of the whisker from the two sources. The diameter distribution shown in Fig. 1 clearly shows that the W1 whiskers have a larger mean diameter than W2 whiskers. The mean diameter for W1 whiskers was 2.14 μm and for W2 whiskers was 0.85 μm. The whisker length distribution is shown in Fig. 2. The mean length of W1 whiskers was 13.3 μm and for W2 whiskers was 8.8 μm. The mean aspect ratios for W1 and W2 whiskers were 7 and 11.8, respectively. Table I shows the statistical data. The data were obtained on approximately 300 randomly selected whiskers in each case.

3.2. Flexural strength

All the data on the cordierite matrix composites was obtained with W1 whiskers. The flexural strength of the composites as a function of whisker volume fraction is shown in Fig. 4. The strength of the composites increases with increasing volume fraction as expected. The flexural strength–volume fraction relationship, however, is nonlinear. In short-fibre–resin matrix systems, the strengths of random short-fibre composites

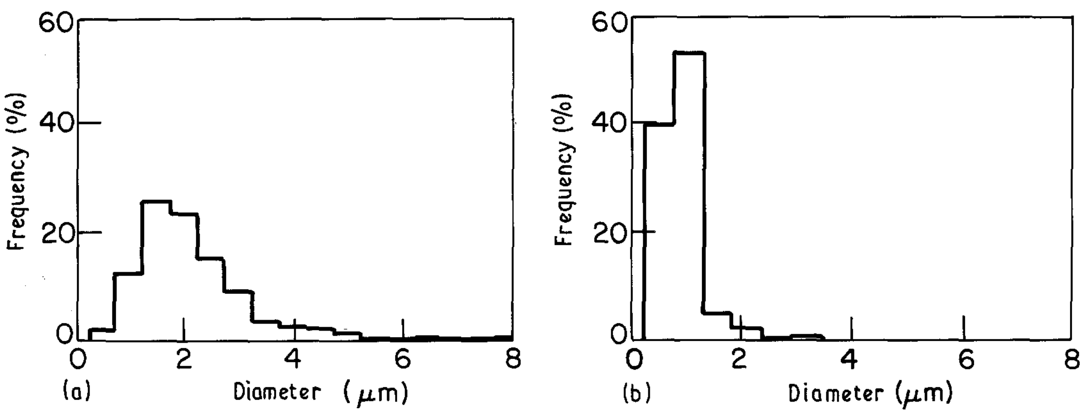

Figure 1 Diameter distribution of the whiskers: (a) W1, (b) W2.

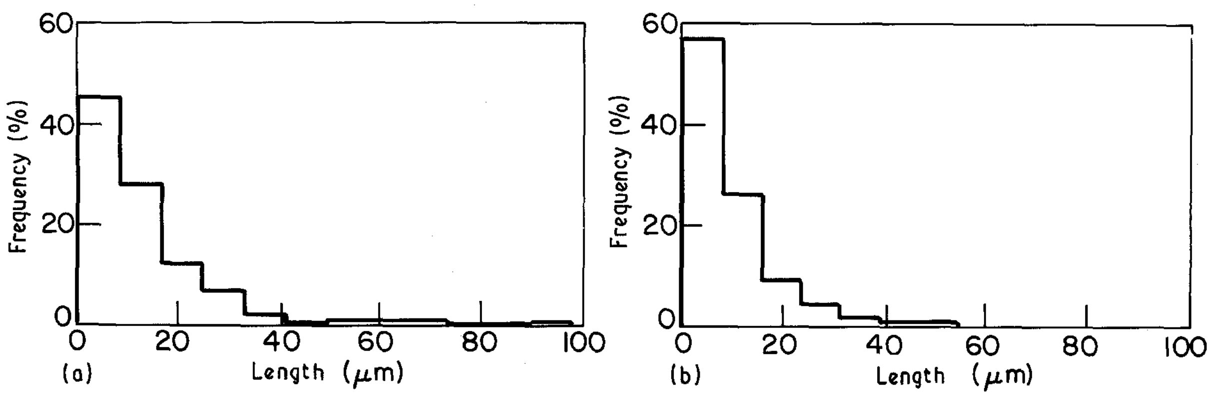

Figure 2 Length distribution of the whiskers: (a) W1, (b) W2.

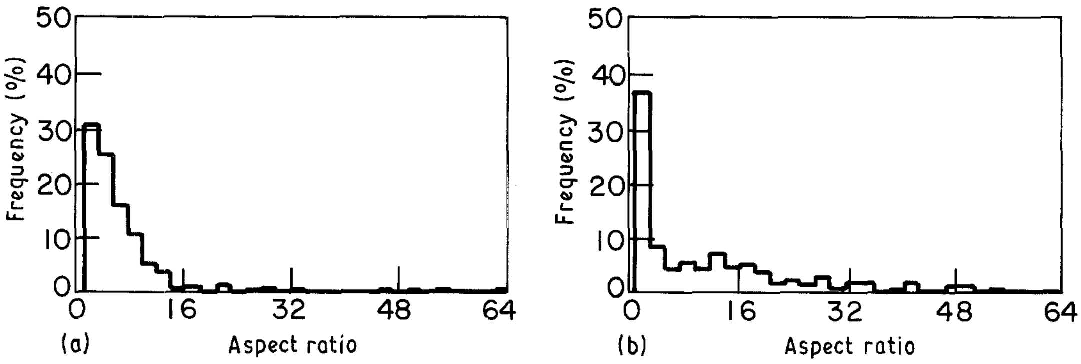

Figure 3 Aspect ratio distribution of the whiskers: (a) W1, (b) W2.

TABLE I A comparison of whisker dimensions

	Whisker type	
	W1	W2
Mean diameter (μm)	2.14	0.85
Mean length (μm)	13.6	8.8
Mean aspect ratio (μm)	7.0	11.8

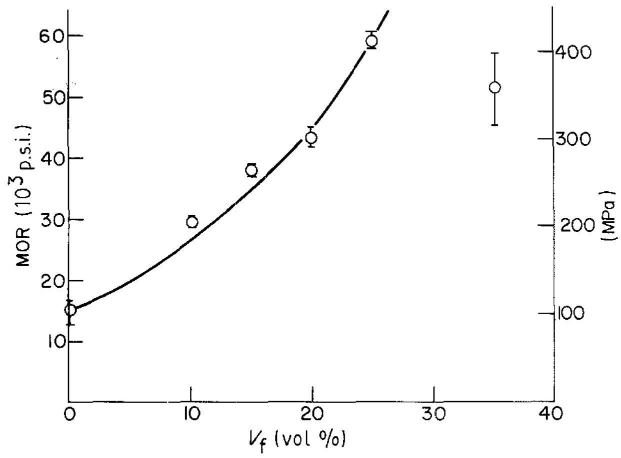

Figure 4 Flexural strength as a function of volume fraction of reinforcement for cordierite–W1 composite.

have been found to increase linearly with volume fraction [13]. A similar correlation may be expected in this case. From Fig. 4 it is seen that the flexural strength increases nonlinearly with increase in volume fraction of the whiskers. At 25 vol % fraction whiskers, the strength is significantly higher than would be expected based on a linear relationship. In other words, a higher percentage of whiskers is effectively reinforcing the composite at higher whisker volume fractions. This phenomenon may be explained as follows.

The critical aspect ratio for the glass or glass-ceramic matrix system may be calculated based on the following equation for well-bonded elastic–elastic systems [14]

$$\left(\frac{L}{d_f}\right)_c = \left[\frac{E_f}{2G_m}(V_f^{-1/2} - 1)\right]^{1/2} \cosh^{-1} \times \left[\frac{1 + (1 - \Phi)^2}{2(1 - \Phi)}\right] \quad (1)$$

where $(L/d_f)_c$ is the critical aspect ratio, E_f the modulus of the whisker, G_m the shear modulus of the matrix, V_f the whisker volume fraction, Φ the fibre efficiency. The critical aspect ratio calculated based on this equation as a function of whisker volume fraction for the cordierite–whisker system is shown in Fig. 5. As seen from the figure, the critical aspect ratio decreases with increasing volume fraction of the whiskers. The critical aspect ratio varies from 8.2 at 10 vol % whiskers to 5.4 at 25 vol % whiskers. The aspect ratio distribution of the W1 whiskers is given in Fig. 3. As seen from the figure, the aspect ratios vary from 2–64 with majority of the whiskers in the 2–16 range. From the distribution it is seen that there is a substantially higher percentage of whiskers above the calculated critical aspect ratio at 25 vol % whisker reinforcement than at 10 vol % whisker reinforcement. This results in more efficient reinforcement of the matrix by the whiskers of any given aspect ratio, i.e. the average stress carried by the whiskers is higher at 25 vol % level than at 10 vol % whisker level as can be easily shown based on Rosen model [14].

The nonlinear increase in composite strength with whisker volume fraction thus is caused by the decrease in critical aspect ratio with increasing volume fraction of the whiskers. As seen from Fig. 4 at whisker volume fraction of 35 vol %, the composite strength has declined compared to 25 vol % whisker level. The composite did not fully consolidate in this case. The incomplete consolidation of the composite is the reason for this strength drop. At high whisker volume fractions consolidation of the composites thus becomes the limiting factor.

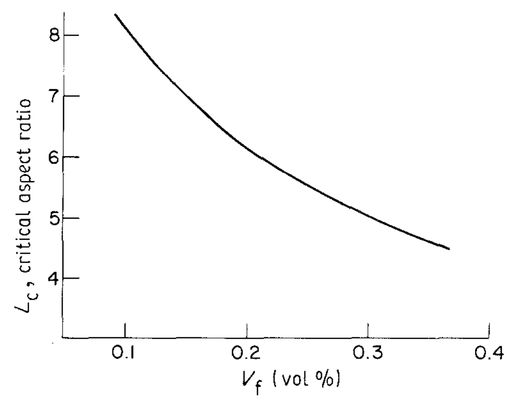

Figure 5 Critical aspect ratio as a function of volume fraction for cordierite–W1 composite.

Anorthite-based system experiments were done with W2 whiskers. The flexural strengths as a function of volume fraction of the whiskers is shown in Fig. 6. Interestingly for these whiskers the flexural strength of the composites is a linear function of the whisker volume fraction. At 25 vol % whiskers the flexural strength is below the linear prediction. This result is contrary to the data obtained with cordierite-based composites reinforced with W1 whiskers. The discussion above, which explains the nonlinear relationship between the whisker volume fraction and the composite strength, i.e. decreasing critical aspect ratio with increasing whisker volume fraction for the cordierite composite, is also applicable in the case of the anorthite composite. A nonlinear relationship is thus expected in the case of the anorthite–W2 system as obtained with cordierite–W1 system. There are three significant differences between the two systems, any one or a combination of which may cause this difference in behaviour of the two composite systems. The differences are (1) a difference in the thermal expansion of the two matrices which may result in residual stresses of different magnitude in the two systems; (2) a difference in the chemical composition of the two matrices which may result in differences in bond strength and hence substantial differences in critical aspect ratio; and, (3) a difference in whisker morphologies of W1 and W2 whiskers.

3.2.1. Thermal expansion differences

The residual stresses in a system, where a very large number of cylindrical particles are randomly oriented in a matrix, are very difficult to quantify. The thermal expansion mismatch-induced stresses are given by the following equation for the case of a cylindrical inclusion in an infinite matrix

$$\sigma = \frac{(\alpha_m - \alpha_f)\Delta T E_m}{(1 + \mu_m)(1 + \mu_w)} \frac{E_m}{E_w} \quad (2)$$

$\sigma_r = -\sigma(a/r)^2$, $\sigma_\theta = \sigma(a/r)^2$, where σ_r, σ_θ are radial and tangential stresses at a distance, r, from the cylindrical particle, α_m and α_w are the thermal expansion coefficients of matrix and whiskers, respectively, and

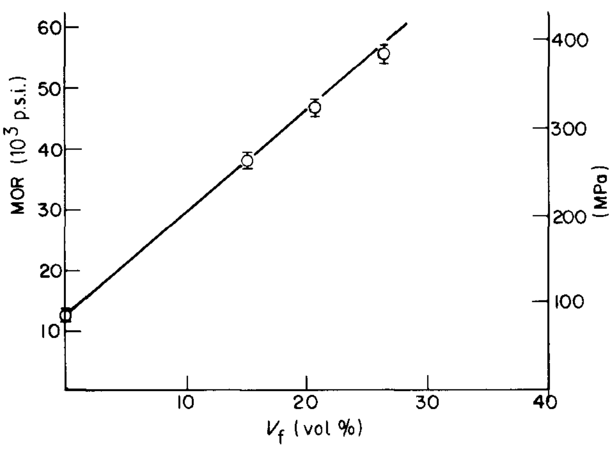

Figure 6 Flexural strength as a function of volume fraction of reinforcement for anorthite–W2 composite.

E_m and E_w are the moduli of matrix and whiskers, respectively.

These equations, however, are valid only for the case of a cylindrical inclusion in an infinite matrix. In the composites there is a large number of whiskers of different morphologies and orientations in close proximity and such model equations may not be applicable. It is thus difficult to evaluate the effect of residual stresses on the composite properties. The radial and tangential stresses of equal magnitude but opposite signs from a large number of particles may nullify each other and, at least in the expansion range studied, may not have a significant effect on the strength of the composites. Some of the experimental results given below support this conclusion.

3.2.2. Bond strength

The difference in the bond strength leading to substantial change in critical aspect ratio is probably not the cause of the different behaviour of these composites in terms of variation of the strength of the anorthite-based composites as a function of volume fraction, compared to the cordierite-based composites. In both cases the flexural strength of the matrices has been increased four-fold by addition of whiskers. Such a substantial improvement in strength cannot be obtained without significant load transfer to the whiskers. For the given low aspect ratios of the whiskers the bond must be an "optimum bond" to allow the load transfer in both cases. Any substantial differences in bond strength, i.e. frictional versus chemical bond, are thus not expected, because a frictional or low-strength bond would result in minimal, if any, strength increases.

3.2.3. Whisker morphology

From Figs 1–3 it is known that the W1 and W2 whiskers are substantially different in terms of the distribution of the diameters, the aspect ratios and the lengths. There are thus two points to be considered which could affect the composite strength. The first is that of the changes in the load transfer to the whiskers and the second is that of the processing issues involved in fabricating a composite with whiskers of different morphologies. From Equation 1 the critical aspect ratio for the anorthite composite system with W2 whiskers may be calculated to be 6.75 at room temperature for 25 vol % fraction whiskers. This is higher than the 5.4 critical aspect ratio value calculated for the cordierite matrix, as expected from the lower modulus of the anorthite system. The ratio of the mean aspect ratio of the whiskers to the critical aspect ratio is 1.29 for the cordierite system and 1.74 for the anorthite system. The load transfer thus should be better, i.e. average fibre stress should be higher, assuming that the whiskers have the same strengths and moduli, for the anorthite system compared to the cordierite W1 system. The anorthite–W2 system should thus result in a higher strength composite than the cordierite-based one.

The deviation from nonlinearity at 25 vol % fraction whiskers should also be as high as in the case of the cordierite–W1 composite system. The discussion given above thus eliminates load transfer considerations related to the whisker morphology as being the cause of the differences in the behaviour between the two systems. The processing related factors, however, are very important because of the difference in whisker morphology. The difference in the mean length and mean diameters of the W1 and W2 whiskers results in a substantial difference in the number of whiskers at a given volume fraction of whiskers. The ratio of the number of W1 to W2 whiskers may be calculated from

$$\frac{N_1}{N_2} = \frac{D_2^2 L_2}{D_1^2 L_1} \tag{3}$$

where N is the number of whiskers, D is the diameter of the whiskers, and L is the length of the whiskers.

A calculation based on mean lengths and diameters of the whiskers clearly shows that at a given volume fraction level the number of W2 whiskers is ten times that of W1 whiskers. This results in difficulties with proper whisker dispersion and consolidation of the composite. An SEM examination showed some evidence of whisker agglomerations becoming failure initiation sites for the W2 whisker composites. All the data mentioned above on the two composite systems were obtained on 10 cm × 10 cm × 0.65 cm specimens cut to proper dimensions for testing. To evaluate whether whisker dispersion and processing could be improved on smaller specimens, a specimen 7.6 cm diameter and 0.3 cm thick was fabricated from anorthite–W2 whisker system at 25 vol % fraction. From this specimen bars of the same standard size were cut and flexural strength measured under the same conditions. The specimens had an average strength of 482 MPa. This data point shows the expected trend similar to the cordierite–W1 whisker system. These data, however, could not be reproduced on the standard sized (10 cm × 10 cm × 0.65 cm) specimens made for the study in spite of repeated experiments. The flexural strength obtained on the smaller specimen clearly shows that the lower than expected strength obtained for the 10 cm × 10 cm × 0.65 cm specimens was not related to thermal expansion mismatch stresses or bond strength differences but to the difficulty of processing fine diameter whiskers and consolidating the composites containing an order of magnitude larger number of whiskers (W2 compared to W1). It has been shown [6] that the addition of whiskers results in up to two orders of magnitude increase in process viscosity. An order of magnitude increase in the number of whiskers at a given whisker percentage is thus expected to increase the process viscosity very significantly. This increase in viscosity leads to difficulties in consolidation of the composites. Thus, the ideal whiskers should have larger diameters (3–5 μm) and high mean aspect ratios (20 or more) with minimum percentage of whiskers of aspect ratios below the critical aspect ratio to obtain improvements in strengths over those already achieved and also to minimize processing difficulties.

3.3. Elevated temperature flexural strength

Fig. 7 shows the flexural strength of the cordierite–W1 composites as a function of volume fraction of the whiskers at 1200 °C. At this temperature the strength–volume fraction relationship is linear, unlike the relationship seen at room temperature. At all the volume fraction whisker reinforcement levels the strength is lower at 1200 °C than at room temperature. At 25 vol % whisker loading level the strength decreases from 415 MPa at room temperature to 248 MPa at 1200 °C. For high-temperature applications it is important to maintain high strengths at elevated temperatures. It is thus important to know the cause of this strength drop. Fig. 8 shows the variation of the strength of the 25 vol % fraction whisker (W1)-reinforced cordierite as a function of temperature. There is a small drop in strength in the temperature range 25–1000 °C. The strength decreases substantially as the temperature increases to 1200 °C from 1000 °C. There must thus be an important change in the reinforcement mechanism at elevated temperatures (1100–1200 °C) compared to room temperature to cause this drop.

The first factor to consider is that of the matrix strength. Although the strength of the composite is derived mainly from the reinforcing whiskers, i.e. the load is mainly carried by the whiskers, the matrix does contribute to the composite strength. A significant

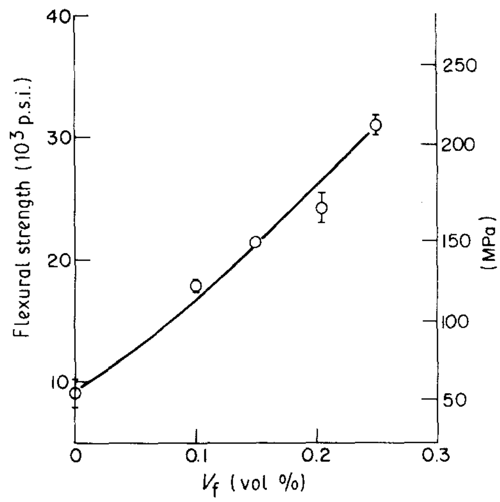

Figure 7 Flexural strength of cordierite–W1 composites at 1200 °C.

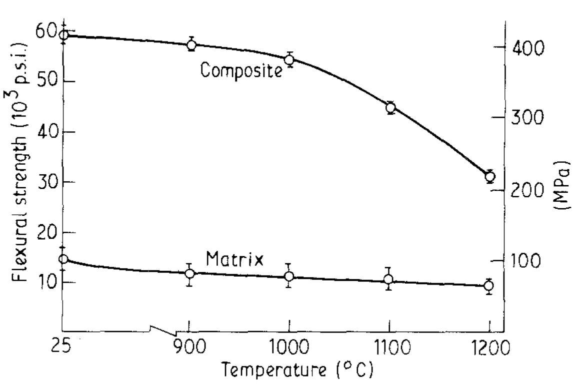

Figure 8 Variation of the composite strength and matrix strength with temperature for cordierite–W1 composite.

drop in matrix strength could account for at least some percentage of the strength loss observed for the composite. Fig. 8 also shows the variation in strength of the matrix with temperature. As seen from the figure, the matrix strength decrease in the temperature range 25–1200 °C is 96–69 MPa. Considering the fractional contribution of the matrix to the composite strength and the fact that the decrease in the matrix strength over the temperature range is only 27.5 MPa, the matrix strength loss may be eliminated as a significant factor in the composite strength decline.

Thermal expansion mismatch stresses could affect the composite strength in that if the matrix has substantial residual stresses, for example a matrix in compression at room temperature, the decrease in residual stresses with temperature could decrease the composite strength. With a large number of randomly oriented whiskers in the composite, the stresses are difficult to quantify.

To verify whether thermal expansion mismatch stresses are an important factor in the strength decline, data were obtained on 25 vol % whisker-reinforced anorthite matrix composite. The thermal expansion mismatch between the whiskers and the matrix is very small for the anorthite–W2 system and that of opposite sign compared to cordierite–W1 case. As seen from Fig. 9, the composite strength variation with temperature shows similar trends as seen with the cordierite matrix composites. The strength decreases slowly from room temperature to 1000 °C. The flexural strength is 379 MPa at 25 °C and is 345 MPa at 1000 °C. It is 276 MPa at 1200 °C. As mentioned above, the thermal expansion mismatch in the case of these composites is $3 \times 10^{-7}\,°C^{-1}$ and hence the residual stress magnitude is also very low. The similarity in behaviour obtained between this composite and the cordierite–W1 composite which might have higher mismatch stresses with thermal expansion mismatch of $15 \times 10^{-7}\,°C^{-1}$ and of opposite sign, thus eliminates the mismatch stresses as a major cause for the strength decline.

The last factor to be considered is that of the change in the fundamental load transfer mechanism. At room temperature both the whisker and the matrix may be assumed to be elastic materials and hence elastic–elastic models apply to the behaviour of the composite materials. At elevated temperatures the elastic–elastic models may not be applicable. The critical aspect ratio for the cordierite–W1 whisker system at 1200 °C may be calculated from the known mechanical properties of the system according to Equation 1, assuming that the elastic–elastic models are applicable at 1200 °C. For the cordierite–W1 whisker system the critical aspect ratio changes from 5.4 to 6 from 25–1200 °C. Although this increase in aspect ratio results in a smaller percentage of whiskers being effective at 1200 °C compared to 25 °C, the variation in the critical aspect ratio is not enough to explain the strength drop. At elevated temperatures, i.e. temperatures above 1000 °C, the matrix may not behave perfectly elastically but in an elastic–plastic manner because of the presence of residual glass, etc. An elastic–perfectly plastic model may be more appropriate for this situation. The critical aspect ratios may be calculated for elastic–perfectly plastic matrix using well known models [15].

A deterministic calculation of the strength decline associated with a given mechanism is very difficult because of the variations in whisker morphology, orientations, etc. However, a clearer idea of the strength declines may be obtained by calculating the average fibre stresses associated with the given mechanism. For the elastic–elastic situation the fractional average fibre stress may be calculated from [14]

$$\frac{\bar{\sigma}_f}{\sigma_{f_{l\to\infty}}} = \left[\frac{1 - \tanh \eta_L}{\eta_L}\right] \quad (4)$$

where

$$\eta = \frac{2}{d_f}\left[\frac{2G_M}{E_f(V_f^{-1/2} - 1)}\right]^{1/2}$$

For elastic–perfectly plastic models the average fibre stress can be obtained from [16]

$$\bar{\sigma}_f = \tau_y\left(\frac{l}{d}\right) \quad (5)$$

because the whisker aspect ratios are less than critical at 1200 °C for this situation. Fig. 10 shows the variation in fractional average fibre stress as a function of aspect ratio at 25 °C based on the elastic–elastic model given by Equation 3. It is reasonable to expect that at room temperature this model is followed. At 1200 °C,

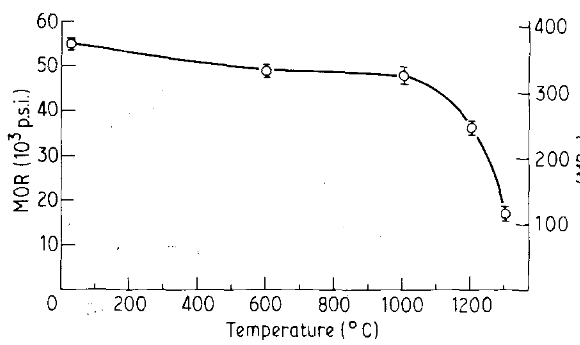

Figure 9 Flexural strength as a function of temperature for anorthite–W2 composite.

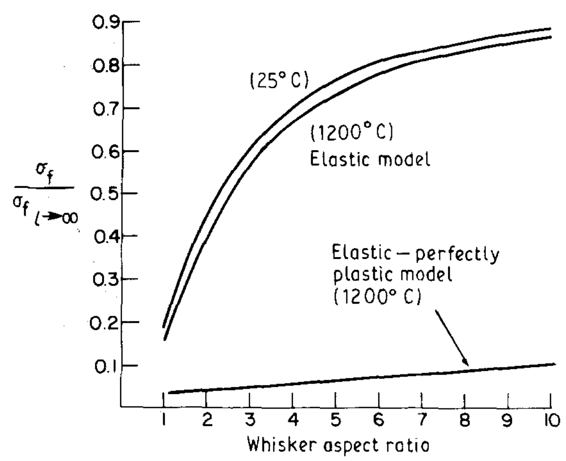

Figure 10 Fractional average fibre stress as a function of aspect ratio for cordierite–W1 composite.

however, this model is not expected to be followed. As seen from the figure, the calculated average fibre stress, assuming Equation 3 to be applicable at 1200 °C, shows very small decline in average fibre stress indicating very small declines in strength. Assumption of elastic–perfectly plastic model, however, results in very large declines in average fibre stress as seen from Fig. 10. The elastic–perfectly plastic model, of course, is an extreme case. The actual decline is expected to be between the two extremes.

The decrease in strength at high temperatures thus appears to be related to change in the elastic–elastic load transfer to elastic–plastic load transfer. High composite strength to elevated temperatures may be thus obtained by avoiding any plastic deformation in the matrix as well as by keeping the matrix modulus high. This may be done by avoiding any residual glass phases in the matrix and utilizing refractory glass-ceramic phases. In addition, if whiskers with high aspect ratios, i.e. 50 or above, are available, these whiskers would increase the composite strengths substantially at elevated temperatures. Fig. 10 shows the expected variation in average fibre stress for the cordierite–W1 system. For the anorthite–W2 system also a very similar calculation may be carried out with similar results. The causes of declines in strength are thus expected to be the same for both the cases.

3.4. Modulus of the composites

The composite moduli may be calculated by using Halpin–Tsai equations [16]. The equations are given as

$$\frac{E_L}{E_M} = \frac{1 + 2(l/d)(\eta_L V_f)}{1 - \eta_L V_f} \tag{6a}$$

and

$$\frac{E_T}{E_M} = \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \tag{6b}$$

where

$$\eta_L = \frac{(E_f/E_M) - 1}{(E_f/E_M) + 2(l/d)}$$

and

$$\eta_T = \frac{(E_f/E_M) - 1}{(E_f/E_M) + 2}$$

where E_f and E_M are fibre and matrix moduli, l/d is the aspect ratio and V_f is the volume function of fibres; E_L and E_T then give longitudinal and transverse moduli of an oriented short-fibre composite. The modulus of a composite with randomly oriented fibres is obtained from

$$E_c = (3/8)E_L + (5/8)E_T \tag{7}$$

The theoretical modulus calculated for the cordierite–W1 whisker system is 209 GPa as opposed to experimentally measured modulus of 186 GPa. For the modulus calculation the aspect ratio of the whiskers was assumed to be 7, equal to the measured mean aspect of the W1 whiskers. In spite of this simplifying assumption there is a good correlation between the predicted modulus and the experimentally obtained modulus. For the anorthite–W2 whisker system the predicted modulus is 161 GPa assuming an aspect ratio of 11.8 (equal to the mean) and the experimentally obtained modulus is 159 GPa. The prediction is very close to the experimental values in this case. For both of the calculations the whisker modulus was assumed to be 579 GPa, the value obtained by experimental measurements on the long silicon carbide whiskers grown by the VLS process [17]. Based on these results, Halpin–Tsai equations may be assumed to be applicable to whisker-reinforced glass-ceramic materials.

Fig. 11 shows the measured Young's modulus, shear modulus, and Poisson ratio for the cordierite–W1 whisker system at 25 vol % fraction whiskers as a function of temperature. The Young's modulus declines from 186 to 165 GPa and the shear modulus declines from 73 to 65 GPa in the temperature range 25–1100 °C. The Poisson ratio varies between 0.25 and 0.26 in this temperature range.

Fig. 12 shows the variation of the Young's modulus, shear modulus and Poisson's ratio for the anorthite–W2 whisker. The Young's modulus declines from 159 to 148 GPa shear modulus from 62 to 59 GPa in the temperature range 25–1000 °C. Poisson's ratio varies from 0.28–0.25 in the same temperature range.

3.5. Fracture toughness

Improvements in fracture toughness of brittle glass-ceramics is also very important if these materials are to be used for load-bearing applications. It has been shown earlier [7] that whisker reinforcement of glass results in up to three-fold improvement in the fracture toughness. The fracture toughness of the composites was measured by the single-edge notch bend (SENB)

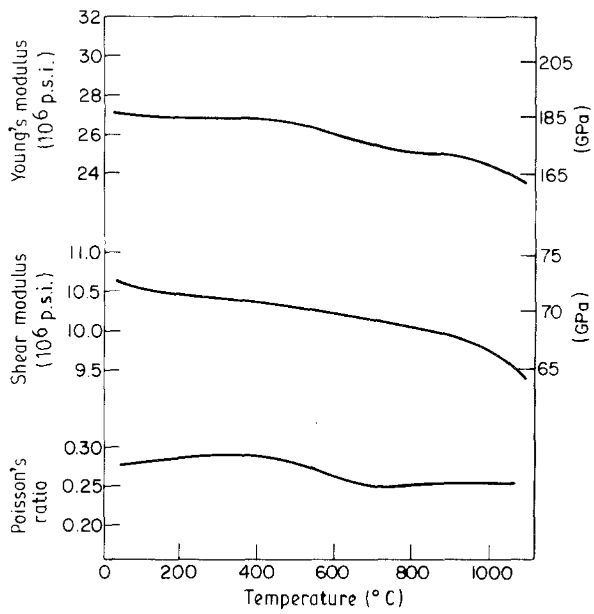

Figure 11 Young's modulus, shear modulus and Poisson's ratio as a function of temperature for cordierite–W1 composite.

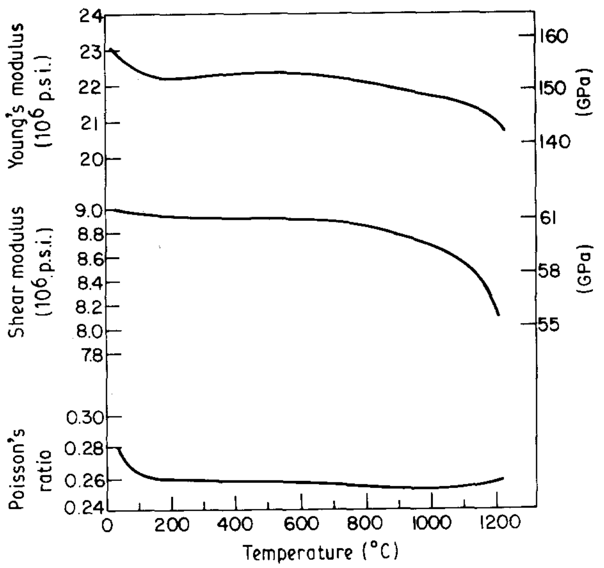

Figure 12 Young's modulus, shear modulus and Poisson's ratio as a function of temperature for anorthite–W2 composite.

technique. It has also been shown [7] that for whisker-reinforced glass matrix composites the SENB method results in more conservative measurements than the chevron notch method. The details of the test methods are given elsewhere [7]. Fig. 13 shows the relationship between the whisker volume fraction and fracture toughness for the cordierite-W1 whisker system. The matrix fracture toughness is 1.4 $\text{MPa m}^{1/2}$. The addition of whiskers results in substantial increases in fracture toughness and at 25 vol % fraction whiskers the fracture toughness is 5.8 $\text{MPa m}^{1/2}$. This four-fold increase in fracture toughness is very significant.

The increase in fracture toughness is obtained essentially because of additional energy absorbing mechanisms such as crack deflection, whisker pull-out, debonding, etc. On examination of several fracture surfaces, crack deflection was found to be the main energy absorbing mechanism. There was little or no evidence of whisker pull-out. Fig. 14 shows a scanning electron micrograph of the fracture surface of a cordierite–W1 whisker composite. As seen from the figure, crack deflection was predominant. A widely quoted theory [15] has been published to predict the increase in strain energy release rate, when the crack

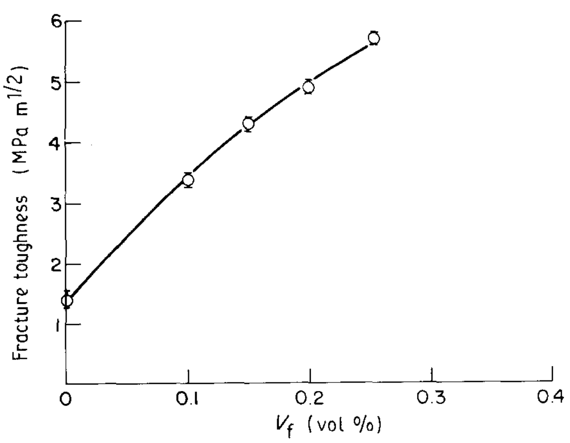

Figure 13 Fracture toughness of cordierite–W1 composite as function of volume fraction of whiskers.

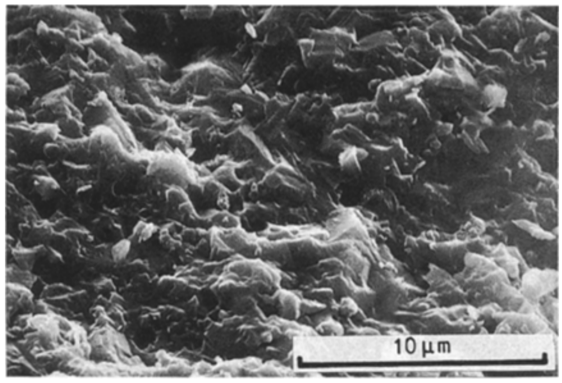

Figure 14 Fracture surface of cordierite–W1 composite.

deflection processes are the predominant energy absorbing mechanisms. Relative strain energy release rates (G_c/G_m where c and m refer to composite and matrix, respectively) have been derived as a function of volume fraction and aspect ratio. At an aspect ratio of 12 and volume fraction of 25%, the predicted ratio of strain energy release rates is 4. The predicted composite fracture toughness, K_{IC}, may be obtained from this as follows

$$\frac{E_c}{E_m}\frac{G_c}{G_m} = \frac{K_{ICc}^2}{K_{ICm}^2} \quad (8)$$

From the known matrix and composite moduli we find:

for the cordierite–W1 system

$$\frac{K_{ICc}}{K_{ICm}} = 2.4$$

for the anorthite–W2 system

$$\frac{K_{ICc}}{K_{ICm}} = 2.77$$

For the cordierite–W1 system the experimentally obtained ratio is 4.14 and for the anorthite–W2 system the ratio is 3.46. The experimentally obtained values of fracture toughness of composites are thus substantially higher than predicted by the theory although mean aspect ratios are lower than 12 in each case. The theory thus does not predict the toughness improvements obtained by whisker reinforcement of glass-ceramics very well. A recent study [18] on whisker-reinforced ceramics has shown that processes such as whisker bridging and pull-out result in additional improvements in fracture toughness of whisker composites. Such processes may also occur in the composites described in this study, which may result in the higher than predicted fracture toughness increases based on crack deflection mechanisms alone. The experimentally obtained relative fracture toughness for the cordierite–W1 system is higher than the relative fracture toughness of the anorthite–W2 system, although the mean aspect ratio is higher for the anorthite–W2 system (11.8) compared to cordierite–W1 (8) system. The reason for this may be related to the higher absolute mean length of W1 whiskers (13.3 µm) compared to W2 whiskers (8.5 µm). Thus, although high aspect ratio is important to improve fracture toughness, high absolute length is relatively more important.

3.6. Thermal properties of the composites

Composite materials are used in engineering applications where transport properties such as electrical conduction, heat conduction, etc., are important. Whisker-reinforced glass-ceramics are expected to be used in high-temperature applications where properties such as thermal shock and thermal conductivity may be important. In some heat engine applications low thermal conductivity may be important to prevent heat losses and improve engine efficiency, whereas in other applications thermal shock resistance might be more important. The thermal expansion coefficients and the thermal conductivities of the two composite systems, i.e. cordierite–W1 and anorthite–W2, have been measured and are presented in Figs 15–18. The coefficient of thermal expansion to 1000 °C is 36×10^{-7} and $46.1 \times 10^{-7}\,°C^{-1}$ for the cordierite-W1 and anorthite–W2 whisker systems, respectively.

The thermal conductivities of the two composite systems are shown in Figs 17 and 18. For the cordierite–W1 composite the conductivity gradually decreases from 5.8 to 3.5 $W\,m^{-1}\,K^{-1}$ in the temperature range 25–1200 °C. The anorthite–W2 composite, however, shows a different behaviour. The conductivity is 9.46 $W\,m^{-1}\,K^{-1}$ at room temperature, significantly higher than the cordierite–W1 system. There is a significant drop in conductivity with temperature and at 500 °C the conductivity is 4.3 $W\,m^{-1}\,K^{-1}$. From 500–1200 °C, the conductivity does not vary substantially. The thermal conductivity versus temperature relationship for the two cases is thus different. There is a gradual decrease for the cordierite–W1 composite, whereas for the anorthite–W2 composite there is a substantial drop from room temperature to 500 °C and very little change beyond 500 °C.

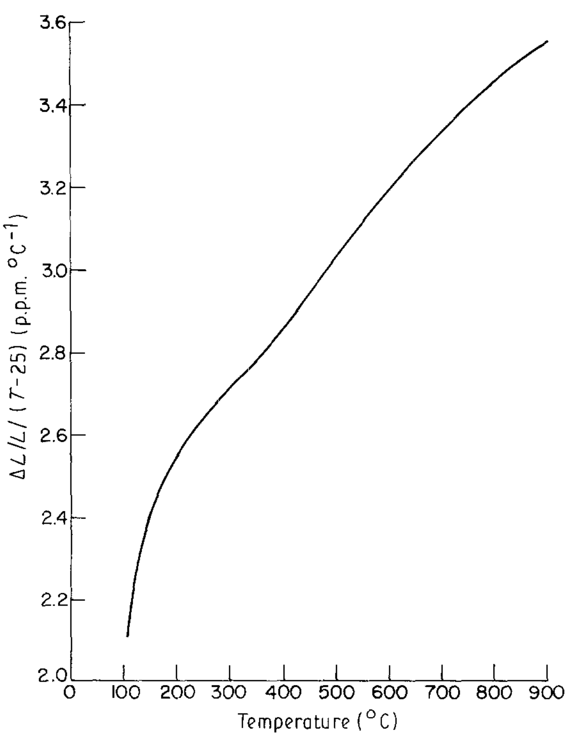

Figure 15 Thermal expansion of cordierite–W1 composite.

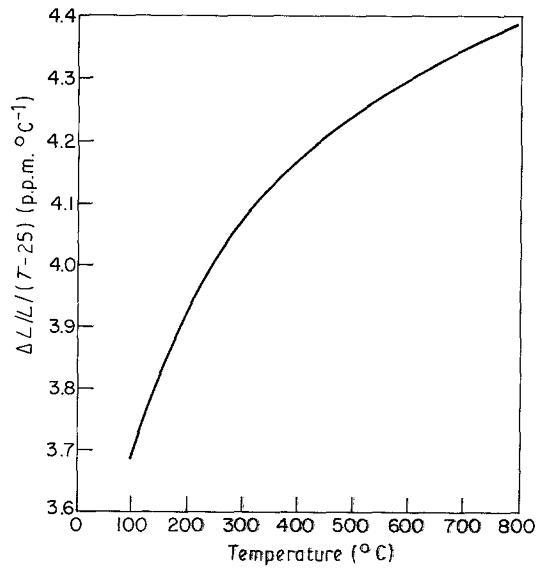

Figure 16 Thermal expansion of anorthite–W2 composite.

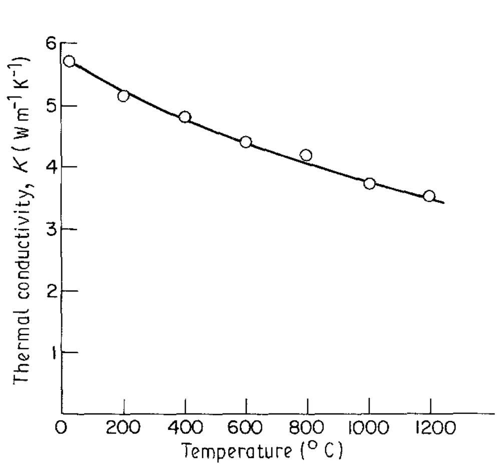

Figure 17 Thermal conductivity of cordierite–W1 composite as a function of temperature.

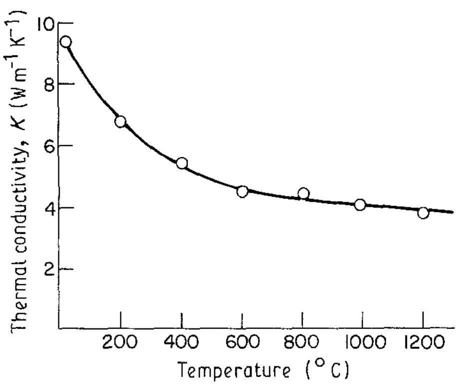

Figure 18 Thermal conductivity of anorthite–W2 composite as a function of temperature.

The thermal conductivity measurements were carried out by a laser flash technique.

A comparison of the thermal and mechanical properties of the two composite systems is shown in Table II.

4. Conclusions

It was found that silicon carbide whisker-reinforcement of glass-ceramics results in several-fold improvement in strength, toughness and modulus of the

TABLE II Properties of whisker-reinforced glass-ceramics

Property	Cordierite–W1 system		Anorthite–W2 system	
	25 °C	1000 °C	25 °C	1000 °C
Flexural strength (MPa)	414	392	380	330
Fracture Toughness (MPa $m^{1/2}$)	5.8	5.0	5.2	4.5
Elastic modulus (GPa)	186	165	158	151
Poisson's ratio	0.27	0.25	0.28	0.27
Thermal conductivity ($W m^{-1} K^{-1}$)	5.8	3.75	9.46	4.10
CTE (25–1000 °C), ($10^{-6} °C^{-1}$)	–	3.62	–	4.61

matrices. The improvement in the mechanical performance is dependent on whisker volume fraction and whisker aspect ratio. The relationship of the composite strength to the whisker volume fraction is nonlinear. At high whisker volume fractions the composite strengths are higher than may be expected based on a linear relationship. The decrease in critical aspect ratio with increase in volume fraction is the cause of this nonlinear relationship.

At elevated temperatures there is a decrease in the flexural strength of the composites. Reduced load transfer efficiency of the matrix is the cause for this decline. At elevated temperatures particularly above 1000 °C the matrix does not remain perfectly elastic, as it is at room temperature. This results in a substantially higher critical aspect ratio necessary for load transfer. The low aspect ratios of the available whiskers thus result in a decrease in the composite strengths. Very fine diameter whiskers (< 1 μm) are difficult to disperse. The agglomeration of whiskers also results in stress concentrations and consolidation problems.

Fracture toughness of the matrices increases several fold on whisker reinforcement. The increases obtained in fracture toughness are substantially higher than predicted by crack deflection-based theory. The composite moduli may be calculated with reasonable accuracy using Halpin–Tsai equations.

The room-temperature and elevated-temperature flexural strengths of the composites may be substantially increased by increasing the whisker diameter to 3–5 μm and increasing the mean aspect ratio of whiskers to 20 or above. The strength decline at elevated temperatures may be minimized by eliminating any residual glassy phases as well as using a high-modulus refractory matrix to eliminate plastic deformation.

The thermal conductivity or the thermal expansion of the composites may be controlled by using an appropriate matrix. The cordierite–W1 and anorthite–W2 system are examples where thermal conductivity is similar although expansions are substantially different.

Because of the availability of a large number of glass-ceramics with a variety of compositions, which in turn control thermal and mechanical properties, it is possible to obtain whisker-reinforced composites with properties tailored for a given application. Thus, whisker-reinforced glass-ceramics are a new class of refractory high-performance materials. For large-scale applications where net shape parts are required for duty at elevated temperatures, these composites may be particularly useful because of the economical glass-processing methods that may be employed.

Acknowledgements

We thank J. F. Mach, M. J. Roach, M. Dandrea, and personnel of Composite Fabrication Center and Corporate Analytical Services group at the Sullivan Park Research Center of Corning, Incorporated, and Professor D. P. H. Hasselman, VPI, Blacksburg, Virginia, for thermal diffusivity measurements.

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Received 20 November 1989
and accepted 19 November 1990