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Fracture Sources and Processing Improvements in SiC-Whisker-Reinforced Mullite–Zirconia Composites

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Abstract

Hot-pressed, SiC-whisker-reinforced mullite–ZrO_2 composites were processed by using two homogenization methods. In method A, the whiskers were admixed to the matrix powder by tumbling. In method B, the whiskers were first ultrasonically dispersed, then separated from coarser impurities by sedimentation, and finally tumbled with plastics balls to reduce their aspect ratio to <20. The composites processed according to method A failed as a result of large inclusions and low-density whisker agglomerates. Method B composites exhibited far better strengths. Correlation between processing, whisker distribution, and strength is discussed.

Heißgepreßte, SiC-Whisker-verstärkte Mullit (–ZrO_2)-Komposite wurden nach zwei Aufbereitungsverfahren hergestellt. In dem einen Verfahren (A) wurden die Whisker nur durch Taumeln dem Matrixpulver zugemischt, während in dem zweiten Verfahren (B) die Whisker zunächst mittels Ultraschall dispergiert, danach durch Sedimentation von groben Verunreinigungen getrennt und anschließend durch Taumeln mit Plastikkugeln auf kürzere Aspektverhältnisse reduziert wurden. Die nach Verfahren B hergestellten Komposite wiesen deutlich verbesserte Festigkeit auf. Der Zusammenhang zwischen Aufbereitung, Whiskerverteilung und Festigkeit wird diskutiert.

On a élaboré des composites mullite–ZrO_2 renforcés par whiskers de SiC, pressés à chaud, par deux méthodes d'homogénéisation. Dans la méthode A, les whiskers étaient mélangés à la matrice par agitation. Dans la méthode B, les whiskers étaient d'abord dispersés par ultrasons puis séparés des impuretés grossières par sédimentation et enfin raccourçis par agitation à l'aide de balles de plastique jusqu'à un rapport d'élongation <20. La rupture des composites élaborés selon la méthode A était causée par des inclusions de grande taile ou par des agglomérats de whiskers de basse densité. Les composites préparés selon la méthode B présentaient des résistances mécaniques bien supérieures. On discute ici de la relation existant entre l'élaboration, la distribution des whiskers et la résistance mécanique de ces matériaux.

1 Introduction

The application of ceramics as engineering materials has been limited by their relatively poor reliability arising from their brittle nature. According to the Griffith fracture criterion, the strength can be enhanced by increasing fracture toughness and by decreasing flaw size. ZrO_2-toughening, SiC-whisker-reinforcement, and combinations of the two toughening methods have been proven to be effective in increasing fracture toughness.[1–5] High strength and therefore reliability critically depend on the fabrication processing used to disperse whiskers homogeneously and to minimize the flaw size.

Initial efforts in developing SiC-whisker-reinforced mullite–zirconia composites have been undertaken to explore fabrication processing, to characterize the fracture origins in the composites, and, iteratively, to

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improve the processing. Some factors that affect flaw formation during powder processing have been considered. The work is intended to be of practical value for developing whisker-reinforced ceramic-matrix composites.

2 Experimental Procedure

Starting materials used for the preparation of the composites were fused mullite,* ZrO_2‡ and SiC whiskers.§ Properties of the SiC whiskers (Tokamax) are summarized in Table 1. The mullite and ZrO_2 powders were milled in an attritor with alumina grinding media ($90\%Al_2O_3$–$10\%SiO_2$) for 4 h in isopropanol and then screened through a 32-μm sieve.

Table 1. Properties of SiC whisker (Tokamax)

Diameter	0·3–1·0 μm
Length	30–60 μm
Density	3·19 g/cm^3
Bulk density	0·1 g/cm^3
Tensile strength	3–14 GPa
Young's modulus	400–700 GPa
Crystal type	β
SiC particulate content	less than 1 wt%
Free carbon	negligible
SiO_2, Si_3N_4 etc.	trace

In attempting to get a homogeneous mixture of SiC whiskers and matrix powders, two powder processes were used. The flow charts of the two processes are shown in Figs 1 and 2.

Powder Processing A (Preliminary Process): SiC whiskers (15 g) were tumbled in 500 ml isopropanol for 20 h and then mixed with mullite or mullite–ZrO_2 powder for 12 h under the same tumbling conditions.

Powder Processing B (Improved Process): SiC whiskers (20 g) were ultrasonically dispersed in 500 ml isopropanol and then poured into 5 litre isopropanol in a glass cylinder. After sedimentation for 20 minutes, the large particles and agglomerates that settled at the bottom were removed. The purified whiskers were tumbled for 12 h in isopropanol with the help of plastics balls (of 3-mm diameter) and then mixed with mullite or mullite–ZrO_2 powder for 4 h by the same tumbling procedure.

* Dynamullit—351 mesh, Dynamit Nobel AG, D-5210 Troisdorf-Oberlar, FRG: in wt% 76·8% Al_2O_3, 22·9% SiO_2, 0·01TiO_2, 0·05 Fe_2O_3, 0·20 Na_2O, 0·04 CaO and MgO.
‡ SC20, Magnesium Electron, Ltd, Manchester, UK.
§ Tokamax, Tokai Carbon Co., Ltd, Tokyo, Japan.

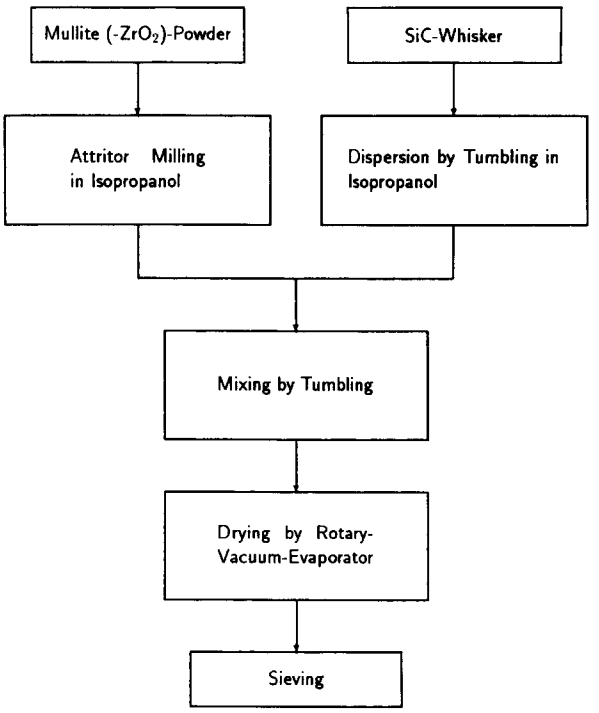


Fig. 1. Flow chart of powder processing A.

In order to avoid the separation of whiskers from matrix powders, a rotary-vacuum evaporator was used to dry the mixed slip at 80°C. The dried powder/whisker mixtures were screened through a 315-μm sieve, cold-pressed in a steel die, and hot-pressed in a BN-washed graphite die in flowing Ar. The hot-pressed discs (35 mm in diameter and

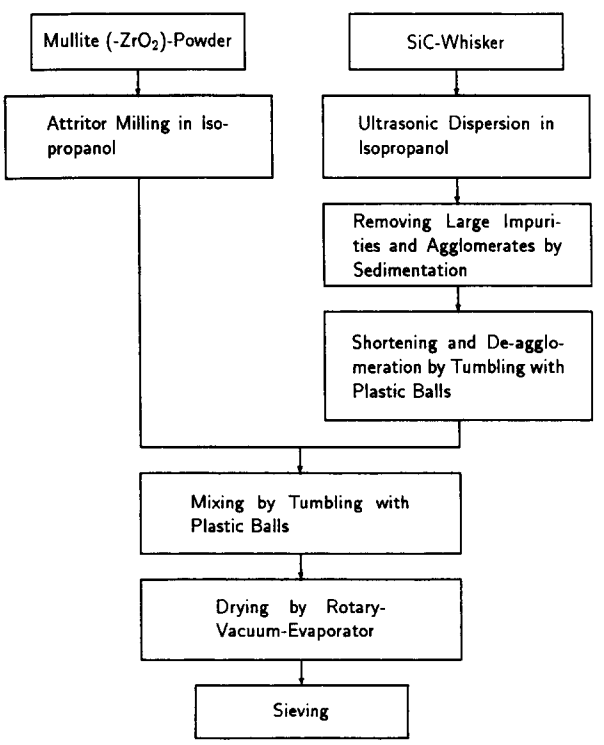


Fig. 2. Flow chart of powder processing B.

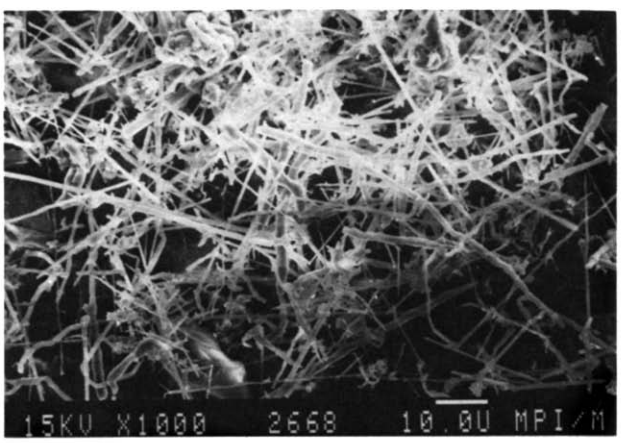
5 mm thick) were cut into rectangular bend bars (28 × 3·5 × 2·5 mm). The tensile surface was perpendicular to the hot-pressing (HP) direction and polished. The flexural strength was measured by four-point bending (20/7 mm), five or six specimens being tested for each condition.

The SiC whiskers and fracture surfaces of the composite specimens were examined by SEM. The Debye–Scherrer X-ray-diffraction technique was used to analyze the impurity particles collected from the SiC whiskers during sedimentation. Wavelength-dispersion X-ray (WDX) analysis was used to analyze the inclusions.

3 Results

3.1 Characteristics of SiC whisker

SEM observation revealed large impurity particles and hard whisker agglomerates removed from the SiC-whiskers by sedimentation, as shown in Fig. 3.



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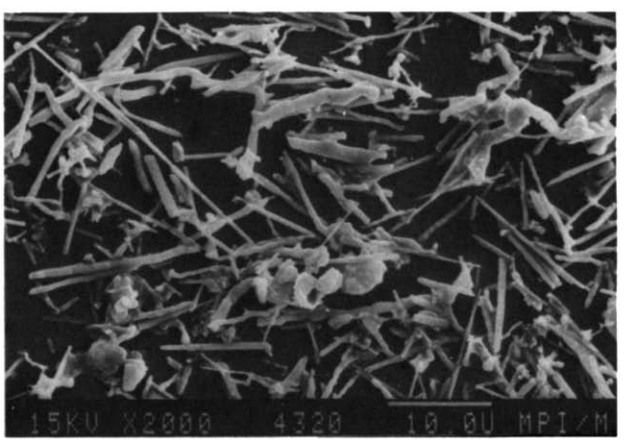
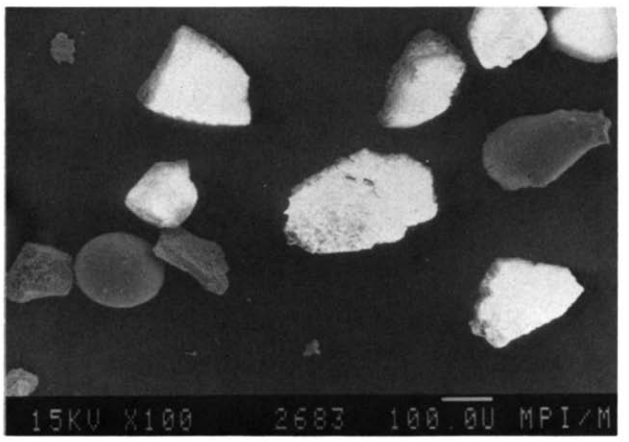
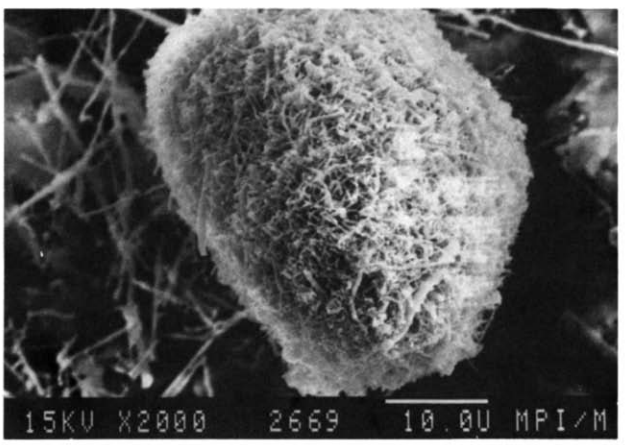


(b)

Fig. 3. SEM-micrographs showing (a) large impurity particles and (b) hard whisker agglomerates removed from as-received SiC whiskers by sedimentation.



(a)



(b)

Fig. 4. SEM-micrographs showing (a) as-received SiC whiskers (Tokamax) with high aspect ratio, agglomerates, and impurity particles; (b) SiC whiskers after sedimentation and 12 h tumbling with plastics balls; large particles (> 10 μm) and whisker agglomerates were removed or broken, and the average length of the whiskers was reduced to about 10 μm.

Powder X-ray-diffraction analysis showed the white particles to be amorphous and the darker particles to be crystalline. The amorphous material was probably a Si–O–C glass phase. The exact crystalline phases could not be identified, though they were iron-rich and could be attracted by a magnet.

Figure 4(a) shows the as-received SiC whiskers with high average aspect ratio (> 50) and impurity particles. Fig. 4(b) shows the whiskers after purification and shortening treatments (Process B). The average aspect ratio was reduced to < 20. Large impurity particles (> 10 μm) and hard whisker agglomerates were removed.

3.2 Bending strength

As shown in Fig. 5, the composite specimens prepared by processing method A display only a small increase or even a slight decrease in strength compared with pure mullite or mullite–zirconia

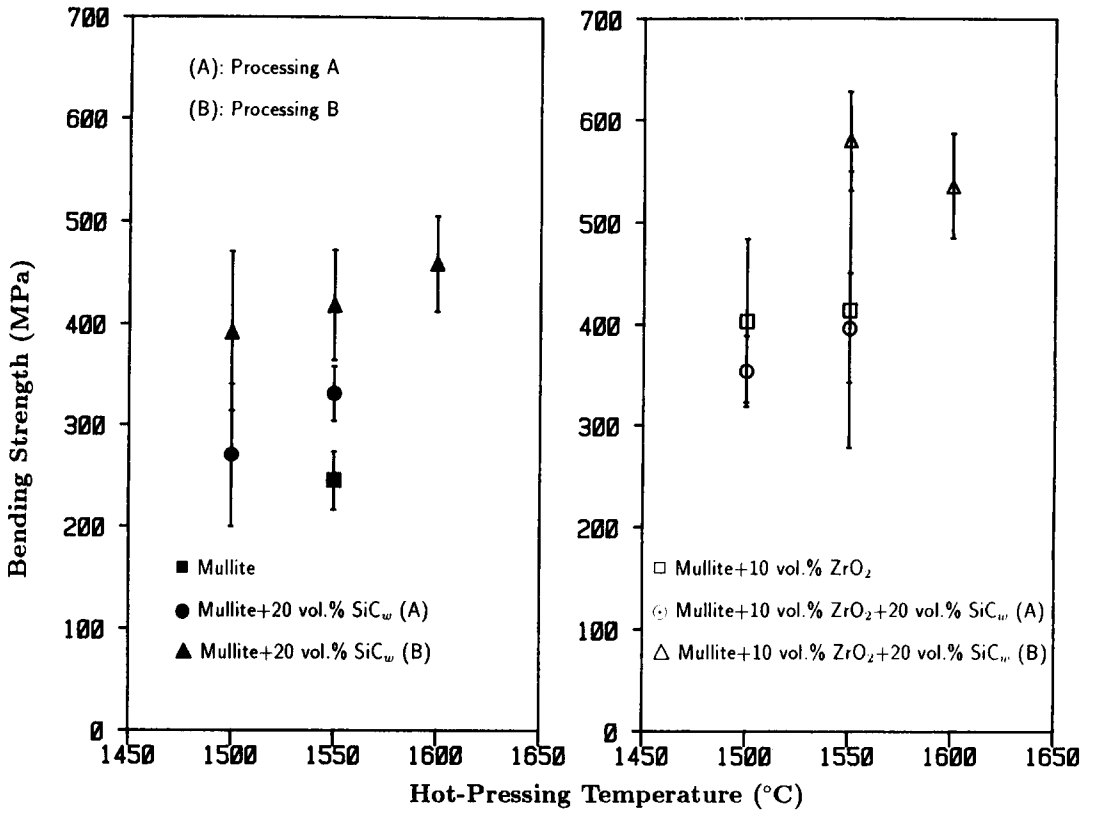
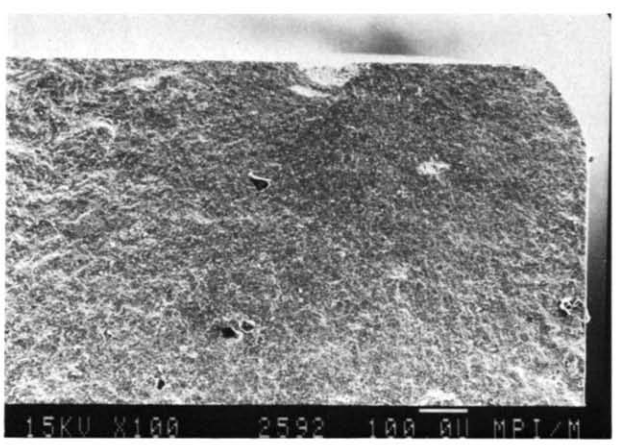
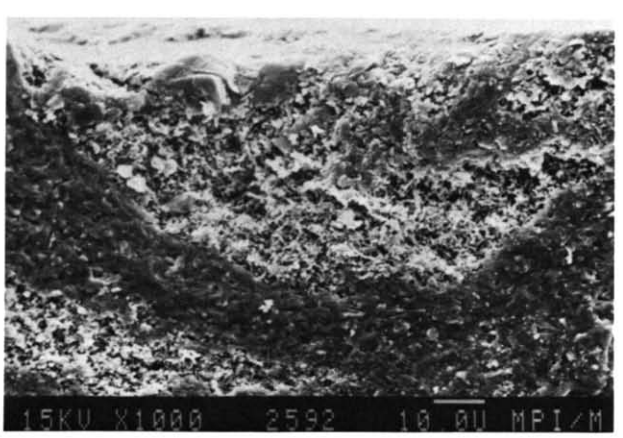


Fig. 5. Room-temperature bending strength of mullite, mullite-matrix composite with 20 vol% SiC whiskers, mullite with 10 vol% ZrO_2, and mullite-matrix composite with 10 vol% ZrO_2 and 20 vol% whiskers as function of powder processing and hot-pressing temperature.

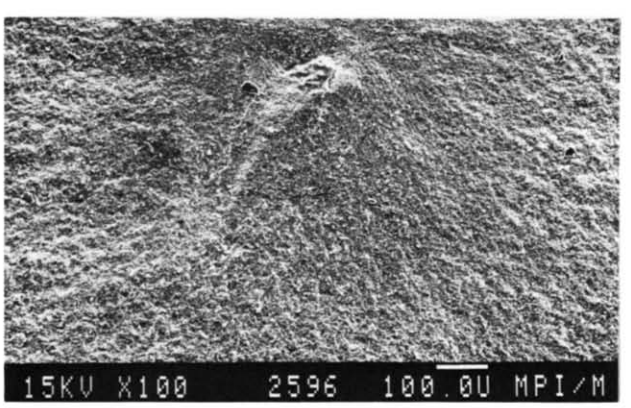


(a)



(b)

Fig. 6. SEM-micrographs showing (a) an elliptical porous region at fracture origin of a mullite-matrix composite with 20% vol% SiC whiskers prepared by processing A, (b) the porous region resulted from whisker agglomerates.



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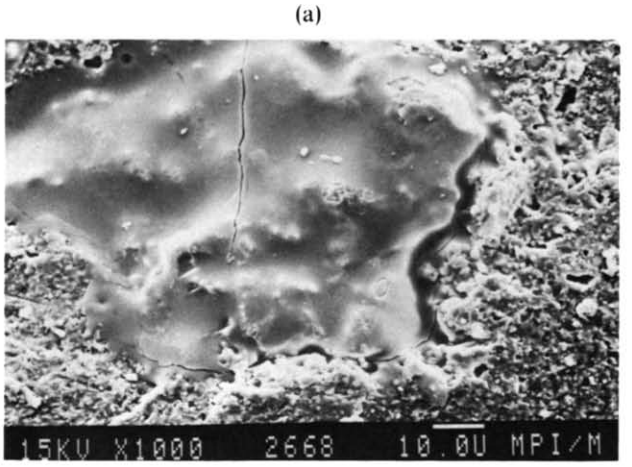


(b)

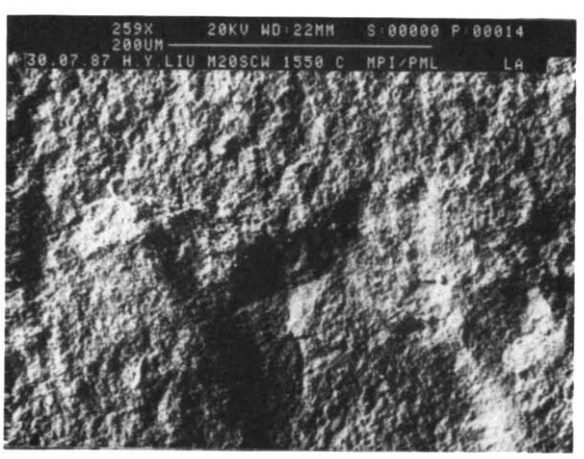
Fig. 7. SEM-micrographs showing (a) a large inclusion at fracture origin of a mullite-matrix composite with 10 vol% ZrO_2 and 20 vol% SiC whiskers prepared by processing A, (b) cracks in and around the inclusion.

ceramics. In contrast, the composite specimens prepared by processing method B showed a clear increase in strength, improvement of approximately 200 MPa being obtainable for specimens hot-pressed at 1550°C.

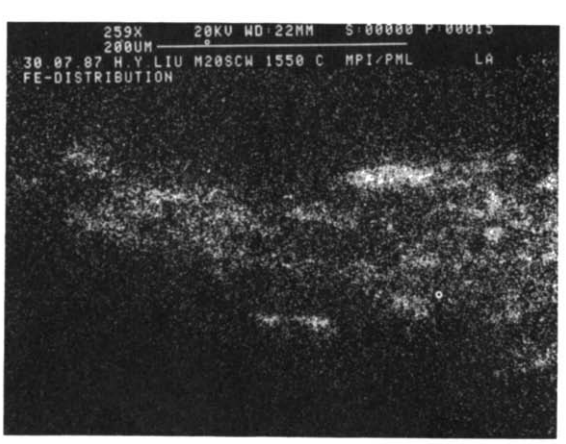
3.3 Fracture sources

The fracture origins in composite specimens prepared by process A were easily located by fractography. They were mainly of two kinds. One was a crack-like, extensive porous region resulting from whisker agglomerates (Fig. 6); the other one was a result of large inclusions (Fig. 7). The sizes of both flaws were about 100 μm. WDX analysis revealed the large inclusions on the fracture surface of the composite to be iron-rich (Fig. 8).

In contrast, large porous regions and large inclusions were not found on the fracture surfaces of the composite specimens prepared by process B (Fig. 9).

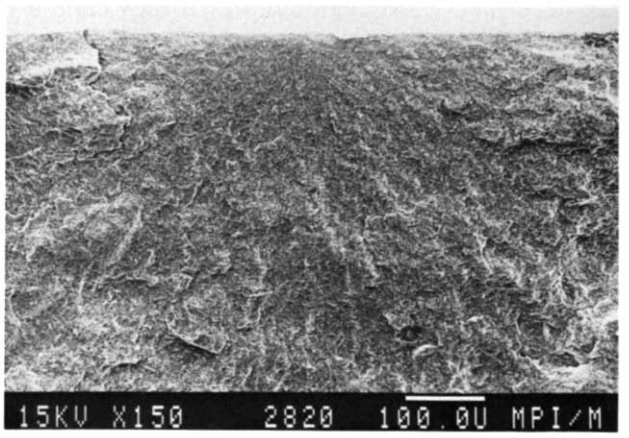


(a)

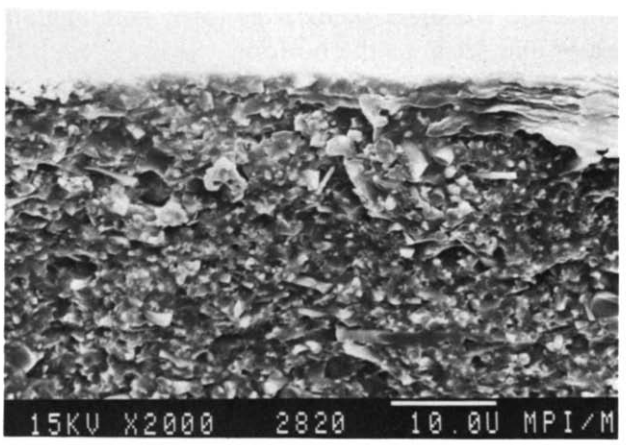


(b)

Fig. 8. SEM-micrographs showing (a) a large inclusion at fracture origin of a mullite-matrix composite with 20 vol% SiC whiskers prepared by processing A, (b) WDX-analysis revealing that the inclusion was an iron-rich particle.



(a)



(b)

Fig. 9. SEM-micrographs (a) and (b) showing fracture origin of a mullite-matrix composite with 10 vol% ZrO_2 and 20 vol% SiC whiskers prepared by processing B; no large processing flaws were identified.

4 Discussion

Strength data and fractography evidence strongly suggest that large inclusions and extensive low-density regions act as fracture sources in the composites prepared by process A. In order to find effective methods to minimize the flaw size, the flaw sources and the factors controlling the formation of flaws during the fabrication process need to be identified and controlled.

4.1 Large inclusions and hard whisker agglomerates

Since attritor-milled mullite–ZrO_2 slip was screened through a 32-μm sieve, the whiskers must have introduced the large inclusions and hard agglomerates. The SiC whiskers used for this study were grown by the VLS (Vapor–Liquid–Solid) Process.[6,7] In this process, small liquid drops of iron act as catalysts; some whiskers can grow together. Because of the high aspect ratio, some of the whiskers tend to bundle together to form agglomerates. For convenience, the whisker agglomerates

can be termed 'hard agglomerates' if they cannot be separated by simple tumbling without balls or by ultrasonic treatment. After the growth of the whiskers, large inclusions and hard whisker agglomerates are not completely removed or destroyed. If such whiskers are used for the fabrication of composites without prior treatment, the formation of flaws is to be expected.

Sedimentation proved to be successful in removing large particles and hard whisker agglomerates. For effective purification of the whiskers, it is important for the whisker suspension to have relatively good stability. It is difficult to remove the impurity particles and hard whisker agglomerates when the whiskers themselves form soft agglomerates and settle to the bottom.

4.2 Soft whisker agglomerates

Suspension stability with respect to agglomeration is determined by particle surface charge, London–Van der Waals forces, and steric effects. Bleier[8,9] found that, of these factors, London–Van der Waals forces are the most important for SiC suspensions prepared in organic liquids. The Van der Waals potential energy of interaction, V_A, for SiC particles (diameter = 0·274 μm) in isopropanol is:

$$V_A = -0{\cdot}91kT$$

Since the average kinetic energy of the suspended particles is $\frac{3}{2}kT$, a liquid with $|V_A| < 1kT$ is a good dispersion medium. Since V_A is proportional to particle size,[9] isopropanol is expected to be a good medium for spherical SiC particles up to a diameter of about 0·3 μm, but unsuitable for SiC whiskers with a submicron diameter and a length of about 10 μm (a typical average size for the whiskers after shortening treatment). There is therefore a tendency to form soft agglomerates in a SiC-whisker–isopropanol suspension. Such agglomerates could be broken by tumbling or by ultrasonic vibration.

When a homogeneously mixed slurry of matrix powders and whiskers is dried without stirring, the whiskers separate from the matrix powders because of their different size and shape. Rotary-vacuum-evaporation prevents this separation, since the stresses resulting from rotation can overcome the Van de Waals attraction. In addition, the increased viscosity of the slurry that is due to evaporation and heating provides increased resistance to sedimentation.

4.3 Packing of whisker and matrix powder

The good purification and mixing techniques mentioned above were not sufficient for the successful fabrication of whisker composites. Milewsky[10,11] has pointed out the importance of controlling the whisker aspect ratio on the basis of considerations of the packaging of fibers and spheres. From this viewpoint, the aspect ratios of the most commerically available whiskers are too high for effective ceramic-powder processing. The packing density of randomly oriented whiskers decreases with increasing aspect ratio. Whiskers with aspect ratio > 50 tend to bundle and clump; the shorter the whiskers, the more easily they can be processed.

In the densification of whisker composites, it has been found that: (i) back stresses will be generated between the non-sintering SiC whiskers and the densifying matrix, which reduce the sintering potential and densification rate,[12] and (ii) a rigid network of whiskers can be formed that inhibits further shrinkage.[13] Although hot-pressing may be used to provide a higher driving force than pressureless sintering, a high green density is helpful to obtain a fully dense composite. Short whiskers (aspect ratio 10–20) are therefore needed.[11] It is also important to note that there is no requirement for long whiskers from the toughening aspect, e.g. the critical aspect ratios for SiC-whisker pull-out for a glass matrix and for a SiC matrix are 20 and 12, respectively.[14]

As shown in Fig. 4, the average aspect ratio of whiskers can be reduced from > 50 to about 20. The reduced aspect ratio benefits a higher green density and a homogeneous dispersion of whiskers in the matrix powders. The combination of efficient whisker shortening with good dispersion/mixing techniques leads to a high final density and reduced flaw size.

5 Conclusions

Whisker reinforcement, ZrO_2-toughening, and the combination of both toughening methods offer great potential for increasing the reliability of ceramic composites. However, realization of this potential depends critically on the fabrication processing. Composite specimens prepared by the preliminary processing did not improve bending strength. Large impurity particles and porous regions (whisker agglomerates) were identified as the fracture sources.

An improved processing method was developed by considering the factors that influence the dispersion and packing processes. Large impurity inclusions and hard whisker agglomerates could be removed by sedimentation. The aspect ratio of the whiskers was reduced to < 20 by tumbling with

plastics balls, which in turn led to a higher green density in the composites. Soft agglomerates could be broken down by tumbling and ultrasonic vibration, and separation of whiskers from matrix powders during drying could be prevented by rotary-vacuum evaporation. Homogeneous distribution of whiskers, high final density, and small flaw size were achieved and led to improved bending strength in the composites.

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References

1. Claussen, N. & Jahn, J., Mechanical properties of sintered, in situ-reacted mullite–zirconia composites. *J. Am. Ceram. Soc.*, **63** (1980) 228–9.
2. Becher, P. F. & Wei, G. G., Toughening behavior in SiC-whisker-reinforced aluminia. *J. Am. Ceram. Soc.*, **67** (1984) C-267–9.
3. Wei, G. C. & Becher, P. F., Development of SiC-whisker reinforced ceramics. *Am. Ceram. Soc. Bull.*, **64** (1985) 298–304.
4. Claussen, N., Strengthening strategies for ZrO_2-toughened ceramics (ZTC) at high temperatures. *Mater. Sci. Engng*, **71** (1985) 23.
5. Becher, P. F. & Tiegs, T. N., Toughening behavior involving multiple mechanisms: whisker reinforcement and zirconia toughening. *J. Am. Ceram. Soc.*, **70** (1987) 651–4.
6. Levitt, A. P. (ed.), *Whisker Technology*. Wiley-Interscience, New York, 1970.
7. Milewsky, J. V., Gac, F. D., Petrovic, J. J. & Skaggs, S. R., Vapor–liquid–solid and melt growth of silicon carbide whiskers. *J. Mater. Sci.*, **20** (1985) 1160–6.
8. Bleier, A., Fundamentals of preparing suspensions of silicon and related ceramic powders. *J. Am. Ceram. Soc.*, **66**(5) (1983) C-79–81.
9. Bleier, A., The roles of Van der Waals forces in determining the wetting and dispersion properties of silicon powders. *J. Phys. Chem.*, **87** (1983) 2493–500.
10. Milewsky, J. V., The packing of fibers and spheres. PhD thesis, Rutgers University, 1973.
11. Milewsky, J. V., Efficient use of whiskers in the reinforcement of ceramics. *Advanced Ceram. Mater.*, **1** (1986) 34–41.
12. Raj, R. & Bordia, R. K., Sintering behaviour of bimodal powder compacts. *Acta Metall.*, **32** (1984) 1003–19.
13. Lange, F. F., Constrained network model for predicting densification behavior of composite powders. *J. Mater. Res.*, **2** (1987) 59–65.
14. Gac, F. D., Milewski, J. V., Petrovic, J. J. & Shalek, P. D., Silicon carbide whisker reinforced glasses and ceramics. Paper presented at the Conference on Composite Materials, Cocoa Beach, FL, 20 January 1984.