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Analysis of Si_3N_4+β-Si_3N_4 whisker ceramics

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Dense Si_3N_4 + β-Si_3N_4 whisker composite ceramics were fabricated by hot pressing powder–whisker mixtures. Addition of β-Si_3N_4 whiskers had no significant influence on the densification behaviour for up to 20 wt% addition. Light microscopy and scanning and transmission electron microscopy were used to study their microstructure and fracture behaviour. An increase in fracture toughness was observed for β-Si_3N_4 whisker additions of up to 10%. The main toughening mechanisms observed were crack deflection, crack branching, whisker–matrix debonding and whisker pull-out.

1. Introduction

Advanced ceramics based on Si_3N_4, SiC and Al_2O_3 are materials that exhibit high hardness, good wear resistance and high strength at elevated temperatures and also good dimensional stability, high elastic modulus and good corrosion resistance. These materials are already used for cutting tools, wear parts and components in heat engines and high-temperature energy conversion systems. However, the reliability of ceramics for structural applications is in general limited by their variability in strength and low fracture toughness. They are also susceptible to subcritical crack growth, which causes delayed failure or static fatigue of components under load. Their variability in strength is caused by inadequate reproducibility of manufacturing techniques (powder production, powder preparation, forming and sintering) and their low fracture toughness is a consequence of the lack of crack tip plasticity in brittle material, while static fatigue is caused by stress corrosion.

The basic ways of improving the reliability of ceramics for structural application are:

1. Improve production techniques, so as to produce materials without large pores, agglomerates of grains, impurities or large grains. This will increase their strength whilst reducing the scatter in strength values [1, 2].
2. Increase their fracture toughness by developing toughened ceramic composites [3, 4].
3. Avoid delayed failure within the planned lifetime of a component by proof testing or by lifetime prediction [5].

The main tasks for improving processing are the development of high-purity, fine-grained powders with good chemical and physical properties and the development of new mixing, forming and sintering techniques. Improvements in fracture toughness can be achieved by developing ceramics reinforced by particle platelets, whiskers or fibres. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), room- and high-temperature testing and non-destructive testing (NDT) all play an important role in developing improved ceramic materials.

Most of the ceramic composites which have been developed so far have contained either an Al_2O_3, mullite ($3Al_2O_3 \cdot 2SiO_2$), SiC or Si_3N_4 matrix [6–12]. Of the Si_3N_4-based materials the most widely studied system has been the Si_3N_4 matrix + SiC whisker composite, while there has only been one previous study of Si_3N_4 + β-Si_3N_4 whisker composites [13].

Whisker reinforcement offers the potential for improvement of fracture toughness due to the outstanding mechanical properties of the whiskers. A significant improvement in fracture toughness has been demonstrated for Si_3N_4 reinforced with SiC whiskers (max. $K_{Ic} = 12.5\ MPa\ m^{1/2}$) [7]. In this study a small amount of whisker pull-out on the fracture surfaces suggested that crack deflection and matrix cracking were responsible for the fracture toughness improvement. In the Al_2O_3 + SiC whisker systems, however, increases in toughness appear to be due to a combination of crack deflection, crack bridging and whisker pull-out mechanisms. It is interesting to note that short whiskers seem to be more effective at crack bridging in this system [14].

In the literature, authors have discussed the different types of strength-degrading defects in Si_3N_4 + SiC whisker and Si_3N_4 + β-Si_3N_4 whisker composites [7, 9, 13]. The most important are porosity, large SiC whiskers, and impurities introduced during whisker

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production or whisker modification. In the case of the β-Si_3N_4-reinforced ceramics, whisker clustering introduced during whisker modification by BN deposition has been reported as a cause of their strength reduction [13]. In Si_3N_4 + SiC whisker composites, clusters of small metal inclusions with composition Co/Fe = 4/1 were found at fracture origins [9].

2. Experimental

The experimental material was Si_3N_4 + 5–30 wt % β-Si_3N_4 whiskers. The Si_3N_4 powder (Starck, W. Germany) had an oxygen content of 1.6 wt %, a carbon content of 0.5 wt % and contained < 500 p.p.m. of other impurities. A mixture of Y_2O_3 and Al_2O_3 powders, both of 99.99% purity, was used as a sintering additive. The β-Si_3N_4 whiskers (Fig. 1) were prepared by self-propagation high-temperature synthesis (SHS) in the Institute of Structural Macrokinetic ASci USSR, Chernogolovka. They had an oxygen content of 0.8 wt % and a mean aspect ratio of 5 [15]. The sintering aid and the whiskers were mixed using one of two different methods (Fig. 2). In the first method a mixture of Si_3N_4 powder, sintering additives and β-Si_3N_4 whiskers was homogenized for 2 h in a polyethylene bottle containing methanol. In the second method the powder mix was prepared by ultrasonic mixing of two suspensions: Y_2O_3, Al_2O_3 and Si_3N_4 in dry acetone and β-Si_3N_4 whiskers in dry acetone. Both suspensions were intensively mixed and then rapidly sedimented. Green compacts, with dimensions of 12 mm × 5 mm, were pressed at 100 MPa in a conventional steel die. The compacts were embedded in BN and then sintered by hot pressing at 1750–1850 °C. The samples were hot-pressed at pressures of 27–32 MPa, applied at 1500 °C during the heating of the samples, and were eventually removed on cooling at 1000 °C. When the samples were not being pressed during the heating/cooling cycle they were kept under a nitrogen atmosphere of 0.1 MPa. The density of the compacts was measured using the mercury immersion method. Some samples were also cold isostatically pressed before hot pressing.

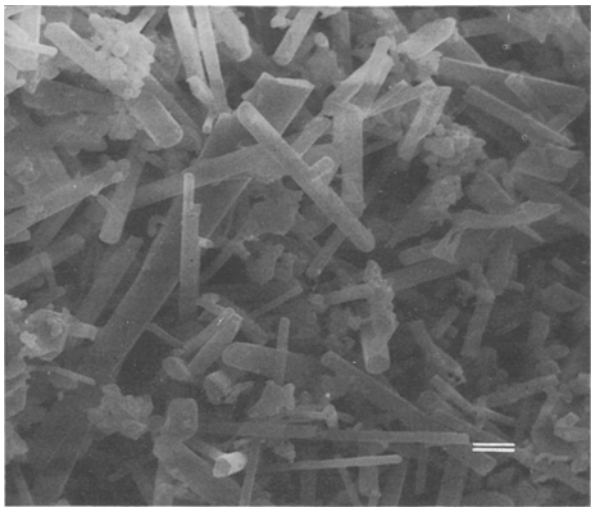


Figure 1 Micrograph of β-Si_3N_4 whiskers (bar = 2 μm).

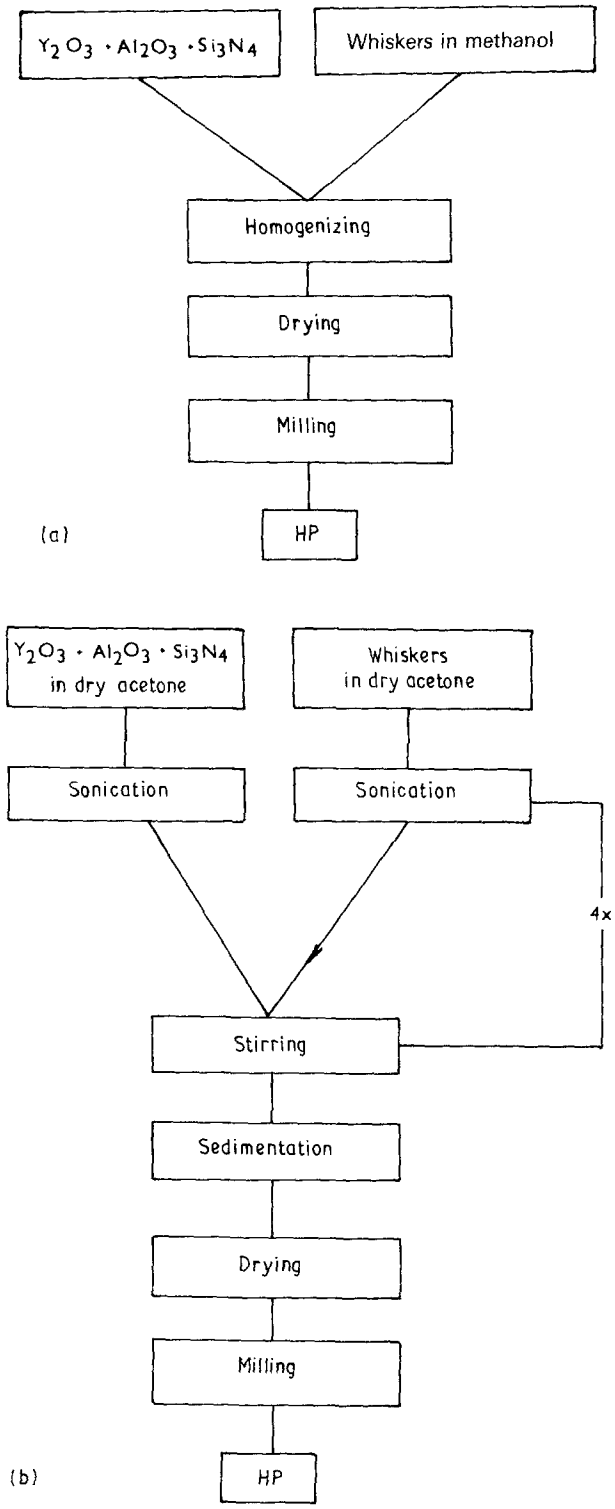


Figure 2 Procedures for processing Si_3N_4 + β-Si_3N_4 whisker composites: (a) homogenizing, (b) stirring.

The microstructure of all of the materials was studied using light microscopy and scanning electron microscopy (SEM). The SEM was fitted with energy-dispersive (EDS) and wavelength-dispersive (WDS) X-ray spectrometers. Before they were examined the samples were either etched at 740 °C in a mixture of K_2CO_3 and NaF or plasma-etched. TEM specimens were prepared by diamond cutting, grinding and polishing, to produce 50 μm thick discs, which were then dimpled and ion beam-thinned. The specimens were coated with a thin layer of evaporated carbon before examination in the microscope. Both X-ray microanalysis and microstructural analysis were made with

a TEM operated at 120 and 200 kV. The fracture characteristics of the specimens were studied by examining fracture lines and fracture surfaces using SEM. The hardness and fracture toughness were measured using Vickers indentation with a load of 10 kg. The values of K_{Ic} were calculated from the formula

$$K_{Ic} = H\, a^{1/2}\, (E/H)^{2/5}\, 10^{Y}$$

where H is the Vickers hardness and a is the semi-diagonal length of the Vickers impression; $Y = \log[(l + a)/a]$, where l is one-half of the median crack length, and E is the Young's modulus [16]. All of the specimens used for indentation fracture toughness tests had relative densities >0.97 of theoretical density (t.d.). Systems containing 0 and 5 wt % β-Si_3N_4 whiskers were prepared by the procedure described in Fig. 2a and the systems containing 10, 20 and 30 wt % of whiskers were prepared by the procedure described in Fig. 2b. The systems with 20 and 30 wt % of β-Si_3N_4 whiskers were hot-pressed at 1850 °C and 32 MPa.

3. Results and discussion

Fig. 3 shows the influence of sintering time (hot-pressing time) on the relative densities of the compacts. The densification behaviour of the materials with 0, 5 and 10 wt % content of β-Si_3N_4 whiskers were similar; however, the behaviour of the 30 wt % systems was very different. It was not possible to sinter the Si_3N_4 + 30 wt % β-Si_3N_4 system to a density of greater than 0.9 t.d., even after hot pressing for 2 h. Fig. 3 shows that for all of the materials the major part of the densification was completed after about 30 min of hot pressing, and practically no increase in density occurred after 60 min. The densities of the systems with 0, 5 and 10 wt % of whiskers after 60 min of hot pressing were all similar. Some additional results for material with 20 wt % of whiskers were also obtained, but have not been included in Fig. 3 because this system was not studied over the full range of hot-pressing times. On the basis of our results and observations, 20 wt % apparently represents a limit for the addition of whiskers in terms of processing difficulties and material quality.

The weight loss of composites prepared by the procedure described in Fig. 2a and hot-pressed at 1750 °C with a pressure of 27 MPa was measured as a function of β-Si_3N_4 whisker content. The addition of β-Si_3N_4 whiskers to Si_3N_4 causes a reduction in its weight loss from 6 wt % for no addition, to less than 3 wt % for additions of 10 wt % or more [15].

The microstructures of the hot-pressed Si_3N_4 + β-Si_3N_4 whisker systems were characterized by a small grain size matrix and elongated β-Si_3N_4 whiskers homogeneously distributed in the matrix. The mean grain size of the matrix was 0.8–0.9 μm, and the mean grain size of the elongated whiskers was 8–10 μm.

The microstructural studies performed using optical microscopy and SEM revealed several types of defects: clusters of large β-Si_3N_4 whiskers, second phases, large β-Si_3N_4 whiskers and microporosity. Clusters of β-Si_3N_4 whiskers were found in all of the materials (Fig. 4). A low number of the clusters were found in the system with 5 wt % of β-Si_3N_4 whiskers, and the highest in the system with 30 wt % of whiskers. It was also apparent from our observations that the composites prepared by the technique described in Fig. 2b contained fewer clusters than the materials prepared according to the procedure described in Fig. 2a. The clusters formed by the whiskers were about 30–50 μm in diameter, and the intergranular phase inside the cluster was thicker than in the matrix.

The clusters in the composites hot-pressed for short times often contained porosity between the whiskers. Other defects, which were observed in all of the materials, were free Si and large β-Si_3N_4 whiskers. The free Si particles (1–5 μm diameter) sometimes formed small clusters. Microporosity was only found in samples which had been hot-pressed for short times, and macropores were only found occasionally. Large β-Si_3N_4 whiskers which were not part of clusters were often surrounded by a coarse region of intergranular phase (Fig. 5).

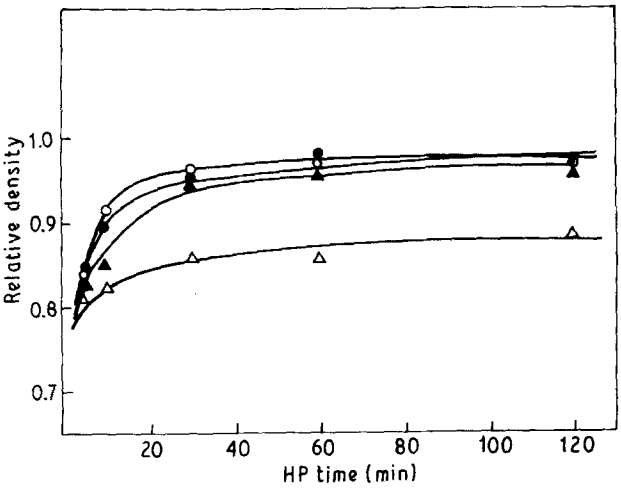


Figure 3 Densification curves for Si_3N_4 + β-Si_3N_4 composites (1750 °C, HP 27 MPa): whisker content (●) 0, (○) 5, (▲) 10, (△) 30 wt %.

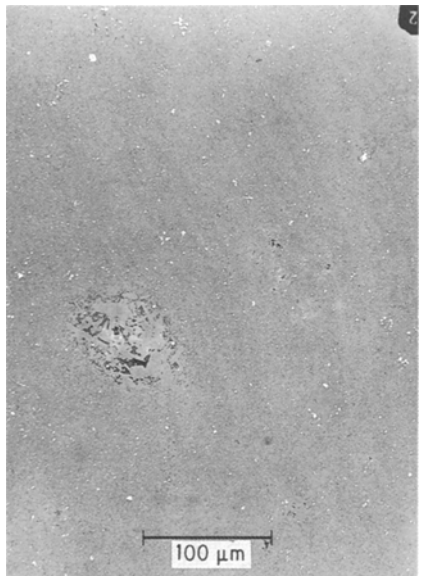


Figure 4 Cluster of whisker in Si_3N_4 + 20 wt % β-whisker system.

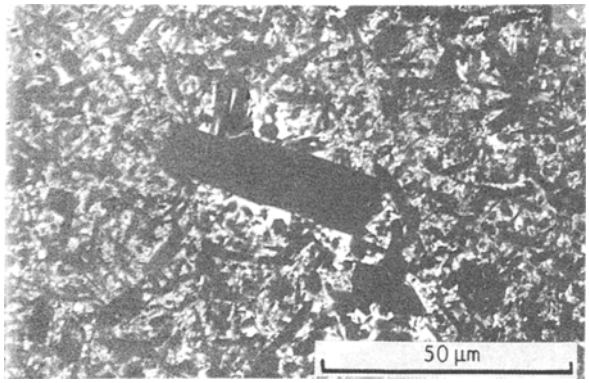


Figure 5 Large β-Si_3N_4 whisker in Si_3N_4 + 10 wt % whisker system.

A detailed analysis of the microstructure was also performed using TEM, which confirmed some of the previous observations made using SEM. For instance, TEM confirmed that large whiskers were sometimes surrounded by large regions of intergranular phase and large Si_3N_4 grains (Fig. 6a). In most cases these large whiskers were surrounded by small Si_3N_4 grains, and in these cases the intergranular phase distribution was usually homogeneous (Fig. 6b). It was found using microdiffraction that the intergranular phase was amorphous.

Using TEM it was possible to obtain more information about second-phase precipitates than was possible using SEM. The precipitates were usually found inside the larger Si_3N_4 grains and only occasionally in the intergranular phase. Precipitates inside the Si_3N_4 grains had irregular shapes and varied greatly in size, and in most cases contained Al and Si. The precipitates in the intergranular phase were often spherical and contained Fe, Cr and Ti but no Si and Al (Fig. 7). Dislocation networks were sometimes found in the larger Si_3N_4 whiskers or grains, and they were often connected to grain boundaries, precipitates or other structural defects (Fig. 8). Dislocations were only very rarely seen in the smaller Si_3N_4 grains.

The fracture characteristics of the materials were studied by examining fracture surfaces and the surface cracks produced by Vickers indentation. The fracture paths showed evidence of several potential toughening mechanisms: crack deflection, crack branching, whisker–matrix debonding, whisker pull-out and bridging (Fig. 9). Crack deflection was the most commonly observed toughening mechanisms on the fracture line. It occurred at the whisker–matrix boundary and was often associated with the cracking of the surrounding matrix and whisker–matrix interfaces. Whiskers with diameters of 5–10 μm appeared to be the most effective at producing crack deflection. Crack deflection was also sometimes found at spherical grains. Extensive whisker–matrix debonding was observed in the crack wake and at the crack front, and was often associated with large β-Si_3N_4 whiskers.

Fig. 10a shows a characteristic fracture surface of the materials with 10 wt % of Si_3N_4 whiskers, on which the cavities left by the pull-out of β-Si_3N_4 whiskers are apparent. Pull-out of whiskers which were parallel and perpendicular to the main crack plane are shown in Fig. 10b and c. Fig. 11a and b, which is a stereo-fractogram, shows that the whiskers in the composites had rough surfaces, which were probably produced by the rupture of adhesive contact between the whiskers and matrix during pull-out since the surfaces of the starting whiskers were smooth. The

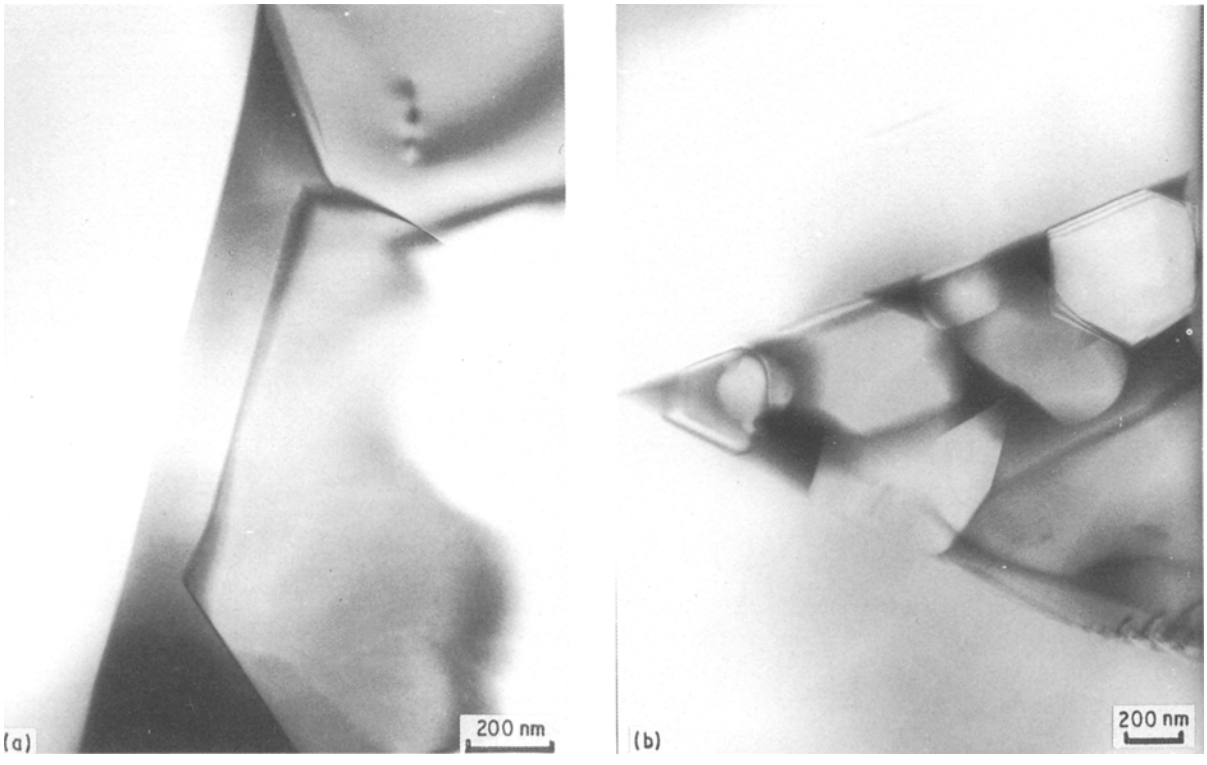


Figure 6 Intergranular phase: (a) between large grains, (b) homogeneous distribution.

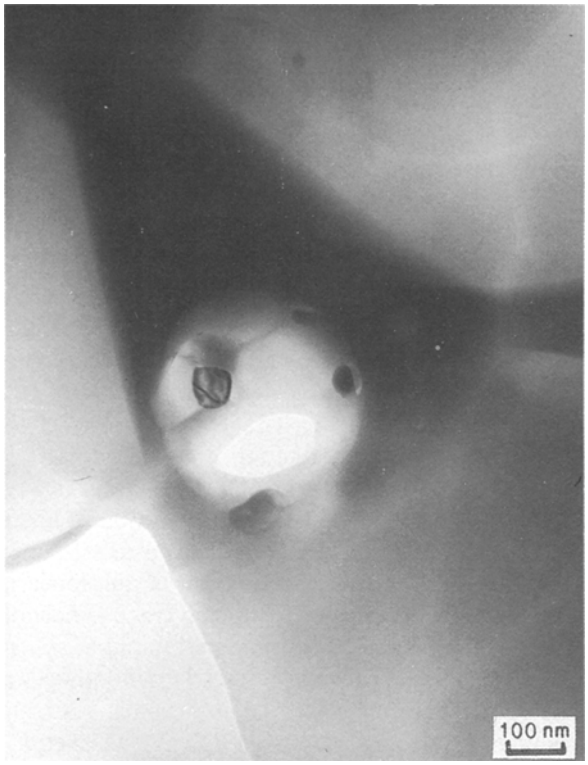


Figure 7 Precipitate in intergranular phase.

Figure 8 Dislocations in Si_3N_4 grains.

surface roughness of the whiskers may affect the sliding friction between the whiskers and matrix in the bridging zone during fracture, and may therefore play an important role in toughening the material. Extremely large β-Si_3N_4 whiskers or clusters usually failed transgranularly and therefore did not contribute to any toughening process. The strength of these large

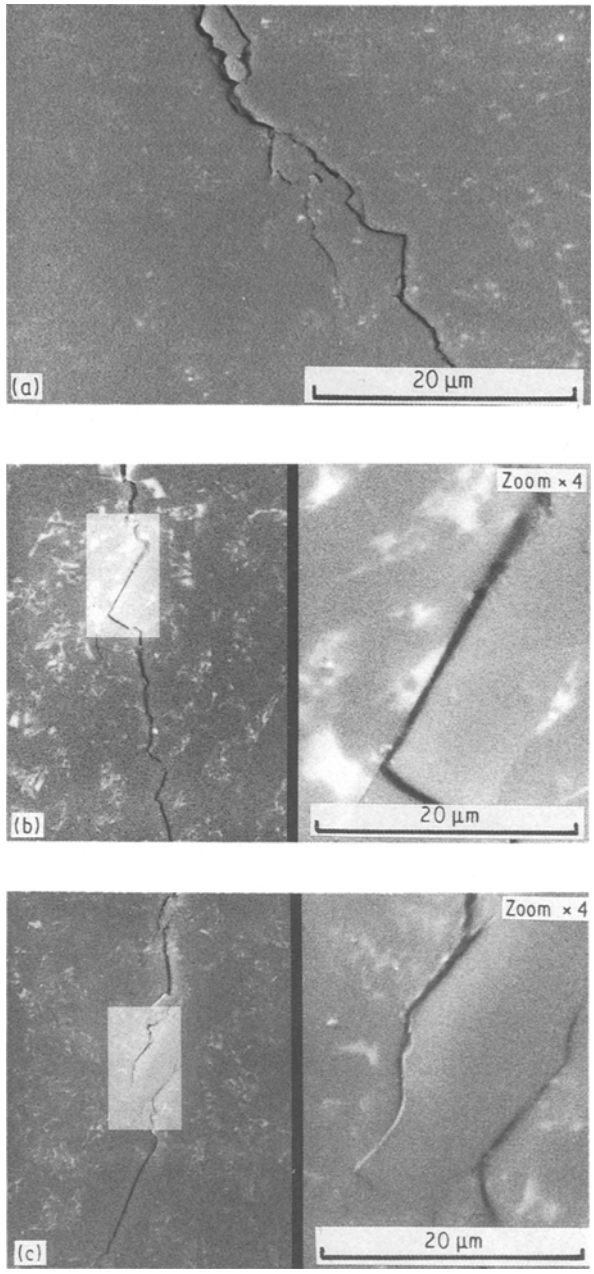
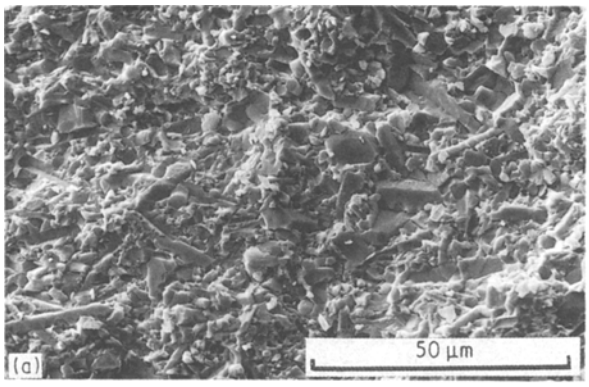
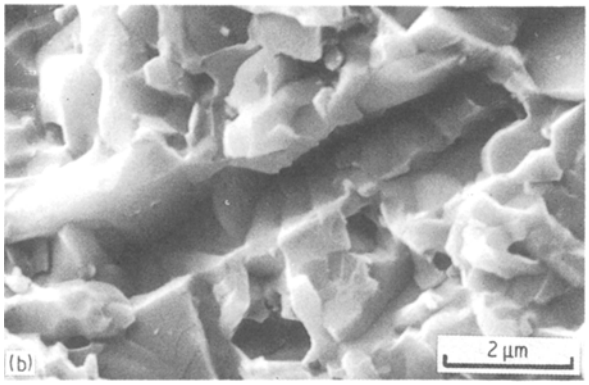


Figure 9 (a–c) Toughening mechanisms observed on fracture line.

whiskers is probably low, and during crack propagation transgranular fracture is presumably easier than intergranular deflection or debonding mechanisms (Fig. 12).

The influence of the whisker content on the hardness of the materials produced for different hot-press times is shown in Fig. 13. The result shows that only materials hot-pressed for 60 min or longer attained a high hardness value. The dependence of fracture toughness on the β-Si_3N_4 whisker content at room temperature is shown in Fig. 14, which also shows the fracture toughness data for Si_3N_4 + SiC whisker composites with different whisker contents reported by other workers [7, 11]. These results show that there is a large difference between the fracture toughness values of different composites, but that in all cases the addition of whiskers increases the fracture toughness of the system.





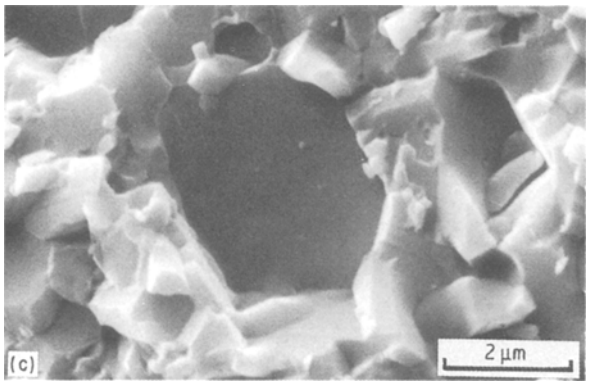
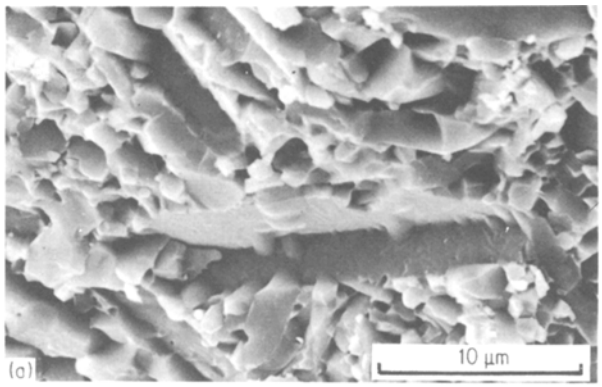


Figure 10 (a–c) Toughening mechanisms observed on fracture surfaces.



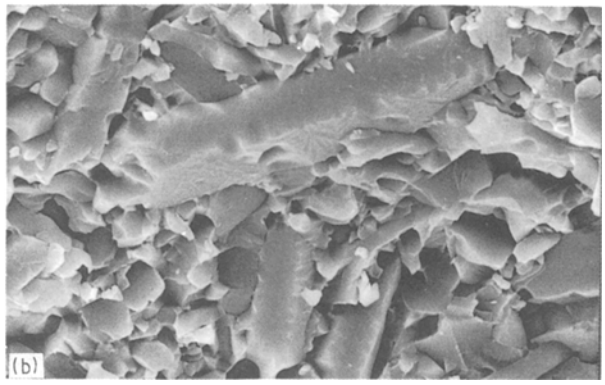


Figure 11 (a, b) Stereo-fractogram of fracture surface of Si_3N_4 + 10 wt % β-Si_3N_4 whisker system.

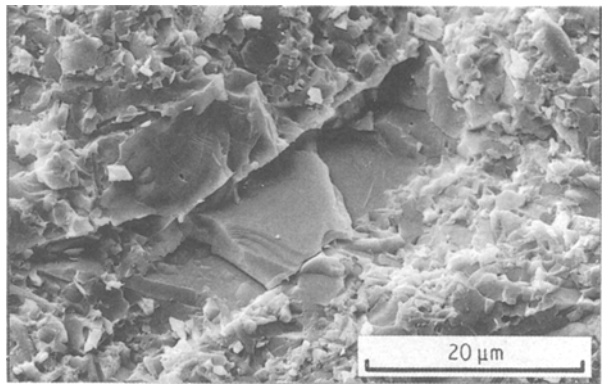


Figure 12 Transgranular failure of large β-Si_3N_4 whisker.

We have observed crack deflection, crack branching, whisker–matrix debonding and whisker pull-out. These toughening mechanisms are sometimes related and are strongly dependent on the debonding between whisker and matrix. Whisker pull-out and crack deflection was most commonly observed for whiskers which were orientated nearly parallel with the plane of the main crack, whereas whisker pull-out perpendicular to the main crack was only occasionally observed and only when the ends of the whiskers were close to the main crack plane. This observation was also made for Al_2O_3 + SiC whisker ceramics [14].

The size and shape of the β-Si_3N_4 whiskers play an important role in the toughening process. The whiskers used for the toughening of ceramic composites reported in the literature had diameters of 0.1–10 μm and high aspect ratios (30 to 40), and the greatest improvements in fracture toughness were achieved by composites with the larger whisker diameters. The diameter of the whiskers used in our work was probably good from the point of view of toughening, but their aspect ratio was probably too low. The low aspect ratio of the whiskers resulted in a short pull-out length which produced only a small increase in fracture toughness. The reason the fracture toughness decreased with increasing whisker content above 10 wt % additions was because of clustering of the whiskers. If materials with a homogeneous whisker distribution and a high whisker content can be prepared, further improvements in fracture toughness will be obtained.

4. Conclusions

1. Si_3N_4 + β-Si_3N_4 whisker composites with high relative densities (>0.97) were successfully prepared

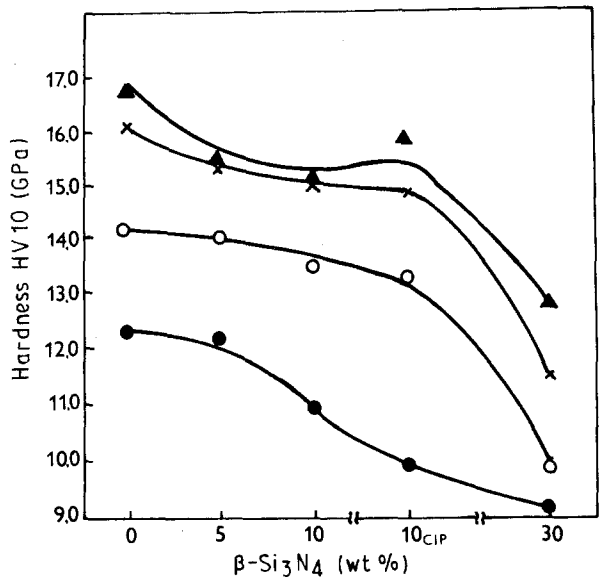


Figure 13 Influence of β-Si_3N_4 addition on hardness for different hot-pressing times: (●) 10, (○) 30, (×) 60, (▲) 120 min.

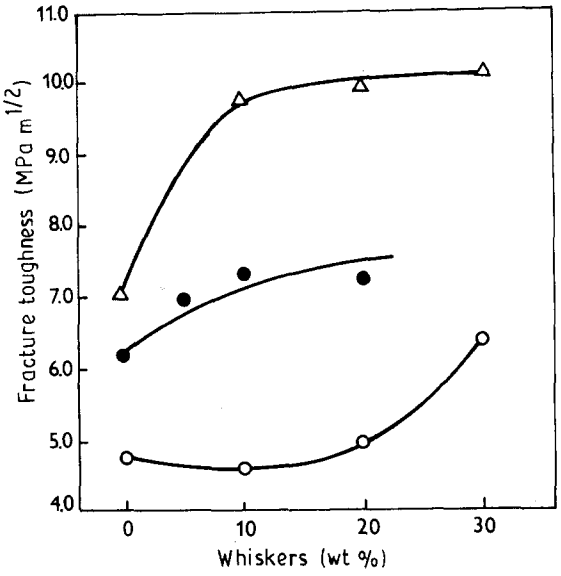


Figure 14 Influence of (●) β-Si_3N_4 and (△, ○) SiC whiskers on fracture toughness: (△) Shalek *et al.* [7], (○) Buljan *et al.* [11].

with small additions of $Al_2O_3 + Y_2O_3$ by hot-pressing at 1750–1850 °C for 1 and 2 h under a pressure of 27–32 MPa.

2. The addition of β-Si_3N_4 whiskers up to 20 wt % had no influence on the densification behaviour of the composites, but at higher whisker contents the maximum attainable density was reduced significantly.

3. The main defects in the material were caused by the presence of large β-Si_3N_4 whiskers in the starting mixture. These formed clusters and caused inhomogenities in the distribution of the intergranular phase.

4. An increase in the fracture toughness of $Si_3N_4 + \beta$-Si_3N_4 whisker composites was observed with increasing whisker content up to 10 wt % addition.

5. The main mechanisms responsible for the toughening were crack deflection, crack branching, whisker–matrix debonding and to a lesser extent whisker pull-out.

6. Future research on $Si_3N_4 + \beta$-Si_3N_4 composites should concentrate on the development of processing techniques which will produce defect-free systems with whisker contents of about 30 wt %. It will also be important to study the influence of whisker characteristics (size, shape) and whisker orientation on interfacial debonding and fracture toughness.

Acknowledgements

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