Journal of the European Ceramic Society **5** (1989) 321–326

Reinforcement of Silicon Nitride Ceramics by β-Si_3N_4 Whiskers

P. Šajgalík

Institute of Inorganic Chemistry, Centre for Chemical Research, Slovak Academy of Sciences, Dúbravská cesta 9, CS-842 36 Bratislava, Czechoslovakia

&

J. Dusza

Institute of Experimental Metallurgy, Slovak Academy of Sciences, Solovievova 47, CS-043 53 Košice, Czechoslovakia

(Received 18 September 1989; revised version received 23 November 1989; accepted 5 December 1989)

Abstract

The silicon nitride based ceramics are reinforced by β-Si_3N_4 whiskers. β-Si_3N_4 whiskers do not influence the sinterability of the composite up to an addition of 10 wt %. The improvement of fracture toughness at room temperature of silicon nitride ceramics reinforced by β-Si_3N_4 whiskers is observed.

Keramiken auf Siliziumnitridbasis wurden mit β-Si_3N_4-Whiskern verstärkt. Bis zu einem Volumenanteil von 10% β-Si_3N_4-Whiskern wurde das Sinterverhaltern der Verbundwerkstoffe nicht beeinflußt. Der Anstieg der Bruchzähigkeit bei Raumtemperatur der verstärkten Siliziumnitridkeramik wurde untersucht.

Des céramiques à base de nitrure de silicium ont été renforcées par des whiskers de Si_3N_4 β. Un ajout de ceux-ci inférieur ou égal à 10% ne modifie pas l'aptitude au frittage du composite. On observe une amélioration de la ténacité à température ambiante de ces céramiques renforcées par des whiskers de Si_3N_4 β.

1 Introduction

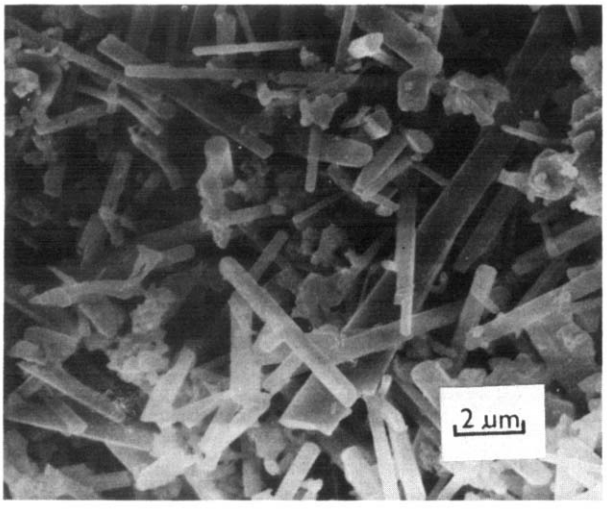
Silicon nitride based ceramics are promising candidates for structural applications. One factor which limits the widespread application of these materials is their brittle failure. SiC fiber (whisker) addition offers a potential for considerable improvement of the material's fracture toughness and strength, because of the superior tensile strength (3 GPa) and tensile modulus (400 GPa).[1] Reinforcing additions must be not only mechanically but also chemically suited to their role. The mechanical suitability mainly concerns the thermal expansion coefficients of SiC and Si_3N_4. Their thermal expansion coefficients are $5{\cdot}2 \times 10^{-6}\,K^{-1}$ (Ref. 1) and $3{\cdot}0 \times 10^{-6}\,K^{-1}$ (Ref. 2), respectively. Chemical compatibility between whiskers and matrix is most crucial at their point of contact. In the case of SiC whiskers and Si_3N_4 matrix composites, reduction reactions could take place, mainly when the oxide additions are used for enhancement of sintering. Both the above-mentioned objections resulted in an idea for replacing SiC whiskers by β-Si_3N_4 rod-like particles (whiskers). In this case the objections against mechanical and chemical suitability of reinforcing additives are unimportant. The aim of the present paper is the estimation of the influence of β-Si_3N_4 whiskers on the sinterability and fracture toughness of silicon nitride based ceramics.

2 Material

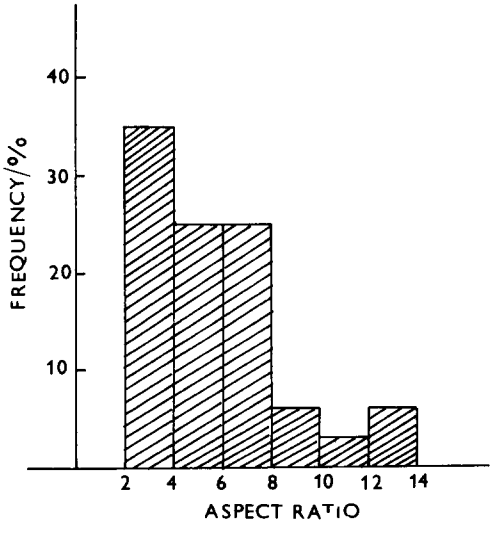
The Si_3N_4 powder (H1, H.C. Starck, West Germany) used in the present study had an oxygen content of 1·6 wt % and a carbon content of 0·5 wt % with <500 ppm of other impurities. A mixture of Y_2O_3 (99·99%) and Al_2O_3 (99·9%) in the molar ratio

Journal of the European Ceramic Society 0955-2219/90/$3.50

corresponding to the yttrium–aluminum garnet (YAG) composition was used as sintering additives. Y_2O_3 and Al_2O_3 were added in the form of a water solution of $Y(NO_3)_3$ and $Al(NO_3)_3$ into an aqueous suspension of Si_3N_4. An appropriate amount of urea was added for the coprecipitation of $Y(OH)_3$ and $Al(OH)_3$. This suspension was heated at 100°C for 1 h, filtered, dried and decomposed at 500°C and then homogenized in ethanol. Calculated resulting weight content of mixture of Y_2O_3 and Al_2O_3 in Si_3N_4 powder was 8 wt %. The β-Si_3N_4 whiskers (prepared by self propagation high temperature synthesis (SHS) in the Institute of Structural Macrokinetics, ASci, Chernogolovka, USSR) (Fig. 1), with oxygen content 0·8 wt % and mean aspect ratio of 5 were added in two ways. According to the first one, the mixtures of Si_3N_4 powder with the sintering additives and β-Si_3N_4 whiskers were homogenized 24 h in a polyethylene bottle in ethanol. In this way prepared powders with weight contents of whiskers larger than 5 wt % formed a large number of agglomerates of β-Si_3N_4 whiskers in a sintered body (Fig. 2(a), (b)). The number of agglomerates significantly decreased when powders with larger amounts of β-Si_3N_4 whiskers were prepared by ultrasonic agitation of two suspensions consisting of dry acetone and Y_2O_3, Al_2O_3, Si_3N_4 and dry acetone and β-Si_3N_4 whiskers. Both suspensions were then mixed together and vigorously stirred. The mixture coalesced with stirring and then rapidly sedimented. Both preparation methods, which are schematically illustrated in Fig. 3, were used for the preparation of green body compacts. The weight content of β-Si_3N_4 whiskers used in this study was 5, 10, 20 and 30 wt %. The green compacts were pressed at 100 MPa in a conventional steel die and so that the prepared green compacts had a diameter of 12 mm and a thickness of about 5 mm. The compacts, embedded in BN, were densified by hot pressing at 1750°C in a nitrogen atmosphere with a pressure of 0·1 MPa. The load, causing a pressure of 27 MPa was applied at 1500°C during heating of the sample and the force

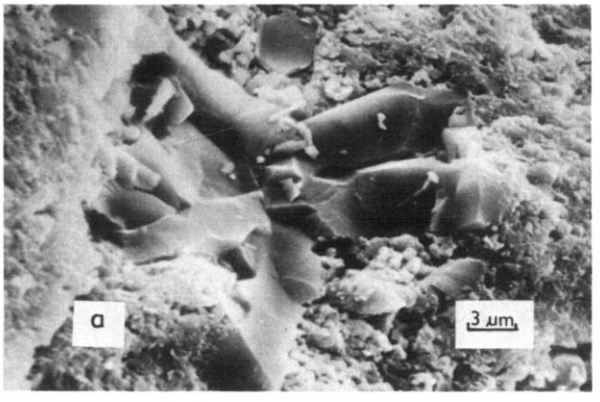


(a)



(b)

Fig. 1. (a) Micrograph of β-Si_3N_4 whiskers, bar = 2 μm. (b) Aspect ratio distribution of β-Si_3N_4 whiskers.



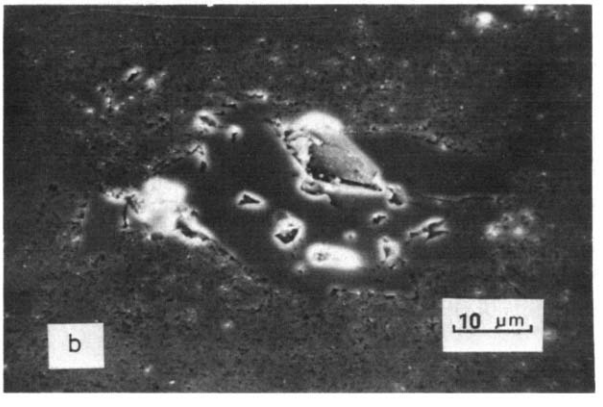
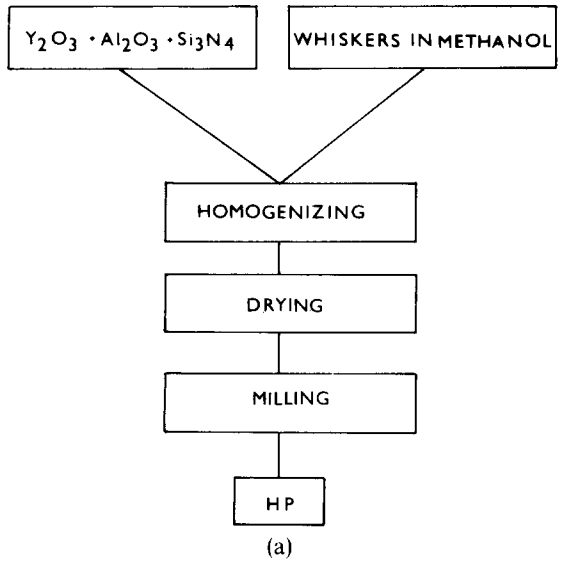


Fig. 2. (a) Micrograph of fractured surface with β-Si_3N_4 whiskers agglomerate, bar = 3 μm. (b) Micrograph of etched surface with β-Si_3N_4 whiskers agglomerate, bar = 10 μm.



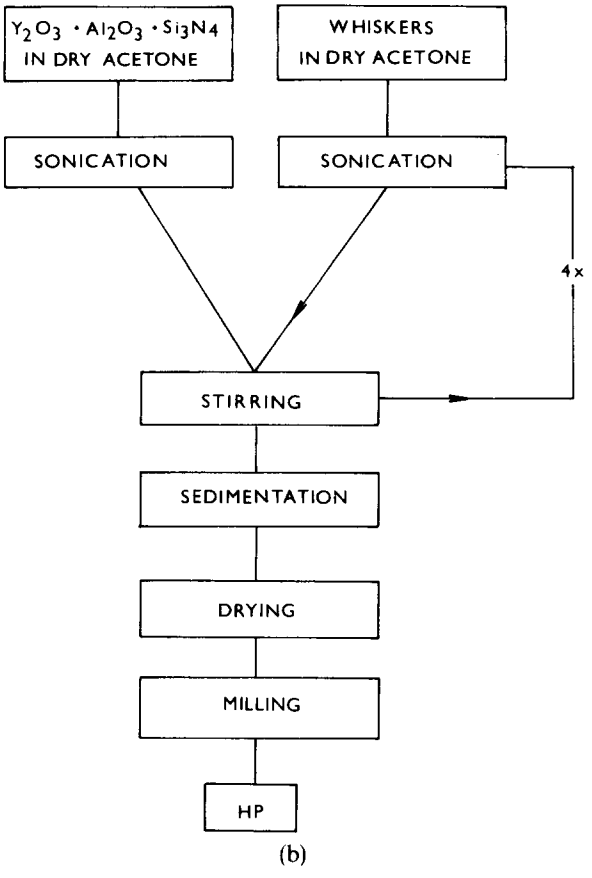


Fig. 3. Procedure of processing of a Si_3N_4–β-Si_3N_4 composite by (a) homogenizing; (b) stirring.

was released after an HP cycle at 1000°C. The densities of the compacts were measured by the mercury immersion method. The densified compacts were ground and then polished for indentation fracture toughness (IFT) measurements. IFT values were determined using a Vickers diamond pyramid indenter at a load of 100 N. The values of K_{IC} were calculated according to the following relation:[3,4]

$$K_{IC} = Ha^{1/2}(E/H)^{2/5}\,10^{Y} \qquad (1)$$

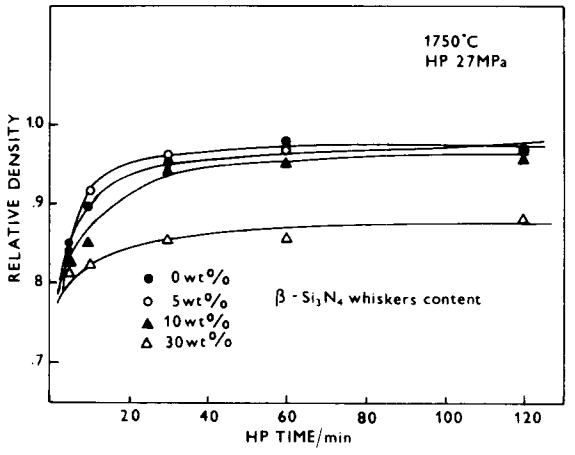


Fig. 4. Densification curves for Si_3N_4–β-Si_3N_4 composites with respect to the different whisker contents.

where H is the Vickers hardness, a is one-half of the length of the diagonal of the Vickers impression:

$$Y = f(\log[(l+a)/a])$$

where $Y = -1{\cdot}59 - 0{\cdot}34q - 2{\cdot}02q^2 + 11{\cdot}23q^3 - 24{\cdot}97q^4 + 16{\cdot}32q^5$, $q = \log[(l+a)/a]$, l is one-half of the median crack length and E is the Young's modulus which was inferred from data for materials of comparable composition as $E = 300\,\text{GPa}$[5].

The microstructural observation was carried out after etching of the polished samples. The hot-pressed samples were etched at 740°C in a mixture of K_2CO_3 and NaF in the weight ratio 6:1. Fractographic methods were used for the study of fracture characteristics.

3 Experimental Results

The Figs 4 and 5 show the relative density as a function of time during isothermal hot pressing and

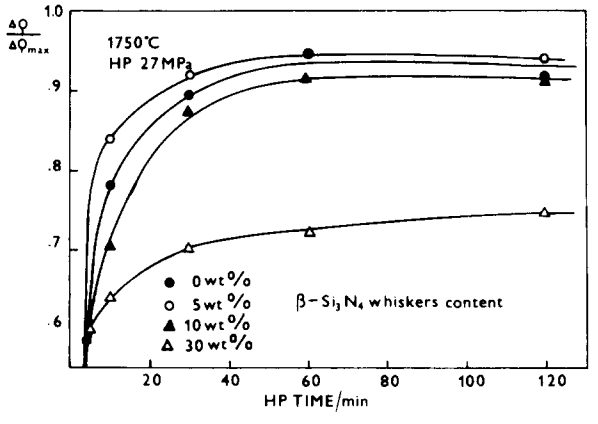


Fig. 5. Normalized change in density during HP of Si_3N_4–β-Si_3N_4 composite; where $\Delta\rho/\Delta\rho_{max} = (\rho - \rho_0)/(1 - \rho_0)$, ρ is the density of the hot-pressed composite, ρ_0 is the density of the green composite compact.

the normalized change in density as a function of time, respectively. Both figures indicate that the density curves are significantly influenced by the β-Si_3N_4 whiskers only in the case of 30 wt % whisker addition. In the other cases when 0, 5 and 10 wt % of β-Si_3N_4 were added, the curves of relative density and normalized change in density differ minimally. These differences are within the precision of the mercury immersion method used for density determination.

The dependence of fracture toughness on the β-Si_3N_4 whiskers content at room temperature is shown in Fig. 6. The values of K_{IC} were calculated according to the eqn (1). The hot-pressed composites containing 0 and 5 wt % of β-Si_3N_4 whiskers were prepared by the procedure described in Fig. 3(a), and composites containing 10, 20 and 30 wt % were prepared by the procedure described in Fig. 3(b). The composites containing 20 wt % of β-Si_3N_4 whiskers were hot-pressed at 1850°C and a HP-pressure of 32 MPa. All IFT tested composite compacts had a relative density >0·97. The composite compacts containing 30 wt % of β-Si_3N_4 whiskers were not sintered to a density suitable for IFT testing (>0·97) even when the last mentioned HP-conditions were applied. Figure 6 also shows the values for K_{IC} of SiC whisker reinforced Si_3N_4 composite ceramics referred to in Ref. 5. The Si_3N_4 matrix powder composite compared in Fig. 6 had similar oxygen content (1·5 wt %) to the oxygen content (1·6 wt %) of the Si_3N_4 powder used in this study; the amount and composition of liquid phase forming additives were similar, i.e. the total amount of sintering additives was 7·5 wt % versus 8 wt % in the present study. The difference in the composition of sintering additives

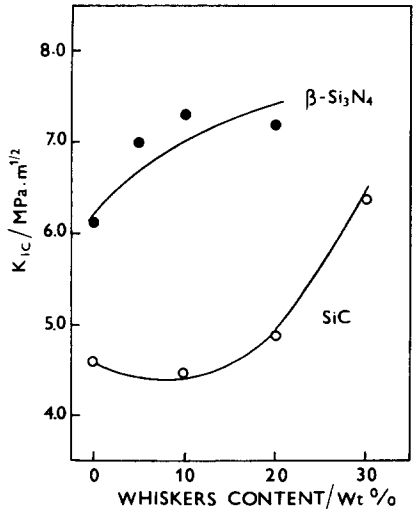


Fig. 6. Room temperature fracture toughness of Si_3N_4–β-Si_3N_4 composite determined by IFT techniques. The values of K_{IC} for SiC taken from the paper by Buljan *et al.*[5]

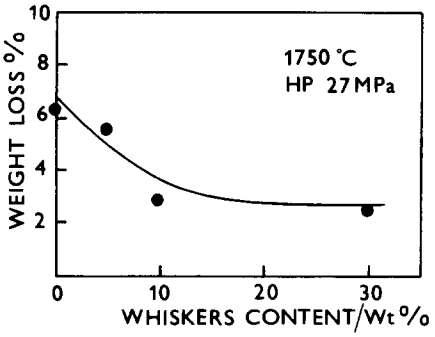


Fig. 7. Weight loss of Si_3N_4–β-Si_3N_4 composite.

within the range of the 6 wt % Y_2O_3 + 1·5 wt % Al_2O_3 versus the YAG composition, does not significantly influence the mechanical properties of Si_3N_4–Y_2O_3–Al_2O_3 material at room temperature.[6] The mean matrix particle size of Si_3N_4 used is a little lower (0·5 μm) in comparison with the Si_3N_4 powder used in this study (0·7 μm). The values of K_{IC} for Si_3N_4–SiC composites presented in Fig. 6 were measured by the controlled surface flaw technique. The authors[5] also refer to the values of indentation fracture toughness for this system, but these are about 25% lower than the quoted ones. The differences between the values produced by the two techniques are caused by the use of Knoop microhardness values in the calculation of indentation fracture toughness as is pointed out in Ref. 5. The comparison of both curves in Fig. 6 is favoring the β-Si_3N_4 whisker application.

Figure 7 shows the weight loss of composites (prepared by the procedure described in Fig. 3(a) and hot pressed at 1750°C with a load of 27 MPa) as a function of β-Si_3N_4 whisker content. The positive effect of β-Si_3N_4 whisker addition on the weight loss is evident.

4 Discussion

The effect of the addition of a second phase on the sintering behaviour of composites was expressed as the ratio of the rate of shear relaxation to the densification rate of the matrix phase.[7–9] Large values of this ratio are desirable, so that the densification behaviour of the composite is the same as that of the matrix. The densification curves of the specimens with 5 and 10 wt % of β-Si_3N_4, Figs 4 and 5, indicate that the densification behaviour of the composite is similar to that of the matrix.

Whisker reinforcement can involve several toughening mechanisms. Whisker pull-out can occur when the stress, transferred to the whisker during fracture of the matrix is less than the fracture strength of

whisker but generates a shear stress that is greater than the interfacial shear strength of the whisker–matrix interface.[10] The interfacial shear strength for a rod-like whisker depends upon the coefficient of friction and the stress acting normal to the interface parallel to the longitudinal axis of the whisker when no chemical bond between the matrix and whisker is supposed. The last mentioned stress is a function of the mismatch of the thermal expansion coefficients of matrix and whiskers. When the values of the thermal expansion coefficients are close to each other, this stress is minimal, thus the interfacial shear strength is minimal and the whisker pull out can occur. Figure 8 shows the whisker-shaped cavities of whiskers that appear to result from whisker pull-out. In the work of Lundberg *et al.*[11] it was pointed out that when the bond between a SiC whisker and the Si_3N_4 matrix is too strong, no whisker pull-out is observed, the fracture toughness of the composite slightly decreases with increasing whisker content.

Another toughening process involves crack deflection around the whiskers. The study of Faber & Evans[12] indicates that rods (whiskers) have an extremely effective geometry for deflecting cracks increasing the tortuosity of the crack path. It is shown[12] that the toughness of composites increases as the aspect ratio of the whiskers increases, if no

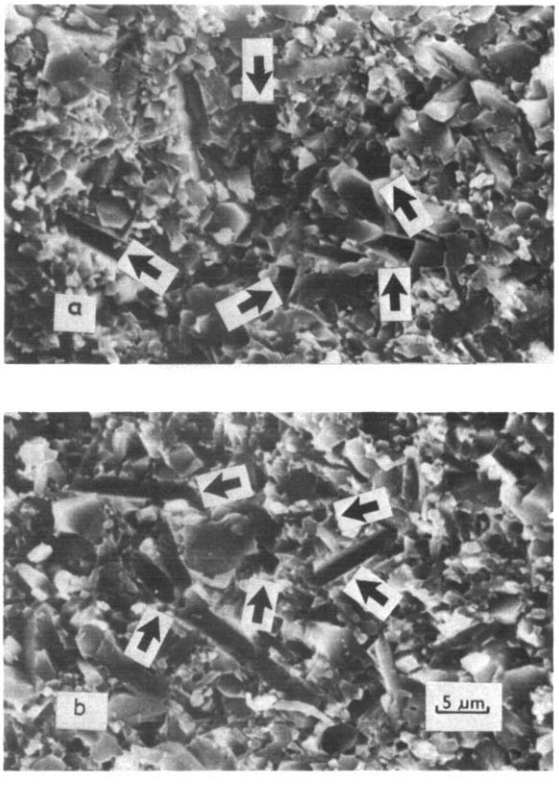


Fig. 8. Micrograph of fractured surface of Si_3N_4–β-Si_3N_4 composite. Whisker-shaped cavities of β-Si_3N_4 whiskers pulled out from the matrix are indicated by arrows, (a) and (b). Bar = 5 μm.

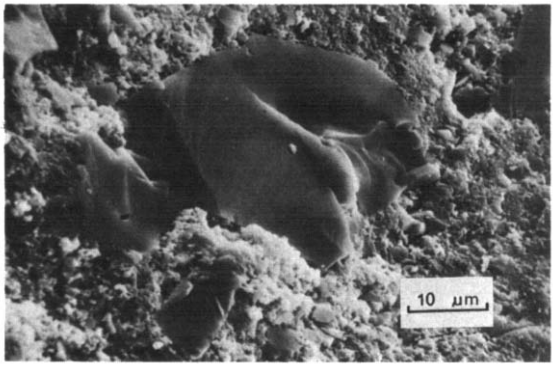


Fig. 9. Micrograph of fractured surface of Si_3N_4–β-Si_3N_4 composite with large β-Si_3N_4 particle, bar = 10 μm.

whisker fracture is supposed. Thus, equiaxed particles are not very effective in energy dissipation of a crack by the deflection mechanism. In the present study the β-Si_3N_4 addition contained not only rod-like whiskers but also equiaxed particles (Fig. 9), and also in the case of the 20 and 30 wt % addition of β-Si_3N_4 whiskers the larger number of agglomerates of whiskers were observed (Fig. 2(a), (b)). It is reasonable to assume that the presence of both the above-mentioned forms contribute little or nothing to the improvement of the fracture toughness, and this could be one reason for the low increase of fracture toughness with addition of β-Si_3N_4 whiskers above 10 wt % (Fig. 6).

A very important strengthening mechanism of composites is crack bridging. The bridging of the crack by the β-Si_3N_4 whiskers is observed and marked by the arrows in Fig. 10.

The fracture toughness curve, Fig. 6, indicates that the highest increase of fracture toughness is gained when 5 and 10 wt % of β-Si_3N_4 whiskers are applied and these additions expose little influence on densification behaviour of the composite compacts as Figs 4 and 5 indicate. Both these results and the positive effect of β-Si_3N_4 additives on thermal

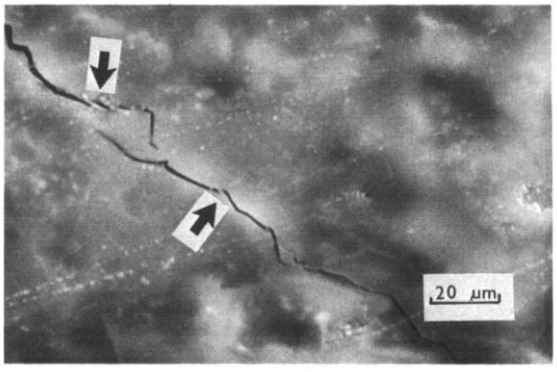


Fig. 10. Micrograph of polished surface with indentation inducted crack at room temperature; the arrows show the bridging of the crack by β-Si_3N_4 whiskers; bar = 20 μm.

decomposition, Fig. 7, make the β-Si_3N_4 whiskers a serious candidate for silicon nitride ceramics reinforcement.

5 Conclusions

(i) An increase in K_{IC} of β-Si_3N_4 whisker reinforced Si_3N_4 composites is observed with an increase in the β-Si_3N_4 content of up to 10 wt %.

(ii) Within this interval of β-Si_3N_4 additions, they indicate no influence on composite densification behaviour.

(iii) A positive effect of increased β-Si_3N_4 whisker content on weight loss suppression is observed.

(iv) The microstructural and fractographic results confirmed presence of the strengthening mechanisms of the composite at room temperature.

References

1. Chou, T-W. & Yang, J-M., Structure-performance maps of polymeric, metal, and ceramic matrix composites. *Metall. Trans. A.*, **17A** (1986) 1547–59.
2. Moulson, A. J. Reaction-bonded silicon nitride: its formation and properties. *J. Mat. Sci.*, **14** (1979) 1017–51.
3. Evans, A. G. & Charles, E. A., Fracture toughness determinations by indentation. *J. Am. Ceram. Soc.*, **59**(7–8) (1976) 371–2.
4. Evans, A. G., Fracture toughness: the role of indentation techniques. In *Fracture Mechanics Applied to Brittle Materials*, ASTM STP No. 678, ed. S. W. Freiman. American Society for Testing and Materials, Philadelphia, 1979, pp. 112–35.
5. Buljan, S. T., Baldoni, J. G. & Huckabee, M. L., Si_3N_4–SiC composites. *Am. Ceram. Soc. Bull.*, **66**(2) (1987) 347–53.
6. Tsuge, A. & Nishida, K., High strength hot-pressed Si_3N_4 with concurrent Y_2O_3 and Al_2O_3 additions. *Am. Ceram. Soc. Bull.*, **57**(4) (1978) 424–31.
7. Bordia, R. K. & Raj, R., Analysis of sintering of a composite with a glass or ceramics matrix. *J. Am. Ceram. Soc.*, **69**(3) (1986) C-55–C-57.
8. Bordia, R. K. & Raj, R., Sintering of TiO–Al_2O_3 composites: a model experimental investigation. *J. Am. Ceram. Soc.*, **71**(4) (1988) 302–10.
9. Bordia, R. K. & Raj, R., Hot isostatic pressing of ceramic/ceramic composites at pressures <10 MPa. *Adv. Ceram. Mat.*, **3**(2) (1988) 122–6.
10. Becher, P. F., Tiegs, T. N., Ogle, J. C. & Warwick, W. H., Toughening of ceramics by whisker reinforcement. In *Fracture Mechanics of Ceramics, Vol. 7*, ed. R. C. Bradt, A. G. Evans, D. P. H. Hasselman & F. F. Lange. Plenum Publishing Corp., 1986, pp. 61–73.
11. Lundberg, R., Kahlman, L., Pompe, R., Carlsson, R. & Warren, R., SiC-whisker-reinforced Si_3N_4 composites. *Am. Ceram. Soc. Bull.*, **66**(2) (1987) 330–3.
12. Faber, K. T. & Evans, A. G., Crack deflection process—I. theory. *Acta Metall.*, **31**(4) (1983) 565–76.