*Journal of the European Ceramic Society* **16** (1996) 1213–1220

PII:S0955-2219(96)00051-9
0955-2219/96/$15.00

# SiC Platelet-Reinforced $Al_2O_3$ Composites by Free Sintering of Coated Inclusions

X. Yang & M. N. Rahaman*

University of Missouri-Rolla, Department of Ceramic Engineering, Rolla, MO 65401, USA

(Received 19 December 1995; revised version received 8 February 1996; accepted 20 February 1996)

***Abstract***

*SiC platelets were coated with a fine-grained $Al_2O_3$ precursor powder by controlled heterogeneous precipitation from solution. After calcination, the coated platelets were compacted and sintered at a constant heating rate of 5°C $min^{-1}$ in a helium atmosphere. The parameters that control the coating process and the sintering behaviour of the coated powders were investigated. For given reactant and platelet concentrations, pH and temperature, the presence of a small amount of poly(vinylpyrrolidone) (PVP) produced a more homogeneous coating which, in turn, produced an improvement in the sinterability of the coated platelets. Composites formed from the coated platelets, with an initial matrix density of 40–45% of the theoretical and containing ≈20 vol% platelets, reached nearly full density after sintering at 1800°C for 30 min. By comparison, similar composites formed by mechanical mixing of the SiC platelets and freely precipitated $Al_2O_3$ powder reached a density of only ≈70% of the theoretical under identical sintering conditions. The strength and fracture toughness of the sintered composites formed from the coated platelets were measured in three-point loading at room temperature. For the composite containing 20 vol% platelets, the strength and fracture toughness values were 240 MPa and 5.4 MPa $m^{1/2}$, respectively. They are comparable to the highest values reported for similar composites produced by hot-pressing of mechanically mixed systems. Copyright © 1996 Elsevier Science Ltd*

## 1 Introduction

Polycrystalline ceramic matrix composites formed by conventional methods are difficult to sinter to the high densities normally required for structural applications, without the application of an external pressure or the use of a large amount of liquid phase. The factors responsible for the reduced sinterability have been considered in detail elsewhere.[1,2] It is now generally accepted that network formation between the reinforcing particles (the inclusions) and inhomogeneous packing of the matrix phase (particularly in the regions surrounding the inclusions) are the key factors that restrict the sintering of polycrystalline ceramic matrix composites. Transient stresses due to the mismatch in shrinkage rates between the matrix and the inclusions may also play a limited role in reducing the densification.[3,4]

For densification by a solid-state mechanism, De Jonghe and co-workers[5,6] and Rahaman and co-workers[7,8] have demonstrated that the sintering impediments due to network formation and packing can be significantly alleviated by the use of an alternative processing route based on the preparation of coated particles. The preparation of coated particles was pioneered by Matijevic and co-workers.[9–11] The method was also used later by Garg and De Jonghe[12] for the preparation of $Si_3N_4$ coated with yttria and yttria–alumina precursors. For particulate composites, the reinforcement phase is coated with the required thickness of the matrix phase by controlled heterogeneous precipitation in a suspension of particles or whiskers. The coated powders are then collected, compacted by normal ceramic powder forming methods (e.g. pressing in a die or isostatic pressing) and densified by conventional, pressureless sintering (referred to as free sintering). Composites reinforced with up to ≈40 vol% particles or 20–30 vol% whiskers have been sintered to almost full density under conditions fairly similar to those used for the unreinforced materials. From the point of view of ease of fabrication, the route based on the use of coated particles may therefore have considerable benefits. Sacks *et al.*[13] employed an alternative method based on the use of coated powders. They prepared amorphous coatings on core particles in order to take advantage of the easier densification

*To whom correspondence should be addressed.

of the coating by viscous flow. After densification, the amorphous phase can be crystallized or reacted with the core particles to produce a crystalline product.

Compared with nearly equiaxial inclusions, the use of whisker reinforcement can provide improvement in the mechanical properties of the ceramic matrix.[14–16] However, various questions have arisen concerning the health hazards posed by the use of whiskers. Platelets may provide an effective reinforcing phase for improvement of the strength and fracture toughness of ceramics.[17,18] At the same time, they are not associated with any known health hazards.

The work described in the present paper forms an extension of the earlier work of Rahaman and co-workers to the fabrication of platelet-reinforced composites from coated inclusions. The factors that control the coating of SiC platelets with an alumina precursor powder and the sinterability of composites formed from the coated platelets were investigated. The strength and fracture toughness of the fabricated composites were measured at room temperature and compared with the values reported for similar composites produced by hot-pressing.

## 2 Experimental Procedure

### 2.1 Preparation of coated powders and mechanically mixed powders

Following the procedure described by Hu and Rahaman[8] for the coating of SiC whiskers with an alumina precursor powder, the key parameters of the process were varied to produce a uniform coating without significant precipitation of free powder. The parameters included the concentration of the reactants in solution, the concentration of SiC platelets in the suspension, the temperature and the pH. The following procedure was initially found to produce coated platelets. A coating solution consisting of 0.18 mol $l^{-1}$ $Al(NO_3)_3$, 0.05 mol $l^{-1}$ $Al_2(SO_4)_3$ and 32 g $l^{-1}$ urea was prepared. (All of the chemicals were reagent grade, obtained from Aldrich Chemical Co., Milwaukee, WI.) SiC platelets (-400 mesh, Type T; Third Millenium Technology Co., Knoxville, TN), at a concentration of 3.2 g $l^{-1}$ were added to the solution. The platelets had a diameter of 0.5 to 3 $\mu$m and an aspect ratio of $\approx 10$. The suspension was heated, under vigorous stirring, for 48 h at 83 ± 2°C. During the process, the pH of the suspension was monitored. This procedure produced coated platelets. However, the coating contained cracks and, in many cases, parts of the cracked coating fell off, leaving uncoated surfaces on the platelets. The addition of poly(vinylpyrrolidone) (PVP, molecular weight ~30 000; Aldrich Chemical Co., Milwaukee, WI) at a concentration of 0.7 g $l^{-1}$ prior to heating the suspension to the coating temperature, produced a relatively smooth coating that did not show any evidence of cracking.

After the coating process, the suspension was cooled quickly. The coated platelets were collected, washed with distilled water and dried for 8 h at 100°C. The dried material was then placed in a high-purity $Al_2O_3$ crucible and heated in helium for 15 min at 1250°C to decompose the alumina precursor powder.

After calcination, the coated powder was doped with MgO (Mg:Al atomic ratio = 250 ppm) for grain growth control during sintering. In the process, the required amount of $Mg(NO_3)_2.6H_2O$ (purity 99.99%; Aesar/Johnson Matthey, Ward Hill, MA) was added to a suspension of the coated powder in ethanol. The mixture was stirred until it was dry and then calcined in air for 2 h at 1000°C to incorporate the Mg into solid solution.

For a comparison of the sintering kinetics, mechanically mixed systems were also prepared. In this case, free alumina precursor powder was precipitated from the solution under the same conditions described earlier for the coating process. The precipitated powder was mixed with the required amount of SiC platelets, while dispersed in ethanol, for 2 h in a ball mill using zirconia balls as the milling media. After drying, the mixture was calcined and doped using the same procedure described earlier for the coated powder.

### 2.2 Sintering of the composites

The coated platelets and the mechanically mixed systems were compacted by pressing lightly in a uniaxial die (under a pressure of $\approx 40$ MPa), followed by cold-isostatic pressing ($\approx 250$ MPa) to form pellets (6 mm in diameter by 5 mm) for sintering. Plates (48 by 28 by 6 mm) for mechanical testing experiments were prepared by compacting the powders in a rectangular die followed by cold-isostatic pressing under the pressures outlined above for the preparation of the pellets. The matrix density of the compacted samples formed from both the coated platelets and the mechanically mixed systems was 40–45% of the theoretical density of $\alpha$-$Al_2O_3$.

Sintering was performed in a high-purity helium atmosphere (flow rate 50 $cm^3$ $min^{-1}$) in a graphite element furnace (model 1000; Thermal Technology, Inc., Santa Rosa, CA) at a constant heating rate of 5°C $min^{-1}$ to $\approx 1800$°C. In the experiments, the powder compacts were placed in a high-purity graphite crucible and surrounded by loose powder of the same composition in order to minimize

weight loss during sintering. The densities of the fired samples were determined from their mass and dimensions. The values were checked by Archimedes' method.

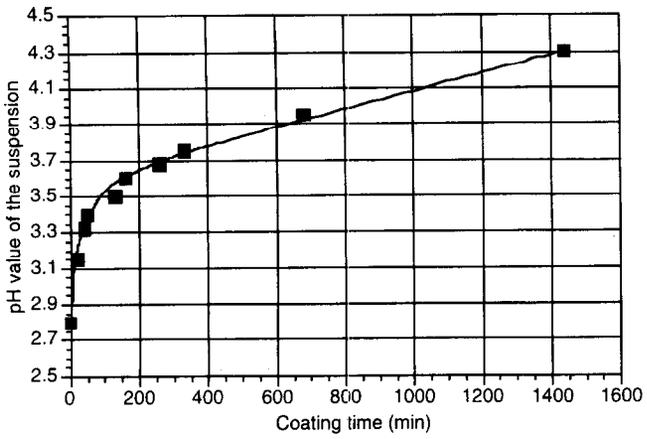


**Fig. 1.** The pH of the suspension during the coating process at 83 ± 2°C.

### 2.3 Measurement of mechanical properties

The flexural strength and fracture toughness of the sintered materials were determined by three-point bending of beams (3 by 4 by 30 mm) at a crosshead speed of 0.5 mm $min^{-1}$. The test samples were cut from the fired plates and then polished with SiC papers to 600-grit. The edges were bevelled during the polishing step. Fracture toughness values were determined using a single-edge notched beam (SENB) technique. The beams were notched at the centre using a diamond wheel (0.6 mm thick) to produce a notch depth ($a$) to the beam width ($w$) ratio of 0.4–0.5. At least five specimens were tested for each reported value.

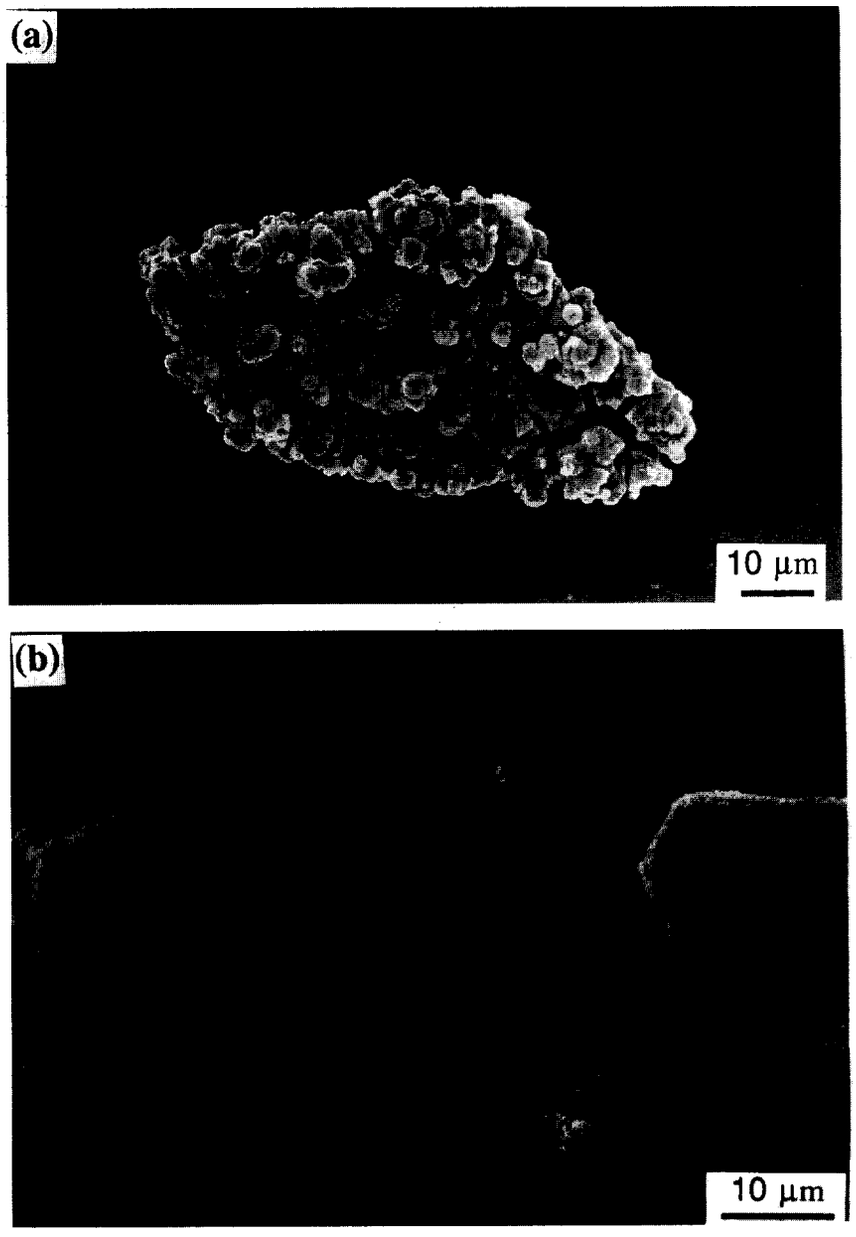


**Fig. 2.** SEM micrographs of the coated platelets prepared by chemical precipitation: (a) without PVP and (b) with PVP.

### 2.4 Structural and microstructural characterization

X-ray diffraction (XRD) was used to analyse the coatings after drying as well as after the calcination step. The structure of the coating on the SiC platelets was observed by scanning electron microscopy (SEM). The microstructure of the sintered samples was observed by SEM and by optical microscopy of fractured surfaces and polished surfaces.

## 3 Results and Discussion

Figure 1 shows the data for the pH of the suspension as a function of time at the coating temperature of 83 ± 2°C. At this temperature, the urea decomposed slowly, leading to an increase in the hydroxyl ion concentration. The pH value of the solution increased until the conditions for precipitation of aluminium hydroxide were reached.

The production of coated particles depends on the ability to achieve heterogeneous nucleation and growth from the solution, in contrast to the case of free powder which is produced by homogeneous nucleation and growth. For the preparation of coated platelets, a general requirement is to achieve a balance between the total available surface area of the platelets in suspension and the rate of precipitation. The total surface area is determined by the specific surface area and the concentration of the platelets, while the rate of precipitation depends on the concentration of the reactants (urea and aluminium salts) and the temperature of the solution. Successful coating of the platelets in suspension therefore requires some trial and error for achieving the proper concentration of platelets and reactants under a set of fixed reaction conditions.

The initial experiments employed the same conditions as those used earlier by Hu and Rahaman[8] for the coating of SiC whiskers with an alumina precursor powder. These conditions produced a mixture of coated platelets and free powder. However, a significant increase in the concentration of the platelets produced coated platelets primarily. Figure 2(a) shows an SEM micrograph of the product from the conditions of increased platelet concentration. The coating suffers from extensive cracking which can be alleviated by the addition of PVP to the solution prior to the coating process [Fig. 2(b)]. The presence of the PVP also leads to a change in the structure of the alumina precursor coating.

The volume fraction of the platelets in the composites is controlled by the total amount of aluminium ion in the solution. By completing the precipitation reaction, almost all the aluminium ions can be precipitated at pH values greater than ≈4.3. For the coated platelets shown in Fig. 2, the volume fraction of the platelets (based on the fully dense composite) is ≈20%. The error in the platelet volume fraction determined by this method is estimated at ±1%.

The quality of the coating on the platelets influences the sintering characteristics. For the highly cracked coating prepared without the addition of PVP [Fig. 2(a)], the composites reached a density of ≈92% of the theoretical after sintering for 30 min at 1800°C. In comparison, the composites formed from the coated powders prepared with the addition of PVP [Fig. 2(b)] reached a density of 98% of the theoretical under identical sintering

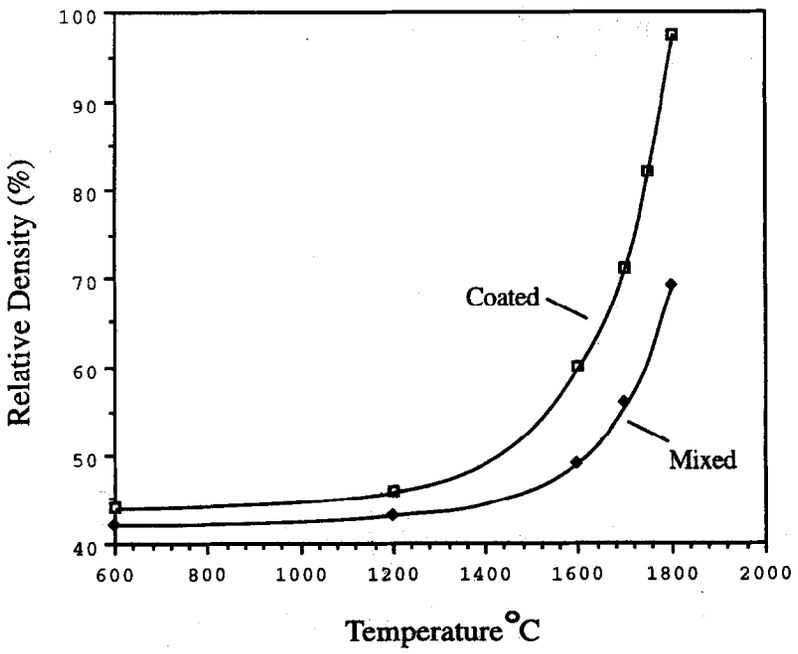


**Fig. 3.** Relative density versus temperature for composites formed from (a) the coated powder and (b) the mechanically mixed powder, during constant heating rate sintering of 5°C $min^{-1}$ to 1800°C.

conditions. The results indicate that the more uniform coating produced with the addition of PVP leads to a higher sintered density.

The sinterability of the composites formed from the coated powders was compared with that for similar composites formed from mechanically mixed systems. Figure 3 shows the sintered densities of composites at various temperatures. The volume fraction of the platelets in the composites was ≈20 vol%. The sintered density of the composite formed from the mixed powders is significantly lower than that for the composite formed from the coated powders.

Scanning electron micrographs of the fractured surfaces of the sintered composites formed from the coated powder and from the mixed powder are shown in Fig. 4. The micrograph of the composite formed from the coated powder [Fig. 4(a)] reveals a dense microstructure in which all the platelets are separated from one another by the matrix phase. However, for the composite formed from the mixed powder [Fig. 4(b)], a highly porous microstructure is observed. Furthermore, most of the porosity is concentrated immediately around the platelets. Several platelets appear to be interconnected, with a large amount of porosity associated with this type of structure. Both microstructures reveal an average grain size of the matrix equal to 5–10 μm.

Figure 5 is an optical micrograph of the polished surface of the composite formed from the coated powder after sintering for 30 min at 1800°C. A fairly uniform distribution of the platelets (light phase) in a highly dense matrix (dark phase) is observed. There is almost no evidence for clustering of platelets, as is normally observed for hot-pressed composites formed from mechanically mixed systems.

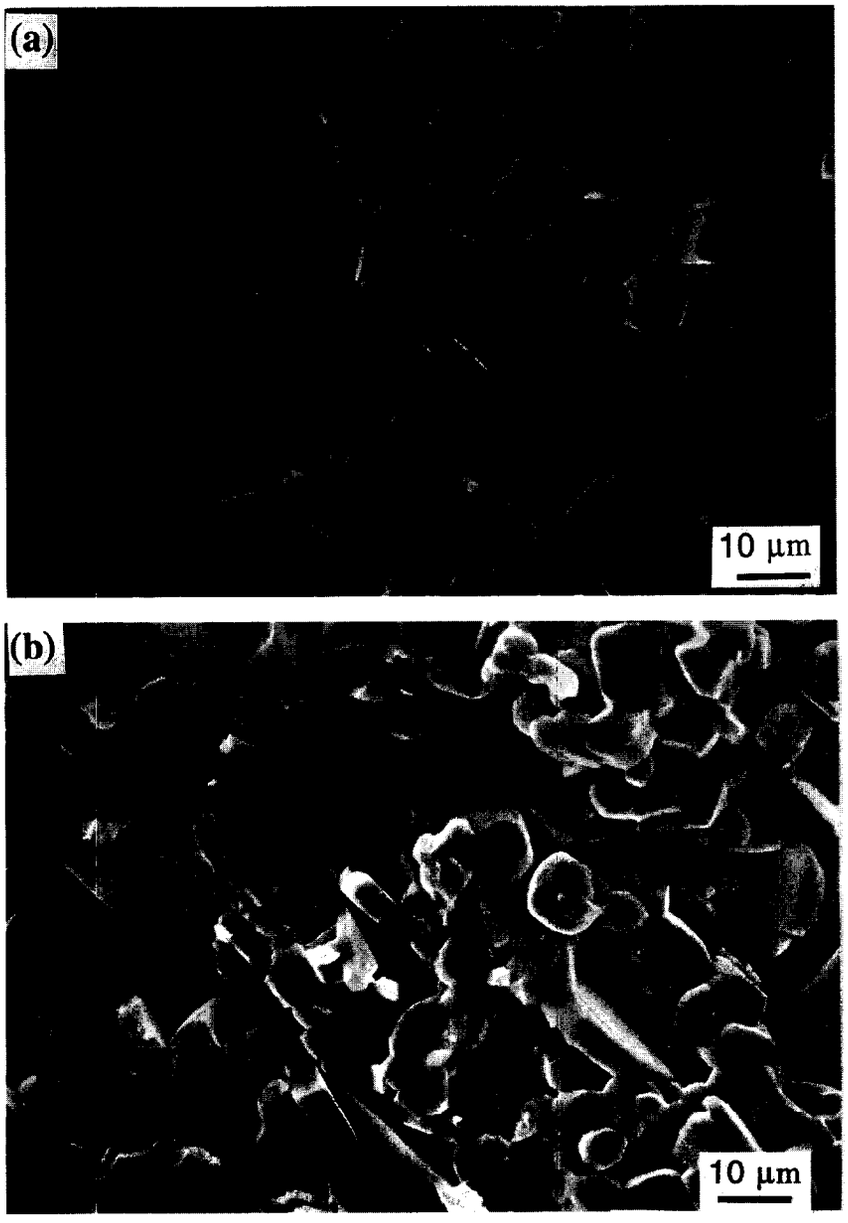


**Fig. 4.** The microstructures of the fractured surfaces of the composites formed from (a) the coated powder and (b) the mechanically mixed powder after sintering.

The data for the flexural strength and fracture toughness of the sintered composites produced from the coated platelets are shown in Table 1. The strength is ≈240 MPa while the fracture toughness is ≈5.4 MPa $m^{1/2}$. For comparison, the data for unreinforced $Al_2O_3$, produced from the

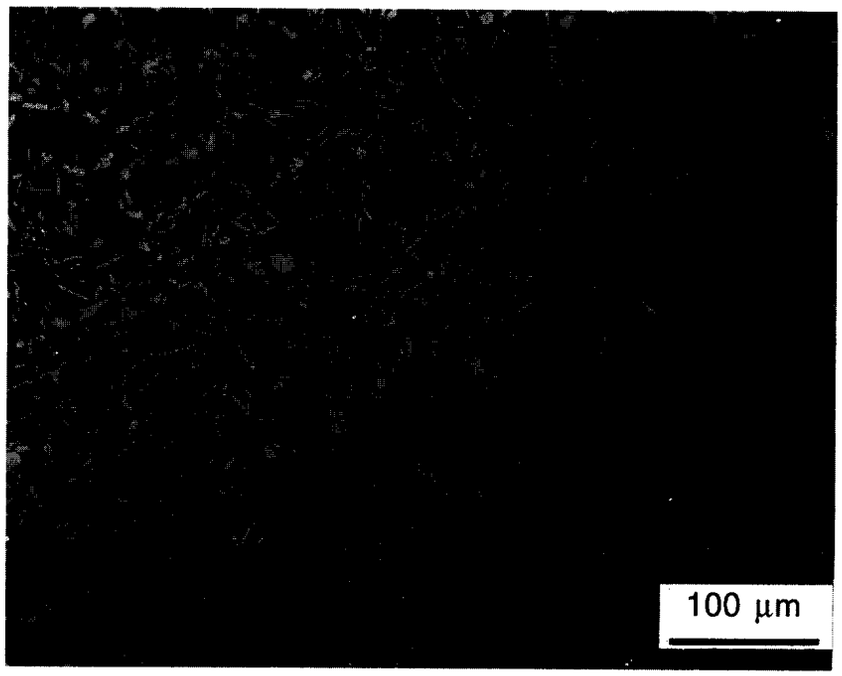


**Fig. 5.** Optical micrograph of the polished surface of the sintered composite formed from the coated powder, showing a fairly uniform distribution of the platelets (light phase) in a highly dense matrix (dark phase).

**Table 1.** Flexural strength and fracture toughness values for unreinforced $Al_2O_3$ and $Al_2O_3$/20 vol% SiC platelet-reinforced composites produced in the present work. Values reported in the literature for similar composites are also shown

| *Composition* | *Fabrication route* | *Flexural strength (MPa)* | *Fracture toughness (MPa $m^{1/2}$)* |
|---|---|---|---|
| $Al_2O_3$ (present work) | Sintering | 262 ± 20 | 3.8 ± 0.4 |
| $Al_2O_3$/20 vol% SiC (present work) | Sintering | 240 ± 14 | 5.4 ± 0.2 |
| $Al_2O_3$/20 vol% SiC (Refs 19,20) | Hot-pressing | 120–280 | 4.5–5.4 |

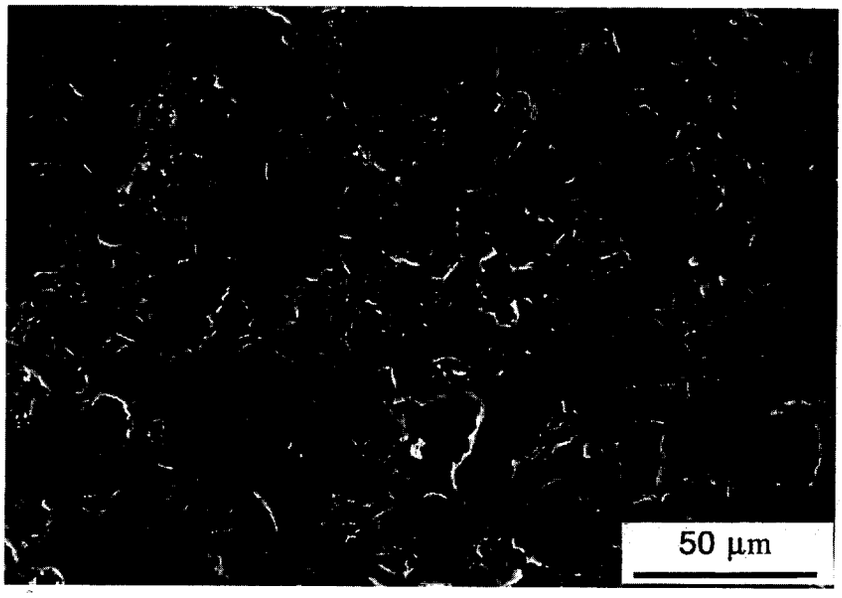


**Fig. 6.** SEM micrograph of a machined surface of the composites (20 vol% SiC platelet) used in the flexural strength tests.

precipitated alumina precursor powder are also included. The calcination, doping and sintering steps for the unreinforced $Al_2O_3$ were similar to those for the composites formed from the coated platelets. In addition, the grain size of the fabricated $Al_2O_3$ material was approximately the same as that of the matrix phase of the composite. Within the limits of experimental error, the strength values are approximately the same but the fracture toughness of the composite is $\approx 1.5$ times higher than that of the unreinforced $Al_2O_3$. Table 1 also shows the range of data reported in the literature[19,20] for similar composites produced by hot-pressing of mechanically mixed systems. For the data reported in the literature, while the average grain size of the $Al_2O_3$ matrix is not known, the SiC platelets were similar to those used in the present work. Furthermore, the methods used to measure the flexural strength and fracture toughness were similar to those employed in the present work. Qualitatively, the data show that the strength and fracture toughness of the composites produced in the present work by the free sintering of coated platelets are approximately the same or even better than the values reported for the hot-pressed composites. At least two factors can have an influence on the strength of the composites: (i) the interfacial bonding between the platelets and the matrix and (ii) the surface finish of the specimens used in the mechanical tests. No detailed work was performed for the characterization of the interface. However, the surface finish of the specimens was observed. As shown in Fig. 6, the surface of the specimens contains defects which are as large as the platelets. The defects were produced during grinding and polishing of the surfaces prior to mechanical testing. Such defects can significantly reduce the strength. An optimized surface finish may therefore be expected to lead to an improvement of the measured strength value.

## 4 Conclusions

Conditions were determined for the coating of SiC platelets with a uniform, crack-free layer of an alumina precursor powder by heterogeneous precipitation from solution. The thickness of the precursor layer was controlled to achieve a platelet volume fraction of 20% based on the theoretically dense composite. After calcination to convert the precursor layer to $Al_2O_3$, the coated platelets were compacted and freely sintered to produce highly dense composites. Under identical sintering conditions, similar composites formed from mechanically mixed systems were highly porous. The flexural strength and fracture toughness of the sintered composites formed from the coated platelets are comparable to the highest values reported for similar composites produced by hot pressing of mechanically mixed systems. The present work provides further demonstration of the effectiveness of the fabrication route based on the use of coated inclusions for the production of ceramic matrix composites by free sintering.

## References


1. Fan, C.-L. & Rahaman, M. N., Factors controlling the sintering of ceramic particulate composites: I, conventional processing. *J. Am. Ceram. Soc.*, **75**[8] (1992) 2056–65.
2. Hu, C.-L. & Rahaman, M. N., Factors controlling the sintering of ceramic particulate composites: II, coated inclusion particles. *J. Am. Ceram. Soc.*, **75**[8] (1992) 2066–70.
3. Sudre, O. & Lange, F. F., Effect of inclusions on densification: I, microstructural development in an $Al_2O_3$ matrix containing a high volume fraction of $ZrO_2$ inclusions. *J. Am. Ceram. Soc.*, **75**[3] (1992) 519–24.
4. Sudre, O., Bao, G., Fan, B., Lange, F. F. & Evans, A. G., Effect of inclusions on densification: II, numerical model. *J. Am. Ceram. Soc.*, **75**[3] (1992) 525–31.
5. Mitchell, T. D. Jr. & De Jonghe, L. C., Processing and properties of particulate composites from coated powders. *J. Am. Ceram. Soc.*, **78**[1] (1995) 199–204.
6. Kapolnek, D. & De Jonghe, L. C., Particulate composites from coated powders. *J. Eur. Ceram. Soc.*, **7**[6] (1991) 345–51.
7. Hu, C.-L. & Rahaman, M. N., Dense $ZrO_2/Al_2O_3$ composites by free sintering of coated powders. *J. Am. Ceram. Soc.*, **77**[3] (1994) 815–19.
8. Hu, C.-L. & Rahaman, M. N., SiC whisker reinforced $Al_2O_3$ composites by free sintering of coated powders. *J. Am. Ceram. Soc.*, **76**[10] (1993) 2549–54.
9. Gherardi, P. & Matijevic, E., Interactions of precipitated hematite with preformed colloidal titania dispersions. *J. Colloid Interface Sci.*, **109**[1] (1986) 57–68.
10. Kratohvil, S. & Matijevic, E., Preparation and properties of coated, uniform inorganic colloidal particles: I, aluminum hydrous oxide on hematite, chromia, and titania. *Adv. Ceram. Mater.*, **2**[4] (1987) 798–803.
11. Garg, A. K. & Matijevic, E., Preparation and properties of uniformly coated inorganic colloidal particles, II: chromium hydrous oxide on hematite. *Langmuir*, **4** (1988) 38–44.
12. Garg, A. K. & De Jonghe, L. C., Microencapsulation of silicon nitride particles with yttria and yttria–alumina precursors. *J. Mater. Res.*, **5**[1] (1990) 136–42.
13. Sacks, M. D., Bozkurt, N. & Scheiffele, G. W., Fabrication of mullite and mullite matrix composites by transient viscous sintering of composite powders. *J. Am. Ceram. Soc.*, **74**[10] (1991) 2428–37.
14. Faber, K. T. & Evans, A. G., Crack deflection processes — I. theory. *Acta Metall.*, **31**[4] (1983) 565–76.
15. Becher, P. F., Hsueh, C.-H., Angelini, P. & Tiegs, T. N., Toughening behavior in whisker-reinforced ceramic matrix composites. *J. Am. Ceram. Soc.*, **71**[12] (1988) 1050–61.
16. Bengisu, M. & Inal, O. T., Whisker toughening of ceramics: toughening mechanism, fabrication, and composite properties. *Ann. Rev. Mater. Sci.*, **24** (1994) 83–124.
17. Brandt, G. & Thelin, A., Ceramic cutting tool with improved toughness behavior. *European Patent Application 0 295 228 A2.*

18. Heussner, K.-H. & Claussen, N., Yttria- and ceria-stabilized tetragonal zirconia polycrystals (Y-TZP, Ce-TZP) reinforced with $Al_2O_3$ platelets. *J. Eur. Ceram. Soc.*, **5** (1989) 193–200.
19. Sakai, H., Matsuhiro, K. & Furuse, Y., Mechanical properties of SiC platelet reinforced ceramic composites. *Mater. Res. Soc. Symp. Proc.*, **271** (1992) 765–71.
20. Fisher, W. F., Haber, R. A. & Anderson, R. M., Mechanical properties of alumina matrix composites reinforced with silicon carbide platelets and particles. *Mater. Res. Soc. Symp. Proc.*, **271** (1992) 773–9.