

Processing of pressureless-sintered SiC whisker-reinforced Al₂O₃ composites

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Silicon carbide whisker-reinforced Al₂O₃ composites were prepared using a processing scheme in which the constituents were dispersed in nonaqueous media, then colloid-pressed and pressureless-sintered under an inert atmosphere. Novel oligomeric and polymeric dispersants were used to sterically stabilize the SiC whiskers in the presence of the Al₂O₃ powder. The sintering studies indicated that in the absence of a suitable sintering aid, the whiskers significantly inhibited densification of the Al₂O₃ matrix. Doped composites containing yttrium isopropoxide as a sintering aid were pressureless-sintered to final densities 95% of theoretical.

1. Introduction

Fibre-reinforced ceramic composites show promise for structural applications where high toughness is required. Researchers at Oak Ridge [1] have recently demonstrated that the fracture toughness of hot-pressed alumina and mullite composites is doubled by the addition of sufficient quantities of SiC whiskers.

The present work describes: (1) the dispersion and sedimentation of SiC whiskers using large organic/organometallic molecules as dispersants for the whiskers, and (2) the pressureless sintering of Al₂O₃/SiC whisker composites made with a dispersant. The organic dispersants may coat the whiskers prior to burnout, preventing contact between the whiskers and the Al₂O₃ matrix. Removal of this coating would therefore allow the Al₂O₃ to "shrink-fit" around the whiskers during pressureless sintering. Since researchers at Oak Ridge have achieved good results using Y₂O₃ powder as a sintering aid in whisker composites [2], some composites in this study were also doped with yttrium isopropoxide.

2. Experimental procedure

2.1. SiC whisker dispersion studies

The dispersion/sedimentation behaviour of SiC whiskers (Silar Grade SC-9, ARCO Metals Co., Greer, South Carolina) in hexane and toluene was investigated using four different dispersants: (1) aluminium *sec*-butoxide stearate, Al₅(*sec*-OC₄H₉)₁₃(C₁₇H₃₅COO)₂ (Alfa Products, Danvers, Massachusetts), (2) a monocarboxy-terminated polystyrene *MW* 250 000 (Aldrich Chemical Co., Milwaukee, Wisconsin), (3) a copolymer of 70:30 polystyrene and methylmethacrylate *MW* 270 000 (Polysciences, Warrington, Pennsylvania), and (4) a silanized version of the polystyrene polymer. Whisker dispersions were prepared by sonicating the whiskers (0.5 g) and a dispersant with hexane or toluene (8 ml) in a 12-ml graduated centrifuge tube for 30 min, then tumbling the dispersion overnight on a ball mill. In the sedimentation experiments, the dispersions were allowed to settle to con-

stant volume and the packing density was calculated as a percentage of theoretical using 3.2 g ml⁻¹ as the density of SiC. Dispersant concentrations were based on the weight of the whiskers.

The silanized polystyrene dispersant was prepared via a Friedel-Crafts reaction [3] with the alkylating agent *p*-chloromethylphenyltrimethoxysilane (Petrarch Systems Inc., Bristol, Pennsylvania). The reaction was carried out under a nitrogen atmosphere in a 250-ml three-neck round-bottom flask equipped with a reflux condenser. A solution of polystyrene (1 g) and the organosilane (1.92×10^{-3} mol) in *o*-dichlorobenzene (40 ml) (MCB Chemicals, South Plainfield, New Jersey) was prepared in a 60-ml pressure-equalizing funnel in a nitrogen-purged glove box, then transferred to the reaction flask under a nitrogen purge and heated to 65°C.

A solution of AlCl₃ catalyst (6.4×10^{-4} mol, using 1 M solution in nitrobenzene from Aldrich Chemical Co.) in *o*-dichlorobenzene (40 ml) was then added dropwise, using a second pressure-equalizing funnel, and the mixture was stirred and heated for 18 h. After the solution was cooled to room temperature, isopropanol was added and the solution was cooled further to precipitate the polymer. The product was collected on a filter and washed thoroughly with isopropanol.

The silicon content of the silanized polymer was determined to be 0.63 wt % by inductively coupled plasma (ICP) analysis (Model 86, I.S.A. Jobin-Yvon, Metuchen, New Jersey). This corresponds to one silane group every 40 styrene units, as shown in Fig. 1. Gel permeation chromatography (GPC) indicated that the molecular weight of the polymer had not changed, and ICP analysis of the GPC effluent confirmed that the polymer contained silicon.

2.2. Sintering studies

Alumina/whisker dispersions were prepared by mixing whisker dispersions (4 vol % solids, 10 wt % polystyrene) with Al₂O₃ dispersions (ALCOA XA-139

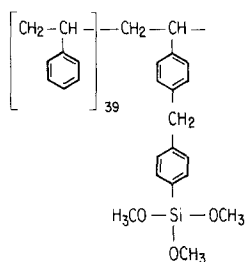


Figure 1 Structure of silanized polystyrene.

alumina, Alcoa Center, Pennsylvania, 20 vol % solids, 2 wt % oleic acid). The whisker dispersion was allowed to stand approximately 15 min before the supernatant, containing approximately 80% of the whiskers, was removed and added to the Al_2O_3 dispersion. For some dispersions, 8 wt % yttrium isopropoxide was added to the Al_2O_3 dispersion before the powder and whisker dispersions were mixed together. The mixed dispersion was then colloid-pressed in a Carver press using 0.20 μm filters; the final pressure applied was 14 k.s.i. The green densities obtained were approximately 60% of theoretical.

Organics were burned out in air at 600°C for 2 h. The composites were then packed in SiC whiskers in a graphite crucible and fired at 1550 and 1800°C in a graphite resistance furnace with a flowing argon atmosphere. The microstructure of the composites was examined using a dual-stage scanning electron microscope (Model S-530, Hitachi, Rockville, Maryland).

3. Results and discussion

3.1. SiC whisker dispersion studies

The SiC whiskers employed in this study were dispersed in nonaqueous media using different dispersants. The dispersant aluminium *sec*-butoxide stearate, "AIBS", is an oligomeric alkoxy carboxylate whose reactive butoxy groups permit grafting to the whisker surface. Similar chemistry is known to occur for analogous monomeric titanium compounds that have been used to disperse BaTiO_3 powders [4, 5]. Since the matrix for the composites was alumina, AIBS was chosen here because it contains aluminium. The polystyrene and polystyrene/methylmethacrylate dispersants were selected based on theta thickness calculations [6] that indicated these polymers would provide a coating approximately 30 nm thick, thereby increasing the effective volume of the whiskers in the green body by 20 to 30%.

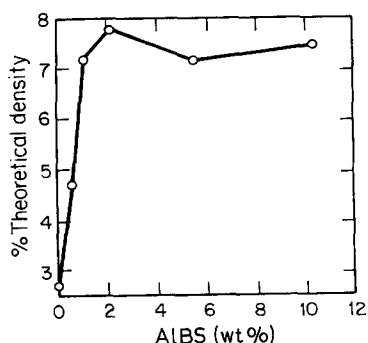


Figure 2 Sediment density of SiC whiskers dispersed in hexane against wt % AIBS.

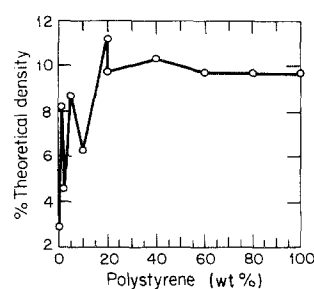


Figure 3 Sediment density of SiC whiskers dispersed in toluene against wt % polystyrene.

Figs 2 and 3 show the sediment density of SiC whiskers as a function of dispersant concentration (AIBS in hexane and as-received polystyrene in toluene, respectively). Small additions (approximately 1 wt % or greater) of AIBS increased the sediment density from less than 3% of theoretical to a maximum of between 7 and 8%. Between 10 and 20 wt % of the polystyrene resulted in maximum densities between 10 and 11% of theoretical. These low sediment densities are due to the high aspect ratio ($l/d = 75$) of the whiskers, which results in poor packing.

Although the whisker sediment densities were low, the steric stabilization achieved by using dispersants did result in a two- to four-fold increase in density over unstabilized dispersions, indicating that the presence of the dispersants improved whisker dispersion. This is evident in the optical microscope photographs of Fig. 4, which compare whiskers dispersed in pure hexane (Fig. 4a) with those dispersed in a mixture of toluene and 20 wt % polystyrene (Fig. 4b). In Fig. 4a the whiskers are clumped together in large bundles, or "haystacks", which reach nearly 500 μm in length. Although there is still evidence of whisker agglomeration in Fig. 4b, none of the large bundles of Fig. 4a are present.

Sedimentation times also increased from a few minutes to a few hours in the presence of dispersants. This phenomenon was important during the colloid-pressing operation, because it provided more time to work with the dispersions.

Mixed alumina/whisker dispersions using the unmodified polystyrene as the whisker dispersant showed a tendency for whisker agglomeration when the dispersed whiskers were added to the alumina/oleic acid dispersion. This was especially pronounced for whisker loadings of less than 5%, in which case agglomeration occurred within seconds after mixing. The destabilization of the whisker dispersions is probably due to the displacement of the weakly adsorbed polystyrene (van der Waals interaction) by oleic acid, which can hydrogen bond to hydroxyl groups at the whisker surface.

In contrast, whiskers did not agglomerate when silanized polystyrene was used as a dispersant. Through the reaction of its alkoxy groups with hydroxyl groups at the surface of the SiC to eliminate a molecule(s) of alcohol, the silanized polystyrene can form a chemical bond (Si-O-Si) with the whisker surface, thereby providing a stable dispersion in the presence of oleic acid. The copolymer of polystyrene and methylmethacrylate was also found to be a suitable dispersant for the whiskers in the presence of

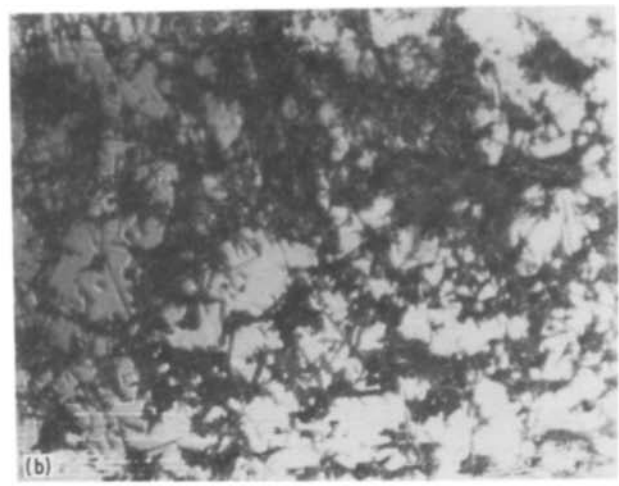
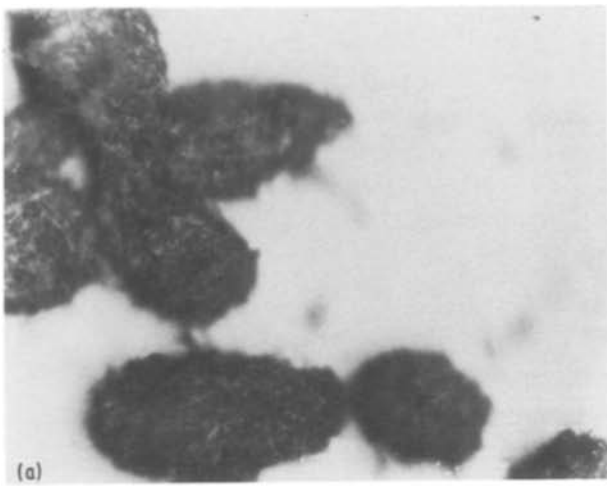


Figure 4 Optical microscope photographs of whisker dispersions in: (a) pure hexane, and (b) toluene with 20 wt % polystyrene. Both are magnified $\times 100$.

oleic acid. This polymer is capable of hydrogen bonding with the whisker surface and does not allow the monomeric oleic acid to compete effectively for surface sites.

These studies demonstrate that it is important to select dispersants that are compatible in mixed systems. Grafting of polymers to the particle surface is one approach to this problem. Polymeric dispersants with reactive silane groups have been grafted to the surface of silica powders in the past [7], but the silane groups have been introduced during the synthesis of the polymer itself. Silanization of commercially available polystyrene using the Friedel–Crafts reaction is a simple, alternative way to obtain chemically active polymers for grafting to ceramic powders or whiskers.

3.2. Sintering studies

Preliminary sintering studies showed that the sintering atmosphere is an important variable in these systems. Sintering to 1550°C in a dilatometer using a static argon atmosphere containing small amounts of oxygen resulted in extensive whisker oxidation and concomitant disappearance of whiskers. X-ray diffraction

results showed the presence of mullite in the final composite, resulting from the reaction of SiO_2 formed from the whiskers with the Al_2O_3 matrix.

When sintering was conducted in a graphite resistance furnace with a flowing argon atmosphere, the problem of whisker oxidation was eliminated. However, the compacts exhibited weight losses on the order of 1 and 10% at 1550 and 1800°C, respectively. Similar results were obtained when an Al_2O_3 compact containing no SiC whiskers was sintered under identical conditions. With the composites, at both temperatures a small amount of yellow crystalline material was deposited at the ends of the graphite crucible and in the whiskers used to pack the compacts; only a small amount was detected in the composites themselves. X-ray diffraction results indicate that this material was $\beta\text{-Al}_4\text{SiC}_4$. It appears that under the sintering conditions used, significant reduction of the Al_2O_3 occurred.

The SiC whiskers significantly inhibited densification of the composites. Fig. 5 shows densities achieved under different sintering conditions as a function of whisker concentration. However, even Al_2O_3 samples without whiskers had densities of only 92 to 94%. It is possible that carbon is inhibiting sintering of the Al_2O_3 . This is supported by the observations that compacts were grey after firing, and Al_2O_3 compacts fired in air achieved densities of 96 to 97%.

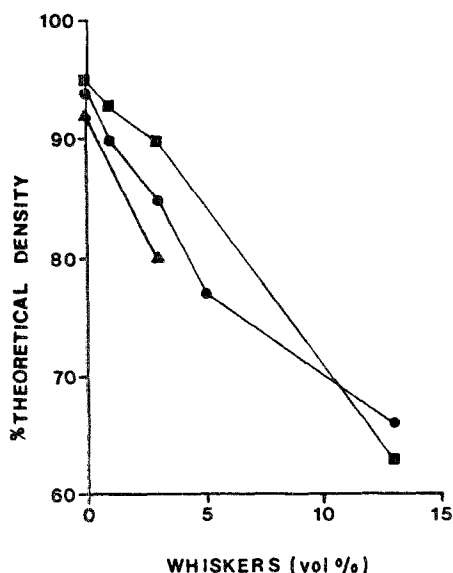


Figure 5 Percentage theoretical density against vol % SiC whiskers for $\text{Al}_2\text{O}_3/\text{SiC}$ whisker composites sintered at different temperatures. (■) 1800°C, 1.5 h (●) 1550°C, 1 h (▲) 1450°C 2.5 h.

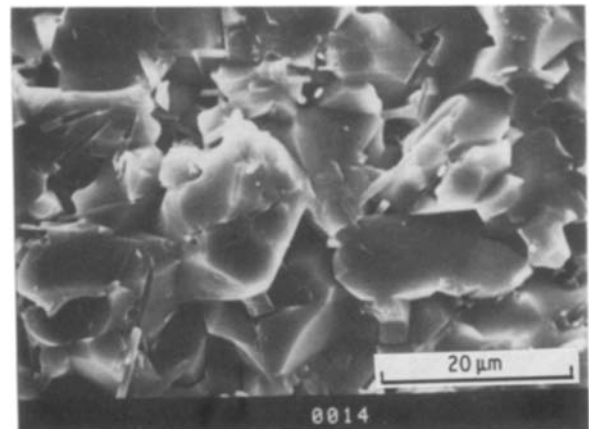


Figure 6 SEM of an $\text{Al}_2\text{O}_3/3$ vol % SiC whisker composite sintered at 1800°C for 2 h.

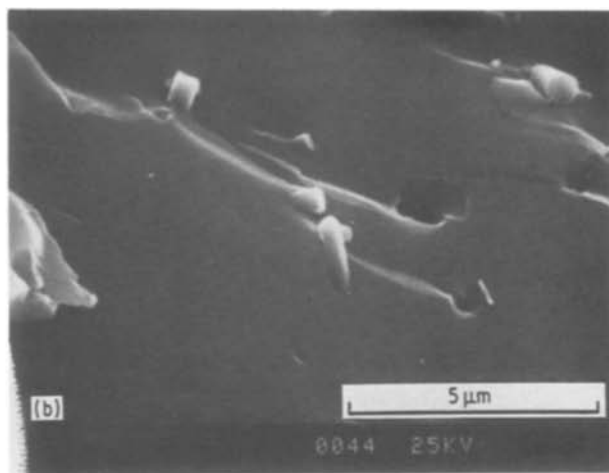
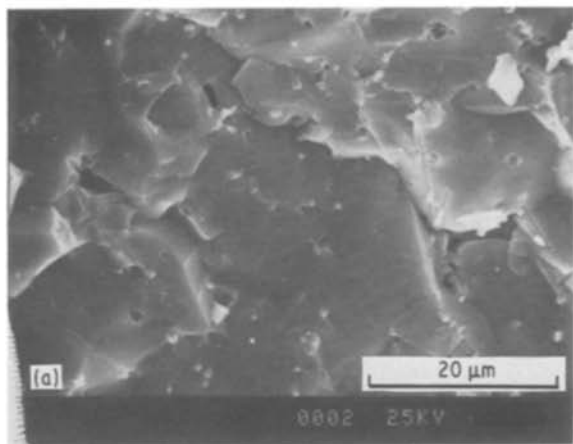


Figure 7 SEMs of an Al_2O_3 /3 vol % SiC whisker/8 wt % yttrium isopropoxide composite sintered at 1800°C for 15 min, magnified: (a) 2000X, and (b) 10,000X.

Porosimetry measurements on sintered compacts (1550°C , 1 h) with whisker loadings of 6 and 13 vol % showed that the average pore size increased from approximately $0.07\ \mu\text{m}$ in the green state to approximately $0.70\ \mu\text{m}$ after sintering.

Fig. 6 is a scanning electron micrograph (SEM) of a fracture surface of an Al_2O_3 /SiC whisker compact sintered at 1800°C for 2 h. This micrograph shows considerable pore coarsening and grain growth with little densification. There is no evidence that densification of the Al_2O_3 around the whiskers was aided by the polymeric dispersant used for the whisker dispersions.

Alumina/3 vol % SiC whisker compacts doped with yttrium isopropoxide and fired at 1800°C for 15 min had final densities of 95%, comparable to densities obtained for Al_2O_3 compacts fired under similar conditions. In contrast, a density of only 87 to 90% was achieved for undoped composites containing 3 vol % SiC whiskers. SEM/EDS results showed approximately 0.6 wt % yttrium in the sintered compact. Large pores were observed, but they were always associated with whisker agglomerates. As shown in Figs 7a and b, the yttrium-doped composite underwent considerable grain growth and the Al_2O_3 densified around the whiskers to a much greater extent than in samples with no added yttrium. Overall, this study indicates that to

obtain high densities in pressureless-sintered whisker composites, it will probably be necessary to use a sintering aid.

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