Sintering and oxidation in gel-coated $\text{SiC}_w/\text{Al}_2\text{O}_3$ composites

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Abstract. Boehmite gel-coated SiC whiskers have been studied as discs and as dispersed in gel and commercial alumina. The coated whiskers oxidize and react to some extent in alumina-rich composite compacts when heated in vacuum. In the absence of alumina as matrix, discs of coated whiskers turned brittle on heating above 1600°C. A density of 3.7g/cc was obtained for compacts of SiC whiskers in submicron alumina when sintered pressureless for 2 h at 1600°C. A smooth interface, compatible with the matrix, has resulted in good mechanical properties.

Keywords. Sintering; gel-coating; coated whiskers; composites.

1. Introduction

A ceramic with good toughness is required for engineering applications and this is achieved in composites by introducing fibres or particles in a suitable matrix. The morphology of the embedded material plays a crucial role in strengthening (Faber and Evans 1983). When whiskers are used for reinforcement, the large aspect ratio that one desires for higher strength results in poor packing and low green density. Consequently post-sintered densities are affected. A high sintered density is considered possible only under pressure (Homeny *et al* 1987). Pressureless sintering is most desirable when conventional forming techniques have to be utilised for the economical production of components with complicated shapes and high volume.

A hypothetical model calculation by Hsueh (1988) sets a limit for the density achievable by pressureless sintering on the basis that the gap between an already dense whisker in a densifying matrix generates a stress which would counteract sintering, the effect of which can be overcome by applying pressure or by coating of whiskers. In this paper it is shown that coating of SiC whiskers with boehmite gel aids sintering of alumina composites. Compacts with 10 wt% coated whiskers in alumina matrix attain a density of 3.66 g/cc after two hours of sintering in vacuum at 1600°C. The coating also protects the whiskers against damage during handling, milling and other reactions. Since the boehmite coating sinters on heating and the whiskers are in an oxide-rich alumina matrix it would be of interest to study their oxidation behaviour. The results on the investigation of monolith composites prepared from boehmite gel and SiC whiskers, discs of SiC whiskers coated with diluted boehmite gel, and composite pellets made from commercial alumina and coated whiskers are presented here.

2. Experimental

2.1 Material preparation

Boehmite gel was prepared by the hydrolysis, condensation and polymerization of aluminum isopropoxide as detailed in an earlier work (Saraswati *et al* 1987). This

gel was used in making monolithic composites and for coating the whiskers. Boehmite gel had nanometer size particles, ≈ 8 nm, and micropores of size 3 nm. The transition phase aluminas, gamma and delta, form on heating the gel at 350 and 950°C respectively (Saraswati 1988a). They have large surface areas and high reactivities. SiC whiskers, commercially obtained, had an average diameter of $0.5\text{ }\mu\text{m}$ and an aspect ratio of 15. They were predominantly in the β -cubic phase and contain small percentages of hexagonal α -phase also as confirmed from X-ray diffraction. Submicron commercial alumina was used for making the composite compacts.

2.2 Monolithic composites

10 wt% of SiC whiskers were well-dispersed in nearly gelled boehmite. The dispersion was dried in petri dishes of 5 cm diameter. The gel composites dried quickly and the shrinkage was lower as compared to alumina xerogels. On heating, the monoliths followed the phase transitions of boehmite from γ to δ to α at appropriate temperatures viz. 350, 950 and 1100°C respectively. The α -phase is crystalline corundum phase whereas γ and δ have partial disorder (Saraswati 1988a). Unlike alumina xerogel, which had a smooth surface and needed no surface finish, the SiC embedded composites have a coarse surface. Polishing had to be done carefully for hardness measurements as the monoliths were porous (Saraswati 1988b).

2.3 Coating of whiskers

The whiskers were dispersed in dilute solution of boehmite gel, ultrasonically homogenized and dried in petri dishes of 10 cm diameter. The dry discs were rigid and crackfree inspite of high porosity (density 0.72 g/cm^3). The discs were convenient for handling and characterization. They were calcined for 10 h at 500°C to convert boehmite to γ -alumina (Saraswati *et al* 1987).

2.4 Composite compacts

Submicron-size alumina powder was mixed with 10 wt% coated and calcined whiskers with 10 wt% yttria. The mixture was dispersed in alcohol and homogenized ultrasonically. The slurry was dried and the powder was cold-pressed into compacts. The green density of the compacts were in the range 1.85 to 1.95 g/cm^3 . The compacts were heated in vacuum for two hours at 1600°C. The density of the sintered compacts were measured by the displacement method.

3. Results

3.1 Density

The monolithic whisker-embedded composites were porous but had a density comparatively higher than alumina xerogels. The values are compared in table 1.

Table 1. Density and microhardness in composites

Materials	Density (g/cm ³ ± 5%)	Hardness (kg/mm ²)
γAl ₂ O ₃	1.37 [†]	116 ± 10 (Vickers)
αAl ₂ O ₃ monolith	3.08 [†]	904 ± 10 (Vickers)
SiC _w /Al ₂ O ₃ monolith	2.65	190 ± 10 (Vickers)
SiC _w /Al ₂ O ₃ monolith	3.3	1300 ± 20 (Vickers)
SiC _w /Al ₂ O ₃ pellet	3.66	1850 ± 50 (Knoop)

[†] Saraswati (1988b)

They did not attain theoretical density even after prolonged heating at 1600°C. The maximum density attained in the monolith was 88%.

The 10 cm diameter discs of gel-coated whiskers had a green density of 0.72 g/cc. They were rigid and crackfree. The discs showed no change in density even after sintering in vacuum for four hours at 1600 and later at 1800°C. On heating above 1600°C the colour of the discs changed to dark grey and they became soft and brittle.

The green density of the composite pellets ranged between 1.85 and 1.95 g/cm³. After sintering at 1600°C for 2 h the compacts had an average density of about 3.7 g/cm³.

3.2 Microstructure

Uniform dispersion of whiskers was seen in both coated disc and monolith composites (figure 1). As the monolith composites did not attain full density the microstructure reveals voids and pores apart from good adhesion of the coating (figure 2). The matrix grains were submicron size after sintering. Oxidation of whiskers can be inferred from micrographs in figure 3, when monoliths were sintered in open air at temperatures above 1200°C.

In the composite pellets, grains are equiaxed and have an average size of 4 μm. The distribution of grains and whiskers appeared uniform at low magnification (figure 2). But at high magnification, > 8000X, nonuniformity appeared in the EDX counts and micrographs. There were whisker-rich regions where the counts of Si was selectively higher and there were yttria agglomerates in some areas. Such inhomogeneities could limit densification and are discussed in later sections.

Whisker pull-outs were evident in the micrographs (figure 2b). They indicate a weak matrix/whisker interface and are desirable for improving the strength of a composite.

3.3 Infrared absorption

FTIR spectra (figure 4) taken in the coated SiC disc, sintered in vacuum at 1800 °C, show a strong absorption band at 785 cm⁻¹. This is characteristic of Si–C stretching.

Figure 1. SEM of fractured surface in (a) gel-coated SiC_w disc, and (b) monolith composite.

This again is present in the composite (figure 5) at 792 cm^{-1} along with other absorptions corresponding to Al–O stretch vibrations. The absorption at 950 cm^{-1} is probably due to the Si–O stretching vibration from non-bridging oxygen as has been seen in some silicates.

Figure 2. SEM of composite compact showing (a) whiskers and grains, and (b) whisker pull-outs.

3.4 X-ray diffraction

The powder diffraction patterns in the monolith composites displayed spectral lines characteristic of SiC and the respective phase of alumina (γ , δ , or α). When heated in air above 1200°C an additional amorphous band was noticed at $d \sim 3.35 \text{ \AA}$ due to silica formation. Coated whisker discs also showed the presence of silica to a small extent when heated in open air while embedded in alumina powder. But this amorphous band had a higher intensity when the disc was powdered and well-dispersed in alumina (figure 6). The coated whisker disc, even after heating at 1800°C in vacuum did not show the presence of silica but the composite did (figures

(a)

(b)

Figure 3.

(c)

Figure 3. Oxidation of monolith composites on heating in air at (a) 1200, (b) 1250, and (c) 1450°C.

Figure 4. FTIR spectrum of coated whiskers heated at 1800°C.

Figure 5. FTIR spectrum in composite compact.

Figure 6. XRD of (a) coated disc and (b) same heated in open air at 1200°C after powdering and dispersing in alumina.

Figure 7. XRD of coated whisker disc (a) before and (b) after heating at 1800°C in vacuum.

Figure 8. XRD of (a) coated disc and (b) composite after heating at 1600°C in vacuum.

7 and 8). These results show that the alumina matrix could itself be a source of oxygen for oxidation of whiskers at high temperatures. In the XRD of dense composite pellets, apart from alumina and silicon carbide weak lines from Al_4SiC_4 are also present. These were not present in the more porous pellets.

3.5 Microhardness

Indentation hardness measurements were carried out in the composite monoliths and compacts. The scatter in hardness values was 5 to 10% depending on the load. Different loads were used for the monoliths and compacts as their thickness and hardness values varied. For monoliths (thickness < 1 mm and low hardness) 25 and 50 g were used as loads whereas for compacts (5 to 8 mm thick with higher hardness numbers) 100 to 500 g were used. Variation with load was minimal. About 20 impressions were taken with a Knoop indenter. The average hardness for composite pellet was 1850 kg/mm^2 , higher than alumina. Halland *et al* (1987) have reported density and hardness values for nanocomposites prepared from colloidal alumina and polysilastyrene. Their observations compare well with ours. Estimation of toughness through the indentation method had some scatter owing to porosity. The indentation impressions with a load of 5 and 10 kg indicated toughness K_{1c} to be about $5.1 \text{ MPa m}^{1/2}$.

4. Discussion

4.1 Sintering

Monoliths of whisker-embedded alumina gel do not sinter to a high density in spite of heating for long durations at 1600°C . This is partly due to an initially low green density apart from the coarse micron size of whiskers in comparison to the nanometer size of gel particles which may inhibit densification owing to differential stress. The micrographs of monoliths reveal that the gel wets and coats the whiskers very well. In these and the porous pellets there was no evidence of reaction of gel with the whiskers as evidenced by XRD.

The boehmite gel coating on the whiskers also sinter with the matrix on heating the composite pellets. This fits the whiskers well into the matrix and prevents stresses or gaps, which are detrimental to densification. Thermal expansion coefficients are also compatible. These factors, we think, are responsible for the good density in the compact. As long as the coating is not very thick the stresses on the whiskers due to shrinking may be expected to be small. On sintering for two hours at 1600°C in vacuum the density of the pellet was 96% for an alumina composite with 10 wt% whiskers. Comparing this with the values obtained by Becher *et al* (1988) for pressureless sintering this is quite high. It is possible to improve upon the density further by optimizing the coating thickness, process conditions and sintering parameters. A better packing and green density would also improve the mechanical properties apart from sintered density.

4.2 Oxidation

The coated whiskers (disc), after heating at 1800 °C in vacuum showed no silica as deduced from XRD and FTIR (figures 4,7,8). The SiC phase alone was observed. The reason for the change in colour and brittleness of the disc is not clear although it is possible that the ratio of cubic to hexagonal phase could have changed on heating above 1600 °C. The composite pellets heated in vacuum at 1600 °C, under identical conditions as the coated whiskers, indicated an amorphous band due to silica showing that an alumina matrix itself could be a source of oxygen when the volume fraction of alumina is high. Furthermore, the presence of weak lines of Al₄SiC₄ in the XRD patterns of some compacts with high density indicate an interaction of alumina with silicon carbide to produce silica and the above compound as,

Increasing the volume fraction of whiskers in alumina may help against oxidation but will reduce density owing to poor packing. As the flexural strength is a function of both the volume fraction of whiskers and the density it is obvious that a compromise has to be reached. No free yttria was detected. As the addition was 10% above the detectable sensitivity of XRD, one can surmise that it has gone into solid solution.

4.3 Mechanical properties

Coating of the whisker with gel is advantageous for improving whisker strength by masking the flaw centres and reducing interface fracture energy by smoothening the interface. As the coating also sinters, there may not be a gap which counteracts sintering rate by introducing undesirable stress. The hardness values in the monolithic composites are higher than in the alumina xerogels (table 1). In the sintered pellets also the average hardness was higher than in alumina (1600 kg/mm²), though the density is not fully theoretical. The scatter of hardness values and the presence of small agglomerates as revealed by microstructure show that a better processing might result in a higher value. The K_{1c} , measured by the indentation method with loads between 5–10 kg was around 5 MPa m^{1/2}, which though good, cannot be considered very high. But with better processing conditions and optimised coating thickness, a higher density and good toughness value could be achieved through pressureless sintering for limited volume fractions of whiskers in alumina. For higher volume fractions, inferring from the coated discs, packing and density could be limited without applied pressures.

5. Conclusions

Our observations show that pressureless sintering of commercial submicron alumina with gel-coated whiskers yields a good density. The coating improves whisker strength, exposes a smoother interface, and better matrix compatibility. Gel-processed alumina is not a good matrix as the whiskers are too coarse in size as compared to nanosized alumina and thus create a differential stress detrimental to sintering rate. An

alumina-rich matrix was found to oxidize the whiskers but with little alumina the coated whiskers turned brittle when heated above 1600°C. It can be concluded that pressureless sintering has advantages and is feasible for limited volume fractions of coated whiskers.

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