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Pressureless sintering of Al_2O_3–SiC whisker composites

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High-density compacts, up to 88% theoretical density, of Al_2O_3–SiC whiskers were prepared by a pressure casting and impregnation technique. Starting with these green bodies, composites of Al_2O_3–20 vol% SiC whiskers were pressureless sintered to higher than 95% theoretical density. They were further densified by hot isostatic pressing up to 99% theoretical density, resulting in a rupture strength of 680 MPa and a fracture toughness of 4.70 MPa $m^{1/2}$.

1. Introduction

SiC whisker-reinforced composites have been investigated extensively in recent years due to their improved mechanical properties compared to the monolithic materials [1–16]. However, whisker-containing powder compacts are difficult to densify, because of formation of a constraining network of whiskers [13, 16]. This network usually exerts tensional stresses on the matrix and severely inhibits particle rearrangement and shrinkage during sintering [13, 17].

Lange [18] proposed a constraining network model for predicting the densification behaviour of composites. He suggested that even a small fraction of an inert phase (less than 20 vol %) could form a short network which could act as a barrier to sintering. Therefore, hot pressing is a common practice for the densification of whisker-containing composites, although sintering or SIN/HIP (sintering followed by hot isostatic pressing) is known to be more economical.

Sacks *et al.* [15] reviewed several possible strategies for enhancing densification in whisker-containing powder compacts:

1. liquid-phase sintering [13];
2. decreasing the aspect ratio of the whiskers [13, 14];
3. use of particle/whisker compacts with higher packing densities [14, 15].

The first two approaches inevitably will result in some disadvantages: reduced mechanical properties at high temperatures due to the residual liquid phase and lessened improvement in fracture toughness due to the lower aspect ratio whiskers, respectively. The third method can avoid these disadvantages and increase the sinterability of compacts. In addition, it can minimize sintering shrinkage and reduce the constraining effect of the whisker network. Sacks *et al.* [15] reported that, starting with high green-density compacts in the range 66%–69% theoretical density, Al_2O_3–15 vol % ZrO_2–15 vol % SiC whisker composites can be densified up to 94% theoretical density [15].

The primary objectives of this study were the preparation of high green-density compacts of Al_2O_3–20 vol % SiC whiskers by pressure casting and an impregnation technique, and densification of them via SIN/HIP close to full density.

2. Experimental procedure

2.1. Materials

α-alumina and β-SiC whiskers were used for the matrix and reinforcing material, respectively. The whiskers were first sorted out by a sedimentation method that eliminates both the particulate portion and large whiskers. They were further treated with 20% hydrofluoric acid solution to remove surface silica, and dried for subsequent processing.

2.2. Pressure casting

First, Al_2O_3 suspensions were prepared at pH 4 using an homogenizer. The pH was adjusted using nitric acid. Subsequently, a precalculated amount of SiC whiskers and dispersant (DAXAD, Grace and Co.) were added to the Al_2O_3 suspensions and the suspensions were then blended for 1 h in homogenizer.

The flow behaviour of the different slips containing 0, 20, 25, and 30 vol % SiC whiskers were characterized using a viscometer. The composite suspensions with a solid content of 48 vol % were cast under various applied pressures using a pressure casting apparatus [19]. The consolidated cylindrical casts (diameter 30 mm) were dried at room temperature for 1 day and subsequently dried at 60 °C for 2 days. To compare pressure casting with dry processing, several samples were uniaxially pressed at 50 MPa followed by isostatic pressing at 170 MPa.

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2.3. Impregnation

Cylindrical cast compacts were partially sintered at 1350 °C for 30 min to impart enough strength to withstand the subsequent processing steps. The partially sintered compacts were cut into 5 mm × 5 mm × 25 mm specimens and they were impregnated for 1 h with boiling saturated aluminium nitrate solution. The impregnated specimens were then immersed in a boiling ammonium hydroxide solution for 5 min to achieve aluminium hydroxide precipitation. The specimens were then heated slowly ($3\ ^\circ\mathrm{C\,min}^{-1}$) to 800 °C in flowing argon to decompose the hydroxide and to form alumina. The amount of alumina picked up by impregnation was calculated by measuring the weight gain. The impregnation, precipitation and decomposition procedures were repeated until the weight gain was negligible.

Pore size distributions of specimens at each procedure were analysed by mercury porosimeter.

2.4. Sintering and hot isostatic pressing

Samples were sintered in a graphite element furnace under helium at 1800 °C for 4 h. A laboratory hot isostatic press was used for the final densification of the sintered samples at 1600 °C for 30 min under 150 MPa Ar. For comparison, several samples were hot pressed at 1800 °C for 1 h with an applied pressure of 45 MPa.

2.5. Property measurements

Densities were measured using the Archimedes principle, and the relative density was calculated based on the densities of Al_2O_3 ($3.987\ \mathrm{g\,cm}^{-3}$) [20] and SiC ($3.215\ \mathrm{g\,cm}^{-3}$) [21] assuming a rule of mixtures. The flexural strengths at room temperature and 1000 °C were determined using a three-point rupture test on 5 mm × 5 mm × 25 mm bars whose surfaces and edges were polished with an 800 grit diamond wheel. The fracture toughness was measured using a Vicker's indentor with a load of 100 N.

3. Results and discussion

3.1. Pressure casting

By using the combination of pH adjustment and polyelectrolytic dispersant addition, Al_2O_3 particles and SiC whiskers were well codispersed at high solid content (48 vol %). As observed by other workers [14], the slip viscosities were increased with increasing whisker content. For example, viscosities of 29, 115, 134, and 140 mPa s were measured at the shear rate of $10\ \mathrm{sec}^{-1}$ for composite slips containing 0, 20, 25 and 30 vol % SiC whiskers. This behaviour is believed to be due to the high aspect ratio of SiC whiskers, which tend to form network structures at high concentrations. However, these viscosities were still low enough for pressure casting of prepared composite slips.

In order to obtain homogeneous green bodies, segregation of particles during casting must be avoided. When SiC whiskers and Al_2O_3 particles are codispersed, SiC whiskers tend to accumulate towards the bottom of the cast samples, whereas fine Al_2O_3 particles tend to concentrate near the top of the cast samples. In order to prevent segregation of whiskers during casting, the slip should have a high solid content and be consolidated rapidly. Rapid consolidation can be achieved by applying pressure during casting. In conventional suspensions, the experimentally determined casting rate is linearly proportional to the applied pressure [22, 23]. The experiment revealed that the casting rate of whisker-containing slips also linearly increased with applied pressure in the range 0.1–0.8 MPa. Although the slip casts well under gravity, the casting time for a 9 mm thick disc was about 2 h. An applied pressure of 0.8 MPa reduced this time to about 15 min. In addition to significantly reducing casting time, pressure casting also helps to produce homogeneous green bodies and eliminate density gradients. Fig. 1 shows the pore size distribution of specimens after each forming process. It indicates that pressure-cast specimen has lower porosity and smaller pores compared to either gravity cast or dry pressed specimen. Relative densities of the pressure-cast discs were quite high (68%–69%) compared to dry pressing (55%–57%).

3.2. Impregnation

Fig. 2 shows that the densities of composite compacts increase with the number of impregnation cycles. Theoretical impregnation densities were calculated assuming that all pores are filled with $Al(OH)_3$ solution at each cycle. A relative density of 88% was obtained after 14 impregnation cycles for Al_2O_3–20 vol % SiC whisker composites.

From a theoretical standpoint, the total amount of shrinkage which can occur during sintering is related only to the initial green density through the expression

$$\frac{\rho_0}{\rho} = \left(1 + \frac{\Delta L}{L_0}\right)^3 \qquad (1)$$

where ρ_0 is the green density, ρ is the sintered density, ΔL is the change in length during sintering and L_0 is the initial length of specimen. The linear shrinkages for full densification with the experimental impregna-

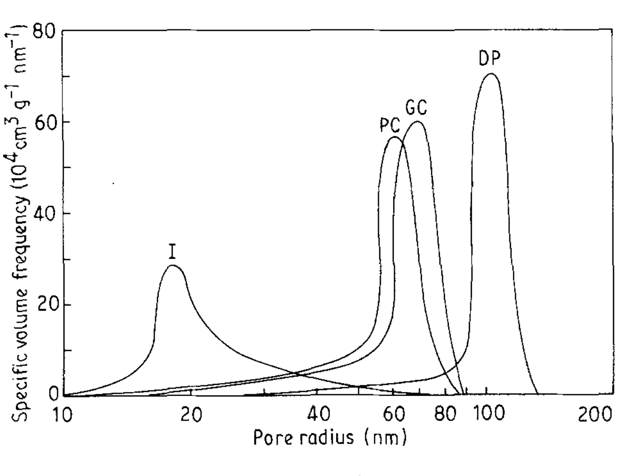

Figure 1 Plots of specific pore volume frequency versus pore radius for dry pressed (DP), gravity cast (GC), pressure cast (PC), and impregnated (I) Al_2O_3–20 vol % SiC whisker compacts.

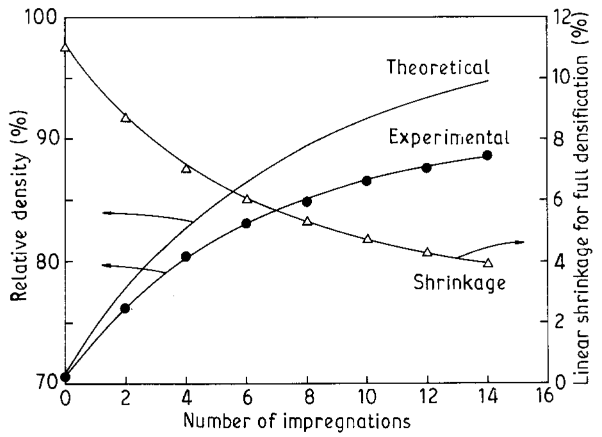

Figure 2 Effect of impregnation on relative density of Al_2O_3–SiC whisker compacts.

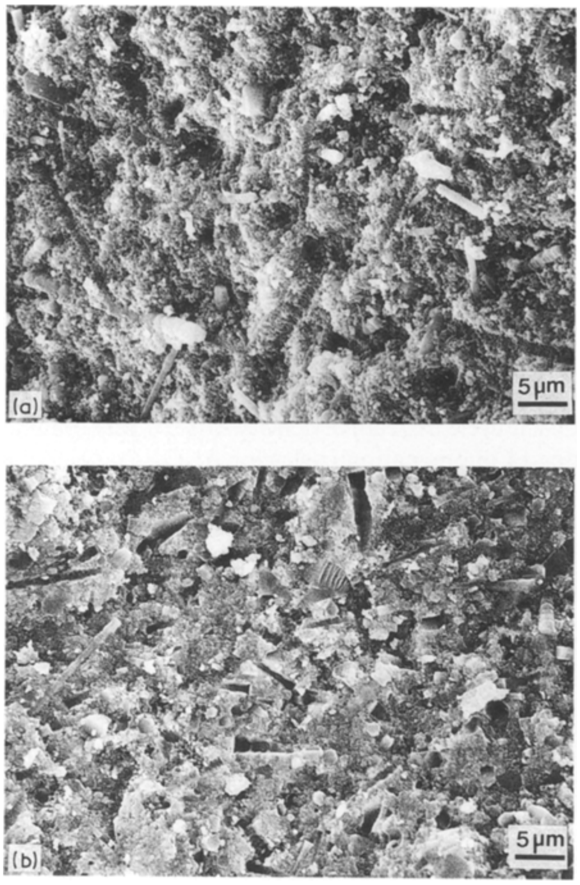

Figure 3 Fracture surfaces of Al_2O_3–20 vol % SiC whisker compacts: (a) before impregnation and (b) after 14 impregnations.

tion densities were calculated from Equation 1 and are shown in Fig. 2. It can be seen that increasing relative green density from 70% to 88% should decrease the shrinkage for full densification from 11.2% to 4.2%. This decrease in total shrinkage would decrease the tensile mean stresses in the matrix during sintering and elevate the sinterability of the composites.

Pore size distribution of the impregnated sample shifts to greatly smaller sizes (~ 18 nm) compared to that of the pressure-cast sample (~ 60 nm) as shown in Fig. 1. The result shows that the impregnation process has a beneficial effect on sintering by not only increasing green density but also reducing pore size. Fig. 3 shows the micrographs of the fracture surface of Al_2O_3–20 vol % SiC whisker bodies as partially sintered and after 14 impregnation cycles. The micrograph of the impregnated sample (Fig. 3b) shows that pores existing after pressure casting are mostly filled with Al_2O_3 derived from the thermal decomposition of the aluminium hydroxide and some sockets due to whisker pull-out can be clearly seen. Fig. 3 also indicates that the SiC whiskers are homogeneously distributed for samples prepared using pressure casting.

3.3. Sintering and hot isostatic pressing

The sintered densities of Al_2O_3–SiC whisker composites (ρ_C) with green density can be predicted by an equation derived from the constrained network model by Lange [18]

$$\rho_C = \rho_{OC}\{1 - \varepsilon_m[1 - (1/\alpha)(f/s)^{1/3}]\}^{-3} \quad (2)$$

where ρ_{OC} is the green density of the composite powder compacts, ε_m is the shrinkage strain of the matrix, f is the volume fraction of the SiC whiskers within the initial composite powder compacts, s is the limiting whisker volume fraction where closest whiskers touch to form a continuous network, and α is the numerical factor. The constrained network model is based on the hypothesis that the densification of the matrix in the composites will occur until the whiskers form a continuously touching network.

The experimentally determined and calculated sintered densities from the constrained network model with impregnated densities are given in Table I. Because Equation 2 was derived for particulate composites, the constraining effect will be larger for whisker composites at the same volume fraction of second phase because of the large aspect ratio of the whiskers. Nevertheless, the sintered densities of the composites show much higher values than the calculated values. This result suggests that when a high sinterability sample is prepared, some rearrangement of the whisker network can occur for further densification.

Fig. 4 shows the sintered densities of Al_2O_3–SiC whisker composites as a function of the SiC content. As observed by other workers [13, 14], densification of Al_2O_3 is severely inhibited by the addition of SiC

TABLE I Comparison of the experimental and calculated sintered densities of Al_2O_3–SiC whisker composites

ρ_{OC} (%)	ε_m	Relative sintered densities (%)	
		Calc.	Exp.
70.5	0.109 99	75.0	75.6
76.2	0.086 62	80.0	82.9
80.4	0.070 14	83.6	88.0
83.0	0.060 22	85.8	91.1
84.9	0.053 10	87.4	92.8
86.5	0.047 19	88.8	93.8
87.6	0.043 17	89.7	94.5
88.6	0.039 54	90.6	95.1

[a] s was taken by averaging the relative tap density (0.08) and relative pressing density (0.48) of SiC whiskers; $f = 0.176$, $\alpha = 1.05$.

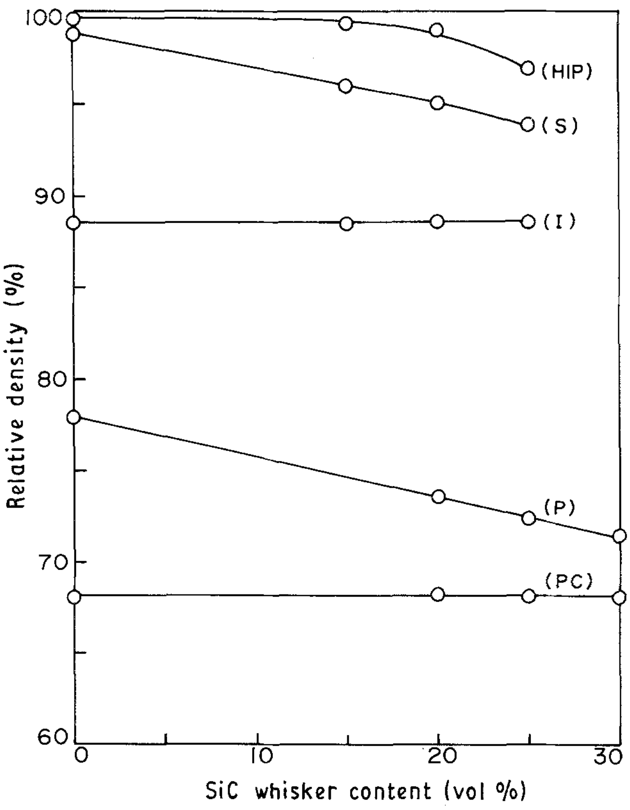

Figure 4 Pressure cast (PC), partially sintered (P), impregnated (I), sintered (S), and sinter-hot isostatically pressed (HIP) densities of Al_2O_3–SiC whisker composites as a function of the SiC content.

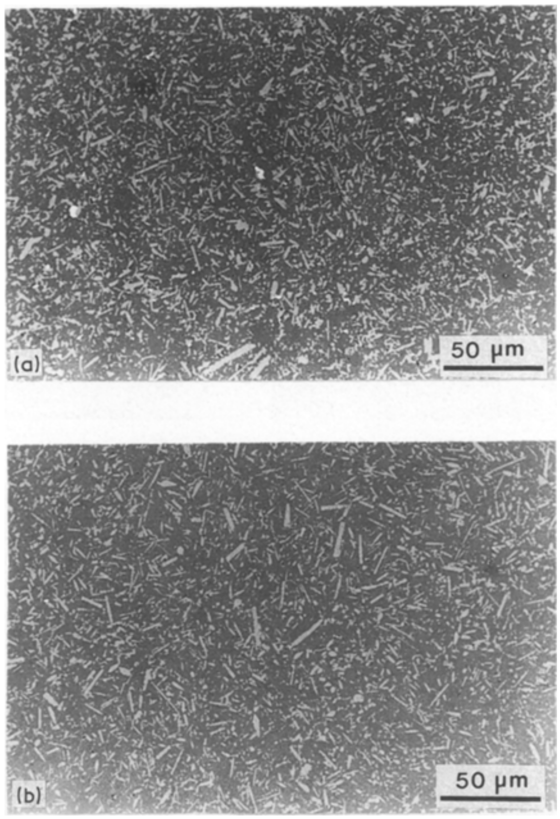

Figure 5 Optical micrographs of polished cross-sections of (a) sinter-hot isostatically pressed, and (b) hot-pressed Al_2O_3–20 vol % SiC whisker composites.

whiskers. Nevertheless, by using a combination of pressure casting and the impregnation technique, substantially improved densification resulted, in the current study. For the 15 and 20 vol % SiC whisker samples, the sintered densities are 3.72 g cm^{-3} (96.0% relative density) and 3.64 g cm^{-3} (95.1% relative density), respectively, whereas the corresponding values for pressure-cast samples are only 2.98 g cm^{-3} (77.0% relative density) and 2.90 g cm^{-3} (75.6% relative density), respectively.

A group of Al_2O_3–20 vol % SiC whisker composite samples with densities ranging from 94.7%–95.8% were hot isostatically pressed under 150 MPa argon for 30 min at 1600 °C. All samples which contained only closed porosity (i.e. relative density > 95%) achieved densities > 99.2% theoretical. Fig. 5 shows optical micrographs of the sinter-hot isostatically pressed and the hot-pressed samples. Both show similar microstructures (white phase is SiC) consisting of well-dispersed SiC whiskers in an alumina matrix with only minimal porosity. The flexural strength and fracture toughness of various samples are summarized in Table II. Properties of SIN/HIP samples show comparable values with those of the hot-pressed samples. They also show that room-temperature strength of the composites is maintained at 1000 °C. Fracture surfaces of the Al_2O_3–20 vol % SiC whisker composites which were sinter-hot isostatically pressed and hot pressed are shown in Fig. 6. As shown, the SiC whiskers are easily observed indicating crack–whisker interaction, which results in the toughness increase. Al_2O_3–SiC whisker composites made from whiskers with surface carbon coatings are under investigation for further improvement of toughness.

TABLE II Properties of various Al_2O_3–SiC whisker composites

Sample	Whisker content (vol %)	Relative density (%)	Fracture[a] toughness (MPa $m^{1/2}$)	Flexural[a] strength (MPa)	
				RT	1000 °C
Sinter-hot isostatically pressed	20	99.2	4.70 ± 0.20	682 ± 96	670 ± 75
Hot-pressed	20	99.9	4.73 ± 0.18	698 ± 105	687 ± 84
	30	99.8	5.11 ± 0.17	775 ± 95	760 ± 82

[a] Average of five samples.

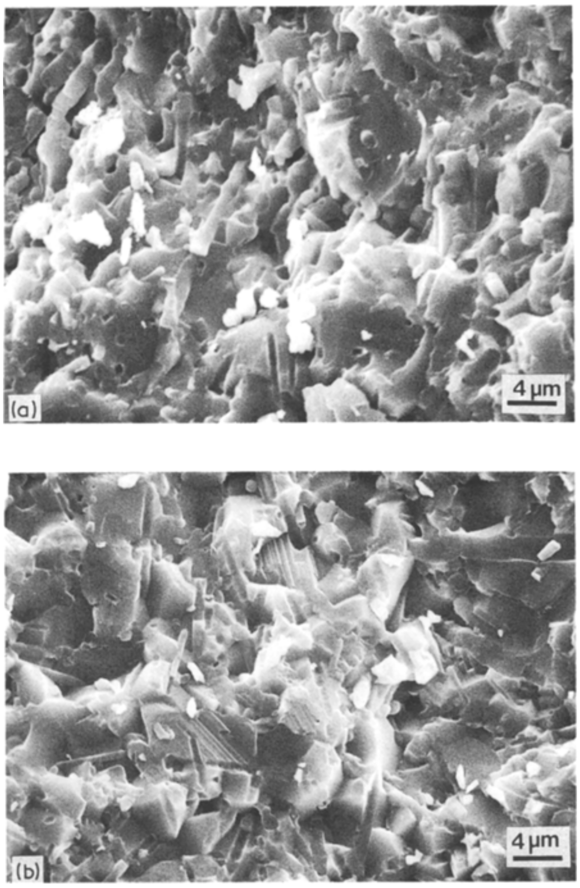

Figure 6 Fracture surfaces of (a) sinter-hot isostatically pressed and (b) hot-pressed Al_2O_3–20 vol % SiC whisker composites.

4. Conclusion

Pressure casting and an impregnation technique were used to prepare homogeneous and highly dense (88% relative density) Al_2O_3–SiC whisker compacts. Starting with these green bodies, Al_2O_3–20 vol % SiC whisker composites can be fully densified by pressureless sintering and subsequent hot isostatic pressing. They show typical flexural strength and fracture toughness values of 680 MPa and 4.70 MPa $m^{1/2}$, respectively.

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