Processing and Microstructure Development in Al₂O₃–SiC 'Nanocomposites'

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Abstract

Composites consisting of $Al_2O_3 + 5\,vol.\%$ $0.15\,\mu m$ SiC particles were prepared by pressureless sintering. The optimum conditions for achieving dense and uniform microstructures by conventional ceramic processing are given in detail. The SiC particles were found to strongly inhibit grain growth of the Al_2O_3 matrix. Densification was also significantly retarded by these ultra-fine particles, and possible explanations for this behavior are discussed.

Verbunde aus Al_2O_3 und 5 Vol.-% SiC (Partikelgröße: $0.15\,\mu m$) wurden mittels drucklosen Sinterns hergestellt. Die besten Bedingungen für die Herstellung dichter und homogener Gefüge mit Hilfe konventioneller Herstellungsmethoden für Keramiken werden im Einzelnen vorgestellt. Es wurde festgestellt, daß die SiC-Teilchen in sehr starkem Maße das Kornwachstum der Al_2O_3-Matrix behindern. Die Verdichtung des Materials wird beträchtlich durch diese ultrafeinen Teilchen verzögert. Mögliche Erklärungen für dieses Materialverhalten werden diskutiert.

Des composés $Al_2O_3 + 5\%$ en volume de SiC ($0.15\,\mu m$) ont été préparés par frittage conventionnel. Les conditions optimales pour obtenir des microstructures denses et uniformes par un processus d'élaboration céramique conventionnel sont détaillées. Il apparaît que les particules de SiC inhibent la croissance cristalline de façon drastique. La densification est également fortement retardée par la présence de telles particules ultrafines et les explications possibles de ce phénomène sont discutées.

1 Introduction

It was recently reported by Niihara and co-workers[1-4] that the incorporation of small amounts (5–10 vol.%) of 'nano'-sized ($0.3\,\mu m$ diameter) SiC particles into an Al_2O_3 matrix could significantly enhance the strength compared to pure Al_2O_3. In fact, the unindented strengths were reported to increase from 350 MPa for Al_2O_3 to over 1 GPa for the 5 vol.% SiC composite. Niihara and coworkers have provided relatively little detail on the processing procedures they used to produce such high-strength samples, other than they they used conventional techniques such as ball-milling (various dispersants have been reported). Research in the present authors' group and elsewhere has shown that small differences in the processing procedure (such as drying schedule, dispersant used, etc.) can have a pronounced effect on the microstructure and properties of these materials. This caused the present authors to experience some initial difficulties in reproducing the findings of Niihara and coworkers, and it was anticipated that other researchers will experience similar problems. The first objective of the present work, therefore, is to provide a detailed description of the experimental conditions found to be favorable for producing nanocomposite powders which subsequently can be fabricated into high-strength ceramics. It should be noted here that after homogeneous samples have been prepared using the methods outlined in this paper, surface preparation is also an important factor in the achievement of high strengths. (Four-point bend strengths greater than 1 GPa have been obtained on samples machined and then annealed at 1300°C in argon for 2 h. The details of the mechanical behavior will be reported elsewhere.[5]) Further, this study has concentrated on using conventional processing techniques as a relatively simple, cost-effective method for producing large quantities of samples.

The second objective of this study is to present preliminary results on the effects of ultra-fine ($0.15\,\mu m$) SiC particles on the sintering behavior of

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Al_2O_3. It has been previously reported that 4 μm SiC particles inhibit grain growth in Al_2O_3;[6] however, the extent to which ultra-fine SiC particles influence grain growth in Al_2O_3 has not been investigated. Also, there are no previous reports on the effect of such fine SiC particles on the densification kinetics of Al_2O_3. It is well known that larger inclusions, fibers or whiskers of SiC constrain densification in Al_2O_3.[7-11] However, ultra-fine SiC particles would not be expected to impose the same constraints on densification as those produced by these larger reinforcing phases. In certain metal systems, dispersions of second-phase particles have been found to retard sintering.[12] However, in ceramic systems, small second-phase particles have been observed to both enhance the overall densification rate (as in $BaTiO_3$ with Ba_2TiO_4 second-phase particles[13]) and to retard it (as in Al_2O_3 with ZrO_2 second-phase particles[14-16]). Thus, the effect of ultra-fine SiC particles on densification in Al_2O_3 is not easily predicted.

2 Experimental Procedure

Ultra-high purity α-alumina (99·995%; Sumitomo AKP-53, Osaka, Japan) with a mean particle size of 0·2 μm and β-SiC powder (Performance Ceramics Co., Peninsula, OH) with a mean particle size of 0·15 μm were used in this study. The powders were kept in a clean room environment in a class 100 laminar flow hood, and, whenever possible, any handling in the green state was performed in the clean room.

The starting powders were weighed in the appropriate amounts to yield a final volume fraction of 5 vol.% SiC particles. In order to promote homogeneous mixing of the two powders, they were dispersed in an organic medium. (The use of an aqueous medium was abandoned due to the tendency of the slurry to form hard agglomerates on drying.) As several different organics have reportedly been used as dispersants for this system,[1,3,17] sedimentation experiments were performed using hexane, acetone, ethanol and methanol. The results are given in Fig. 1. It is clear from this bar graph that hexane and acetone led to considerable flocculation. Methanol was chosen for processing because it produced the best dispersion but, for comparison, some samples were also prepared using hexane. For dispersion, the slurry was placed in a strong ultrasonic bath for 40 min. High purity ZrO_2 milling balls (Tosoh Ceramics Division, Bridgewater, NJ) were then added to the slurry, and it was milled for
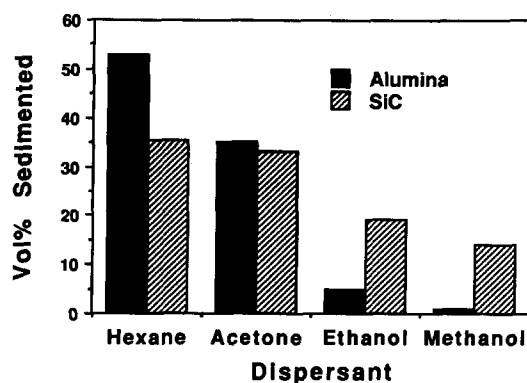

Fig. 1. Volume fraction of powder sedimented in graduated cylinder as a function of organic used for dispersing. The solid content was 8 vol.%, and measurement of vol.% sedimented was taken every 24 h—this data corresponds to the readings after 5 days.

48 h to further promote homogeneous mixing of the Al_2O_3 and SiC. The slurry was poured into a Teflon® bowl in the laminar flow hood, and dried under an infrared heat lamp. The height of the lamp was adjusted so that the slurry dried over a period of 24 h. The lamp was then removed and the slurry continued to dry in the hood for another 24 h. Although seemingly trivial, these details are extremely important, as it was found that drying for less time or under higher heat (lamp closer to slurry) led to hard agglomerates which could not be removed without compromising the purity of the powder. After slow drying under low heat, the powder was very uniform in color, and contained only soft agglomerates which were easily broken up using a Teflon® rod. Before pressing, the powder was crushed in 2-g lots between pieces of weighing paper for further homogenization. The powder was then uniaxially pressed at 42 MPa into discs 1·44 cm in diameter using a high-purity alumina punch and die set, and isostatically pressed at 350 MPa. Calcining was performed at 600°C for 10 h in air. This temperature was found to be low enough not to oxidize the SiC but high enough to burn off any residual organics from powder processing. The samples were then sintered in flowing nitrogen at various temperatures for 2 h. For calcining and sintering, the samples were surrounded by SiC powder in a covered alumina crucible.

For preparation of the Al_2O_3 samples, the Al_2O_3 powder was used without any special processing (i.e. dispersion, milling, crushing, etc.). Some Al_2O_3 samples were prepared by ball-milling, however, in order to check for any effects of ZrO_2 from the milling media on densification, as it has been reported that very small amounts of ZrO_2 can inhibit densification in Al_2O_3.[14] No difference in

densification behavior was observed between Al_2O_3 samples prepared by both methods, so it was concluded that there was no contribution from ZrO_2 contamination. Discs were uniaxially and isostatically pressed as already described, but a separate alumina die set was used to prevent cross-contamination. The samples were surrounded by alumina powder in a covered alumina crucible, and were calcined and sintered under the same conditions as the composite samples.

Sintered densities were measured using the Archimedes method with an immersion medium of deionized water plus a wetting agent. The theoretical density of the composite samples was calculated to be $3.948 \, g/cm^3$, based on theoretical densities of Al_2O_3 and SiC of 3.986 and $3.217 \, g/cm^3$, respectively. For the grain growth experiments, some Al_2O_3 and composite samples were hot-pressed to full density (vacuum, 1400°C, 50 MPa, 1.5 h for Al_2O_3; nitrogen, 1640°C, 50 MPa, 1 h for the composite). These samples were then annealed in flowing nitrogen for various times at 1700°C. For microscopic observation, samples were polished using diamond paste to a 1 μm finish. The composite samples were thermally etched in argon at 1450°C for 1 h in order to reveal the grain boundaries. The Al_2O_3 samples used for microscopic observation were those which were sintered at 1450°C, and they were thermally etched in air at 1400°C for 2 h. The polished sections were examined using a high-resolution scanning electron microscope (SEM). Grain size was measured using the linear intercept method with at least 400 intercepts for each measurement. Samples were prepared for observation by transmission electron microscopy (TEM) using grinding, dimpling and ion beam thinning.

3 Results and Discussion

Figure 2 ((a)–(c)) shows microstructures of Al_2O_3 and the composite materials prepared using methanol. It is evident from Fig. 2(b) and (c) that the SiC particles are well distributed throughout the Al_2O_3 matrix. Also, note that the particles are present inside the grains as well as on the grain boundaries. The grain boundaries of the composite are somewhat wavy and irregular compared to the quite straight boundaries of the Al_2O_3 sample. For comparison, Fig. 2(d) shows the microstructure of the composite prepared using hexane, a poor dispersant. This sample was sintered at 1800°C for 2 h, and reached a density of 92%, whereas the methanol-prepared sample was 99% dense after 2 h

at 1700°C. The hexane-prepared samples contained large voids, due to agglomeration of the SiC particles during mixing. Also, this microstructure shows a smaller grain size than the methanol-prepared sample, most likely due to considerable pore drag in the hexane-prepared sample, as it was only 92% dense.

Figure 3 shows a plot of grain size as a function of annealing time for Al_2O_3 and the composite (methanol-prepared). Here, zero annealing time corresponds to attainment of the setting temperature (1700°C). It is clear that the SiC particles significantly inhibited grain growth of the Al_2O_3 matrix. For instance, after 24 h at 1700°C, the Al_2O_3 grains were about 20 μm in diameter, while the composite grain size was 4.78 μm after 24 h. It is interesting to note that the grain size of the composite material is larger than would be predicted by particle pinning analyses.[18–20] For instance, the weakest pinning (largest limiting grain size) is given by Zener's original model,[18] which predicts a limiting grain size for 5 vol.% 0.15 μm particles as 2 μm. Further, the stronger pinning models[19,20] predict grain sizes an order of magnitude smaller than this.

The densification behavior is shown in Fig. 4 for Al_2O_3 and the composite (methanol-prepared). It can be seen that the Al_2O_3 samples sintered to nearly full density at 1400°C. However, the composite samples reached only 87% theoretical density at this temperature. In fact, a temperature of 1700°C was necessary to achieve 99% density in these samples (for the same sintering time). From this data it is clear that the presence of only 5 vol.% SiC particles severely inhibits densification. According to classical sintering theory, a reduction in grain growth rate should lead to an indirect enhancement of densification {densification rate $\propto 1/(\text{grain size})^n$, where $n = 3$ for lattice diffusion and $n = 4$ for grain boundary diffusion[21,22]}. However, in this case it appears that the retardation of densification was so severe that it overcame the inhibition of grain growth to result in an overall reduction in the densification rate. Similar behavior has been observed in Al_2O_3 containing small amounts (up to 10 vol.%) of ZrO_2,[15,16] but the mechanism for densification inhibition has not been determined. Two possible explanations for the retardation of densification in the Al_2O_3–SiC system are suggested. Firstly, consider that densification of Al_2O_3 is controlled by diffusion along the boundaries.[22] Due to the strong, directional bonding of both Al_2O_3 and SiC, diffusion at the Al_2O_3–SiC interface is expected to be slow. Consequently, the first possibility is that
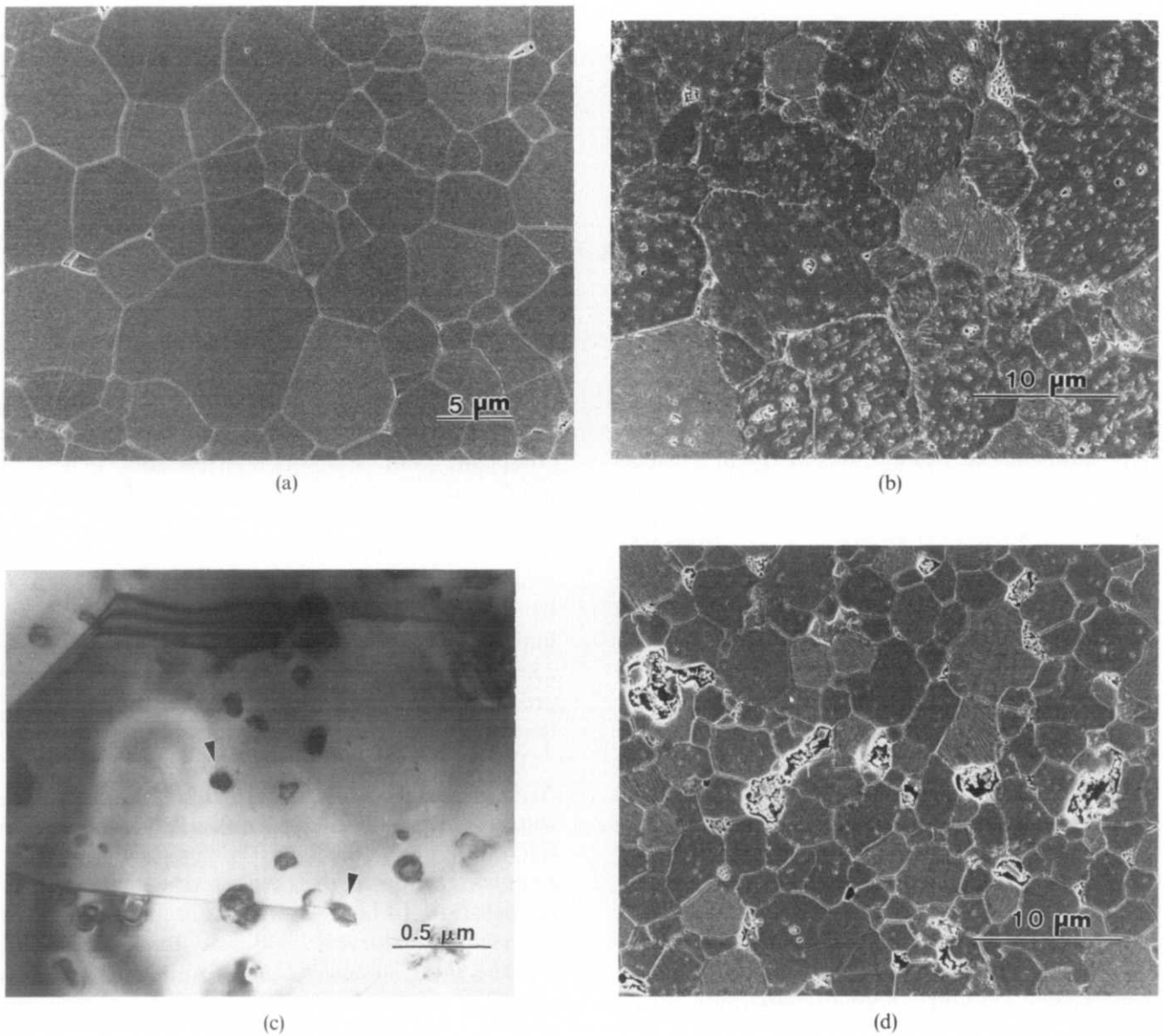
Fig. 2. (a) SEM micrograph of Al_2O_3 sintered at 1450°C; (b) SEM micrograph of composite prepared using methanol, sintered at 1700°C; (c) TEM micrograph of composite prepared using methanol (arrows indicate SiC particles); (d) SEM micrograph of composite prepared using hexane, sintered at 1800°C. All samples were sintered in flowing nitrogen for 2 h.
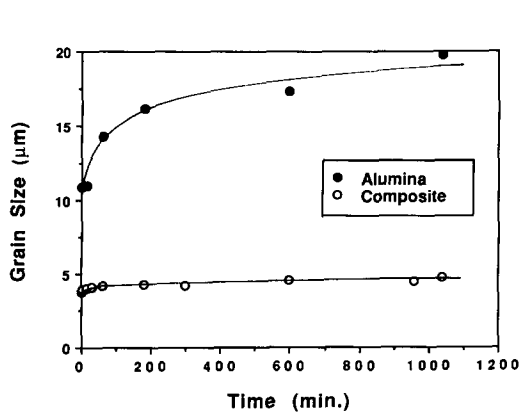

Fig. 3. Grain size as a function of time for Al_2O_3 and the composite annealed at 1700°C in flowing nitrogen.
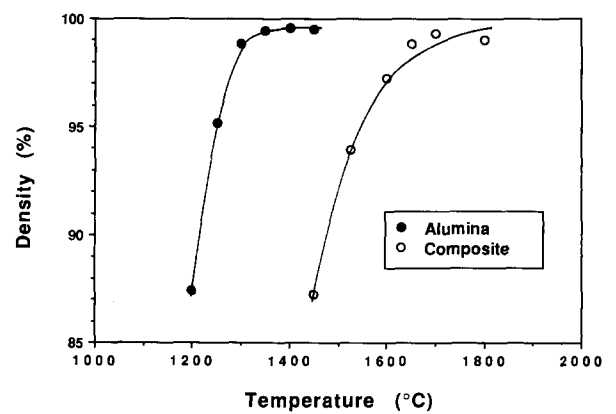
Fig. 4. Density as a function of temperature for Al_2O_3 and the composite. Sintering was conducted in flowing nitrogen for 2 h.

diffusion of atoms along the grain boundaries to the pores may be limited by the presence of SiC particles on those boundaries, and thus densification will also be slowed. For the second possibility, consider that matter must be removed uniformly from all regions of the boundary for uniform shrinkage. This requires that material be removed from the Al_2O_3–SiC interface if a particle is on the boundary. The process of removing Al^{3+} and O^{2-} ions from this interface may be more difficult than the diffusion of these ions along the interface. Thus, this would cause a reduction in the densification rate. A full kinetics study is necessary to test these hypotheses.

4 Summary

A processing method which utilizes relatively conventional techniques has been developed for reproducibly fabricating Al_2O_3–SiC 'nanocomposites'. Dense microstructures with uniformly distributed SiC particles were obtained via pressureless sintering. As may have been expected, the SiC particles strongly inhibited grain growth of the Al_2O_3 matrix. The ultra-fine particles also significantly retarded overall densification, despite this beneficial influence on grain growth. Possible mechanisms for the densification inhibition have been discussed, but a full study of the kinetics is necessary to test these hypotheses.

Acknowledgement

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