PROCESSING OF NANOCOMPOSITE SILICON NITRIDE-MULLITE-ALUMINA BY REACTION SINTERING

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Abstract—We describe a new method for processing Si₃N₄-mullite-Al₂O₃ nanocomposites by reaction sintering of the green compacts after partial oxidation treatment. Bimodal powder compacts used in this process were prepared by a colloidal filtration method. Si₃N₄ and Al₂O₃ powders were dispersed in aqueous suspensions at pH=10 with the aid of an electrosteric stabilizer, polymethacrylic acid. A binary mixture of Al₂O₃ powder was used to attain high green densities. This process results in the following morphology: nanometer-sized Si₃N₄ particles that are distributed in the mullite phase which is embedded in an Al₂O₃ matrix.

I. INTRODUCTION

Advanced ceramic matrix composites are used in many fields, such as electronic, structural, or biomaterial applications. Recently, ceramic matrix nanocomposites have been receiving increasing attention largely due to their significantly enhanced mechanical properties, low-temperature densification, machinability, and superplastic behavior (1-3). Nanocomposites can be classified into two general categories (3). One category consists of composites of only nanometer-sized grains. The other consists of composites where nanosized particles are distributed within the intra-and/or intergrain regions of micron-sized grains. The main advantage of using nanocomposites of the first category is that they can be shaped by superplastic deformation, whereas the main advantage of the nanocomposites of the second category is their enhanced high temperature stability against grain coarsening and mechanical properties. In this paper, we deal with the processing of the second type of nanocomposite with a novel reaction sintering method.

In a recent study, we illustrated the use of reaction sintering as an economical and reliable method for the processing of SiC-mullite-Al₂O₃ nanocomposites (4,5). In this study, we extend this technique to the processing of Si₃N₄-mullite-Al₂O₃ nanocomposites. Our procedure consists of three steps shown in Figure 1 (4,5). First, we consolidate submicron-sized Si₃N₄ and Al₂O₃ powders homogeneously through colloidal consolidation. For the composite material processing of submicron size powder, colloidal dispersion and consolidation techniques have high potential.
in controlling pore volume and pore size distribution of compacts and achieving a desired microstructure (6,7).

Here, the effect of using bimodal $\text{Al}_2\text{O}_3$ powders (8-10) on the microstructure of the green compacts is also examined. Second, partial oxidation treatment is conducted to oxidize the surface of the $\text{Si}_3\text{N}_4$ particles to $\text{SiO}_2$. This reduces the size of the $\text{Si}_3\text{N}_4$ particles to nanometer size. Finally, we react the surface oxide and $\text{Al}_2\text{O}_3$ to produce mullite. As we illustrate in the following sections, the advantages of this method are that (1) the reduction of the inclusion phase to nanoscale can be achieved without milling, (2) due to a volume increase during reaction sintering, the sintering shrinkage is low, and (3) since the oxidation product silica is in amorphous form, the viscous deformation of silica allows the densification process to occur at lower temperatures (11,12), and aids in the formation of dense sintered bodies without pressure.

II. EXPERIMENTAL PROCEDURE

Two types of $\alpha$-$\text{Al}_2\text{O}_3$ powders were used in this study, Sumitomo Chemical's high-purity alumina ($\geq 99.995\%$): the fine powder (AKP-50, indicated as $\text{Al}_2\text{O}_3(F)$) with a mean particle diameter of 0.21 $\mu$m and specific surface area of 9.5 $m^2/g$, and the coarse powder (AKP-15, indicated as $\text{Al}_2\text{O}_3(C)$) with a mean particle diameter of 0.78 $\mu$m and specific surface area of 2.4 $m^2/g$. Bimodal powder where the ratio of $\text{Al}_2\text{O}_3(C)$ to $\text{Al}_2\text{O}_3(F)$ was 7/3 is designated as $\text{Al}_2\text{O}_3(B)$. The $\text{Si}_3\text{N}_4$ powder used was Ube Industries' $\alpha$-$\text{Si}_3\text{N}_4$ (SN-E10; $\alpha$ content above 95\%) with a mean particle diameter of 0.2 $\mu$m and specific surface area of 10.0 $m^2/g$. The data presented here for the alumina and silicon nitride are the manufacturer's reported data except the specific surface area. The specific surface areas were measured by standard BET $N_2$ adsorptions.

Stable colloidal suspensions with a solids content of 45 vol\% were prepared electrosterically in distilled water with an NH$_4$ salt of polymethacrylic acid (PMAA, Darvan C) at pH = 10 as described in the next section. NH$_4$OH was used to adjust the pH. After ultrasonic vibration (Sonic Materials VibraCell 600W Unit, Danbury, CT) was applied for 10 min to facilitate the dispersion of the powders agglomerates, the suspension was stirred for over 12 h at room temperature. Degassing of the suspension was performed in a bell jar connected to a vacuum pump for about 30 min. A colloidal consolidation technique (slip cast) employing a gypsum mold was used to consolidate the colloidal particles. The compacts were then dried overnight at 100°C.

![Figure 1. Schematic illustration of the process steps used to produce nanocomposites by reaction sintering.](image)
Rheological properties of the suspensions were measured by a cone and plate viscometer (Viscomic EMD type, Tokyo Keiki Co., Tokyo, Japan) at 20°C as a function of shear rate over a range of shear rates of 1.92 to 383 s⁻¹.

Thermogravimetric analysis (TGA; TGA7 Thermogravimetric analyzer, Perkin Elmer, Norwalk, CT) was conducted to determine the oxidation level of the Si₃N₄ by weight increase. The dried compacts were put in a platinum pan and heated to soaking temperatures between 1000 and 1300°C at a heating rate of 10°C/min in a stream of dry air. Reaction between the Pt and the Si₃N₄ powder was not observed.

The reaction sintering for the samples after partial oxidation treatment in air was conducted in an alumina crucible in a stream of Ar (above 99.9 % purity) using a graphite furnace at a heating rate of 25°C/min and a cooling rate of 5°C/min. The densities of the green compacts and the sintered bodies were measured by the Archimedes' method using kerosene or distilled water, respectively. Pore channel size distribution of the compacts was investigated by mercury porosimetry (9,10). The pore channel size distribution was obtained using standard values for the mercury surface energy (0.48 N/m) and the contact angle (140°). Phase analysis was conducted by X-ray diffraction (XRD; X-ray Diffractometer, Rigaku RU-300, Tokyo, Japan) using Ni-filtered CuKα radiation.

Sintered samples were polished down to 1 μm surface finish with diamond paste and then thermally etched at 1450°C for 20 min in an Ar atmosphere. The resulting microstructures were evaluated by scanning electron microscopy (SEM; Philips 515 Scanning Electron Microscope) and transmission electron microscopy (TEM; Philips 300 Transmission Electron Microscope). A coating of gold and palladium was sputtered on the surface of the samples for SEM.

III. RESULTS AND DISCUSSION

Dispersion and Consolidation

In the preparation of the colloidal suspensions, controlling the interactions between particles has a significant influence on the stability of a suspension. In our system, an electrosteric stabilization approach was preferred over an electrostatic one since it was not possible to disperse both Si₃N₄ and Al₂O₃ equally well at the same pH level. When only electrostatic dispersion was used, Si₃N₄ dispersed best under basic conditions, whereas Al₂O₃ dispersed best under acidic conditions (13-16). Consequently, an NH₄ salt of PMAA was used as an electrosteric stabilizer (0.4 g/m²) (13,14) to improve the stability of Al₂O₃ under basic conditions so that a low viscosity composite suspension could be prepared at pH = 10. Figure 2 shows the rheological behavior of the Al₂O₃(F)-15Si₃N₄ suspensions with and without the PMAA. A significant decrease in viscosity of the 45 vol% solids suspension with PMAA is seen in comparison with 30 vol% solids suspension without PMAA. Adding PMAA decreased the viscosity significantly, which indicates the suspension dispersion is significantly improved. Figure 3 shows the rheological behavior of 45 vol% solids suspensions using the three types of Al₂O₃ powders. All the suspensions were fluid enough for slip casting and the suspension with bimodal Al₂O₃ had the lowest viscosity due to space filling of smaller particles into a matrix of larger particles. At a fixed solids content, nearly an order of magnitude decrease in viscosity can be realized simply with addition of smaller particles into a nearly monosized matrix (29).
During colloidal consolidation of multi-component suspensions, a key problem is the segregation of particles either due to gravitational (9,10,17) or thermodynamic phase separation (18,19) effects. The best solution for minimizing particle segregation is to prepare the suspensions as highly concentrated as possible (9,10,17-19). Since significant segregation and/or phase separation did not occur while using a 45 vol% solid suspension of Al₂O₃-SiC systems (5), we also prepared 45 vol% solid suspensions in this system. Homogeneous microstructure (Figure 4) and narrow pore channel size distributions (Figure 5) were obtained with all these compacts. The relative green densities of Al₂O₃(F)-15Si₃N₄, Al₂O₃(B)-15Si₃N₄ and Al₂O₃(C)-15Si₃N₄ were 61.5, 65.7 and 65.1%, respectively. Increase of density in Al₂O₃(B)-15Si₃N₄ system is not significant in comparison with that in Al₂O₃(C)-15Si₃N₄ system. This may be due to the fact that the mixtures of Al₂O₃(C) and Si₃N₄ are a binary combination of the coarse Al₂O₃ and the fine Si₃N₄ powders and thus they also display the advantages of binary mixtures.

*Oxidation Process*

A typical weight loss during heating Al₂O₃(F)-15Si₃N₄ at a heating rate of 10°C/min is shown in Figure 6. Upon heating to 700°C weight loss was observed in two regions; in the first
region (up to 300°C) the weight decrease is due to the desorption of water and the second region (around 350°C) is mainly due to decomposition of the surfactant. Above 500°C, the weight loss reaches a maximum value, and due to the onset of Si$_3$N$_4$ oxidation, a weight gain is observed at higher temperatures. The plateau value at the maximum weight loss was used as the reference point to determine the fraction of silica that forms as the oxidation product on the surface of the Si$_3$N$_4$ particles.

The size of the Si$_3$N$_4$ core particles was controlled by determining the fraction of Si$_3$N$_4$ oxidized during heat treatment. Figure 7 shows the oxidation fraction in weight. The oxidation behavior of the Si$_3$N$_4$ powder in this temperature range is believed to follow a passive oxidation reaction (20):

$$\text{Si}_3\text{N}_4 + 3\text{O}_2 \rightarrow 3\text{SiO}_2 + 2\text{N}_2$$  \[1\]

Many authors have reported that oxidation of Si$_3$N$_4$ powders in various oxidizing atmospheres follows parabolic kinetics (21-24). The oxidation fraction is represented by the following Jander's equation (25).
where $f$ is the oxidation fraction, $t$ is the reaction time, and $k$ is the rate constant. As shown in Figure 8, when the $[1 - f^{1/3}]$ is plotted versus the square root of time, a linear variation is observed, suggesting that oxidation is rate limited by a diffusion process. Using eq. [2] we can calculate the rate constants at every temperature. An Arrhenius plot of the rate constants in the temperature range of 1000-1300°C is shown in Figure 9. The activation energy for Al₂O₃(F)-Si₃N₄ system is 340 kJ/mol. Activation energies reported in the literature vary from 250 to 480 kJ/mol (21-24). This large amount of scatter has been attributed to the different types of materials (powder, polycrystal and single-crystal), with varying concentrations of impurities, which can alter the oxidation kinetics significantly. The activation energies obtained in our study are close to the activation energy of the oxygen diffusion in vitreous silica (298 kJ/mol) (26) but not to that of the molecular oxygen diffusion (113 kJ/mol) (27), or not to the formation of an intermediate phase Si₃N₂O (480 kJ/mol) (24). The present oxidation reaction seems to proceed via oxygen diffusion through the silica film.
Figure 5. Hg porosimetry pore channel size distributions of the Al₂O₃·15Si₃N₄ compacts consolidated by the colloidal consolidation.

Figure 10 shows the X-ray diffraction patterns of Al₂O₃·15Si₃N₄ oxidized at 1300°C for 2 h in air. The decrease in the amount of Si₃N₄ can be seen from the figure, where amorphous SiO₂ might be produced as is the case of Al₂O₃-SiC system using fine powders (5).

**Reaction Sintering and Microstructure**

The comparison of the X-ray diffraction patterns in Figure 10 confirms the premise of this study, that SiO₂ phase is formed as the oxidation product and is then consumed to form mullite during the final stage heat treatment in Ar. Transformation of α-Si₃N₄ to β-Si₃N₄ was observed for the samples sintered at 1700°C but not at 1600°C. The existence of Si₂N₂O phase is not observed.

In calculating the theoretical densities of the compacts, two types of volume expansion had to be considered (28). Volume expansion of Si₃N₄ upon oxidation is 76% and formation of stoichiometric mullite from the reaction of 3Al₂O₃ and 2SiO₂ results in a volume increase of 5% (5). The theoretical densities were determined by the following equation:
Figure 6. TGA curves of colloidal consolidated compacts of $\text{Al}_2\text{O}_3(\text{F})-15\text{Si}_3\text{N}_4$ at a heating rate of 10°C/min in a stream of dry air.
Figure 7. Oxidation fraction in weight of Al$_2$O$_3$(F)-15Si$_3$N$_4$ system during isothermal holding in a stream of dry air.

\[ \rho = [V_s \rho_s + (1-V_s) \rho_A]W/K \]  \[3\]

where $\rho_s$ and $\rho_A$ are the theoretical densities of Si$_3$N$_4$ and Al$_2$O$_3$, respectively, $V_s$ the volume fraction of Si$_3$N$_4$, and $W$ is the oxidation weight increase ratio. $K$ is a factor controlled by the composition and the respective volume expansions, as

\[ K = \frac{f_0 (1.76 \times 1.05 - 1)}{[1 + (1-f)V_s]} + 1 \]  \[4\]

where $f$ is the oxidation fraction of Si$_3$N$_4$. The linear shrinkage $L$ is calculated by the following equation:

\[ L = (K \rho / \rho_k)^{1/3} - 1 \]  \[5\]

where $\rho_k$ is the green density. It is easily calculated using above equation that sinter shrinkage is lower due to the two types of volume increase.

Figure 11 shows the relative sintered densities of the samples which partially oxidized at 1300°C for 2 h and reaction-sintered at 1600°C for 2 h. Higher sintered densities were obtained by sintering at 1600°C for 2 h in an Ar atmosphere without pressure. As is the case in transient
viscous phase processing of mullite in homogeneously mixed compacts of amorphous SiO$_2$ and Al$_2$O$_3$ powders (11,12), viscous deformation of silica is the most likely mechanism contributing to the enhanced densification of the compacts in this study.

Figure 12 shows a SEM image of a polished and etched Al$_2$O$_3$-15Si$_3$N$_4$-mullite sample that was oxidized at 1300°C and sintered at 1600°C for 2h. At this resolution, although small second phase inclusions are observed, it is not obvious whether these inclusions extend to the nanoscale range. Figure 13 shows a TEM image of the same samples of Figure 12. Nanometer-sized spherical Si$_3$N$_4$ particles are observed as inclusions within a mullite matrix as confirmed by energy dispersive X-ray spectroscopy (EDS). This morphology shows that the surface of the Si$_3$N$_4$ is oxidized uniformly and nanometer-sized Si$_3$N$_4$ particles remain in the mullite matrix as illustrated in Figure 1.

IV. CONCLUSIONS

Si$_3$N$_4$-mullite-Al$_2$O$_3$ nanocomposites were processed through a novel colloidal consolidation and reaction sintering process. First, micron-sized Si$_3$N$_4$ and Al$_2$O$_3$ particles were colloidal...
Figure 9. Arrhenius plot of the passive oxidation rate constants.

Figure 10. X-ray diffraction patterns of Al₂O₃(F)-15Si₃N₄ (a) as colloidal consolidation, (b) after oxidation, and (c) after reaction sintering at 1600°C for 2 h in Ar.
Figure 11. Density after an initial oxidation at 1300°C in air and then a final sintering at 1600°C for 2 h in Ar.

Figure 12. SEM image of polished and a thermally etched Al₂O₃(F)-15Si₃N₄-mullite nanocomposite first oxidized at 1300°C for 2 h and followed by a 1600°C sintering for 2 h in Ar.
dispersed and consolidated to form uniformly mixed compacts. Second, Si₃N₄ particles were partially oxidized until the Si₃N₄ particles was reduced to a nanometer-sized core. Third, these nanometer-sized core particles were trapped within a mullite matrix as the silica oxidation product reacted with the alumina to form the mullite matrix.

This process offers several advantages and thereby warrants further research: (1) it eliminates the need to reduce the particle size of the inclusion phase to the nanometer range by milling and thus provides better control in minimizing impurities; (2) due to volume increase during reaction sintering, sintering shrinkage are lower, and (3) the presence of amorphous silica as a transient phase results in enhanced densification by viscous deformation and thus provides an opportunity to process these composites without pressure.

Figure 13. TEM image of Al₂O₃(F)-Si₃N₄-mullite nanocomposites first oxidized at 1300°C for 5 h in air and followed by final sintering treatment at 1600°C for 2h in Ar. (Spherical particles are Si₃N₄.)
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