Effect of submicron silicon carbide powder addition on the processing and strength of reaction-sintered mullite-silicon carbide composites

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Mullite-silicon carbide composites were fabricated via a reaction sintering using SiC and alumina (Al₂O₃) powders. The mullite phase was in situ synthesized from the reaction between the oxidation-derived SiO₂ and alumina. The effects of incorporating submicron (~0.5 μm) SiC powder (in addition to the coarser (~65 μm) SiC powder) on the microstructures, densities, and flexural strengths of the composites were investigated. The addition of submicron SiC powder was found to increase the mullite content, relative density, and flexural strength of the composite. The 6-h-sintered composite containing 40 mass% submicron SiC powder had the highest flexural strength. A slightly lower strength was observed for the composite containing 50 mass% submicron SiC powder. This was attributed to there being insufficient alumina in the starting powder for synthesizing the mullite. The composites sintered for 6 h typically had flexural strengths of ~90 MPa at 25% porosity.

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1. Introduction

One approach for tailoring material properties is to combine materials that have different properties. Examples include mullite-coated silicon carbide (SiC) ceramics and mullite-SiC composites. It has been reported that the oxidation resistance of recrystallized SiC was improved by the incorporation of a mullite coating on the SiC. Similarly, the corrosion resistance of SiC in contact with coal slag was improved by introducing a chemically vapor-deposited mullite coating on the SiC. Ando et al. reported that mullite-SiC composites have the ability to heal semicircular cracks having diameters of up to 200 μm.

A new approach that has received much less attention is the formation of mullite-SiC composites in situ. Mullite has good chemical compatibility with SiC, and both materials have similar thermal expansion properties. Thus, the combination of mullite and SiC to form mullite-SiC composites is an attractive approach. Composites of mullite and SiC can be fabricated by pressureless sintering, or by hot-pressing, or by polymer impregnation and pyrolysis. Recently, Tian and Shobu reported a melt infiltration method for fabricating mullite-SiC composites. The method involved obtaining the mullite from a SiO₂–Al₂O₃ powder mixture by melting it above 1830°C. The melt was then infiltrated into a porous SiC preform, resulting in a dense mullite-SiC composite.

In this research, mullite-SiC composites were fabricated via reaction sintering of SiC and alumina (Al₂O₃) powders. The mullite phase was synthesized in situ from the reaction between the oxidation-derived SiO₂ and the alumina. The effects of incorporating submicron (~0.5 μm) SiC powder (in addition to the coarser (~65 μm) SiC powder) on the microstructures, relative densities, and flexural strengths of the composites were investigated.

2. Experimental procedure

Commercially available α-SiC powders (~65 μm, ESK, Germany and ~0.5 μm, Norton AS, Norway) and Al₂O₃ powder (~0.4 μm, 99.9% pure, Sumitomo Chemical Co., Tokyo, Japan) were used as the starting materials. They were used as received. Six batches were mixed, each containing 63 mass% SiC and 37 mass% Al₂O₃ (see Table 1). All of the batches were milled separately within a polypropylene jar for 24 h using distilled water and SiC grinding balls. Polyethylene glycol and polyvinyl alcohol were added as binders. The milled slurry was dried and uniaxially pressed into porous SiC preforms. These were sintered in a vacuum to form dense mullite-SiC composites.

Table 1. Batch Composition of Mullite-SiC Composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Batch Composition (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiC (~65 μm)</td>
</tr>
<tr>
<td>S10F0</td>
<td>63</td>
</tr>
<tr>
<td>S9F1</td>
<td>56.7</td>
</tr>
<tr>
<td>S8F2</td>
<td>50.4</td>
</tr>
<tr>
<td>S7F3</td>
<td>44.1</td>
</tr>
<tr>
<td>S6F4</td>
<td>37.8</td>
</tr>
<tr>
<td>S5F5</td>
<td>31.5</td>
</tr>
</tbody>
</table>

* 4% poly(ethylene glycol) + 2% poly(vinyl alcohol)
ally pressed under a pressure of 28 MPa. The resulting compacts were sintered at 1550°C for 2 h and 6 h in air.

Raw SiC powders were separately oxidized at 1550°C for 2 h and 6 h in order to measure the weight gain after oxidation. The SiC and SiO₂ contents in each specimen after sintering were calculated from the weight gain of each component powder when heated under the same conditions. The calculation was based on the following reaction:

\[
\text{SiC}_{(s)} + 2\text{O}_{2(g)} \rightarrow \text{SiO}_2 + \text{CO}_2(g) \quad (1)
\]

The bulk density (\(D_b\)) of each composite was computed from the weight-to-volume ratio of the samples. By assuming that all of the oxidation-derived SiO₂ reacted with the Al₂O₃ and formed mullite, the theoretical density (\(D_{th}\)) of each composite could be estimated from the rule of mixtures,

\[
D_{th} = D_{mullite}V_{mullite} + D_{SiC}V_{SiC} + D_{alumina}V_{alumina} + D_{silica}V_{silica} \quad (2)
\]

where \(D_{mullite}\), \(D_{SiC}\), \(D_{alumina}\), and \(D_{silica}\) are the theoretical densities of mullite (3.160 g/cm³), SiC (3.218 g/cm³), Al₂O₃ (3.987 g/cm³), and cristobalite (2.330 g/cm³), and \(V_{mullite}\), \(V_{SiC}\), \(V_{alumina}\), and \(V_{silica}\) are the volume fractions of mullite, SiC, Al₂O₃, and cristobalite, respectively. \(V_{mullite}\), \(V_{SiC}\), \(V_{alumina}\), and \(V_{silica}\) can simply be calculated from both the weight change of the specimen in the sintering process and the weight change of each SiC powder when oxidized under the same conditions.

The relative density of each composite was calculated from \(D_b\) and \(D_{th}\) of the composites according to:

\[
\text{Relative density (\%)} = \left(\frac{D_b}{D_{th}}\right) \times 100 \quad (3)
\]

The fracture surfaces were observed using scanning electron microscopy (SEM; S4300, Hitachi Ltd., Japan). X-ray diffractometry (XRD) was performed on the specimens on a diffractometer (D8 Discover, Bruker AXS GmbH, Germany) using Cu Kα radiation. For the flexural strength measurements, bar-shaped samples were cut to a size of 3 mm × 4 mm × 30 mm. These were used for bend tests, which were performed on an Instron machine (4465, Instron Co., Ltd., USA) at room temperature using a four-point method with inner and outer spans of 10 and 20 mm, respectively.

3. Results

The change of calculated phase content as a function of submicron SiC powder is shown in Fig. 1. The mullite content increased with increasing the submicron SiC content. The oxidation of the ~65 μm SiC powder at 1550°C for 2 h resulted in 97.7 mass% SiC and 2.3 mass% SiO₂, whereas the oxidation of the submicron (~0.5 μm) SiC powder under the same conditions resulted in 60.6 mass% SiC and 39.4 mass% SiO₂. The oxidation of the ~65 μm SiC powder at 1550°C for 6 h resulted in 94.3 mass% SiC and 5.7 mass% SiO₂, whereas the oxidation of the submicron (~0.5 μm) SiC powder under the same conditions resulted in 51.9 mass% SiC and 48.1 mass% SiO₂. Thus, adding more submicron SiC powder leads to a higher oxidation-derived SiO₂ content, resulting in a higher mullite content, as shown in Fig. 1. For the same submicron SiC powder contents, increasing the sintering time from 2 h to 6 h increased the mullite content slightly. For example, the mullite contents of 2-h-sintered and 6-h-sintered S5F5 specimens were 46.6% and 51.5%, respectively.

The 6-h-sintered S5F5 specimen contained 2.4% residual SiO₂ because of the insufficient alumina in the starting powder for synthesizing the mullite. Thus, each composite has different amounts of SiC, mullite, and residual Al₂O₃ or SiO₂, depending on the submicron SiC content and the sintering time.

As shown in Fig. 2, the XRD analyses of the mullite-SiC composites showed the peaks of α-SiC, mullite, and α-Al₂O₃, indicating the formation of the mullite phase. The intensity of the mullite peaks becomes stronger with increasing the submicron...
SiC content in the starting powder composition, as expected from the calculation (Fig. 1). Some specimens showed a very weak cristobalite peak, indicating that the mullite synthesis reaction had not gone to completion during the sintering process. Increasing the sintering time from 2 h to 6 h increased the intensities of the mullite peaks slightly, as expected from the calculation (see Fig. 1). One advantage of this process for fabricating mullite-SiC composites is that it can be performed at a relatively low temperature (1550°C) in air. By comparison, previously reported fabrication methods involved pressureless sintering at 1750°C in nitrogen⁵ and melt infiltration at >1830°C in argon.⁴

**Figure 3** shows typical fracture surfaces of the mullite-SiC composites. The microstructure consisted of large SiC grains embedded in fine mullite-SiC-alumina grains and some residual pores. The SiC, mullite, and alumina grain sizes ranged from 0.5 to 2 μm and the pore sizes ranged from 1 to 5 μm. The SiC, mullite, and alumina grains could not be clearly distinguished in the microstructure. It was expected that the number of coarse SiC grains increased with increasing the submicron SiC content in the starting composition. However, the number of coarse SiC grains in specimen S8F2 seems to be larger than that in S10F0. It would be due to the presence of local inhomogeneity in the specimens because of too large difference in the particle size of starting powders. **Figure 4** shows higher magnification images of two regions: (1) an interface region between a large SiC grain and fine grains and (2) a fine-grained region in the specimen S8F2. The fine-grained region consisted of submicron SiC embedded in mullite and residual alumina grains. Lower porosity was observed in the fine-grained regions than in the interface region. The grain morphology of all of the grains in the fine-grained region was equiaxed. The *in situ*-synthesized mullite and submicron SiC particles acted as an adhesive, binding the larger SiC grains together, as shown in **Fig. 5**. Bonding between the large SiC grains and the *in situ*-synthesized mullite grains was observed, as shown in **Fig. 5**. This bonding imparts strength to the composites. The effect of sintering time on the microstructure of the composite is shown in **Fig. 6**. There was no remarkable difference between the microstructures of both specimens. However, the 6-h-sintered composites contained more dense regions locally, i.e., more dense submicron SiC and mullite regions, due to the higher amount of mullite phase.

**Figure 7** shows the relative densities of the mullite-SiC composites as functions of the submicron SiC content and the sintering time. The densities of the mullite-SiC composites ranged from 2.16 to 2.46 g/cm³. These densities correspond to the porosities ranging from 30% to 22%, respectively. The relative density increased with increasing the content of the submicron SiC powder in the starting composition and with increasing the sintering time. This is consistent with the microstructures shown in **Fig. 3**. The low relative densities of the S10F0 specimens were attributed to the limited amount of mullite formation, which is in turn due to the small amount of oxidation-derived SiO₂ in the specimens. The mullite-SiC composites containing 50 mass% submi-

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**Fig. 3.** Typical fracture surfaces of the mullite-SiC composites sintered at 1550°C for 2 h in air: (a) S10F0, (b) S8F2 and (c) S5F5.

**Fig. 4.** Typical fracture surfaces of mullite-SiC composites (S8F2) sintered at 1550°C for 2 h in air: (a) an interface region between a large SiC grain and fine grains and (b) a fine grain region.

**Fig. 5.** Typical fracture surfaces showing SiC-mullite bonding phase between coarse SiC grains in the S9F1 specimen sintered at 1550°C for (a) 2 h and (b) 6 h in air.

**Fig. 6.** Typical fracture surfaces of the mullite-SiC composites (S6F4) sintered at 1550°C for (a) 2 h and (b) 6 h in air.

**Fig. 7.** Relative densities of the mullite-SiC composites as functions of submicron SiC content and sintering time.
The higher strength of the 6-h-sintered specimen is attributed to the presence of residual cristobalite in the composites. This hypothesis is also supported by the fact that the mullite phase content increased with prolonged sintering time because of the formation of mullite-SiC composites (Fig. 1(b)) because of the Al$_2$O$_3$ deficiency in the starting composition. The presence of cristobalite in the composites may induce some microcracking or residual stress in the composites due to the phase transformation of the cristobalite during cooling.

The strengths of the 6-h-sintered specimens were higher than those of the 2-h-sintered specimens, e.g., the strengths of the 2-h-sintered and the 6-h-sintered S10F0 specimens were 26 MPa and 57 MPa, respectively. This result indicates that the mullite phase forms a layer on the surface of the SiC particles, protecting them against further oxidation. Otherwise, the strength would decrease with prolonged sintering time because of the formation of a large amount of cristobalite phase. This hypothesis is also supported by the fact that the mullite phase content increased when the sintering time was increased from 2 h to 6 h (Fig. 1). The higher strength of the 6-h-sintered specimen is attributed to its higher mullite phase content and its higher relative density (Fig. 7).

4. Discussion

The formation of mullite phase in between coarse SiC grains occurred in two steps: (i) the formation of SiO$_2$ phase on the surface of SiC particles, which involves the oxidation of SiC particles during heating in air, as suggested in Eq. (1), and (ii) the formation of mullite phase by a reaction between the oxidation-derived silica and alumina upon increasing the temperature. The amount of mullite phase formed in the 6-h-sintered composites was larger than that for 2 h, as expected by the calculation (Fig. 1) and as evidenced by XRD results (Fig. 2).

The in situ-synthesized mullite acted as an adhesive, binding the larger SiC grains together, as shown in Fig. 5. However, some long pores (up to ∼40 μm in length) were frequently observed in the low magnification micrograph (see Fig. 3(b)). It seems that the following processes take place sequentially during the sintering process: (i) oxidation of the SiC powders, which results in the oxidation-derived silica phase covering the SiC particles; (ii) in-situ synthesis of the mullite phase by a reaction between the alumina and the oxidation-derived SiO$_2$; and (iii) local densification of the mullite and submicron SiC composite, resulting in local shrinkage. The linear shrinkage observed in the S10F0 and S5F5 specimens sintered for 6 h were 0.80% and 2.71%, respectively. The constrained network of large SiC grains in the specimens hindered the total shrinkage of the composites. Therefore, the local shrinkage due to the local densification of the mullite and submicron SiC composite regions led to relatively large pores near the large SiC grains (see Fig. 3) within the composites.

Studies on refractory-grade SiC ceramics have been quite limited. Silica and silicon nitride (Si$_3$N$_4$), and mullite phases have been investigated as bonding phases for SiC ceramics. A silica bonding phase is formed by heating SiC powder compacts in air. The SiC particles in the compacts are bonded to each other by an oxidation-derived SiO$_2$ glass. A silicon nitride bonding phase is formed by nitridation of the silicon (Si) powder in compacts containing SiC and Si powders. However, the SiO$_2$ bonding phase usually contains a considerable amount of cristobalite phase. The cristobalite phase is transformed from cubic to tetragonal on cooling below 250°C, causing considerable mechanical damage to the ceramics. The Si$_3$N$_4$ bonding phase is oxidized under the oxidizing atmosphere and transformed into a silicon oxynitride phase, causing a degradation of mechanical properties. The mullite-SiC composites fabricated herein were processed in the air and the SiC particles were covered with mullite phase. This indicates that the mullite-SiC composites fabricated by this reaction sintering process are highly resistant to oxidation. This makes them suitable materials for objects, such as refractory plates, kiln furniture, and filter applications, which are all exposed to oxidizing conditions.

Recently, Ding et al. suggested an in situ reaction bonding technique for fabricating porous mullite-bonded SiC ceramics. They heated SiC compacts containing Al$_2$O$_3$ and graphite powders in air. In the process, the graphite is burned out to produce pores and the surface of the SiC is oxidized to SiO$_2$ at high temperature. Upon increasing the temperature, the SiO$_2$ reacts with the Al$_2$O$_3$ to form mullite. 20 μm-SiC powder was used as a starting powder and the resulting material showed a maximum strength of 24 MPa. The same authors also found that the addition of Y$_2$O$_3$ to the same material increased the resulting material's strength to 28 MPa. By contrast, the strength of the mullite-SiC composites fabricated in this research ranged from 50 to 90 MPa, depending on the submicron SiC content. This superior strength is attributed to the formation of finer mullite grains from the use of the submicron SiC powder.

5. Conclusions

Composites of mullite-SiC were fabricated from SiC powder...
mixtures and alumina by reaction sintering in air. Oxidation-derived silica reacted with alumina at 1550°C and formed a mullite phase on the surface of SiC particles. The mullite phase bound the SiC particles together and served to protect them against further oxidation. The addition of the submicron SiC powder increased the relative densities and flexural strengths of the composites. Typical sintered density and flexural strength values of the mullite-SiC composites were \(\sim 2.5 \text{ g/cm}^3\) and \(\sim 90 \text{ MPa}\), respectively, when 40 mass% submicron SiC powder was added and the mixture was sintered at 1550°C for 6 h.

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References