Microwave and Radio Frequency Applications

Proceedings of the Fourth World Congress on Microwave and Radio Frequency Applications

"Bridging Science, Technology and Applications"

Edited by: R.L. Schulz, D.C. Folz
MICROWAVE SYNTHESIS AND SINTERING STUDIES ON ALUMINA-SILICON CARBIDE COMPOSITES

L. N. Satapathy a, b, P. D. Ramesh a, Dinesh Agrawal a, and Rustum Roy a

a Microwave Processing and Engineering Center, Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA
b Ceramic Technological Institute, Bharat Heavy Electricals Limited, Bangalore 560012 INDIA

ABSTRACT

Alumina–silicon carbide composite powders were synthesized by reacting silicon metal, amorphous carbon and fine alumina powder mixture in the 2.45 GHz microwave field. Wide ranging compositions were attempted with SiC content varying from 2, 5, 10, 35, and 55 to 75 vol. %. Compositions with < 10 vol. %SiC were difficult to synthesize using this method. The x-ray diffraction (XRD) revealed a mixture of only SiC and Al₂O₃ phases in the high volume compositions. The size distribution in the synthesized composite powder particles was bimodal in nature. Sintering experiments with the synthesized powders were carried out at 1853 K in a 6 kW microwave furnace using MgO as an additive. Addition of MgO enhanced the densification for the compositions containing less than 10 vol.% SiC in alumina.

INTRODUCTION

Alumina is a versatile material with high hardness, strength and corrosion resistance and these properties are being exploited for room temperature structural applications. However, monolithic alumina exhibits only moderate strength and creep resistance and, like most monolithic ceramics, it is very brittle. The main reason for this behavior is associated with high grain boundary energy coupled with stress assisted grain growth and cavitation during high temperature deformation. Thus, methods to improve the high temperature creep properties and mechanical reliability in alumina pose a huge challenge. One way to achieve this is by the introduction of second phase in the form of particles, fibers or whiskers to form a composite microstructure.

Silicon carbide in alumina matrix has been found to serve a dual purpose namely, to control the alumina grain growth and to strengthen the alumina-alumina grain boundaries resulting in a tough ceramic matrix composite [1]. Hence, these composites find diverse use in structural, wear-resistant and aerospace applications. Bulk residual stresses arising from the thermal expansion mismatch between Al₂O₃ and SiC are substantial. A strengthening mechanism of Al₂O₃ grain boundaries was possible only when SiC particles were embedded in the Al₂O₃ matrix grains. Since the probability of finding intergranularly located particles increases with increasing volume fraction, therefore only composites with a low SiC content show high strength. A detectable strengthening effect was reported at low SiC content (Vf < 10 %) by Ferroni and Pezzotti [2]. However, a comprehensive study on the effect of wide ranging compositions of SiC is lacking in the literature.

The widespread applications of such structural ceramic composites were largely hindered by processing difficulties [3]. Such attempts resulted in a non-homogeneous dispersion of the SiC particles in the alumina matrix, which resulted in detrimental effects on densification and mechanical properties due to agglomeration. Alternative preparation techniques were based on sol-gel [4], self-propagating...
high temperature synthesis [5], microwave drying of the coated gels [6] and microwave combustion synthesis [7], which were all used to avoid agglomeration problems. However, the authors have found no reports of the fabrication of in-situ SiC-Al2O3 composites using microwave energy. Also, reports on densification of these engineering materials using microwave process are not available. Various research groups have used microwave energy to process ceramics, metals and composites [8-11]. Though some reports are available on the effect of additives like MgO and Y2O3 [12], SiO2 [13] and more recently ZrO2 [14], a comprehensive report is not available on the effect of sintering aid on a wide range of SiC-Al2O3 composites. Further, in earlier experiments, very high temperatures have been used to process these materials.

Keeping these points in view, in this work the in-situ synthesis of silicon carbide in alumina by reacting silicon (Si), amorphous carbon (C) and alumina in a controlled atmosphere microwave furnace is reported. The synthesis of a wide range of compositions was attempted in this study. Further, the densification of these composites was carried out at temperatures below 1873 K, with and without MgO.

EXPERIMENTAL

The raw materials used in this study were silicon (Aldrich chemical Co., Milwaukee, WI, USA, 99% purity, -325 mesh), amorphous carbon (Aldrich chemical Co., Milwaukee, WI USA) and CR-6 grade of high purity aluminum oxide (Baikowski International Corporation, NC, USA). d90 = 0.6 μm, BET surface area = 6 m²/g powders. In order to synthesize silicon carbide (SiC) powder, one mole of silicon and two moles of carbon powders were milled using a plastic container for about six hours in ethanol using zirconia-grinding media. The mixed powder was completely dried under an infrared lamp and transferred to a one end closed mullite tube, which was then placed at the center of a 2 kW tubular microwave furnace (Model RC20SF, Amana Refrigeration Inc., Amana, CA, USA). The details of microwave furnace and its operation have been reported elsewhere [11]. All the present synthesis experiments were carried out in argon atmosphere. A constant flow rate of 200 ml/min was maintained throughout the experiments. Temperatures were measured using a single wavelength infrared (IR) pyrometer (Model MA2SC, Raytek Co., Santa Cruz, CA, USA) that was focused through a transparent quartz window on the center of the charge. The syntheses were carried out at a temperature of 1573 K with a holding time of 30 minutes. To remove excess carbon, the as-synthesized powders were calcined in air at 923 K for eight hours.

Details of pure SiC powder synthesis procedure have been provided elsewhere [15]. A similar method was adopted to prepare the composite powder. One mole of silicon and two moles of carbon powders were added to alumina, and the synthesized powder had a composition of Al2O3 + x vol. % SiC. The value of 'x' varied from 2, 5, 10, 35, and 55 to 75 vol%. The powders corresponding to these compositions were coded as AS0, AS2, AS5, AS10, AS35, AS55, AS75 and AS100. The mixed powders of all compositions were heat treated in a similar manner in a tubular microwave furnace as described above and followed by calcination at 923 K for 8 hours. The resulting powders were tested for particle size distribution using a Malvern particle size analyzer and surface area by a BET surface area analyzer. Phase identification studies were carried out by a Scintag X-ray diffractometer (XRD) and the particle morphology and size were studied using a Hitachi scanning electron microscope (SEM).

For the densification study, a stoichiometric amount of pure SiC powder (as synthesized above) corresponding to a given volume percentage was added to alumina using a mortar and pestle and mixed for 15 minutes. Thereafter, 250 parts per million (ppm) of magnesium oxide (MgO) was added to the same composition in the form of a solution of Mg(NO3)2·6H2O. The dried powder was added with 2% polyvinyl alcohol (PVA) binder and uniaxially pressed using a steel die at a pressure of 600 kgs/cm² to form a cylindrical pellet of 12 mm diameter and 3 mm thickness. These pellets were then cold
isostatically pressed (CIP) using a rubber mold at a pressure of 2100 kgs/cm² prior to green density measurement.

For sintering experiments, the CIPed pellets were placed in an alumina crucible and heated in a 6 kW microwave furnace (Cober Electronics, CA, USA) in flowing nitrogen gas (200 ml/min). The temperature was measured by an optical pyrometer. The soaking time at 1853 K was 60 min. The density of the sintered pellets was measured using the Archimedes procedure.

RESULTS AND DISCUSSION

Solid state synthesis of a wide range of SiC-Al₂O₃ composite powders were easily achieved using microwave energy. The reaction between Si and C under a microwave field was observed even below 1273 K, however, phase pure SiC was obtained only at a minimum temperature of 1473 K. Composites containing 35, 55 and 75 vol.% SiC could be synthesized by this method and the XRD patterns are shown in Figure 1. In the figure, comparison between composite XRD patterns and XRD patterns of pure alumina and SiC can be made. It was observed that with the increase of Si and C content in the reactant mixture, the amount of SiC formation increased. The complete conversion of Si and C to SiC occurred only at 1573 K and 30 minutes.

![Figure 1.](image)

**Figure 1.** The x-ray diffraction patterns of alumina-silicon carbide composite powders which are compared with those of pure alumina (as received powder) and β-SiC powder (as synthesized in our laboratory using similar method).

Another important observation in these experiments was alumina containing less than 10 vol.% Si and C mixtures could not be reacted to form the end product, SiC. It may be that during the experiment, the isolated carbon particles in the mixture ignite in the microwave field and thus became unavailable for reaction with Si to form the carbide phase. This is explained on the basis that the solid state reaction occurring in such situation is based on the particle-to-particle contact. A homogeneous mixture with less than 10 vol.% Si and C mixture, hypothetically, may not possess any contact between the Si and C particles and thus resulted in no reaction. In these compositions, it was also difficult to reach the desired temperature of 1573 K after the burning out of carbon, there are no susceptor particles
available to absorb and maintain the temperature of the mixture. Accordingly, the XRD patterns revealed presence of $\text{Al}_2\text{O}_3$ and Si peaks for these compositions. This was, however, not the case with higher volume of Si and C mixture. In such situations, the probability of contact between Si and C particles is increased and then the formation of SiC was observed in XRD.

The as synthesized and calcined powders varied in color depending on the amount of SiC present. By visualization, it was not easy to distinguish the white alumina particle in the grey SiC matrix and vice versa qualitatively suggesting homogenous mixing of the two phases. Figure 2 compares the particle size distribution of alumina containing 35, 55 and 75 vol.% SiC with those of pure alumina (as received) and SiC (as synthesized). Both $\text{Al}_2\text{O}_3$ and SiC show a bimodal size distribution.

![Figure 2. Particle size distribution of alumina-silicon carbide composite powders synthesized under microwave field by reacting Si and C in alumina matrix.](image)

The average particle size of alumina as specified by the supplier was 0.6 µm which was confirmed as shown in the first peak of alumina plot in Figure 2. The corresponding peak for SiC was 0.40 µm. The second peak in both the cases was considered to be arising from the agglomerates and lies at 1.98 µm and at 2.57 µm respectively, for alumina and silicon carbide. The patterns for the composite powders revealed that the composition containing lower SiC content (35%) was influenced by $\text{Al}_2\text{O}_3$ size and the higher SiC content (75%) was influenced by SiC particle size. The AS55 composition was intermediate between these particle size ranges. The values for the first peaks were 0.70 µm, 0.42 µm and 0.33 µm for the compositions of alumina containing 35, 55 and 75 vol. % SiC respectively. The corresponding values for the second peaks were 2.67 µm, 2.40 µm and 2.30 µm respectively (Table 1). This analysis indicates that homogenous and submicron sized alumina-silicon carbide composite powders were synthesized by this procedure.

The SEM observation of the AS55 composition (Figure 3a) revealed a mixture of particles, whiskers and agglomerates. Pure SiC synthesized earlier also displayed a similar type of microstructure [15]. The energy dispersive x-ray analysis (EDAX) of all the three points marked in Figure 3a indicated...
EDAX patterns with identical Si/Al ratio (F). The EDAX of one of the agglomerates at four points is depicted in Figure 3b. This agglomerate is a mixture of SiC and alumina as indicated by its EDAX pattern. The areas 1 and 3 are silicon carbide rich and areas 2 and 4 are alumina rich, respectively. This implies that SiC is distributed in the alumina matrix during in-situ formation from its constituents under the microwave field.

![Images of EDAX patterns](image)

**Figure 3.** (a) Typical scanning electron micrograph of AS 55 powder. Particles (P), whiskers (W) and agglomerates (A) are observed and (b) One of the typical agglomerate in AS 55 which is an intimate mixture of SiC and Al₂O₃ as observed from EDAX at different points. Locations 1 and 3 are SiC-rich (Right peak) and locations P, 2 and 4 are alumina-rich (left peak) regions.

After cold isostatic pressing, the green density of the samples lie in the range of 50 – 54% of their respective theoretical density, which was calculated for each composition using the rule of mixtures (Table 1). The samples were sintered using a 6 kW microwave furnace at 1853 K with a holding time of 60 min. The effective power required for this purpose was 3.0 kW and the total duration of the experiment was about 4 hours. The densification study was carried out with and without 250 ppm MgO additive. MgO was chosen as additive because it is an effective sintering aid for alumina [16].
### Table 1. Properties of Alumina-Silicon Carbide Composite Material.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AS0</td>
<td>0.60</td>
<td>1.98</td>
<td>3.98</td>
<td>53.0</td>
<td>98.0</td>
<td>98.0</td>
</tr>
<tr>
<td>AS2</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>53.0</td>
<td>90.5</td>
<td>92.0</td>
</tr>
<tr>
<td>AS5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>53.4</td>
<td>78.7</td>
<td>88.7</td>
</tr>
<tr>
<td>AS10</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>52.3</td>
<td>69.1</td>
<td>78.3</td>
</tr>
<tr>
<td>AS35</td>
<td>0.70</td>
<td>2.30</td>
<td>3.70</td>
<td>54.3</td>
<td>62.1</td>
<td>65.6</td>
</tr>
<tr>
<td>AS85</td>
<td>0.42</td>
<td>2.40</td>
<td>3.55</td>
<td>53.7</td>
<td>60.3</td>
<td>59.2</td>
</tr>
<tr>
<td>AS70</td>
<td>0.33</td>
<td>2.67</td>
<td>3.40</td>
<td>53.0</td>
<td>55.4</td>
<td>55.3</td>
</tr>
<tr>
<td>AS150</td>
<td>0.40</td>
<td>2.57</td>
<td>3.20</td>
<td>50.0</td>
<td>54.4</td>
<td>54.0</td>
</tr>
</tbody>
</table>

* : Th. Den. : Theoretical density of the composite as calculated by rule of mixture considering 3.98 g/cc and 3.2 g/cc as the theoretical densities of α-Al₂O₃ and β-SiC respectively.

The main aim of choosing this additive was to densify the alumina, which may eventually help in densification of the composite. The densification of alumina containing lower SiC content could be enhanced significantly (Fig. 4) with the 250 ppm MgO addition. This result is in line with earlier data of Jeong et al. [12], where the authors reported an increase of density of AS5 composition from ~89 % to ~93 % at a temperature of ~ 1853 K. The density values reported in this work were slightly different but follow similar kinetics. The anomaly may be due to the finer alumina used in Jeong’s work (d₃₀ ~ 0.2 μm with BET surface area of 4.7m²/g) and the high amount of MgO (0.1 wt. %) used in their experiments. They could sinter the composite to 0.98 of theoretical density at a very high temperature of 2073 K with 0.1 wt. % MgO. Similar results were also reported recently by Hareesh et al. [3] on AS5 composition wherein the sol-gel processed composite showed an increase in density from 0.94 to 0.96 at ~ 1853 K by α-Al₂O₃ seeding. However, in the present case, for compositions containing higher volume percentage of SiC, there was little effect with MgO additions. This result is not surprising since, MgO is not an effective sintering aid in SiC. Similar results were also reported earlier by Yang and Troczyński [16] wherein the authors reported a decrease in relative density of SiC-Al₂O₃ composites from 0.985 to 0.81 when the SiC content increased from 5 to 60 vol. %. In the present work, the apparent porosity was also significantly reduced in AS5 with MgO addition (Table 1). As noticed from Figure 5 and the earlier results described above, the temperature of 1853 K was insufficient to densify these composites to theoretical density. However, it was expected that the widely used alumina-5 % SiC composite material could be sintered to full density in a microwave field using MgO as an additive at a lower temperature than that employed by other researchers.
Figure 4. Variation of percentage theoretical density of alumina–silicon carbide composites, sintered at 1853 K for 60 min. in a 6 kW microwave furnace in nitrogen atmosphere.

CONCLUSIONS

The in-situ microwave synthesis and sintering of a wide range of alumina-silicon carbide composite powders were achieved. The low volume SiC compositions could not be synthesized by this method due to the early burn out of isolated carbon particles in the mixture. This synthesis procedure yielded submicron sized β-SiC particles in an alumina matrix. The bimodal particle size distribution of β- SiC was not altered in the presence of alumina. The SEM and EDAX results suggested that homogenous distribution of SiC and Al₂O₃ was obtained after the synthesis procedure. The densification study of the composites was carried out with and without MgO additive. It was noted that MgO was an effective additive for composites containing higher volume of alumina. From the experiments, it was understood that the sintering of high volume SiC composites require sufficiently higher temperatures for complete densification to occur.

ACKNOWLEDGEMENTS

One of the authors (LNS) would like to acknowledge the financial support from Department of Science and Technology, Govt. of India on BOYSCAST fellowship to carry out this work at The Pennsylvania State University, USA. The LNS would also thank the management of Ceramic Technological Institute, Bharat Heavy Electricals Limited, Bangalore, India for deputing him to take up this activity.
REFERENCES


