Pressureless Sintering and High-Temperature Strength of SiC–AlN Ceramics

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Pressureless sintering of the SiC–AlN system with Y2O3 as a sintering aid was carried out. Composites with <50 vol% SiC were densified to above 98% of the theoretical density in N2 atmosphere of 0.1 MPa at temperatures below 1900 °C using commercial SiC and AlN powders. The densification behavior was investigated and analyzed on the basis of microstructural observation. The strength and deformation of the densely pressureless-sintered AlN and SiC–AlN composites were measured from room temperature to 1500 °C by small punch testing. The sintered AlN and SiC–AlN composites showed no strength decrease at temperatures below 1200 °C, whereas the SiC–AlN composites showed higher strength at room temperature and retained them to higher temperature. At 1500 °C, plastic-like deformation was observed in the SiC–50 and 70 vol% AlN composites. The microstructural observation suggested that the fine microstructure with a uniform and fine grain size in the SiC–AlN composites was a dominant factor responsible for the plastic-like deformation at high temperature.

Key-words: Pressureless sintering, Silicon carbide, Aluminum nitride, Solid solution, Ceramic composite, High temperature strength, Plastic deformation, Small punch testing

1. Introduction

Both silicon carbide (SiC) and aluminum nitride (AlN) have many potential applications mainly in electronic and high-temperature fields. Furthermore, it has been found that a series of solid solutions are formed between SiC and AlN over a wide composition range,1)–4) which will provide much freedom in designing the material properties in this system by controlling the composition and microstructure. During the past decade, the synthesis and properties of the SiC–AlN solid solutions have received considerable attention.2)–4),5)–16) Hot-pressing was commonly used to prepare the SiC–AlN solid solution samples from the mixture of SiC and AlN powders,3),4),5),6)–14) but high temperature over 2100 °C was required to obtain dense solid solution samples with homogeneous compositional distributions. The alternative method is a way to synthesize the solid solution and/or composite powders by carbothermal reduction, subsequently densified by hot and hot-isostatic pressing.2),6),7)

From an industrial point of view, pressureless sintering is more attractive than hot and hot-isostatic pressing. However, less work has been reported on the pressureless sintering of the SiC–AlN system, probably because of their poor sinterabilities. As is used generally in the sintering of silicon nitride, liquid phase sintering is useful for the pressureless sintering of non-oxide ceramics.17) Alumina (Al2O3), yttria (Y2O3) and calcia (CaO) are used as sintering aids for hot-pressing of SiC powder and pressureless sintering of AlN.18),19) Wei and Lee20) investigated the pressureless sintering of SiC–AlN composite powders, and found that Y2O3 was a better sintering aid than the others. In the present study, we focused on the pressureless sintering of the SiC–AlN system with Y2O3 as a sintering aid. The high-temperature strength of the densely pressureless sintered SiC–AlN ceramics was also investigated, because the mechanical properties at elevated temperature would be of the first concern as for non-oxide ceramics containing oxide sintering aids.

2. Experimental procedures

2.1 Sintering and characterization

The commercial powders shown in Table 1 were used in this work. The compositions of SiC–25, 50, 70, 80, 90, 100 vol% AlN were selected for the present work, and Y2O3 powder was added by 2 vol% relative to the total amount of SiC and AlN. The powder mixtures were prepared by ball-milling for 24h in ethanol solution with a silicon nitride pot and balls and subsequently drying in air at 80 °C. Green compacts with dimensions of 10 mm in diameter and about 10 mm in height were formed by die-pressing at 100 MPa, followed by isostatic pressing at 200 MPa. Sintering experiments were performed at temperatures between 1650 and 1900 °C in

Table 1. Characteristics of Starting Powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>Average particle size (μm)</th>
<th>Purity</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-SiC</td>
<td>0.37</td>
<td>&gt;98.5%</td>
<td>Showa Denko K. K.</td>
</tr>
<tr>
<td>AlN</td>
<td>1.39</td>
<td>&gt;98.5%</td>
<td>Toyo Aluminum K. K.</td>
</tr>
<tr>
<td>Y2O3</td>
<td>1.31</td>
<td>&gt;99.9%</td>
<td>Shin-Etsu Chemical Co., Ltd.</td>
</tr>
</tbody>
</table>

(*) major impurities: 0.70% free carbon, 0.37% free oxygen; # major impurities: 0.89% free oxygen, 0.03% free carbon
nitrogen at 0.1 MPa using a tungsten mesh resistance furnace. The green compacts were placed in a BN crucible and buried in a powder premix of SiC-50 vol% AlN as packing powder, which was confirmed to be more effective than SiC or AlN powder. The furnace temperature was controlled to ±10°C with a W-Re thermocouple placed near the specimen. The heating rate and holding time were 10°C·min⁻¹ and 1h, respectively.

The density of the sintered samples was measured by Archimedes’ method. The relative density was calculated from the theoretical density of SiC (3.21 g·cm⁻³), AlN (3.26 g·cm⁻³) and Y₂O₃ (5.03 g·cm⁻³) according to the rule of mixture by ignoring the influence of any reaction on the density. X-ray diffraction analysis was done on the sintered bodies to determine the constituent phases. The microanalysis of the composition in the sintered bodies was performed on a scanning transmission electron microscope (STEM) equipped with an energy dispersive X-ray spectrometer (EDX).

2.2 Measurement of strength
Specimens sintered to 98% of the theoretical density were used for mechanical evaluation. The strength was measured from room temperature to 1500°C in Ar atmosphere by a small punch (SP) test,¹⁶,¹⁷ which is a newly developed semi-empirical testing method suitable and effective for the evaluation of mechanical behavior including high temperature deformation of ceramics using a small-sized specimen. Figure 1 schematically shows the configuration of SP testing jig built in the chamber of an electric furnace. The loading was controlled with a universal testing machines at a crosshead speed of 0.1 mm·min⁻¹. The operation principle of this testing method is that a disk specimen is loaded by a small puncher and the deflection is monitored. Compared with the bending test widely used for measuring the strength of ceramics, the SP test has several advantages. That is, a small sized specimen (approximately 10 mm in diameter and 0.5 mm in thickness) can be used; the fixture of specimen to the testing jig is easier. And the deformation of a tested specimen can be directly and accurately measured as a deflection in the z-axis. The fracture strength is given by the following equation from the maximum load (P) in the deformation curve,¹¹,²¹

\[ \sigma_{SP} = \frac{3P}{2\pi t^2} \left[ 1 - \frac{1}{4} \frac{v^2 b^4}{a^4} + (1 + \nu) \ln \frac{a}{b} \right] \]  

(1)

where t is the thickness of a specimen, a and b are radii of the lower hole and the puncher, 2.25 mm and 0.9 mm, respectively, in the present work. \( v \) is Poisson’s ratio. It has been found that a linear relationship holds between the strengths by the SP and bending tests, allowing that the SP-strength is slightly smaller than the 4-point bending strength by a factor of 0.89 for the present material.¹¹

Disk specimens for the SP test, approximately 0.7 mm in thickness, were sliced from the densely sintered bodies using a diamond wheel. The specimens were then ground on both faces to obtain flat and parallel faces. The tensile surface was finally polished with 1 μm diamond paste to achieve a mirror-like surface finish. The SP testing was conducted in argon atmosphere.

The Vickers hardness and fracture toughness of the densely pressureless sintered compacts were also measured by the Vickers indentation method, the experimental details of which have been given elsewhere.⁷

3. Results and discussion
Figure 2 shows the sintered density of AlN and SiC–AlN composites as a function of sintering temperature. It was clear that there was no apparent increase in density in the samples without additives, even if the sintering temperature was raised to 1850°C. As for the AlN with 2 vol% Y₂O₃, the density of AlN increased sharply from 1750°C and reached about 100% of the theoretical density at 1850°C. The densification of AlN is mainly attributed to the formation of aluminates between the added Y₂O₃ and oxide compounds on the surface of AlN,¹⁹ which will give a liquid phase at temperature above 1760°C according to the phase diagram of Y₂O₃-Al₂O₃ system.²²

It should be noted that higher densities were achieved in the compositions with 10–30 vol% SiC at temperatures below 1800°C. This fact is probably because the densification was promoted by a new liquid phase, which was formed between the added Y₂O₃ and the oxides on the surfaces of SiC (SiO₂ or SiO) and AlN (Al₂O₃) at lower temperature. In fact, the eutectic points of the Al₂O₃–SiO₂ and Y₂O₃–SiO₂ sys-
terns are 1595°C and 1660°C, respectively.

Figure 3 shows the X-ray diffraction patterns of mixed powders and sintered body with a composition of SiC-70 vol% AlN (containing 2 vol% Y2O3). The peaks of SiC and AlN were still split after sintering with slight change in the relative intensity. The fact suggests that the sintered body was not a single-phase solid solution under the present conditions of the pressureless sintering. Compared with the conventional hot-pressing temperature, usually above 2100°C, the sintering temperature in the present study is rather lower to complete the solid-solution reaction. The unindexed weak peak in the sintered body is expected to belong to the grain boundary phase of oxides, as described later.

Figure 4 shows the typical transmission electron micrographs (TEM) of the pressureless sintered AlN and SiC-70 vol% AlN. The indicated areas were analyzed by STEM-EDX, and the compositions were listed in Table 2. The contents of oxygen and nitrogen were not determined, because their analysis was impossible in the EDX equipment used in the present study. As shown in Fig. 4(A), a typical microstructure of liquid phase sintering was observed in the pressureless sintered AlN, in which pure AlN grains were surrounded by the grain boundary phase composed of Y2O3 and Al2O3. The grain boundary phase enhanced the densification when it was liquid phase at the sintering temperature. On the other hand, the SiC-70 vol% AlN showed a complicated and fine-grained microstructure. Each individual grain was composed of SiC and AlN with different composition ratio, but no pure SiC and AlN were detected. The grain boundary phase was found to contain Al, Si and Y elements, which were thought to be in the form of oxide. The grain boundary phases were not connected as in the AlN, but most of them tended to concentrate in the region of fine

<table>
<thead>
<tr>
<th>Material</th>
<th>Point</th>
<th>Atomic Percentage (at%)</th>
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<tbody>
<tr>
<td>AlN</td>
<td>A</td>
<td>89 0 31</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>100 0 0</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>100 0 0</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>88 0 32</td>
</tr>
<tr>
<td>SiC-70vol% AlN</td>
<td>E</td>
<td>25 56 19</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>15 71 14</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>88 14 0</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>71 29 0</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>99 1 0</td>
</tr>
<tr>
<td></td>
<td>J</td>
<td>3 97 0</td>
</tr>
</tbody>
</table>
grains with SiC-rich compositions. The difference in wettability of liquid phase onto the SiC and AlN grains was supposed to be one of the reasons why such a specific microstructure was formed.

Figure 5 shows the typical load–deflection curves from room temperature to 1500°C for AlN, SiC–70 vol% AlN and SiC–50 vol% AlN sintered bodies as determined by the SP test. The sintering temperature and some related properties are given in Table 3. For all compositions, the specimen was elastically deformed at the testing temperature below 1350°C. The AlN sintered body maintained linear deformation up to 1500°C, but nonlinearity appeared in the deformation curves of the SiC–50, 70 vol% AlN samples at 1500°C. Furthermore, the amount of nonlinear deformation in the SiC–50 vol% AlN was greater than that in the SiC–70 vol% AlN. The temperature dependence of average fracture strength for the same three materials in Fig. 5 is given in Fig. 6, where the strength values were calculated using Eq. (1). Equation (1) is rigorously applicable for elastic deformation like those below 1350°C shown in Fig. 5 and the strength in the SiC–50 and 70 vol% AlN sintered bodies at 1500°C was calculated using the maximum load of the linear deformation range of the load–deflection curve for comparison. The SiC–AlN composites showed higher strength and retained the strength up to a higher temperature than the AlN. Above 1350°C, the strength of the SiC–AlN composites decreased remarkably from 1350°C to the same level as the AlN at 1200°C.

As shown in Fig. 3, the oxide grain boundary phase must be detrimental to the high temperature strength. However, in a previous study, it was found that high temperature strength decreased with the appearance of nonlinear (or plastic-like) deformation in the fine-grained SiC–AlN solid solutions fabricated by the combination of carbothermal reduction and hot-isostatic pressing without additives. It was concluded that a fine-grained microstructure plays a main role in yielding the high temperature strength decrease presumably due to a superplastic deformation. The studies on the superplasticity of ceramics have shown that a fine-grained microstructure is essential to the plastic deformation of ceramics, because grain refining will enhance micro deformations as grain boundary slidings. Figure 7 shows the scanning electron micrographs (SEM) of the fractured surfaces of the AlN and SiC–AlN composites. The grain size of the SiC–AlN composites was much smaller than that of the monolithic AlN, and it decreased with increasing SiC content. Therefore, it is reasonable to attribute the

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**Table 3. Sintering Temperature, Density and Other Properties of the Materials Used for the Measurement of High Temperature Strength and Deformation**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sintering Temp. (°C)</th>
<th>Bulk Density (g/cm³)</th>
<th>Relative Density (%)</th>
<th>Vickers Hardness (GPa)</th>
<th>Fracture Toughness MPa m¹/²</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>1850</td>
<td>3.28</td>
<td>99.5</td>
<td>14.7</td>
<td>2.01</td>
</tr>
<tr>
<td>SiC–70vol%AlN</td>
<td>1875</td>
<td>3.23</td>
<td>98.5</td>
<td>17.7</td>
<td>3.83</td>
</tr>
<tr>
<td>SiC–50vol%AlN</td>
<td>1900</td>
<td>3.21</td>
<td>98.1</td>
<td>20.0</td>
<td>4.25</td>
</tr>
</tbody>
</table>

Fig. 5. Variations on load–deflection curves by the SP testing for the pressureless sintered AlN and SiC–AlN composites from room temperature to 1500°C.

Fig. 6. Change in SP-strength for the pressureless sintered AlN and SiC–AlN composites with 2 vol% Y₂O₃ as a sintering aid.
nonlinear deformation in the SiC–AlN composites to the uniform microstructure having grain size of submicrometer order. The SiC–50 vol% AlN showed larger amount of nonlinear deformation than the SiC–70 vol% AlN, since its grain size was smaller than that of the latter. No plastic-like deformation occurred in the monolithic AlN probably because of its coarse-grained microstructure, even though one would expect the grain sliding deformation should be promoted by the continuous grain boundary phase.

4. Conclusions
Dense SiC–AIN composites were obtained by the pressureless sintering of fine-grained SiC–AIN powder mixture with 2 vol% Y$_2$O$_3$ as a sintering aid. The composites with <50 vol% SiC contents were densified to above 98% of the theoretical density in N$_2$ atmosphere of 0.1 MPa at temperatures below 1900°C. The densification was enhanced by the formation of liquid phase from the added Y$_2$O$_3$ powder and surface oxide of SiC and AlN.

The strength and deformation behavior of the pressureless sintered AlN and SiC–AIN composites were investigated from room temperature to 1500°C. No apparent decrease in strength was found in the AlN and SiC–AIN at testing temperature below 1200°C. Compared with the AlN, the SiC–AIN composites have higher strength and retained it to higher temperature. At 1500°C, the SiC–AIN composites showed a remarkable decrease in strength with the appearance of plastic-like deformation. Considering the fact that the SiC–AIN composites had a fine microstructure of uniform grain size, the plastic-like deformation was thought to be due to the grain boundary sliding, apart from the softening of glassy grain boundary phase.

References