MICROWAVE SINTERING OF A COMBUSTION SYNTHESIZED AlN POWDER

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ABSTRACT

We report our preliminary study on microwave sintering of a combustion synthesized AlN powder. The combustion synthesis method was previously developed by Chung et al. at National Cheng Kung University, and the microwave sintering experiments were carried out at the Microwave Processing and Engineering Center in the Pennsylvania State University. The samples were sintered by microwave at 2.45 GHz in a multi-mode cavity. The power used ranged from 200 W to 1 kW, and the sintering temperature ranged from 1600°C to 2000°C. The percent theoretical densities of some of the sintered specimens reached 99% and higher. These specimens were also characterized by XRD and SEM. The thermal conductivity of the specimens was also measured. These results will be presented and the effects of several important experimental parameters on the sintering will be discussed.

INTRODUCTION

Aluminum nitride (AlN) has been acknowledged as an important industrial material because of the unique combination of its properties such as high thermal conductivity, high electrical resistivity, low thermal expansion coefficient, low dielectric constant, good thermal shock resistance, and good corrosion resistance. It has been considered for many applications such as electronic substrates, microelectronic packaging materials, filters in high thermal conductivity materials, heat sinks and crucibles for containing and processing molten metals and salts.

We have recently developed a combustion synthesis method for the synthesis of aluminum nitride. This method has advantages including simple processing, fast production, low production cost, high product purity, and being capable of mass production. It has thus a high potential to be used as a method for commercial production of the AlN powder. Since sintering is a necessary step in the fabrication of many AlN related ceramic products, understanding of the sintering behavior and the properties of the sintered specimens is essential to the applications of the AlN powders produced by a newly developed method. Besides, it is also desirable to reduce the cost of sintering, and this is especially important for the case of AlN. Due to its
c... at bond nature, AIN is usually sintered with relatively severe conditions su... a sintering temperature of 1800°C and a soaking time of 1 h or higher.

Application of microwave for sintering ceramic materials has recently attracted much attention. Advantages of microwave heating and sintering include fast heating rate, energy efficiency, uniform heating, enhancement of mass transport during sintering, and superior properties of the sintered product. For the sintering of AIN ceramics, it has been reported [7] that lower sintering temperatures, shorter soaking times, and better sintered specimens properties can be realized by using microwave as compared to the conventional sintering techniques. One of our research programs has thus been aimed at studying the microwave sintering of the AIN powders synthesized by our newly developed combustion synthesis method. In this work, we report our preliminary results of this study.

EXPERIMENTAL
Combustion Synthesis of AIN
All of the AIN powders used in the present study were prepared by our newly developed combustion synthesis method. Al (99.99% purity, 250g) and a small amount of ammonium chloride powder (0.1-3 wt%) were thoroughly mixed and then poured into a perforated aluminum container, which was cylindrical in shape with 80 mm in diameter and 100 mm in height. The container holding the reactants was then placed in a reactor, which has been described and shown schematically in our previous study. The reactor was evacuated (to 600 Pa) and then was refilled with nitrogen gas to the desired pressure (0.05-0.5 MPa). The combustion reaction was ignited by heating the top surface of the reactants powders with an electric current (~1200 W) through the tungsten heating coil. It took ~30 sec to ignite the combustion reaction and the heating power was turned off after ignition. A regulated flow of nitrogen was supplied to the reactor to maintain a constant pressure inside the reactor. It took ~30 min for the combustion reaction to complete. The products were taken out of the reactor after cooling to near the room temperature. The conversion (defined as the mass fraction of the Al converted to AIN) was higher than 99.9% as determined by the method described previously [9].

Table 1: Properties of the AIN Prepared in the Present Study

<table>
<thead>
<tr>
<th>Type of AIN</th>
<th>Average particle size ( D_{50} ) (μm)</th>
<th>Si (wt%)</th>
<th>O (wt%)</th>
<th>Fe (wt%)</th>
<th>Zr (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-synthesized</td>
<td>-</td>
<td>&lt;0.035</td>
<td>0.2</td>
<td>&lt;0.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>AIN-1</td>
<td>0.9</td>
<td>0.04</td>
<td>4.0</td>
<td>0.256</td>
<td>0.528</td>
</tr>
<tr>
<td>AIN-2</td>
<td>3.0</td>
<td>0.03</td>
<td>3.0</td>
<td>0.087</td>
<td>0.215</td>
</tr>
</tbody>
</table>

The microwave furnace used in the present study consists of a 2.45 GHz microwave generator with a power output continuously adjustable from 0-6 kW, and a water-cooled multi mode cavity. As shown in figure 1, a quartz tube which was insulated by fiberglass insulation packages, was placed vertically at the center of the cavity. The BN crucible was placed on the perforated BN support, which was at the center of the quartz tube and the top end of the quartz tube was covered with a copper lid. The quartz tube was evacuated to 1 torr by flushing with nitrogen between evacuations. After the evacuations, the reactor was back filled with nitrogen at the desired pressure (0.1 MPa) and the heating process was performed in a flowing nitrogen gas atmosphere with a flow rate of 750 ml/min. Variation of the temperature at the top surface of the sample was measured by using an optical pyrometer through the quartz window at the center of the copper lid.

![Schematic illustration of the microwave cavity](image)

**Figure 1**: Schematic illustration of the microwave cavity.

a: view window ; b: optical pyrometer ; c: quartz tube (D=62 mm); d: tuner ; e: microwave source ; f: insulated package ; g: BN crucible containing AIN green compacts ; h: BN support.

Microwave Sintering of AIN
In the present experiment, samples of different levels of \( Y_2O_3 \) additions from 0-10 wt% were fabricated by uniaxial pressing. The compact was ~15.5 mm in diameter and ~3 mm in thickness and the green density was ~64% of the theoretical density. The compact was placed in a BN crucible, which served as a microwave absorber to preheat the compact. The BN crucible was packed in an insulation packet.
In this set of experiment, AlN-1 powder was used for microwave sintering. Figure 2 shows the shrinkages as a function of Y₂O₃ content at various sintering conditions. The measured densities and the calculated percent theoretical densities of the sintered specimens are also provided and marked on the respective data points. As shown in figure 2, a nearly fully densification can be achieved with a sintering temperature of 1800°C and a soaking time of 30 min when the Y₂O₃ content is 5wts. A sintering temperature of 1700°C is obviously not high enough to achieve a high densification when the soaking time is 30 min or shorter. A sintering temperature of 1800°C and a soaking time of 15 min is also seen to be not long enough to achieve a high densification. With a sintering temperature of 1800°C and a soaking time of 30 or 60 min, the shrinkage is seen to increase rapidly as the Y₂O₃ content increases from 0 to 3 wts, but is relatively unaffected with further increase in the Y₂O₃ content. An increase of the soaking time from 30 to 60 min has little effect on densification when the sintering temperature is 1800°C. A sintering temperature of 1800°C and a soaking time of 30 min with a Y₂O₃ content of 3-5 wts, thus can be considered as a set of optimum sintering conditions for the AlN-1 powder.

Figure 2 The shrinkage as a function of Y₂O₃ content under various sintering conditions for AlN-1 powder.

Experiment II

In this experiment, AlN-2 powder was used for microwave sintering under conditions of 4 different sintering temperatures and a soaking time of 30 min. As shown in figure 3, the shrinkages (and the densities) obtained at the sintering temperature of 1600°C are much smaller than those obtained at 1800°C and higher, indicating that 1600°C is not high enough as a sintering temperature for the AlN-2 powder. The shrinkage is seen to increase with increasing sintering temperature at all the Y₂O₃ contents used. For the three higher sintering temperatures (i.e., 1800, 1950 and 2000°C), the shrinkage increases rapidly with increasing Y₂O₃ content when the Y₂O₃ content is less than 3wts. The increases become relatively small as the Y₂O₃ content is increased beyond 3wts.

Phase Analysis with XRD

Typical XRD patterns (Fig. 4.) shows that Al₃(Y₀.₃Ti₀.₇O₁₂) is the only second phase detected at 3wts Y₂O₃ content specimen. YAlO₃ and Al₄Y₂O₇ are being to be detected as the Y₂O₃ content increased to 5wts. Al₃Y₂O₇ becomes the major second phase and, in some cases, Y₂O₃ is also detected as the Y₃ content is increased to 10wts.

Microstructure Analysis

Figure 3 shows typical SEM photographs of the fractured surfaces of the specimens composed of AlN-1 powder sintered under various conditions. The specimens with Y₂O₃ contents of 0, 3, 5, or 10wts contain numerous pores and have little grain growth when they are sintered at 1800°C with a soaking time of 15 min. This can be seen in Fig. 5(a), where the grain size = 5µm, similar to the particle size of the starting powder. As shown in figure 5(b), 5(c) and 5(d), the specimens are nearly fully dense when they are sintered at 1800°C with a soaking time of 30 min. The grains are seen to be well-defined hexagonal in shape and uniform in size distribution (the grain size = 2µm).

Figure 3 The shrinkage as a function of Y₂O₃ content at various sintering temperatures with a soaking time of 30 min for AlN-2 powder.

Figure 6 contains two SEM photographs of the fractured surfaces of the specimens composed of AlN-2 powder and sintered at 2000°C with a soaking time of 30 min. The specimens are also seen to be nearly fully dense with grain sizes ranging from 5 to 10µm. The grain shapes are, however, more like sphere rather than hexagonal. Back-scattered electron SEM photographs of the fractured and polished surfaces of the specimens shows that the second phases are formed along the grain boundaries. This also can be seen in figure 6.

Thermal Conductivity Measurement

Listed in Table II are the thermal conductivities of the specimens sintered under various conditions. For the AlN-1 specimens sintered at 1800°C with a soaking time of 30 min, the thermal conductivity increases significantly (from 90 to 122w/m·k) as the Y₂O₃ content is increased from 3 to 5wts. As the Y₂O₃ content is further increased (from 5 to 10wts), the increase in the thermal conductivity is relatively small (from 122 to 126 w/m·k). For the AlN-2 specimens sintered at 2000°C with a soaking time of 30 min, the thermal conductivity is almost unaffected by the increase of the Y₂O₃ content from 3 to 5wts. The thermal conductivity, however, decreases (from 132 to 122w/m·k) as the Y₂O₃ content is increased from 5 to 10wts.
Combustion synthesized powders have been claimed to have superior sintering properties as compared to those produced by conventional methods. Because the materials experience large temperature gradients and high heating and cooling rates during the SHS processes, the powders produced are expected to have high defect concentrations, thus being more reactive for sintering. Xu et al. studied the microwave sintering of AlN produced Al2O3 powder and found that a high densification (98.7% of theoretical density) can be achieved by sintering the powder (with 3wt% Y2O3 added) at 1600°C for 4 min. In the present study, the AlN-1 powder, which has a similar particle size distribution with that used by Xu et al., is seen to be unable to be sintered to high densities (98.0%) at 1700°C for 30 min with 3wt% Y2O3 added (see Fig. 2). When using a sintering temperature of 1800°C and a soaking time of 15 min, the maximum theoretical density obtained was 97.3% with 10 wt% of Y2O3 was added. A sintering temperature of 1800°C, a soaking time of 30 min and a 3-5wt% Y2O3 content are thus considered to be optimum conditions to achieve high densifications for the AlN-1 powder. The AlN-2 powder is seen to be less sinterable than the AlN-1 because the former has much larger particle sizes than the latter. When sintered at 1800°C with a soaking time of 30 min and a 5wt% Y2O3 content, the specimens from the AlN-2 powder reach 92.5% of theoretical density, compared to 99.1% for the specimens from the AlN-1 powder. A sintering temperature of 1950°C or higher is thus required to achieve high densifications (e.g., 99% or higher) for the AlN-2 powder when a soaking time of 30 min is used.

Figure 4 XRD patterns of the specimens composed of AlN-2 powder and sintered at 2000°C with a soaking time of 30 min, contents of Y2O3: (a), 3wt%; (b), 5wt%; and (c), 10wt%.

Figure 5 SEM photographs of the fractured surfaces of the specimens composed of AlN-1 powder and sintered at 1800°C with different soaking times and Y2O3 contents: (a), 15 min and 5wt%; (b), 30 min and 3wt%; (c), 30 min and 5wt%; and (d), 30 min and 10wt%.

Figure 6 SEM photographs of the fractured surfaces of the specimens composed of AlN-1 powder and sintered at 2000°C with a soaking time of 30 min, Y2O3 content: (a), 5wt% and (b), 10wt%.
Thermal Conductivities of the Specimens Sintered at 1800 or 2000°C with a soaking time of 30 min

<table>
<thead>
<tr>
<th>AIN powder</th>
<th>sintering temperature (°C)</th>
<th>Y₂O₃ content (wt%)</th>
<th>density (g/cm³)</th>
<th>linear shrinkage (%)</th>
<th>thermal conductivity (W/m·K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIN-1</td>
<td>1800</td>
<td>3</td>
<td>3.26</td>
<td>17.1</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>1800</td>
<td>5</td>
<td>3.32</td>
<td>17.9</td>
<td>122</td>
</tr>
<tr>
<td>AIN-2</td>
<td>2000</td>
<td>3</td>
<td>3.16</td>
<td>15.1</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>5</td>
<td>3.23</td>
<td>15.7</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>2000</td>
<td>10</td>
<td>3.33</td>
<td>16.1</td>
<td>122</td>
</tr>
</tbody>
</table>

When using a 3 or 5 wt% Y₂O₃ content, the specimens made from the AIN-2 powder possess higher thermal conductivities than those from the AIN-1 powder although the densities of the former are lower than the latter (see Table I). As pointed out by many researchers, the oxygen content within the AIN grains poses the most detrimental effect on the thermal conductivity. The difference in the oxygen content between the AIN-1 and AIN-2 powders (see Table I) may thus be a primary factor causing this in the difference in thermal conductivity between their sintered specimens.

It has also been pointed out that cation impurities have significant effects on degradation of the thermal conductivity of AIN ceramics. Although the AIN-1 powder contains much higher cation concentrations than the AIN-2 powder does, the concentration of each cation of the two powders exceeds its respective soluble limit in the AIN lattice. The cation impurities may thus pose an equal effect on degradation of the thermal conductivities of the two types of specimens made from AIN-1 and AIN-2 powders.

Second phase distribution has also been pointed out (44) to affect the thermal conductivity of AIN ceramics. As mentioned previously, the second phases are formed along the grain boundaries. This may thus be another factor causing low thermal conductivities of the specimens in the present study. Harata, et al. (13) studied the effect of second phase on the thermal conductivity of AIN ceramics and found that high contents of sintering aid caused a decrease in thermal conductivity. Although the thermal conductivity of a specimen is affected by many other factors (e.g., oxygen content and degree of densification), this effect would be more pronounced for the specimen with larger grains. Since the specimens with larger grains have less grain boundary area, the second phase present along the grain boundary would be thicker, thus causing a greater extent of decrease in thermal conductivity for such a specimen. This may explain the opposite effects on the thermal conductivities of the AIN-2 specimens, when the Y₂O₃ content is increased from 5 to 10 wt%.

The thermal conductivities measured in the present study are relatively low as compared to those reported in many other studies where the AIN powder from Tokuyama Soda, Grade F has been mostly used. Nevertheless, by employing proper equipment for processing the powder produced by our

CONCLUSION

A combustion synthesized AIN powder was preliminarily tested for its sinterability and the thermal conductivities of the sintered specimens were measured. The AIN powder (AIN-1) with an average particle size (D₅₀) of 0.9 μm could be sintered to ~ 99% of theoretical density at a sintering temperature of 1800°C with a soaking time of 30 min and a Y₂O₃ content of 3.5 wt%.

The AIN powder with a D₅₀ of 3.0 μm (AIN-2) was seen to be less sinterable than AIN-1. In this case, 97% of theoretical density was obtained at a sintering temperature of 2000°C with a soaking time of 30 min and a Y₂O₃ content of 3 wt%.

The thermal conductivities reached 122 and 132 W/m·K for the specimens made from AIN-1 and AIN-2, respectively, when 5 wt% of Y₂O₃ was added. The higher thermal conductivity of the AIN-2 specimen is attributed to its lower oxygen content in spite of its lower densification. The thermal conductivities are relatively low as compared to those reported in many other studies. This is considered to be caused by high oxygen contents, high contents of other impurities, and that the second phases exist along the grain boundaries. A significant improvement in thermal conductivity is expected by employing proper grinding equipment with which AIN powders with higher purity can be produced.

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REFERENCES


