Microwave Sintering of Combustion Synthesized AlN Powder towards High Thermal Conductivity Ceramics

S.L. Chung*, T. I. Tsai and S.C. Huang

Department of Chemical Engineering
National Cheng Kung University
Tainan, Taiwan, 70101
Republic of China
email: slchung@mail.ncku.edu.tw

*To whom all correspondence should be addressed.
TEL: +886-6-2757575 ext. 62654
FAX: +886-6-2344496
email: slchung@mail.ncku.edu.tw
Abstract

Combustion synthesized AlN powders were investigated for use as starting material for obtaining high thermal conductivity specimens by microwave sintering and reheating. Microwave sintering and reheating was carried out in a TE_{103} single mode cavity with an adjustable microwave power in the range of 0-3KW at 2.45 GHz. Densification was found to be a primary requirement to obtain a high thermal conductivity AlN. AlN powders with good sinterability are required to achieve a high densification. AlN powder with $D_{50}$ of ~6μm was found to have a poor sinterability and that with $D_{50}$ of ~3μm or finer to have a good sinterability. Oxygen content was found to be an another important factor determining the thermal conductivity. The thermal conductivity can be enhanced from ~130 to ~155 W/mK when the oxygen content is reduced from 2.3 to 1.4 wt%. The thermal conductivity can be significantly improved by microwave reheating the sintered specimen under the reducing atmosphere. This is considered to be due to enhanced removal of the second phases by the reducing atmosphere.

Key words: SHS, Combustion synthesis, Aluminum nitride, Sintering, Thermal conductivity.
1 Introduction

Aluminum nitride (AlN) has been acknowledged as an important industrial material because of its unique combination of the properties such as high thermal conductivity, high electrical resistivity, low thermal expansion coefficient, moderately low dielectric constant, good thermal shock resistance and good corrosion resistance.\(^1,2\)

It has been considered for many applications such as a filler for EMC (epoxy molding compound) for microelectronic encapsulation, substrates for semiconductor chips, and an insulating material for RF and microwave packages.\(^3,4\)

Recently, it is also considered\(^3\) for application as a loading substrate for high power LED chips because of its high thermal conductivity.

In our laboratory, a SHS\(^5\) (Self Propagating High Temperature Synthesis or combustion synthesis) process has been recently developed\(^6-8\) for synthesis of AlN powder and this process is considered to possess many advantages such as low energy consumption, high production rate, low production cost and being capable of mass production. The use of the AlN powder as a filler for EMC has been studied\(^9\) and a thermal conductivity of 14 W/mK was obtained for a specimen made up of 80 wt% AlN and 20 wt% cresol novolac epoxy. Sintering of the AlN powder using microwave has also been investigated\(^10\) and a thermal conductivity of 186 W/ mK was obtained for a specimen sintered at 1900\(^\circ\)C for 30 min with addition of 3 wt% Y\(_2\)O\(_3\) as
sintering aid. The thermal conductivity of AlN was further found to be significantly improved by microwave reheating the sintered specimen under the reducing atmosphere\textsuperscript{11}.

When compared to traditional techniques, microwave heating and sintering has been shown to possess many advantages such as rapid heating, energy efficiency, volumetric and uniform heating, enhancement of mass transfer during sintering, superior properties of the sintered products and so-called “microwave effect”\textsuperscript{12-14}. Although many studies\textsuperscript{15,16} have been carried out to investigate the microwave sintering of AlN, few of them have been aimed at improving the thermal conductivity by employing techniques such as reheating treatment. The data concerning the effects of AlN properties (e.g., particle size and oxygen content) on the sinterability and thermal conductivity has also been rare. In this study, AlN powders with different particle size and oxygen content were used as the starting material for microwave sintering. The effects of particle size and oxygen content on sinterability and thermal conductivity were investigated. Microwave reheating under reducing atmosphere was also carried out to study its effect on the thermal conductivity.
2 Experimental

2.1 Preparation of AlN powder and green compact

The AlN powders used in the present study were produced by the SHS method developed in our laboratory. The as-synthesized AlN product was crushed to under 60 mesh and then milled for the desired periods of time by using an attritor (Union Process, Szegvari Attritor, USA) with ZrO₂ balls of 5 mm diameter as milling media and acetone as milling fluid. Listed in Table I are the properties of the as-synthesized AlN and the AlN powder thus obtained for use in the present study. Powder A, B and C were obtained by milling for 4, 6 and 8 hr and their average particle sizes (D5₀) were 6.2, 3.4 and 1.8 μm, respectively. To minimize oxidation, the milling for powders A, B and C was carried out under N₂ atmosphere and their oxygen contents were measured to be 1.0, 1.3 and 1.4 wt%, respectively. To obtain a powder with a higher oxygen content, powder D was obtained by milling for 8 hr but under ambient air. As can be seen, powder D has the same D5₀ as powder C but has a higher oxygen content, i.e., 2.3 wt%.

Y₂O₃ of 99.99% purity and with a D5₀ of 2 μm (TG-007, Echo Che Co., Ltd) was used as sintering aid. The AlN powder, 3-7 wt% sintering aid and 5 wt% cellulose (serving as binder, both percentages were based on the weight of AlN) were mixed in
acetone for \( \sim 3 \) hr by using a magnetic stirrer. The slurry was then dried. The product thus obtained was ground to under 60 mesh and then uniaxially pressed (250 MPa) into green compacts with a diameter of 15.5 mm and a thickness of 5 mm. The green compact was then placed in an electrical oven to have the binder burned out in air at \( 350^\circ C \) for 1 hr before microwave sintering.

2.2 Microwave sintering of AlN

Figure 1 is a schematic illustration of the microwave cavity. The AlN crucible containing the AlN specimen was placed on a Al\textsubscript{2}O\textsubscript{3} fiber support inside a quartz tube (inside diameter: 46 mm), which was installed vertically at the center of the cavity. The quartz tube was surrounded with Al\textsubscript{2}O\textsubscript{3} fiber blocks in order to minimize heat loss. The microwave cavity was TE\textsubscript{103} single-mode and was cooled by circulating water. Microwave at 2.45 GHz was generated by a generator with a power output continuously adjustable in the range of 0 - 3 KW. The quartz tube was purged with nitrogen at a flow rate of 1 l/min for 10 min before operating. The sintering was performed in a flowing nitrogen gas atmosphere with a flow rate of 450 ml/min. The heating rate was controlled by adjusting the microwave power with a variac. For each sintering experiment, the microwave power was increased by 100 W for every 10 min during heating until reaching the desired sintering temperature and the power was held constant during soaking. After soaking, the microwave power was decreased by
100 W for every 10 min to decrease gradually the specimen’s temperature. The specimen was embedded at the center of a volume (7.8 cm$^3$) of AlN packing powder contained in an AlN crucible (31 mm in diameter and 25 mm in height). The temperature of the specimen was measured by both a two-color pyrometer and a thermocouple with an extrapolation technique. The detailed specimen arrangement, insulation package, temperature measurement and experimental procedure were described in our previous study$^{10}$ and were not repeated here. All the specimens were sintered at either 1750 or 1900$^\circ$C with various soaking times (5 ~ 180 min) under a constant flow of N$_2$ gas (450 ml/min).

2.3 Microwave reheating under reducing atmosphere

To study the effect of heat treatment on sintered specimens under a reducing atmosphere, some of the specimens after sintering for a period of time (5 ~ 180 min) were placed back into the cavity and were microwave reheated. The specimen arrangement and insulation package for reheating were both the same as that for sintering with the only difference that the AlN packing powder was uniformly mixed with a small amount of carbon powder (under 150 mesh and 0.5 wt% based on the weight of the AlN packing powder). The reheating was carried out at 1800$^\circ$C with a holding time ranging from 60 to 180 min.

2.4 Characterization of specimens
The densities of the sintered specimens were measured by Archimedes displacement method using deionized water as the immersion medium. Theoretical densities of the specimens were calculated by assuming that the specimens were composed of AlN and Y$_2$O$_3$ according to their compositions. The crystalline phases were determined by X-ray diffraction analysis (XRD) (Rigaku, DMAX-200, Japan) and the microstructures were characterized by using a scanning electron microscope (SEM) (Hitachi, S4200, Japan). To measure the oxygen content of the sintered specimen, the sintered specimen was crushed to under 60 mesh and then measured by a N/O analyzer (LECO, TC300, USA). The thermal diffusivity was measured by a laser flash method (Holometrix, Microflash 300, USA). A room temperature heat capacity of 0.718 J/kg · K from JANAF thermo-chemical tables was used to calculate the thermal conductivity based on the equation: \[ K \text{ (thermal conductivity)} = C_p \text{ (heat capacity)} \cdot \rho \text{(density)} \cdot \alpha \text{(thermal diffusivity)}. \]
3 Results and Discussion

Figure 2 shows the density of the sintered specimens as a function of Y$_2$O$_3$ content when the specimens were sintered at 1750 or 1900$^\circ$C. As can be seen, the sintered specimen densities all increase with increasing Y$_2$O$_3$ content. In addition, the densities of the specimens sintered from powders B, C and D (will be referred to as specimens B, C and D) are all much higher than that from powder A (will be referred to as specimen A), indicating that AlN powder with a D$_{50}$ of around 6μm has a poor sinterability when microwave-sintered in the temperature range from 1750 to 1900$^\circ$C and that the sinterability can be significantly improved by reducing the D$_{50}$ to around 3μm or smaller. The densities of specimens C and D are seen to be essentially the same, indicating that oxygen content (in the range of the present study, 1.4-2.3 wt%) does not affect the sinterability.

Figure 3 shows typical SEM photographs of the fractured surfaces of the sintered specimens. Specimens A and B sintered at 1750$^\circ$C both contain large volumes of pore while specimens C and D sintered at 1900$^\circ$C are seen to be fully densified. Both the pore size and pore volume decrease with decreasing D$_{50}$ of the powder and with increasing sintering temperature. These are all in good agreement with the measured
densities. The grains sintered at 1750°C are more spherical but those sintered at 1900°C are sharp-edge in shape with a grain size of ~8μm. Besides, in all the cases, second phases can be seen along grain boundaries.

Figure 4 shows typical XRD patterns of the sintered specimens. At a Y2O3 low content (i.e., 3 or 5 wt%) YAG (Y3Al5O12) or YAP (YAlO3) was detected and at a high Y2O3 content (i.e., 5 or 7 wt%) YAM (Y4Al2O9) and Y2O3 was detected.

Shown in Fig. 5 are the thermal conductivities of the sintered specimens. As can be seen, the thermal conductivity of the specimen sintered at 1900°C is higher than that sintered at 1750°C when using the same size of powder. This indicates that densification is an important factor to enhance the thermal conductivity. The same principle is also seen when one compares the thermal conductivities of the specimens sintered from different sizes of powders, where one sees that the thermal conductivity of the specimen sintered from finer powder is higher than that sintered from coarser powder. When sintered at 1900°C, the thermal conductivities of specimens B and C both increase as the Y2O3 content is increased from 3 to 5 wt%, indicating that densification enhanced by increasing Y2O3 content predominates. However, as the Y2O3 content is further increased to 7 wt%, the thermal conductivity decreases, revealing that thermal conductivity reduction caused by a larger amount of second phases formed between grain boundaries predominates. (Note that the thermal conductivities of YAG, YAP and
YAM are 7.4, 4.3 and 2.5 W/mK, respectively, which are all much lower than that of AlN.) Same argument can also explain the variation of thermal conductivity with Y$_2$O$_3$ content at the sintering temperature of 1750°C. Furthermore, one sees that the thermal conductivity of specimen D is much lower than that of specimen C. This indicates that oxygen content is an important factor affecting the thermal conductivity: The thermal conductivity is significantly reduced as the oxygen content is increased from 1.4 to 2.3 wt%.

Figure 6 shows the effects of reheating under reducing atmosphere on the density, oxygen content and thermal conductivity of specimen C (with 5wt% Y$_2$O$_3$) which had been sintered at 1900°C for 30 min before the reheating. As can be seen, the density and the oxygen content of the specimen both decrease with reheating time but the thermal conductivity increases with increasing reheating time and reaches 185 W/mK after being reheated for 180 min. During reheating under reducing atmosphere, oxygen is believed to be removed primarily by diffusion of the secondary phases out to the surfaces of the specimen where the secondary phases, in addition to evaporation and sublimation, can react with carbon by reactions such as:

$$\text{Al}_2\text{Y}_4\text{O}_9 + \text{N}_2 + 3\text{C} \rightarrow 2\text{Y}_2\text{O}_3 + 2\text{AlN} + 3\text{CO} \quad (1)$$

and

$$\text{Al}_2\text{O}_3 + \text{N}_2 + 3\text{C} \rightarrow 2\text{AlN} + 3\text{CO} \quad (2)$$
Since the second phases contain oxygen and have higher densities than AlN, the removal of the second phases thus causes the decreases in both the density and the oxygen content. Since the specimen had been sintered to nearly fully dense before reheating, the densification was maintained and was not affected by the reducing atmosphere during reheating. Because the second phases have much lower thermal conductivities than AlN and are removed by reheating, the thermal conductivity is therefore significantly increased by the reheating.
4 Conclusion

Several conclusions can be drawn based on the present study:

(1) Densification is a primary requirement for obtaining a high thermal conductivity AlN.

(2) AlN powders with good sinterability are required to achieve a high densification. AlN powder with $D_{50}$ of ~6μm is found to have a poor sinterability and that with $D_{50}$ of ~3μm or finer has a good sinterability.

(3) Oxygen content is another important factor determining the thermal conductivity. The thermal conductivity can be significantly enhanced when the oxygen content is reduced from 2.3 to 1.4 wt%. (The thermal conductivity is increased from ~130 to ~155 W/mK.)

(4) Removal of second phases can significantly enhance the thermal conductivity and this can be achieved by reheating the sintered specimen under reducing atmosphere.
Acknowledgment

The authors would like to thank the Bureau of Energy, Ministry of Economic Affairs of Taiwan, R.O.C. for the partial financial support under Contract No. 100-D0204-6 and the LED Lighting Research Center, NCKU for the assistance of product characterization.
References


8. Lin, C. N. and Chung, S. L., combustion synthesis method for synthesis of


Table 1. Properties of as-synthesized and ground AlN

<table>
<thead>
<tr>
<th>AlN</th>
<th>Milling time(hr)</th>
<th>average particle size D50 (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>—</td>
<td>0.015</td>
<td>0.2</td>
<td>0.012</td>
<td>N*</td>
</tr>
<tr>
<td>powder A</td>
<td>4</td>
<td>6.2</td>
<td>0.015</td>
<td>1.0</td>
<td>0.086</td>
<td>0.07</td>
</tr>
<tr>
<td>powder B</td>
<td>6</td>
<td>3.4</td>
<td>0.015</td>
<td>1.3</td>
<td>0.087</td>
<td>0.09</td>
</tr>
<tr>
<td>powder C</td>
<td>8</td>
<td>1.8</td>
<td>0.015</td>
<td>1.4</td>
<td>0.087</td>
<td>0.10</td>
</tr>
<tr>
<td>powder D</td>
<td>8</td>
<td>1.8</td>
<td>0.015</td>
<td>2.3</td>
<td>0.088</td>
<td>0.10</td>
</tr>
</tbody>
</table>

*N: not detected.
Figure Captions

Figure 1  Schematic illustration of the microwave cavity.
a: view hole; b: quartz tube ($D_{in}$: 46mm : $D_{out}$: 50mm); c: Al$_2$O$_3$ fiber blocks; d: tuner; e: microwave source; f: short adjust; g: AlN crucible containing AlN specimen; h: N$_2$ gas inlet; i: gas outlet.

Figure 2  Density of the sintered specimens as a function of Y$_2$O$_3$ content when the sintering temperature is 1750 or 1900°C. (Specimen and sintering temperature : ○, specimen A, 1750°C; □, specimen B, 1750°C; △, specimen C, 1750°C; ●, specimen A, 1900°C; ■, specimen B, 1900°C; and ▲, specimen C, 1900°C)

Figure 3  Typical SEM photographs of fractured surfaces of the sintered specimens. Type of specimen, Y$_2$O$_3$ content and sintering temperature: (a) and (b): specimen C, 7wt% and 1750°C; (c) and (d): specimen C, 7wt% and 1900°C; (e) and (f): specimen B, 7wt% and 1900°C.

Figure 4  XRD patterns of specimen B sintered at 1900°C for 30 min with different contents of Y$_2$O$_3$.

Figure 5  Thermal conductivities of specimens sintered at 1750°C or 1900°C for 30 min with different Y$_2$O$_3$ contents. ( Specimen and sintering temperature: □, specimen B, 1750°C; △, specimen C, 1750°C; ■, specimen B, 1900°C; ▲, specimen C, 1900°C; ▼, specimen D, 1900°C.)

Figure 6  Effects of reheating time on the density, oxygen content and thermal conductivity of specimen C that had been sintered at 1900°C for 30 min (with 5wt% Y$_2$O$_3$) before the reheating.
Figure 1  Schematic illustration of the microwave cavity.

a: view hole; b: quartz tube (D_in: 46mm ; D_out: 50mm); c: Al_2O_3 fiber
blocks; d: tuner; e: microwave source; f: short adjust; g: AlN crucible containing AlN specimen; h: N₂ gas inlet; i: gas outlet.
Figure 2. Density of the sintered specimens as a function of Y$_2$O$_3$ content when the sintering temperature is 1750 or 1900℃. (Specimen and sintering temperature: ○, specimen A, 1750℃; □, specimen B, 1750℃; △, specimen C, 1750℃; ●, specimen A, 1900℃; ■, specimen B, 1900℃; and ▲, specimen C, 1900℃)
Figure 3. Typical SEM photographs of fractured surfaces of the sintered specimens. Type of specimen, Y\textsubscript{2}O\textsubscript{3} content and sintering temperature: (a) and (b): specimen C, 7wt\% and 1750°C; (c) and (d): specimen C, 7wt\% and 1900°C; (e) and (f): specimen B, 7wt\% and 1900°C.
Figure 4. XRD patterns of specimen B sintered at 1900°C for 30 min with different contents of Y₂O₃.
Figure 5. Thermal conductivities of specimens sintered at 1750°C or 1900°C for 30 min with different Y$_2$O$_3$ contents. (Specimen and sintering temperature: □, specimen B, 1750°C; △, specimen C, 1750°C; ■, specimen B, 1900°C; ▲, specimen C, 1900°C; ▼, specimen D, 1900°C.)
Figure 6. Effects of reheating time on the density, oxygen content and thermal conductivity of specimen C that had been sintered at 1900°C for 30 min (with 5wt% Y₂O₃) before the reheating.