Direct Synthesis of Large Scale AlN Sheet

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Abstract. Centimeter scale AlN sheet has been successfully synthesized by the direct nitridation method with an Al–NH₃–N₂–H₂ system. The starting material is Al sheet with 16-300 micron thickness. Al sheet was gradually transformed into AlN sheet in a tube furnace with NH₃–N₂–H₂ atmosphere at 900-1200°C. Synthesized a large scale AlN sheet has highly crystalline. The size of the AlN sheet with 30×100×0.0016mm has only AlN crystal phase. In microstructure analysis, there are fine AlN particles in an AlN sheet. AlN particle size decreased from 250 to 100 nm with decreasing reaction temperature in the tube furnace. Large scale AlN sheet synthesized at high reaction temperatures have low oxygen contents.

1. Introduction
Components for electronic packing require high thermal conductivity to dissipate heat generated in devices especially during running the devices. Polymer/ceramic composites have attracted considerable attention [1–3] because with refined structures can greatly increase performance after proper orientation of fillers in the polymer matrix. One-dimensionally aligned fillers in a polymer matrix can achieve electrical and thermal properties at a remarkably low volume fraction, compared to the pristine powder [4,5]. The anisotropic alignment of graphite sheets in a polymer has attracted interest for the fabrication of polymer/graphite sheet composites, which can exhibit high thermal and electrical conductivity [3,6,7]. However, because the electrical properties of graphite range from metallic to semiconducting, its application as an electrical insulator is restricted [8].

AlN is a functional ceramics with high thermal conductivity (319 W/mK), the coefficient of thermal expansion (4×10⁻⁶/°C), similar to that of silicon, and high electrical insulation (9×10¹³ Ωcm) [9]. AlN can be prepared by several techniques such as: (1) carbothermal reduction from alumina in nitrogen atmospheres; (2) direct nitridation of aluminum metal in N₂ atmospheres; (3) chemical vapor deposition from alkyl-aluminum and ammonia gas; (4) polymer depolymerization (breakdown); and (5) self-propagating high-temperature synthesis [10]. The effect of AlN fillers with high electrical insulation reinforcement on the thermal conductivity of polymer composites has been studied in many papers [11,12] These properties are used in the heat sink system of semiconductor chips, component parts in manufacturing of semiconductor [9].

Theoretically, the thermal resistance is caused by phonon scattering [13], thus it has to be minimized to increase thermal conductivity. Materials with high thermal conductivities can be obtained by using fillers with high intrinsic conductivities. However, as discussed by Bigg [14], when the intrinsic thermal conductivity of the filler is greater than 100 times that of the polymer matrix, there is no significant improvement in the thermal conductivity of the composite. On the contrary, the aspect ratio of the filler is more considerable that dictates the conductivities of a composite, because the fillers with large aspect ratios easily form the bridges between them, known as conductive network.

However, these properties of functional materials could be realized in sintered AlN bulk and sheet types. Then AlN powder was formed into bulk and sheet types and then sintered in inert atmosphere.
at high temperature. Also, we have to control the morphology of AlN to use filler. High aspect ratio of AlN filler can improve the properties of composites [1–3]. However, there is little information regarding the direct synthesize method of centimeter scale AlN sheet. In this paper, we try to synthesize a centimeter scale AlN sheet by the direct nitridation method with an Al–NH$_3$–N$_2$–H$_2$ system. In addition, this study evaluates properties of AlN sheet and polymer composites.

2. Experimental procedure

Commercial aluminum foil with 16-300micron thickness (99.9% purity, Goodfellow Cambridge Limited, U.K.) was used as the starting materials. Aluminum foils have polycrystaline as shown in Fig. 1. Aluminum foil was placed into a graphite plate and subjected to thermal nitridation for one and three hours at 900-1,200 °C in an electronic furnace for ammonia nitridation. The atmosphere within the electronic furnace consisted of N$_2$ (99.999%) carrier gas and NH$_3$ (99.8%) gas, which were injected at rates of 1.0 l/min. The temperature was raised by 5 °C/min until reaching the maximum temperature (i.e. 1,200 °C). With an aim of optimizing the nitridation conditions, ammonia gas was first injected at a temperature of 50 °C; to maintain a stable nitridation atmosphere, the injection of ammonia gas continued after the retention time at maximum temperature was over and until reaching 50 °C, even during the furnace cooling process. Crystal phase analysis depending on reduction atmosphere was done by using XRD (X-ray diffraction, Right D/max 2500v/pc, Rigaku, Japan).

Figure 1. Microstructures and XRD patterns of aluminum foils

50 volume % of multilayered AlN sheets(50*50 mm) were set in a plastic mold and then unsaturated polyester with 0.01% hardner (Butanox, M60) was injected in it. These samples were vacuum dried at room temperature for 6 h. The dimensions of specimen injection molded or machined after curing process were 12.5mm diameter and 2 mm thickness.

The lase-flash method is one of the most popular techniques for determining the thermal diffusivity of materials. In this study, the thermal diffusivity was measured using a Ninseis system (XFA 600, Germany). Then thermal conductivity was calculated from thermal diffusivity by the following equation [15]:

$$k=\alpha \rho C_p$$  \hspace{1cm} (1)

where $k$ is the thermal conductivity of the material, $\alpha$ is the thermal diffusivity of the materials, $\rho$ is the density, and $C_p$ is the specific heat capacity under constant pressure.

3. Results and discussion

Figure 2. AlN sheets (50*50mm) with various thickness synthesized at 1100 °C (a) and magnifications (b)
Aluminum foils with various thicknesses were synthesized at 900-1,200 °C for 1-3 hours. Figure 2 shows that AlN sheets synthesized at 1100 °C for 3 hours look like ceramics. In the case of low temperature (under 1000 °C), metallic surface was remained on the samples. However, synthesizing temperature increased at 1200 °C, aluminum foils was explosively reacted partially.

Figure 3. XRD patterns of AlN sheets with 16 microns thickness samples synthesized at 1,000 °C for 1 hour ((a)-(1)), 1,000 °C for 3 hours ((a)-(2)), 1100 °C for 3 hours ((b)-(1)) and 1100 °C for 2 hours ((b)-(2)).

Figure 3(a) shows XRD patterns of AlN sheets with 16 microns thickness samples synthesized at 1,000 and 1,100 °C for one and three hours. Un-reacted aluminum peaks are remained in the samples synthesized at lower temperature and for short holding times. Also alumina peak is confirmed around 35 degree in XRD patterns (figure 3(a)). Because alumina is generated from the oxygen gas reaction included ammonia gas. However, in the high temperature ammonia gas generates hydrogen gas. These hydrogen gases trap the oxygen gas. So we could remove the alumina in the samples synthesized at above 1,100 °C. AlN peak intensity increased with increasing synthetic temperature and holding time.

Figure 4. Conversion rate of aluminum foils with 16 micron thickness (a) and 0.1mm thickness (b) synthesized at 1050-1200 °C for one and three hours.

Using phase analysis results, the conversion rates of aluminum to AlN were calculated. Figure 4(a) shows the conversion rate of aluminum foils with 16 microns thickness synthesized 1,050 and 1,100 °C for various holding times. To get a fully transformed AlN sheet in the samples with 16 microns thickness, they were synthesized at 1,100 °C for above 2 hours or 1,000 °C for 3 hours. In the case of samples with 0.1mm thickness, samples were synthesized at above 1,200 °C for 3 hours to obtain only AlN phase. However, in the samples with 0.2 and 0.3mm thickness, it is not fully transformed into AlN in this experimental condition. To prepare a multilayered AlN sheets, we only used AlN sheets with 16 microns thickness synthesized at 1,100 °C for 3 hours.

In microstructure analysis (figure 5), there are fine AlN particles in AlN sheet. Mean particle size of them is around 250nm. Figure 5(b) shows the microstructure of AlN cross-section. There are some pores in the sheet. To increase the thermal conductivity of AlN, we have to increase the density of samples. However, in this study, we could not get a dense microstructure.
Composite samples with 50 volume % of multilayered AlN sheets (50*50mm) were prepared. They were set in a plastic mold and then unsaturated polyester with 0.01% hardener (Butanox, M60) was injected in it. These samples were vacuum dried at room temperature for 6 h. The dimensions of specimen injection molded or machined after curing process were 12.5mm diameter and 2 mm thickness.

Figure 6 shows the AlN multilayered structure and microstructure. One-dimensionally aligned AlN sheet with 16 microns thickness in a polymer matrix could be obtained. Then we prepared horizontal (parallel direction of AlN sheet) and vertical direction of samples to measure the thermal diffusivity. To calculate the thermal diffusivity, we use theoretical specific heat value (1.031J/gK). Thermal conductivity of the horizontally aligned AlN sheet composite is 22.4 W/mK and vertically aligned AlN sheet composite is 0.97W/mK. Polyester has a thermal conductivity less than 0.1 W/mK and therefore is basically a thermal insulator. However, by incorporating AlN sheets into it, the resulting composites exhibit marvelous improvement in thermal conductivity.

![Figure 5: Microstructure of AlN sheet with 16 microns thickness synthesized at 1,100 ℃ for 3 hours (a) cross-section of sheet and (b) magnification of (a)](image)

![Figure 6: Composites with multilayered AlN sheet (a) and magnification of (a)](image)

3. Conclusion

Aluminum foils with various thickness was transformed into AlN sheet in a tube furnace in NH₃–N₂–H₂ atmosphere at 900–1,200°C for 1 and 3 hours. We successfully synthesized centimeter scale of AlN sheet (50*100mm, 16 microns thickness) using by ammonia synthesizer. Using vacuum infiltration method, we could fabricate the one-dimensionally aligned AlN-polymer composite. Thermal conductivity of composite with 50vol% AlN sheets is 22.4W/mK (horizontally aligned direction) and 0.9W/mK (vertically aligned direction). In the future, we try to evaluate the effect of filler contents on the thermal conductivity of composite.
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