Evaluation of Nitrogen Conversion Ratio on Reaction between BN and Aluminum

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The fundamental reaction behavior between aluminum powder and boron nitride (BN) powder was investigated, and a quantitative evaluation of aluminum nitride (AlN) formation was carried out. As a result of differential scanning calorimeter (DSC) analysis, an exothermic reaction between BN and aluminum was detected at temperatures between 1073 and 1173 K. The conversion ratio of BN to AlN increased with increasing heating temperature. However, the nitrogen conversion ratio appeared to saturate with a holding time of 3.6 ks at temperatures above 1273 K. The nitrogen conversion ratio increased by using 1 μm BN powder instead of 10 μm BN powder. The effect of using the fine BN powder was significant especially when the heating time was short (<300 s). [doi:10.2320/matertrans.M2011184]

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1. Introduction

Among several kinds of ceramics, aluminum nitride (AlN) is noted for its excellent properties such as a high thermal conductivity, high-temperature mechanical properties, and low dielectric constant.^{1–4)} However, a high sintering temperature is regarded as a serious disadvantage for this material. Since AlN is a covalently bonded material, it has a low diffusivity and requires high temperatures (~ 2200 K) and a long heating period (3–8 h) for densification.^{5–9)} Another disadvantage is that AlN exhibits a low fracture toughness and has not, therefore, been considered as a candidate material for structural applications. However, the fracture toughness of AlN can be improved by dispersing hard second phases such as titanium boride (TiB_2) particles in the material.^{10–12)} The authors have investigated a reactive processing technique for producing TiB_2 dispersed AlN composites with the help of a reaction between aluminum, titanium, and boron nitride (BN) as shown in the following equation.^{13–16)}

In previous research,¹⁶⁾ we found that the reaction between aluminum and BN was a dominant factor which controlled the conversion behavior of BN to AlN, and the conversion ratio was strongly affected by the heating temperature. Therefore, fundamental research focusing on the reaction between aluminum and BN is essential. In this paper, compacted powder blends consisting of aluminum and BN powders were prepared, and a quantitative analysis of the reaction product after heat treatments was carried out to determine the effects of important processing conditions (heating temperature, holding time, and BN powder size) on the conversion behavior of BN to AlN.

2. Experimental Procedure

Starting materials used in this experiment were aluminum powder (size: <45 μm , purity: 99.8%) and BN powders ((1)

size: under 1 μm , purity: 99.5%; (2) size: 10 μm average, purity 99.9%). First of all, aluminum and BN powders were blended with an Al/BN molar blending ratio of 3.0/2.0. The blended powder (2.5 g) was then compressed under a pressure of 200 MPa to make a compacted powder preform (cylindrical shape: $\phi 10$ mm $\times$ 15 mm height), and this is denoted as the [Al+BN] preform in this paper. The [Al+BN] preform was inserted into an Al_2O_3 crucible and placed in an infrared furnace. The preform was heated at a rate of $1.0 \text{ K} \cdot \text{s}^{-1}$ to various predetermined temperatures (1073–1673 K) in an Ar atmosphere and held at the designated temperature for 0–3.6 ks. The cross section of the specimen was analyzed by X-ray diffraction (XRD). The quantitative analysis of the reaction product was carried out by a calibration curve method. The calibration curve was obtained from the XRD data of AlN and BN powder mixtures (where the $\text{AlN}/(\text{AlN}+\text{BN})$ molar ratio was varied from 0.1 to 0.9).

Figure 1(a) shows the XRD data for preparing the calibration curve. The integrated intensity (J) of (002) peak of BN and the (100), (002), (101) peaks of AlN were measured from the XRD data, and J_{AlN} and J_{BN} were derived by the following equations:

$$J_{\text{AlN}} = J_{\text{AlN}(100)} + J_{\text{AlN}(002)} + J_{\text{AlN}(101)} \quad (2)$$

$$J_{\text{BN}} = J_{\text{BN}(002)} \quad (3)$$

Figure 1(b) shows the calibration curve obtained from the XRD data. In this paper, the mole fraction of AlN is used to evaluate the nitrogen conversion ratio, which indicates the fraction of nitrogen converted from BN to AlN.

3. Results

To begin with, a differential scanning calorimeter (DSC) analysis of the [Al+BN(10 μm)] preform was carried out. Figure 2 shows the DSC curve of the [Al+BN] preform together with the results obtained from monolithic powders. An endothermic peak at 933 K in the monolithic aluminum data exhibits a phase transformation ($\text{Al}(\text{solid}) \rightarrow \text{Al}(\text{liquid})$). No clear peaks are observed within this temperature range for the monolithic BN powder. A broad exothermic peak is found at around 1150 K from the [Al+BN] preform. From this result, it is obvious that the

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Fig. 1 (a) XRD data of blended powders consisting of Al and BN and (b) calibration curve derived from XRD data.

Fig. 2 Differential thermal analysis curves of aluminum, BN and [Al+BN] powders (BN powder size: $10\mu\text{m}$).

exothermic reaction starts at a temperature between 1073 and 1173 K.

Figure 3 shows the XRD data obtained from the [Al+BN($10\mu\text{m}$)] preforms heated to temperatures ranging from 1073 to 1673 K (holding time: 0 s). The AlN peak intensity increased and the Al peak intensity decreased with increasing heating temperature. As the reaction product, aluminum diboride (AlB_2), was detected at temperatures below 1273 K. The following reaction might take place below 1273 K:

Fig. 3 XRD data of [Al+BN] preforms heated at 1073 K~1673 K (BN powder size: $10\mu\text{m}$, holding time: 0 s).

Fig. 4 Conversion ratio of BN to AlN as a function of heating temperature (BN powder size: $10\mu\text{m}$, holding time: 0 s).

However, no AlB_2 peaks were observed above 1473 K. According to the Al-B phase diagram, AlB_2 is not a stable phase at high temperatures and, therefore, decomposes as shown in the following equation.

D. Mirkovic *et al.*¹⁷⁾ reported the onset temperature of reaction (5) was 1275 K when the heating rate was $5\text{ K}\cdot\text{s}^{-1}$, and the onset temperature increased with increasing the heating rate. This agrees well with the present results, in which no peaks of AlB_2 are found at temperatures above 1473 K. Although the X-ray peak of AlB_{12} was not detected in this experiment, it might be present as reported by Y. Seimiya.¹⁸⁾ The reason why AlB_{12} was not detected in this experiment is uncertain.

The integrated intensity of the AlN and BN peaks were measured, and the nitrogen conversion ratio was estimated as shown in Fig. 4. The conversion ratio was not high ($\sim 50\%$) when the heating temperature was below 1173 K and increased to more than 70% by increasing the heating temperature above 1273 K.

The nitrogen conversion ratio as a function of the holding time is shown in Fig. 5. It is apparent that the nitrogen

Fig. 5 Effect of holding time on nitrogen conversion ratio at temperatures ranging from 1073 K to 1673 K (BN powder size: 10 μ m).

Fig. 6 Effect of BN powder size on nitrogen conversion ratio at 1673 K.

conversion ratio can be increased by increasing the heating temperature and the holding time. As much as 95% of the nitrogen was converted from BN to AlN by heating the specimen for 3.6 ks at 1673 K. However, the conversion ratio seemed to saturate for the holding time of 3.6 ks, and probably would not be improved drastically by only increasing the holding time. These data agree with the results shown in previous research,¹⁶⁾ in which the conversion of BN to AlN and TiB₂ was not increased by increasing the holding time from 3.6 to 10.8 ks.

From the results above, the nitrogen conversion ratio was shown to increase by increasing the heating temperature. However, the motivation of this study is to develop an energy saving process for producing TiB₂/AlN composites, and therefore, it is undesirable to raise the heating temperature. Thus, the effect of reducing the BN powder size on the nitrogen conversion ratio was investigated. The nitrogen conversion ratio was evaluated by using a fine BN powder (average size: 1 μ m). The results are shown in Fig. 6. It is clear that the nitrogen conversion ratio is improved by using the 1 μ m BN powder instead of the 10 μ m BN powder at both

1473 K and 1673 K. In particular, when the holding time is 300 s or less, the effect is significant. Therefore, it is expected that both the heating temperature and the holding time can be shortened when using fine BN powders. The authors are currently attempting further refinement of BN powders to a nano-order level by a mechanical milling process and intend to investigate the effects for reducing the synthesis temperature of AlN matrix composites.

4. Summary

- (1) As a result of the DSC analysis, a broad exothermic peak was found at around 1150 K from the [Al+BN] preform.
- (2) The nitrogen conversion ratio was not sufficient (~50%) when the heating temperature was below 1173 K. The conversion ratio was increased by increasing the heating temperature. As much as 95% of the nitrogen was converted from BN to AlN by heating at 1673 K.
- (3) The conversion ratio seemed to saturate with the holding time of 3.6 ks. This result agrees well with the data shown in previous research, in which the conversion of BN to TiB₂ and AlN did not increase by increasing the heating time from 3.6 to 10.8 ks.
- (4) The nitrogen conversion ratio was improved by using 1 μ m BN powder instead of the 10 μ m BN powder. When the holding time was 300 s or less, this effect was significant.

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