Direct bonding of AlN and graphite by spark plasma sintering

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AlN powders were simultaneously sintered and bonded to isotropic graphite disks at temperatures of 1800 and 1900°C under 30 MPa by spark plasma sintering (SPS). The effects of temperature and Y₂O₃ additive content on the bonding strength were investigated. The bonding mechanism is proposed as follows: as the temperature increases, a molten Al–Y–O phase forms and flows into the open pores of graphite. As the material cools, a Al₂Y₄O₉ phase forms, resulting in a physical bond between the graphite and AlN. The bonding strength of AlN/graphite increased with an increase of temperature and Y₂O₃ content. When 10 mass % Y₂O₃ was used as a sintering additive, the bonding strength of AlN/graphite reached 19 MPa at 1900°C.

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1. Introduction

High-density isotropic graphite has high temperature resistance, excellent thermal shock and chemical resistance, adding to its self-lubricating and light weight. These properties make it suitable for many applications, including crucibles and heaters used for silicon semiconductor manufacturing, continuous casting dies, electrodes for electric discharge machining, and other industrial applications. However, graphite has a lower mechanical strength than ceramics and metals at room temperature. In addition, it cannot be used with certain metals at high temperatures, including iron, cobalt, titanium, and tungsten because carbon atoms diffuse into these metals. When this diffusion occurs, the melting temperatures are reduced and the metals react with graphite to form carbides.

Studies have shown that coating graphite with carbide ceramics, such as SiC and B₄C, can improve oxidation resistance.^{1)–3)} However, few studies have reported on the bonding of graphite with nitride ceramics, such as AlN. Such bonding between AlN and graphite is of importance in its applications such as heat sinks and heating trays for metals because AlN has both a high electric insulation and thermal conductivity. It can prevent carbon diffusion into metals at high temperature as well.

Spark plasma sintering (SPS) is an efficient process to sinter ceramics and metals.^{4)–8)} It is also used for joining of dissimilar ceramics or metals, and ceramic-to-metal combinations. For example, Kondo et al. reported that stacked powders of TiN and apatite were sintered and simultaneously joined by SPS.⁹⁾ A functionally graded alumina-carbon nanotube system consisting of four alumina layers with different concentrations of carbon nanotubes has also been fabricated by SPS.¹⁰⁾

In this study, SPS was successfully used to bond graphite and AlN together without any interlayer. The effect of Y₂O₃ additive and heating temperature on the bonding strength was investigated, and the bonding mechanism was discussed.

2. Experimental procedure

AlN powder (H-grade, Tokuyama Co. Ltd.) with a particle size of 1 μm and Y₂O₃ powder (particle size = 1 μm, RU-P, Shin-Etsu Chemical Co., Ltd.) as a sintering additive were used as starting materials. Isotropic graphite disks (IG-12, Toyotanso Co., Ltd.) of 25-mm diameter and 4-mm thickness were used for the bonding with AlN. The physical properties are listed in **Table 1**. It has been used in many conventional applications. The relative density is 79% of the theoretical density (2.25 Mg/m³). The coefficient of thermal expansion (CTE) is 4.7 × 10^{−6}/K, which is similar to that of AlN (4.5 × 10^{−6}/K).¹¹⁾ AlN powder was mixed with Y₂O₃ of different mass ratios of 0, 2.5, 5.0, and 10% by using a planetary centrifugal mixer (ARE-310, Thinky Corporation). The mixed powder (1.8 g) was placed on top and beneath the graphite disk in a graphite die with an inner diameter of 25 mm, as illustrated in **Fig. 1**. Graphite sheets of 500-μm thickness (PF-50, Toyotanso Co., Ltd.) were placed between the bonded sample and graphite punches. The sintering and bonding were simultaneously carried out at temperatures from 1700 to 1900°C under 30 MPa for 5 min under vacuum by SPS (SPS-1050, Sumitomo Coal Mining Co., Ltd.). The bonding temperature was measured by focusing a pyrometer into a hole with 1 mm diameter made at the side of the die.

The sandwich-type samples of AlN/graphite were ground and polished to a size of 25-mm diameter × 6-mm thickness, and then cut into test bars of 4-mm in width × 4-mm in length × 6-mm in height for measuring bonding strength. The microstructure observation and elemental analysis of these samples were also performed by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS, ERA-8800FE, ELIONIX Co.,

Table 1. Physical properties of isotropic graphite used in the present study

Raw material	Bulk density (Mg/m ³)	Relative density (%)	Tensile strength (MPa)	CTE (10 ^{−6} /K)
Isotropic graphite	1.78	79	28	4.7

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Fig. 1. SPS setup to make bonding between AlN and graphite.

Table 2. Bonding strength of the AlN/graphite samples in relation to the amount of sintering additive

Amount of Y ₂ O ₃ (mass %)	Bonding strength (MPa)	
	1900°C	
0	3	(3)
2.5	9	(6)
5	13	(4)
10	19	(4)

Numbers in parentheses denote the standard deviation of bonding strength.

Fig. 2. Schematic drawing of jigs used for measuring bonding strength.

Fig. 3. Cross-sectional SEM image at the interface of the AlN/graphite samples prepared at (a) 1700°C, and (b) 1900°C with 5 mass% Y₂O₃ additive.

LTD). Crystalline phases were examined by X-ray diffraction (XRD, Ultima IV, Rigaku Corporation). Bonding strength of AlN/graphite samples was measured by tensile testing (EZ-L, Shimadzu Corporation). **Figure 2** shows a schematic drawing of jigs used for measuring the bonding strength. Stainless steel jigs were adhered to the top and bottom of seven AlN/graphite samples using an epoxy resin adhesive (E-60HP, Henkel AG & Co. KGaA) at 80°C for about 24 h and subjected to tensile testing.

3. Results and discussion

3.1 Effect of heating temperature on bonding

Figure 3 shows the interface of the AlN (5 mass% Y₂O₃)/graphite samples prepared at 1700°C (a) and at 1900°C (b). In the AlN/graphite samples prepared at 1700°C, some gaps are observed at the AlN/graphite interface. The grain growth of AlN does not developed, resulting in low density of AlN layer. This

sample is easily separated by hand. In contrast, AlN and graphite were tightly bonded at 1900°C. As seen in Fig. 3(b), no gaps and delaminations are observed at the interface. Grain growth occurs and the AlN sintered layer is densified.

Figure 4 shows the SEM images and elemental analysis of C, Al, and Y at the bonding interface at different temperatures of 1700 and 1900°C. Yttrium is distributed only in the sintered AlN layer of the sample when prepared at 1700°C. For the sample prepared at 1900°C, there was little Y found in the AlN layer, but a high concentration was found in the graphite disk. A similar Y distribution in graphite was observed in the sample prepared at 1800°C, although it is not shown here.

During sintering of AlN with Y₂O₃, a liquid phase of the Al–Y–O system forms at around 1800°C¹²⁾ and solidifies as a grain boundary phase during cooling. Since the graphite disk used in this study has an open porosity over 10%, it is believed that the

Fig. 4. Cross-sectional SEM images and elemental mapping images of C, Al, and Y at the interface of the AlN/graphite samples prepared at (a) 1700°C, and (b) 1900°C with 5 mass % Y_2O_3 additive.

Fig. 5. Change in XRD patterns of the AlN/graphite samples prepared at different temperatures.

liquid phase of Al-Y-O flows into the open pores under the external pressure of 30 MPa during SPS.

Figure 5 shows the change in XRD patterns at the interface of the AlN/graphite samples prepared at different temperatures. The crystalline phase of $\text{Al}_2\text{Y}_4\text{O}_9$ solidifies from the Al–Y–O melt during cooling. Because no chemical reaction occurs between AlN and graphite, the bonding is of a physical type. In other words, the molten Al–Y–O phase fills into gaps at the interface and flows into open pores located at the surface of the graphite disk at temperatures over 1800°C .

Figure 6 shows the average bonding strength as a function of bonding temperature. The bonding strength increases sharply above 1800°C, at which the Al–Y–O phase penetrates into the graphite. The AlN/graphite sample prepared at 1900°C shows a high strength of 13 MPa. The viscosity of the molten Al–Y–O phase decreases with an increase in bonding temperature. Thus, the Al–Y–O phase flows easily into the graphite pores. During cooling, a strong bond forms between the sintered AlN layer and graphite.

3.2 Effect of Y_2O_3 content on bonding

In order to understand the effect of the sintering additive, the content of Y_2O_3 was increased from 0 to 10 mass% for the bonding at 1900°C. **Figure 7** shows the relationship between the

Fig. 6. Bonding strength of AlN/graphite samples as a function of heating temperature.

Fig. 7. The relationship between bonding strength of AlN/graphite samples and the amount of Y_2O_3 additive.

average bonding strength and the Y_2O_3 content. The strength increases from 3 to 19 MPa by adding 10 mass % Y_2O_3 . In the AlN/graphite sample containing no Y_2O_3 , the joint failed at the interface during tensile testing. In the sample containing Y_2O_3 , the joint failed in the graphite near the interface. Since the tensile strength of graphite is 28 MPa as listed in Table 1, the strength of graphite decreases after bonding. During cooling, the residual stress caused by the bonding between graphite and AlN may have lowered the tensile strength of graphite. The average strength and the standard deviation are listed in **Table 2**.

Fig. 8. Cross-sectional SEM images and elemental mapping images of C, Al, and Y at the interface of the AlN/graphite samples prepared (a) without Y_2O_3 , and (b) with 10 mass % Y_2O_3 additive.

Figure 8 shows the interface of AlN/graphite sample without Y_2O_3 (a), and that with 10 mass % Y_2O_3 (b). Both samples were prepared at $1900^\circ C$. In the sample without Y_2O_3 , some gaps are observed at the interface, indicating weak bonding between AlN and graphite. In contrast, no gaps and delaminations are observed at the interface of the sample with 10 mass % Y_2O_3 . Large grains are formed in the AlN layer, indicating sintering was completed. In addition, Y distribution is clearly observed in the graphite by EDS analysis, as seen in Fig. 8(b). The Al–Y–O phase increases with increasing Y_2O_3 . The molten Al–Y–O phase contributes not only to the densification of AlN, but also to the bonding strength: the Al–Y–O phase fills the pores in graphite and then during cooling, converts to $Al_2Y_4O_9$ phase.

4. Conclusions

A strong bond was formed between graphite and AlN by using Y_2O_3 as sintering additive at 1800 and $1900^\circ C$ during SPS. No gaps and delaminations were observed at the interface of the AlN/graphite samples. The bonding mechanism is explained as follows: As the temperature increases under pressure, a molten Al–Y–O phase forms and flows into the open pores of graphite. As the material cools, a $Al_2Y_4O_9$ phase forms, resulting in a physical bond between the graphite and AlN. The bonding strength reached 19 MPa at $1900^\circ C$ for the sample containing 10 mass % Y_2O_3 . These joints are simple to make and have potential for high-temperature industrial applications.

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