

Corrosion behavior and creepage discharge character for machinable AlN/h-BN ceramic composites

Hai-yun Jin^{a,*}, Bo He^a, Nai-kui Gao^a, Zong-ren Peng^a, Ji-qiang Gao^b

^aState Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, P. R. China

^bState Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China

AlN particles coated with nano-BN were synthesized. The AlN/BN ceramic composites were sintered by Plasma Active Sintering (PAS). Because the nano-BN crystals were homogeneously dispersed around the AlN grains of the matrix, the chemical corrosion resistance of AlN/nano-sized h-BN ceramic composites was higher than that of AlN/micro-sized h-BN ceramic composites and monolithic AlN ceramics. Due to the better hydrophobic property of h-BN, the AlN/BN composites had a better hydrophobic property than the monolithic AlN ceramic, at the same time, because of the homogeneous dispersion of the nano-BN, the creepage discharge voltage of AlN/nano-sized BN composites was the highest.

Keyword: AlN, h-BN, Corrosion, properties, hydrophobic

Introduction

Aluminum nitride (AlN) ceramics have high thermal conductivity, thermal-expansion coefficient match with the silicon, low permittivity, good dielectric properties, high corrosion resistance to halogen and plasma, etc. Thus, they have been used in various fields, especially in electronic applications, for instance AlN could replace Al₂O₃ as a substrate to be used in IC/LSI package [1, 2]. However, AlN has the defects such as low toughness and high hardness. Therefore, it is very difficult to use in precision components. In order to process precision AlN components, the machinability of AlN needs to be improved. Hexagonal boron nitride (h-BN) has a high thermal conductivity, better dielectric properties, and so it is possible to design a machinable AlN-BN ceramic composite having the excellent thermal and electrical properties of AlN ceramics [3, 4]. But some components are sometimes exposed to aqueous solution, after corrosion, the creepage discharge (discharge along the surface of the solid dielectric materials in liquid, gas or vacuum) will be different from the original material, which can lead to failure at a lower voltage. However, there are few reports about the corrosion behavior of AlN/h-BN ceramic composites. In this study, the corrosion behavior and creepage discharge character of AlN and AlN/h-BN ceramic composites in several acid and basic solutions were studied. This study is supported by Natural Science foundation of Shaanxi province, No. SJ08-ZT04.

*Corresponding author:
Tel: +86-29-82669929
Fax: +86-29-82665443
E-mail: jhaiyun@yahoo.co.jp

Experimental Procedure

Preparation of materials

For comparison, 2 series of specimens were prepared. The contents of BN and sintering aids (Y₂O₃) of each specimen in the series are shown in table 1.

The A series specimens were obtained by mechanical mixing powder of AlN(2 μm) and BN, and sintered in a plasma active sintering (PAS) system (Ed-PASIII, Elenix Ltd., Japan) at 1,800 °C for 5 minutes under a uniaxial pressure of 30 MPa in a nitrogen atmosphere.

For the B series, boric acid (H₃BO₃, analytically pure) and urea (CO(NH₂)₂) (H₃BO₃ : CO(NH₂)₂ = 1 : 3 mol) were selected for producing the h-BN precursor coating film on the AlN powder. The AlN powder, H₃BO₃, and CO(NH₂)₂ were mixed by ball milling to ensure homogeneity of the mixture, and dried. The dried mixtures were put into a graphite-heater furnace and kept at 850 °C (temperature rise: 2-5 K·minute⁻¹) for 21 hours in a nitrogen atmosphere, and capsule-like t-BN-coated AlN was produced. Then the temperature was raised to 1,100°C and held at this temperature for 6 hours for the BN phase transformation. Y₂O₃(3 wt.%) was added into each sample as a sintering

Table 1. The content of BN and sintering aids of each specimen (The rest is AlN)

Series A	BN wt.%	Y ₂ O ₃ wt.%	Series B	BN* wt.%	Y ₂ O ₃ wt.%
AN	0	3	-	0	3
ABm10	10	3	ABn10	10	3
ABm20	20	3	ABn20	20	3
ABm30	30	3	ABn30	30	3

*The contents of BN of series B are the calculated contents

aid. The mixtures were put into a graphite mould and sintered in a plasma active sintering (PAS) system at 1,800 °C (temperature ramp speed: 600 K·minute⁻¹) with a 5 minutes holding time under a uniaxial pressure of 30 MPa in a nitrogen atmosphere at a pressure of 0.02 MPa and the temperature was dropped to 300°C within 5 minutes.

Both A and B series specimens were obtained by milling and polishing to $\Phi 30 \times 4$ mm wafers.

Measurement of properties and observation of microstructures

The crystalline phases of the composite powders and PAS sintered specimens were identified by X-ray diffraction (XRD) analysis. The microstructures were characterized by a transmission electron microscope (TEM, Model JEM200CX, JEOL Co. Ltd., Tokyo, Japan).

Corrosion test

The following aqueous solutions (5 wt.%) were prepared: H₂SO₄; HNO₃; NaOH; KOH. The specimens were set in each solution at room temperature for 5, 10 and 25 hours. After soaking, the specimens were set in distilled water and acetone and dried, the residual mass (m_2) of the specimen was measured, the weight loss (ΔW) can be described by:

$$\Delta W_L = \frac{m_1 - m_2}{S} \quad (1)$$

Here, m_1 is the initial mass of specimen and S is the initial surface area. The bending strength was measured after 25 hours soaking.

Creepage discharge tests

The specimens for creepage discharge tests were sized to 3 mm × 4 mm × 30 mm, all surfaces of specimens were finally ground on an 800 grit diamond wheel, the edges were beveled, and specimens were cleaned with distilled water and acetone. At both ends of a specimen, electrodes (electro sheet copper) were set and the span of both electrodes was 24 mm. The frequency of the power supply was 50 Hz. Because the leakage current was very small, it could be ignored. The dry tests were carried out at room temperature and 40% relative humidity. All data were averaged over 5 samples.

Results and Discussion

Phase composition and microstructure

Fig. 1(a) shows the XRD pattern for 20 wt.% BN-coated AlN powder synthesized at 850 °C and Fig. 1(b) shows the XRD pattern of the composite with a 1,800 °C PAS. Peaks from AlN and the weak/wide peaks arising from amorphous BN (about 26° and 41°) are seen in Fig. 1(a). Fig. 1(b) also shows the XRD pattern of the corresponding hot-pressed body. It shows that the amorphous BN is

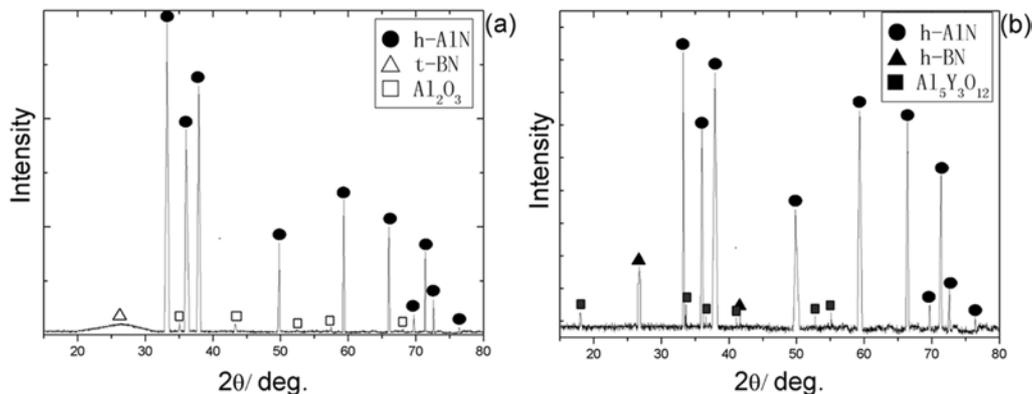


Fig. 1. XRD Pattern for 20 wt.% BN coated AlN powder and a PAS specimen (a) XRD pattern of the powder synthesized at 850 °C; (b) XRD pattern of a PAS composite.

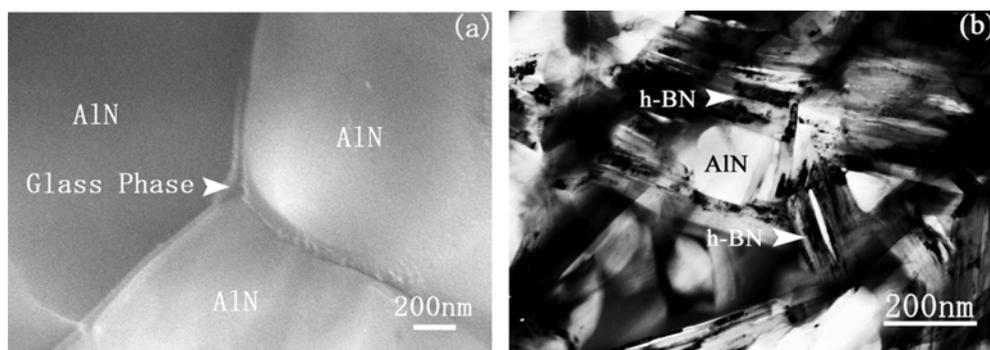


Fig. 2. TEM micrographs of AN (a) and ABn30 (b).

transformed to h-BN after hot-pressing, and the Al_2O_3 on the surface of the AlN grains changes to $\text{Y}_3\text{Al}_5\text{O}_{12}$ under the reaction with the Y_2O_3 . This promotes the sintering process.

In the TEM micrographs of Fig. 2, it can be seen that the microstructures of monolithic AlN ceramic and the AlN/h-BN ceramic composite are different. There are only AlN grains and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) glass phase at grain boundaries in the AlN ceramic, the AlN grain size is also larger than in the AlN/h-BN ceramic composite. In the AlN/nano-sized h-BN composite, nano-sized h-BN crystals are homogeneously dispersed around the matrix grains of AlN during sintering, the AlN grain growth is resisted, and the matrix grain size remains small, and the glass phase at the grain boundaries are separated by the h-BN crystals. The chemical stability of h-BN is better than that of AlN and YAG, therefore, the chemical stability of AlN/h-BN ceramic composites should be better than monolithic AlN ceramics.

Corrosion and weight loss

Fig. 3 and Fig. 4 show the weight loss of AlN ceramics and AlN/BN composites with different aqueous solutions. Comparing Fig. 3 and Fig. 4, it can be found that the weight loss in basic aqueous solutions is far larger than in acid aqueous solutions, and the weight loss increases with the soak time. It is also found that the weight loss of the AlN/micro-sized h-BN composites is less than monolithic

AlN ceramics, and the weight loss of the AlN/nano-sized h-BN composites is less than that of AlN/micro-sized h-BN composites. In acid aqueous solution, because YAG easily dissolves in acid aqueous solutions, therefore, the grain boundaries of AlN ceramics are mainly corroded. In basic aqueous solutions, because the AlN has the Würtzite structure similar to ZnO and ZnS [5, 6], the corrosion behavior of the piezocrystal is affected by the positive and the negative surface charges by polarization caused by strain related to the surface structure and therefore, the AlN grains are mainly corroded [7].

For AlN/h-BN composites, h-BN protects the AlN grains and the grain boundaries and therefore, the AlN/nano-sized h-BN composites are difficult to corrode. In AlN/nano-sized h-BN composites, because the nano-sized h-BN crystals are homogeneously dispersed around the matrix grains of AlN, the corrosion behavior is better than for monolithic AlN ceramics and for AlN/micro-sized h-BN composites.

Creepage discharge character

Fig. 5 shows the relationship between the creepage discharge voltage (E_b) and BN content in NaOH, HNO_3 with and without corrosion. For the ABm series, there is little influence to E_b after corrosion of both basic and acid solutions. For the monolithic AlN ceramic, the E_b is lower than for the AlN/BN composites, this is because that the hydrophobic property of h-BN is better than that of AlN, it is difficult to form the water film on the

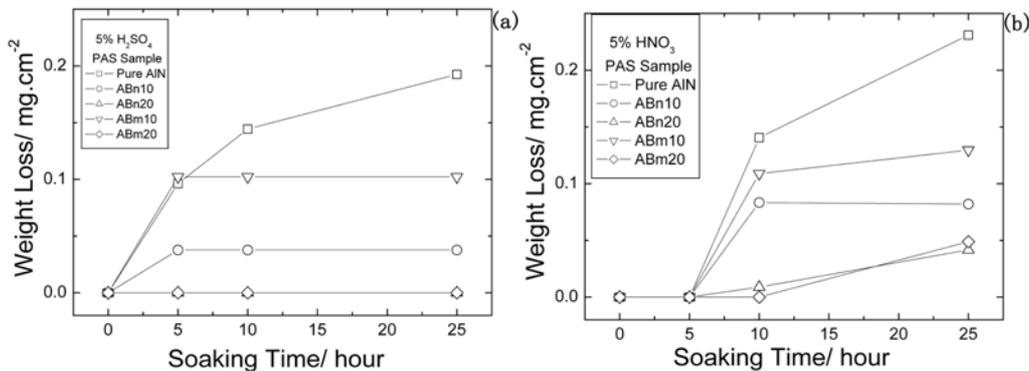


Fig. 3. Weight loss of AlN ceramics and AlN/BN composites with different acid aqueous solutions. (a) H_2SO_4 ; (b) HNO_3 .

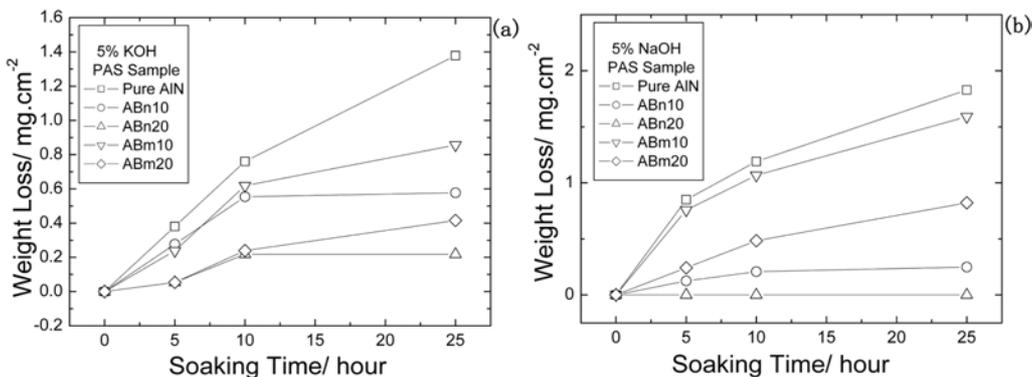


Fig. 4. Weight loss of AlN ceramics and AlN/BN composites with different basic aqueous solutions. (a) KOH; (b) NaOH.

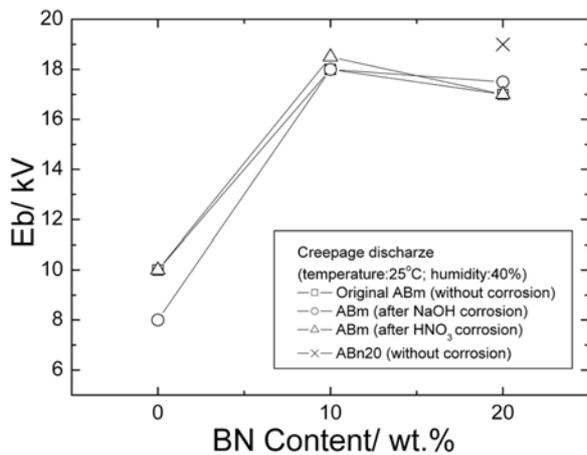


Fig. 5. Creepage Discharge Voltage with different h-BN content

surface of AlN/BN composites, therefore, the E_b of AlN/BN composites is higher than for the monolithic AlN ceramic. In a basic aqueous solution, because the corrosion of AN is more severe, therefore, the E_b of AN after basic aqueous solution soaking is lower. For nano composite ABn30, due to the homogeneous dispersion of nano-sized h-BN, the water film is most difficult to form and therefore, the E_b is highest.

Conclusions

1) For both monolithic AlN ceramics and AlN/h-BN composites, the corrosion in basic aqueous solutions is

more severe than in acid aqueous solutions.

2) h-BN is helpful in protecting the grain boundaries and AlN grains from corrosion, therefore, the corrosion resistance of AlN/h-BN composites are better than monolithic AlN ceramics.

3) For AlN/ nano-sized h-BN composites, due to the homogeneous dispersion of nano-sized h-BN, the corrosion resistance is the best.

4) There is little influence on E_b after corrosion in both basic and acid solutions for AlN/BN composites. Due to the better hydrophobic property of h-BN, the creepage discharge voltage of AlN/BN composites is higher than for monolithic AlN ceramics, at the same time, because the nano-BN crystals were homogeneously dispersed around the AlN grains of the matrix, the creepage discharge voltage of AlN/nano-sized BN composites is the highest.

Reference

1. K. Watari, H.-J. Hwang and M. Toryama, *J. Am. Ceram. Soc.* 79(1996) 1979-1981.
2. Y. Bail, R.A. Drew, *Key Eng. Mater.* 122-124(1996) 553-556.
3. H.-Y. Jin, W. Wang and J.-Q. Gao, *J. Mater. Lett.* 60(2006) 190-193.
4. T. Kusunose, *J. Ceram. Soc. Jpn.* 114(2006) 167-173.
5. G.A. Slack, *J. Phys. Chem. Solids* 34[2] (1973) 321-335.
6. T. Ogawa, in "Fundamentals on Crysta Technology" (Shokabo, Japan, 1987).
7. C.H. Lin, J. Tatami and T. Meguro, *Key Eng. Mater.* 247 (2003) 235-238.