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Effects of adding yttrium nitrate on the mechanical properties of hot-pressed AlN ceramics

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ABSTRACT

Aluminum nitride (AlN) ceramics were prepared by hot-pressing with $Y(NO_3)_3{\cdot}6H_2O$ as sintering additive. The mechanical properties including flexural strength, Vickers' hardness, and fracture toughness were studied. The relative density and mechanical property of the monolithic AlN were improved by adding $Y(NO_3)_3{\cdot}6H_2O$, which decreased the porosity. At 2 wt% Y_2O_3, the AlN ceramic exhibited the highest strength of 383 MPa, the highest hardness of 15.39 GPa, and the highest fracture toughness of 3.1 MPa m$^{1/2}$. However, doping with more additive, the strength, hardness, and toughness of AlN ceramics decreased because of the weak interfacial bonding between AlN matrix and the yttrium aluminates phase.

1. Introduction

Aluminum nitride (AlN) may be highly suitable as substrates and packages for IC/LSI because of its high thermal conductivity (theoretical value of 319 W m^{-1} K^{-1}), low dielectric constant (8.0 at 1 MHz), and thermal expansion coefficient (~4.8×10^{-6} K^{-1} at 20–500 °C) that is close to that of silicon [1–3]. However, because of its high covalent bonding, it is difficult to sinter. Y_2O_3 is widely used as a sintering additive because it forms binary eutectics at temperatures around of ~1800 °C with native Al_2O_3, which is present on the surface of AlN particles, resulting in a material with high density and high thermal conductivity [4,5]. As substrates and packages, the mechanical properties of AlN ceramics are very important. Most studies look at the influence of different sintering additives on the mechanical properties of AlN ceramics [6–8]. Very few studies focus on the effects of the method of adding the sintering additive on the mechanical properties of AlN ceramics. Here, we aim to develop an advanced hot-pressed method to fabricate $Y(NO_3)_3{\cdot}6H_2O$-sintered AlN ceramics and clarify the strengthening mechanism, phase reaction, and sintering behavior by systematically altering the $Y(NO_3)_3{\cdot}6H_2O$ content.

2. Experimental procedures

Commercially available AlN powder (Table 1), was used as a starting material. First, the $Y(NO_3)_3{\cdot}6H_2O$ (99.99% purity) was dissolved in ethanol, and the AlN powders were dispersed in the solution using ultrasonic technology. The mixture was ball-milled by planetary milling for 5 h. After dried and sieved, the mixed powders were densified by hot pressing at 1850 °C for 2 h under a pressure of 25 MPa in flowing N_2. The sintering additive of $Y(NO_3)_3{\cdot}6H_2O$ was added in the following amounts: 3.24, 6.47,12.94, and 19.41 wt% (equivalent to 1, 2, 4, and 6 wt% Y_2O_3 respectively), referred to hereafter as AY1, AY2, AY4, and AY6 for the sintered samples. For comparison, monolithic AlN was also prepared in the same process.

The decomposition profile of $Y(NO_3)_3{\cdot}6H_2O$ from 70 to 600 °C were recorded by thermo gravimetric analysis (TGA). All the samples for mechanical test were prepared by diamond saw and then grinded by diamond disc. Vickers hardness (H_V) was quantified by Vickers indentation tests under a load of 98 N. Specimens chopped into prisms of 3 mm × 4 mm × 30 mm were used for the three-point bending test with a span of 18 mm. Single-edge notched beam (SENB) specimens (2 mm × 4 mm × 20 mm) were prepared for examining fracture toughness. These experiments were repeated three times. Frcature surfaces of the pellets were observed by scanning electron microscopy (SEM, JSM-5600LV).

3. Results

3.1. Decomposition of $Y(NO_3)_3{\cdot}6H_2O$ and reactions between Y_2O_3 and Al_2O_3

The TG-DTA curve (Fig. 1) shows the decomposition of $Y(NO_3)_3{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ completely decomposes into Y_2O_3 at 600 °C. The conversion rate agrees with the theoretical values for the conversion of $Y(NO_3)_3{\cdot}6H_2O$ to Y_2O_3 (29.5%).

From previous reports [9,10], the Y_2O_3 decomposed from $Y(NO_3)_3{\cdot}6H_2O$ reacts with Al_2O_3, which is also present on the surface of AlN particles, to form yttrium aluminates:

$$Al_2O_3 + 2Y_2O_3 = Y_4Al_2O_9 \tag{1}$$

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Table 1
Chemical composition of AlN powder.

Chemical composition (wt%)									Average particle size (μm)
Al	N	O	C	W	Zr	Fe	Si	Co	
65.19	32.66	1.49	0.18	0.19	0.12	0.06	0.07	0.02	5.38

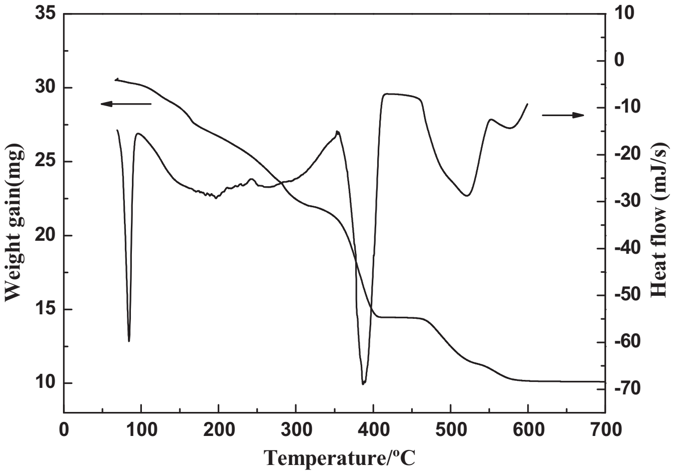


Fig. 1. TG-DTA curve about the decomposition process of $Y(NO_3)_3{\cdot}6H_2O$.

$$5Al_2O_3 + 3Y_2O_3 = 2Y_3Al_5O_{12} \quad (2)$$

The formation of liquid phase ($Y_4Al_2O_9$ and/or $Y_3Al_5O_{12}$) during sintering process will play an important role in the densification of the AlN ceramics.

3.2. Microstructure characterization

Fracture surface profiles of each sample are shown in Fig. 2. Numerous pores are for the monolithic AlN ceramic (Fig. 2(a)). In contrast, the sintered AY samples show dense microstructures (Fig. 2(b)–(d)). Compared with AY4, AY1 and AY2 have no obvious secondary phase at the AlN grain boundaries. In addition, another phase, seen as white particles, are found (indicated by the arrow) and identified by EDS analysis as metal impurities derived from the raw materials.

3.3. Density and mechanical properties

The densities and mechanical properties of the sintered AlN ceramics are summarized in Table 2. The density increases with the additive content. Compared with monolithic AlN, better mechanical properties, such as Vickers' hardness, flexural strength and fracture toughness, are obtained for sintered samples when the additive is $\leq$2 wt% Y_2O_3, AY2 exhibits the highest strength of 383 MPa, hardness of 15.39 GPa, and toughness of 3.1 MPa m$^{1/2}$.

4. Discussions

4.1. Effects of density and grain size on the mechanical properties

Fig. 3 is the sketches of microstructure of the monolithic AlN, AY2, and AY6 according to their SEM observations as shown in

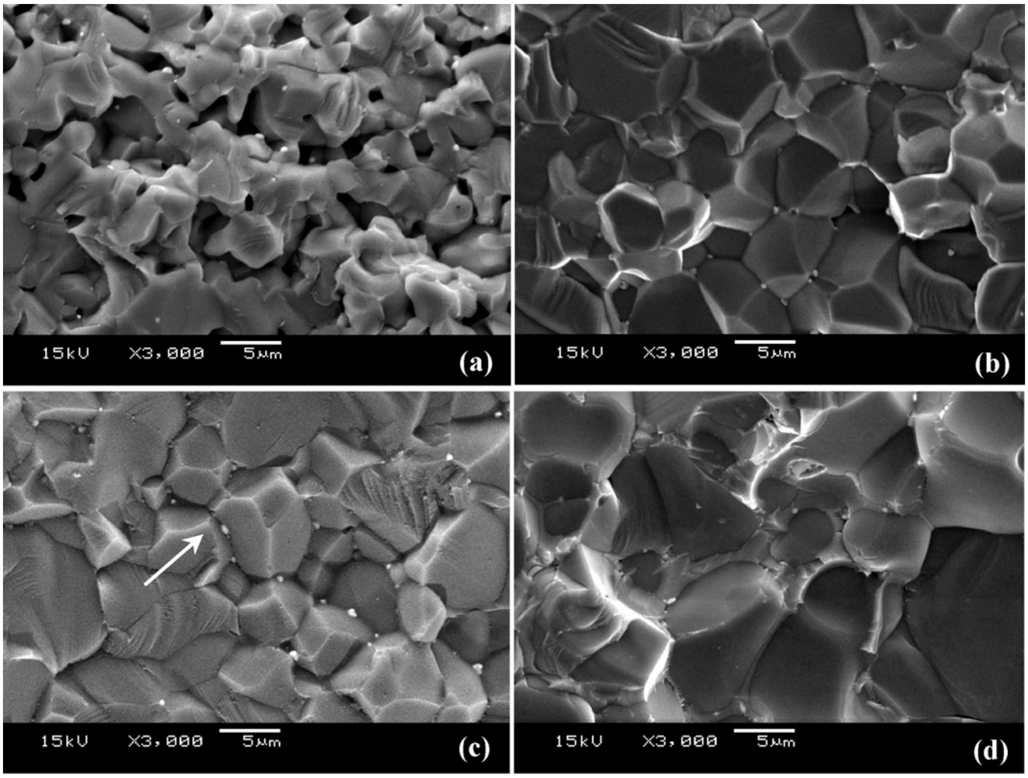


Fig. 2. SEM images of fracture surface for (a) monolithic AlN, (b) AY1, (c) AY2, and (d) AY4.

Table 2
Densities and mechanical properties of sintered samples.

Sample	Density (g cm^{-3})	Vickers' hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa m$^{1/2}$)
Monolithic AlN	2.96	5.85 ± 0.13	245.0 ± 28	2.88 ± 0.28
AYN1	3.15	–	320.0 ± 27	–
AYN2	3.27	15.39 ± 0.26	383.0 ± 36	3.10 ± 0.10
AYN4	3.30	12.56 ± 0.19	369.5 ± 20	2.83 ± 0.16
AYN6	3.33	11.98 ± 0.22	302.9 ± 37	2.87 ± 0.12

Fig. 2. In monolithic AlN, the numerous massive pores are due to the low self-diffusion coefficient of pure AlN. Meanwhile, AY2 and AY6 have dense microstructures because of the formation of $Y_4Al_2O_9$ and/or $Y_3Al_5O_{12}$ liquid phase during the sintering process. On the one hand, the liquid phase accelerates the rearrangement of the AlN particles. On the other hand, the oxide impurities on the surface of AlN are removed; this increases the contact area of the AlN particles and improves the sintering driving force.

Porosity significantly influences the mechanical properties of ceramic materials. The existence of few pores can lead to a considerable decrease in strength and hardness because pores reduce the force-bearing area under the loaded state and stress concentration at pores makes them possible crack sources, which can lead to fracture. In this study, monolithic AlN has lower mechanical properties due to of its numerous pores. Introducing the additive eliminates the pores in the matrix and improves the mechanical properties of the ceramic.

The mechanical properties of samples AY4 and AY6, however, are worse than those of sample AY2, even though they have higher densities. This indicates that other factors also influence the mechanical properties of AlN ceramics.

4.2. *Effects of thermal residual stress on mechanical properties*

In addition to porosity, another important factor which influences mechanical properties is the residual stress for sintered bulk ceramics [11,12]. In the present work, residual stress is generated during the cooling process because of the mismatch between the thermal expansion coefficients (TEC) of AlN matrix and yttrium aluminates. The average TEC of yttrium aluminates ($\sim 7.8 \times 10^{-6}\,^{\circ}C^{-1}$) is much larger than that of AlN ($\sim 4.2 \times 10^{-6}\,^{\circ}C^{-1}$); hence, the shrinkage of yttrium aluminates is larger than that of the AlN matrix during cooling (to room temperature). The distribution of the residual stresses at the AlN/Yttrium aluminate interfaces because of the difference in the shrinkages of these two phases are showed in Fig. 4.

When the additive content is less than or equal to 2 wt% Y_2O_3, the yttrium aluminate contents are small, and mainly located at the trigeminal grain boundary of AlN matrix. The distribution of the residual stress under this situation is shown in Fig. 4(a). The grain boundary of AlN is under the compressive stress state due to the relative shrinkage of yttrium aluminates, so the grain boundary is strengthened because of compressive stress. The tensile stress at AlN/yttrium aluminate interface weakens the interfacial bonding. The distribution of the residual stress when yttrium aluminate covers the matrix grain boundaries is in Fig. 4(b). The residual stress value increases with the increase in additive content. The greater the amount of additives is, the greater the number of AlN/yttrium aluminate interfaces under tensile stress state there also is. Because of the tensile stress perpendicular to the AlN/yttrium aluminate interface, crack propagates along the interface more easily. The AY samples which are doped with much higher additive contents (i.e., AY4 and AY6), thus, exhibit poorer mechanical properties, such as low fracture toughness.

4.3. *Effects of interfacial bonding of AlN/yttrium aluminate on mechanical properties*

Fig. 5 shows the fracture images of samples AY4 and AY6. The wettability between AlN matrix and the yttrium aluminate phase is quite poor; this results in a poor interfacial bonding. Some yttrium aluminate phases are separated from the AlN matrix, as indicated by the open cycle in Fig. 5. In addition to poor wettability, the residual tensile stress at the interface as analyzed above also contributes to the low interfacial bonding strength.

The AlN matrix and yttrium aluminate has a lower interfacial bonding strength, which makes crack propagation easier because of the decrease in fracture energy. Due to the brittleness of the yttrium aluminate and the mismatch of its TEC with that of the AlN matrix, numerous micro-cracks will be generated at the AlN/yttrium aluminate interface. Hence, the mechanical properties such as Vicker's hardness, flexural strength, and fracture toughness decrease with the addition of excess yttrium aluminate phase. Because of this, AY4 and AY6 have poorer mechanical properties compared with AY2 even though they have higher densities.

In addition, grain size is another main factor influencing the mechanical properties of the ceramic materials. Ceramic materials of small grain size and homogeneous particle size have better mechanical properties [13,14]. In this work, the AlN samples with $Y(NO_3)_3{\cdot}6H_2O$ as a sintering additive have similar grain sizes because they have the same sintering temperature (Fig. 2). The

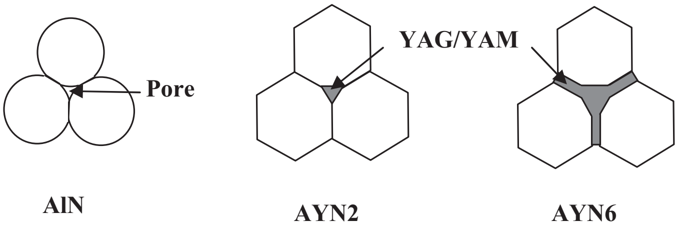
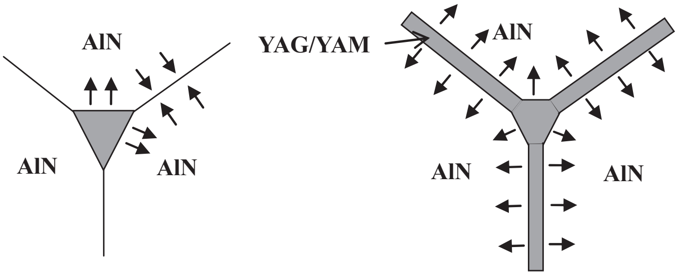


Fig. 3. Schematic illustration of microstructure of monolithic AlN, AY2 and AY6.



(a) less yttrium content

(b) more yttrium content

Fig. 4. The residual stress of AY samples.

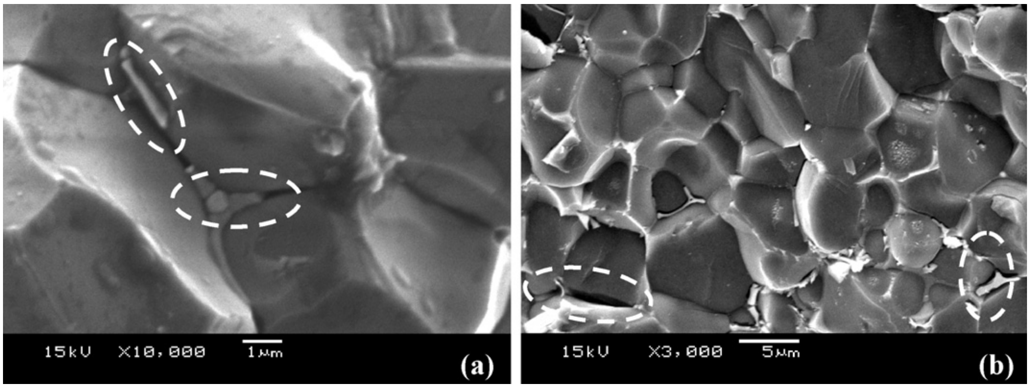


Fig. 5. Fracture pattern of AlN ceramics sintered at 1850 °C: (a) AYN4, (b) AYN6.

effects of grain size on mechanical properties can, therefore, be neglected.

5. Conclusions

AlN ceramics have been prepared by the addition of $Y(NO_3)_3{\cdot}6H_2O$ as the sintering additive. The mechanical properties of the AlN ceramics are mainly affected by their porosity when the microstructure is not dense. When the microstructure is almost completely dense, the bonding between the matrix and the second phase has a significant influence on the strength, Vickers' hardness, and fracture toughness. When the additive amount is 2 wt% Y_2O_3, the AlN ceramic exhibits the highest strength, Vickers' hardness and fracture toughness, (383 MPa, 15.39 GPa, and 3.1 MPa $m^{1/2}$, respectively). Compared to monolithic AlN, the improved properties are attributed to the decrease in porosity. When excess additive is added, the weak bonding between the matrix and yttrium aluminates phases, which is due to the poor wettability and tensile stress on the interface, results in lowering of strength and fracture toughness of AlN ceramics.

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