



Sintering behavior of direct nitrided AlN powder

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Abstract

Classified direct nitrided (DN) aluminum nitride (AlN) powders were examined by dilatometry to study the effect of particle size on sinterability. The shrinkage behavior of three DN powders was compared to that of a commercial, carbothermally produced, AlN powder. Yttrium oxide was added to AlN powder as a sintering aid. Two distinct features of the resulting shrinkage curves, corresponded to particle rearrangement coincident with yttrium aluminate formation and high temperature sintering. The presence of coarse particles in the original DN powder, greater than 8 μm , distinguished it from the other powders studied and appeared to have the greatest influence on the sintering behavior. For fine powders without coarse particles ($> 8 \mu\text{m}$), the synthesis method did not seem to affect the shrinkage. The grain size distribution of the sintered parts mirrored the particle size distribution of the four powders studied. Thermal conductivity (TC) of the sintered AlN bodies was strongly dependent on the oxygen content of the starting powders. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aluminum nitride powder; Particle size distribution; Sintering; Shrinkage; Microstructure; Thermal conductivity

1. Introduction

After years of development, aluminum nitride (AlN) is now the ceramic substrate of choice for heat management of high power semiconductors because of its excellent combination of thermal conductivity (TC) and electrical properties [1,2]. Key to this development has been the introduction of high quality

powders [3,4], and the discovery of the alkaline and rare earth compounds as effective sintering aids for AlN [5–7]. Due to the improved understanding of critical raw material, processing, and property relationships, appropriate cost performance alternatives for AlN have been developed. There are currently three AlN synthesis methods that have been commercialized:

- (a) Carbothermal reduction from alumina and carbon in nitrogen atmosphere [3,4]
- (b) Direct nitridation of aluminum metal in nitrogen atmosphere [8,9]
- (c) Chemical vapor deposition from alkyl-aluminum and ammonia gas [10].

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Table 1
Impurities of starting AlN powders

Sample	Oxygen (wt.%)	Carbon (wt.%)	Metallic impurities (ppm)		
			Fe	Ca	Si
C-0	1.20	0.045	20	71	50
D-0	1.34	0.060	1690	115	520

Historically, direct nitrided (DN) AlN powders have shown poorer sinterability and TC compared to carbothermal powders. Despite their suitability for yielding high thermally conductive AlN ceramics, high production costs for the carbothermal reduction process has limited the market penetration of this high quality product. Because of the inherent price advantage due to lower production costs, interest in

DN AlN powders has increased rapidly. However, a more thorough understanding of its sintering behavior is still needed.

Komeya and Inoue [11] examined the sintering behavior of DN AlN powders with no additives, which were classified by sieving, and it was reported that the particle size had a strong effect on AlN sintering. Weimer et al. [12] proposed a “Rapid Process” for the production of DN AlN powder and studied its sinterability. It was also shown that sinterability was dependent upon the particle size of AlN powder though densification was not completed by 1850°C. Furthermore, Nagai and Lai [13] reported the sintering results of a ground DN AlN powder that was prepared by ball milling in an organic solvent. It was shown that the ball-milled AlN powder densified at lower temperature compared to the raw powder. In the present study, densification be-

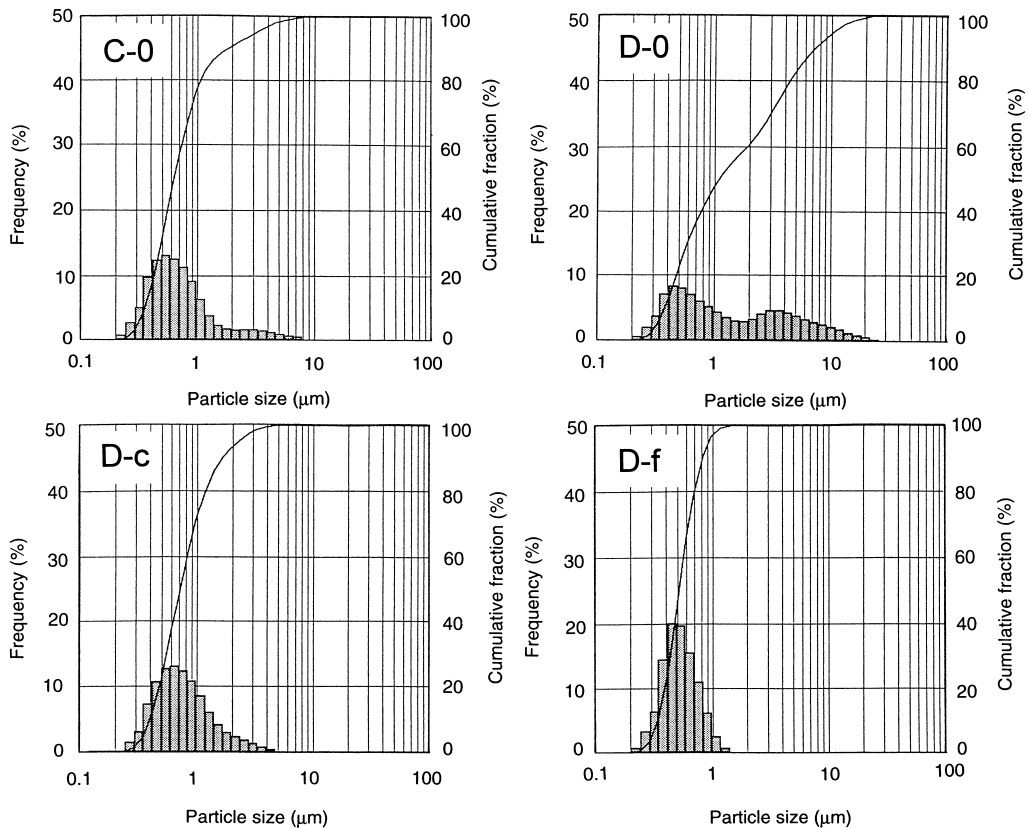


Fig. 1. Particle size distribution of AlN powders.

haviors of as-received and classified DN powders were examined using a dilatometer. The effects of particle size on sinterability, microstructure, and TC of the sintered body were also evaluated.

2. Experimental procedure

2.1. Classification of AlN powder

AlN powders prepared by two distinct methods, direct nitridation and carbothermal reduction, were used in this study. The DN AlN powder (XU35569, The Dow Chemical, MI, USA), designated as D-0, was also classified to generate two finer powders with discrete particle size distributions, using an air classifier (Turbo Classifier, Nissin Flour Milling, Tokyo, Japan). The carbothermally reduced AlN

powder (XU35562, The Dow Chemical), designated as C-0, was used as a benchmark and was studied without any particle classification. The impurities present in the starting powders are shown in Table 1. D-0 has significantly higher levels of metallic impurities than C-0, though oxygen and carbon contents are almost the same for the two powders. The two powders produced by classification of D-0 were designated, D-f and D-c. D-f was the finest powder among the samples evaluated in this study. D-c was fairly similar to D-0. The particle size distributions and SEM photomicrographs of these powders are shown in Figs. 1 and 2, respectively. The properties of the classified powders are summarized in Table 2. Fig. 1 indicates that C-0 has coarse particles in the range of 5–8 μm compared to D-c. However, as shown in Fig. 2, SEM observation shows that C-0

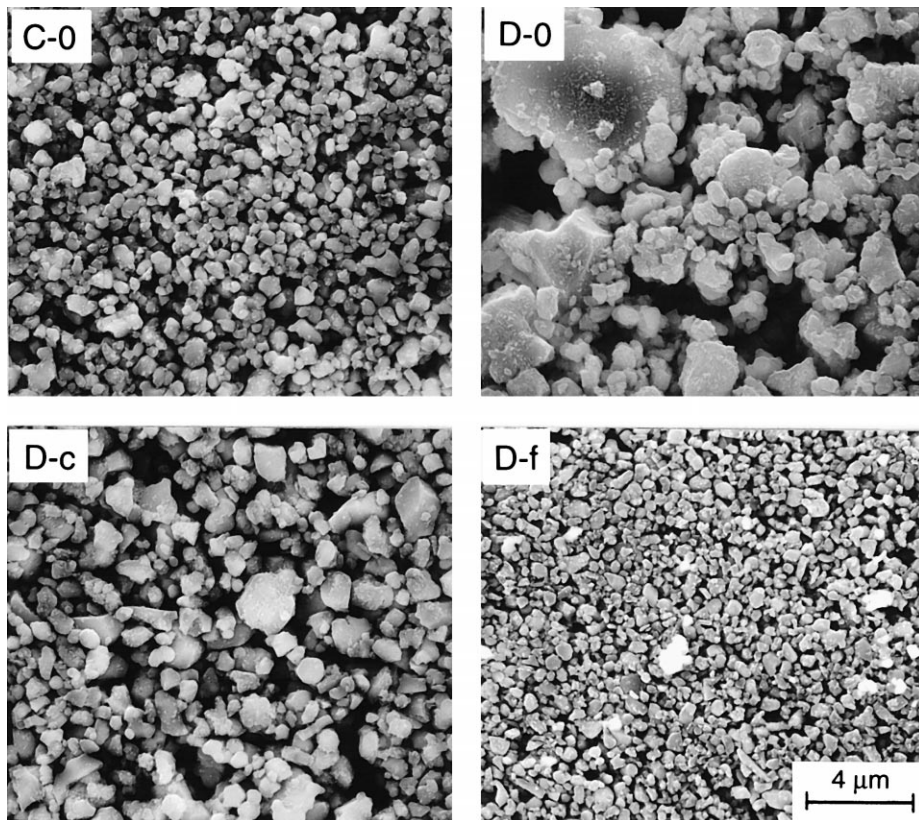


Fig. 2. SEM photographs of AlN powders.

Table 2
Properties of various AlN powders

Sample	Particle size distribution (μm)			Oxygen (wt.%)
	D_{10}	D_{50}	D_{90}	
C-0	0.36	0.63	1.77	1.20
D-0	0.38	1.08	7.13	1.34
D-c	0.39	0.71	1.62	1.69
D-f	0.34	0.51	0.80	2.01

consists of finer particle than D-c. This inconsistency was considered due to the agglomeration of powder in sample C-0.

2.2. Measurement of sintering behavior of AlN powder compacts

The effect of particle size on sintering behavior of AlN powder compacts was examined by dilatometry. Yttrium oxide (RU grade, Shin-Etsu Chemical, Tokyo, Japan) was added as a sintering aid to the AlN powder. The amount of Y_2O_3 added was 6 wt.% for samples D-0, D-c and D-f, and 4 wt.% for the C-0 sample. These powders were mixed by milling in ethanol using urethane coated steel balls. The ball milling was done for 20 h and the slurry was vacuum-dried in a vibration drier. After that, the dried powder was pressed uniaxially at 19.6 MPa into $9 \times 9 \times 40$ mm beams. These were then isostatically pressed at 294 MPa. The compacts were placed in a high temperature dilatometer (Model HPHT-TMA, Rigaku Denki, Tokyo, Japan) for measuring shrinkage behaviors. The samples were heated up to 1000°C at $30^\circ\text{C}/\text{min}$ in vacuum and kept at this temperature for 30 min. Nitrogen gas was introduced into the furnace and the heating continued up to 1900°C at $10^\circ\text{C}/\text{min}$, and held at the maximum temperature for 5 min. The samples were cooled at $10^\circ\text{C}/\text{min}$ to 1500°C when the furnace was shut down and natural cooling occurred.

2.3. Analysis of microstructure and TC of sintered AlN body

After the dilatometry work, the AlN specimens were cut near the sample center to yield a small

wafer about 2 mm thick. Microstructural analysis was done by examining polished cross-sections coated with a thin gold film using a scanning electron microscope (S-800, Hitachi, Tokyo, Japan). TC of the AlN specimens was also measured using the laser flash method. The laser flash apparatus consisted of a 5J CO_2 laser, non-contacting infrared detector, and computer control and data acquisition system. The specific heat capacity value for AlN which was used in the TC calculation was $0.176 \text{ cal}/\text{g}^\circ\text{C}$.

3. Results and discussion

3.1. Shrinkage behavior of AlN powder compacts

Fig. 3 shows the shrinkage behaviors up to 1900°C of the four AlN powder compact. Differential plots of the shrinkage curves are shown in Fig. 4. In all samples, the first shrinkage observed was minor and occurred between 1300°C and 1500°C . Although this temperature range is below the lowest reported melting point in the yttria–alumina system, it has been shown that this is consistent with the solid state reaction of the yttria sintering aid with the surface

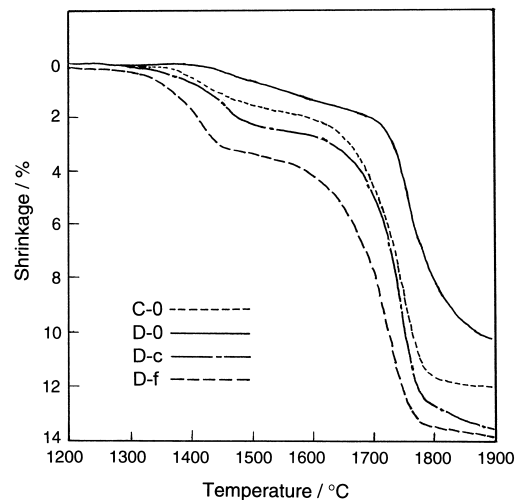


Fig. 3. Shrinkage behaviors of AlN powders containing Y_2O_3 additive.

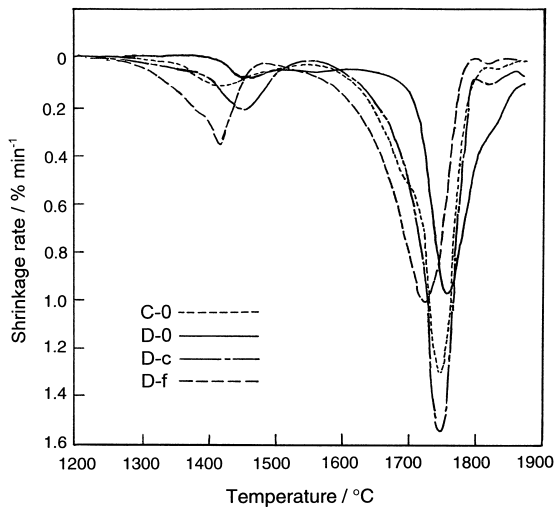


Fig. 4. Differential plots of shrinkage curves of AlN powders containing Y_2O_3 additive.

oxide of the AlN particles [14]. It is also believed that this shrinkage, coincident with the oxide compound formation, is caused by particle rearrangement. The major shrinkage and densification started between 1550°C and 1700°C.

While all four shrinkage curves consisted of two primary peaks, there were significant differences observed in both their magnitude and starting points. Green density differences, shown in Table 3, and the surface state of the AlN powders are considered to be the primary determinants for the plots' low temperature characteristics. It has been reported that DN powders have an aluminum hydroxide layer on the surface of the particle while carbothermally produced powders have an aluminum oxide surface layer [15]. Based on the findings of Hashimoto et al. [16], this surface chemistry difference affects the Y–Al–O compound formation. However, in this study, the magnitude of the rearrangement is clearly controlled by the packing densities of the compacts. Overall, D-f, D-c and C-0 compacts had similar shrinkage behavior. Slight differences in the onset temperature of the second and primary shrinkage region were consistent with the average particle size of these three AlN powders. The D-0 sample was clearly different. The densification curve was shifted to substantially higher temperatures. Unlike the other

samples, which had already leveled off by 1900°C, D-0 was still densifying. From these results, shrinkage behavior is largely influenced by the amount of coarse ($> 8 \mu\text{m}$) AlN particles. For fine powders without coarse particles more than 8 μm , powder synthesis method did not have a significant effect on AlN sinterability.

3.2. Microstructures and TC of sintered AlN bodies

Microstructures of the sintered AlN compacts used in the high temperature (1900°C) dilatometry studies are illustrated in Fig. 5. D-f and C-0 had fairly homogeneous microstructures, while D-0 and D-c had broad grain size distributions reflecting the particle size distributions of the AlN powders. Because of the higher additive level used with the DN powders, the volume percent of the yttrium aluminate grain boundary phase was larger in these samples. In all samples, the second phase was present at both grain boundaries and at grain junctions, consistent with a wetted system.

TC of the sintered AlN samples is presented in Table 3. C-0 had the highest TC among the samples, while D-f had the lowest value. From Tables 2 and 3, the strong dependency of TC of sintered AlN bodies with the oxygen content of the starting AlN powders can be seen. Kuramoto et al. [17] reported the negative effect of metallic impurities on AlN TC. Although there was a large difference in metallic impurities between D-c and C-0 as shown in Table 1, the TC values were essentially the same. This apparent discrepancy can be rationalized since in this TC range, oxygen substitution in the AlN lattice dominates the disruption in photon conduction such that

Table 3
Properties of sintered AlN bodies

Sample	Density (g/cm^3)		Thermal conductivity ($\text{W}/\text{m K}$)
	Green compact	After sintering	
C-0	1.96	3.20	135
D-0	2.13	3.21	120
D-c	1.85	3.24	119
D-f	1.81	3.25	84

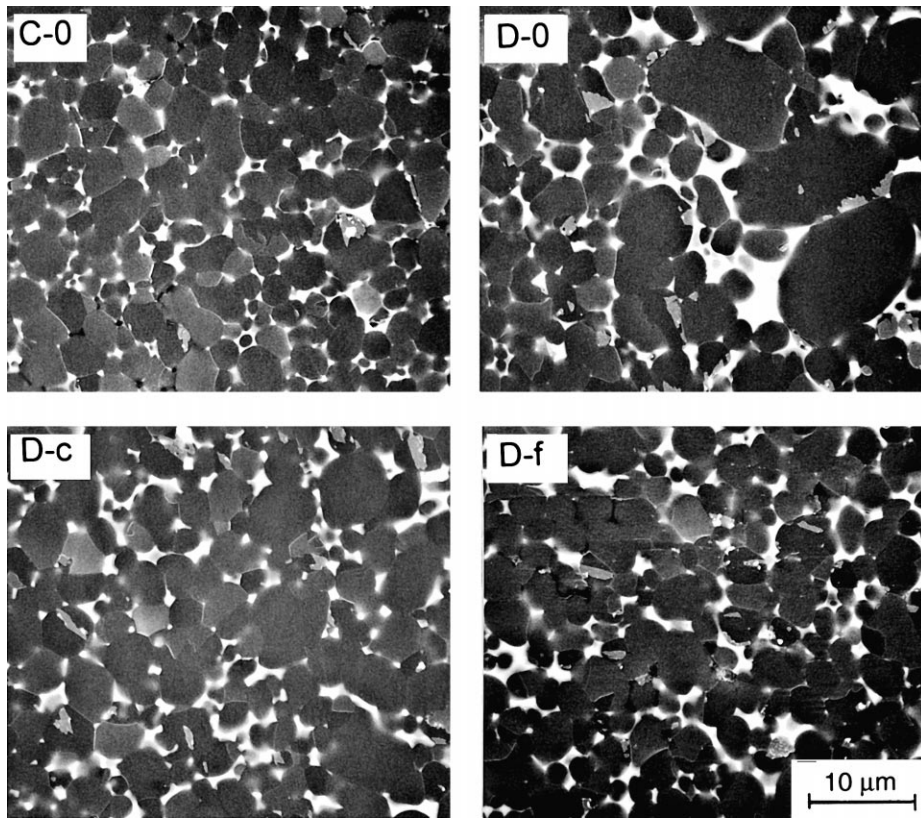


Fig. 5. SEM photographs of microstructures of AlN ceramics.

the presence of metallic impurities has a negligible effect.

4. Conclusions

Sinterability of DN AlN powders with different particle size distributions were examined by dilatometry up to 1900°C in a nitrogen atmosphere. A standard AlN material prepared with a carbothermally produced powder was also included in this study.

Two stages in the shrinkage curves were observed for all samples. These were attributed to the particle rearrangement coincident with the formation of Y–Al–O compounds at low temperature and high temperature sintering.

While there was a strong dependency between the resultant microstructures and the powders' initial

particle size distribution, sinterability was controlled largely by the amount of coarse particles ($> 8 \mu\text{m}$) present in the AlN powder. There were no major differences evident in shrinkage behavior among the three fine AlN powders studied despite the distinct powder manufacturing methods used in their preparation. TC of the sintered AlN bodies was effectively dependent on the oxygen content of AlN powder and was influenced little by the metallic impurities present.

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