Sintering Behavior, Microstructure, and Thermal Conductivity of Dense AlN
Ceramics Processed by Spark Plasma Sintering with Y₂O₃-CaO-B Additives

Ryota Kobayashi*

Department of Chemistry and Energy Engineering, Faculty of Engineering, Tokyo City University

1-28-1, Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

Tel: +81-3-5707-3811, Fax: +81-3-5707-1171, E-mail: rkobaya@tcu.ac.jp

*Corresponding author

Katsuyoshi Oh-ishi

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University

1-13-27, Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Rong Tu, Takashi Goto

Institute for Materials Research, Tohoku University

2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

Abstract

We fabricated dense aluminum nitride ceramics by spark plasma sintering (SPS) with Y₂O₃-CaO-B sintering additives and evaluated their microstructures and thermal conductivities. Samples were perfectly densified after 5 min of SPS at 1650 or 1600 °C or 10 min at 1550 °C and had fine microstructures. Thermal conductivities of the samples were 80–90 W m⁻¹ K⁻¹ and tended to increase with increasing sintering temperature.

Keywords: Aluminum nitride; SPS; Ceramics; Densification; Thermal conductivity

Introduction

Aluminum nitride (AlN) ceramics have high thermal conductivity, high electrical insulation, and excellent corrosion resistance to halogens and plasma [1,2]. These properties of AlN ceramics favor their use as substrate materials for power electronics and structural parts for semiconductor devices. AlN is a typical sintering resistive non-oxide ceramic; its fabrication involves high-temperature sintering with sintering additives to obtain dense ceramics.

Komeya et al. developed dense AlN ceramics by pressureless sintering (PLS) at 1800 °C for several hours, using Y_2O_3 as a sintering additive [3]. Liquid phases composed of Y-Al-O complex oxides form when the natural oxide layer on AlN particles reacts with Y_2O_3 , promoting the densification of AlN ceramics. Since then, there has been ongoing research into additives that lower the sintering temperature. By using Y_2O_3 -CaO sintering additives, the temperature can be lowered to 1700 °C [4,5]. The formation of Y-Al-Ca-O complex oxides having low eutectic melting points (around 1600 °C) appears to promote densification [6]. Further, the addition of boron or borides such as LaB_6 to the Y_2O_3 -CaO system can lower the sintering temperature below 1700 °C [7,8]. We reported that Y_2O_3 -CaO-B sintering additives can sinter AlN ceramics at 1650 °C in 2 h [8]; however, when using the PLS process, densification was insufficient at lower temperatures (below 1650 °C) and a shorter sintering time (1 h).

In recent years, the spark plasma sintering (SPS) process [9], which is also called pulsed electric current sintering (PECS) [10], has been widely used for densification of sintering resistive ceramics such as carbides and nitrides [11-14]. In the SPS process, raw powders are put into a mold fabricated from an electrically conductive

1 material such as graphite and then quickly heated by supplying a large pulse of electric
2 current to the mold while applying uniaxial pressure. The fast heating and uniaxial
3 pressure in SPS help mass transfer during densification without abnormal grain growth.
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5 Therefore, the SPS process can shorten sintering time and lower sintering temperature.
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7 There are several reports on densification of AlN ceramics by SPS. Khor et al.
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9 successfully fabricated dense AlN ceramics with thermal conductivities of 70–95 W m⁻¹
10 K⁻¹ by 1–2 cycles of SPS at 1500–1600 °C with Sm₂O₃ sintering additives [15]. In
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12 contrast, sintering at 1800 °C for several hours is necessary for densification by
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14 pressureless sintering (PLS) with the same additives, clearly indicating the effects of
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16 SPS. Qiao et al. reported fabrication of dense AlN ceramics by SPS without sintering
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18 additives at 1600 °C, but the thermal conductivities of the samples were lower than 60
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20 W m⁻¹ K⁻¹ [16]. These results show that the use of sintering additives is necessary for
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22 obtaining fully densified AlN ceramics by the SPS process with favorable thermal
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24 conductivity.
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28 In our previous work [8], we fabricated dense AlN ceramics with a thermal
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30 conductivity of 95 W m⁻¹ K⁻¹ by PLS at 1650 °C for 2 h with Y₂O₃-CaO-B additives. If
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32 we use both the SPS process and Y₂O₃-CaO-B additives, the sintering temperature may
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34 be decreased below 1600 °C, as reported by Khor et al [15]. In this work, we fabricate
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36 dense AlN ceramics by SPS with Y₂O₃-CaO-B additives, and investigate the sintering
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38 behavior, microstructures, and thermal conductivities of the samples produced.
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52 Experimental procedure

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54 Commercially available AlN powder (Tokuyama Corp., Grade-E, 0.6 μm) was
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56 used as a raw material. Y₂O₃ (Rare Metallic Corp., 99.99%), CaO was produced by
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1 calcining CaCO_3 (Rare Metallic Corp., 99.99%), and B (Rare Metallic Corp., 97%)
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3 powders were added to the AlN raw powder as sintering additives. Composition of the
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5 mixture was 95.92 mass% AlN, 3 mass% Y_2O_3 , 1 mass% CaO, 0.08 mass% B (named
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7 0.08B). The powder mixtures were ball-milled in butanol for 4 h using ZrO_2 balls (ϕ : 5
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9 mm). The slurry was dried using a rotary evaporator, then sieved with 212- μm Nylon
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11 mesh to form granules. The granules were put into a graphite mold (ϕ : 10 mm) lined
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13 with graphite sheet and covered with carbon fiber insulation felt, then sintered using an
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15 SPS system (Sumitomo Coal Mining Co., Ltd., Dr. Sinter SPS-1050) under 1 atm N_2 .
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17 Heating rates were 200 $^\circ\text{C}/\text{min}$ from room temperature to 600 $^\circ\text{C}$, then 100 $^\circ\text{C}/\text{min}$ from
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19 600 $^\circ\text{C}$ to the holding temperature. For sintering temperatures of 1550 $^\circ\text{C}$ and 1650 $^\circ\text{C}$,
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21 the heating rate was decreased to 50 $^\circ\text{C min}^{-1}$ 1 min before the holding temperature due
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23 to limitations in setting the heating profiles. The holding temperatures and times were
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25 1550 $^\circ\text{C}$ for 10 min, 1600 $^\circ\text{C}$ for 5 min, and 1650 $^\circ\text{C}$ for 5 min. A constant uniaxial
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27 pressure of 50 MPa was applied during the SPS process. After holding, the power
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29 supply of the SPS apparatus was shut down and the uniaxial pressure released
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31 immediately. The change in the relative density during SPS was estimated from the
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33 press displacement by using the method described in the previous paper [14].
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43 Densities of samples were measured at room temperature by Archimedes'
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45 method using pure water as buoyancy fluid. Phase identification and elemental analyses
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47 of samples were carried out by X-ray diffraction (XRD) with CuK α radiation and X-ray
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49 fluorescence (XRF), respectively. Microstructures of the samples were evaluated by
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51 scanning electron microscopy (SEM). Thermal conductivities of the samples were
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53 measured at room temperature by laser flash method.
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Results and discussion

Table 1 lists relative densities of the SPS samples in this work and the PLS samples from our previous work [8]. For comparison, the relative densities of the samples sintered using Y_2O_3 -CaO sintering additives without B (named 0B) are also listed. The relative densities of the SPS samples were over 99% of theoretical values, indicating perfect densification even with very short sintering time. In contrast, densities of the PLS samples were drastically decreased by lowering the sintering temperature. In the PLS samples, 0.08B samples had higher relative densities than 0B samples specifically in the sample sintered at 1600°C . These results clearly show the effect of the SPS process on densification of AlN ceramics sintered with Y_2O_3 -CaO-B additives.

Figure 1 shows the shrinkage curves of the SPS samples at 1550 – 1650°C . For comparison, the shrinkage curves of the SPS samples sintered using Y_2O_3 -CaO sintering additives without B (0B) are also shown. The vertical axis indicates the change of relative density, calculated from the press displacement during SPS and the final density of the sample (Table 1) [14]. The lower and upper horizontal axes indicate temperature rising and elapsed time at the holding temperatures, respectively. In all samples, the sintering shrinkage started around 1300°C and accelerated above 1500°C . In the SPS samples at 1550°C , relative density had reached 80% of its theoretical value by the beginning of the holding stage, and densification was almost complete after 5 min. The degree of shrinkage increased between 1500 and 1550°C due to the decrease of heating rate. In the SPS sample held at 1600°C , the relative density also approached 80% of theoretical by the start of holding and achieved almost 100% of theoretical after 2 min, similar to the SPS sample at 1550°C . In the SPS sample at 1650°C , the relative density was drastically increased over 1600°C , and the densification was almost completed at

the start point of holding time. A comparison of the shrinkage curves of the samples sintered using 0.08B and 0B sintering additives showed that the densifications of samples sintered with 0.08B were slightly faster than those of 0B. These results show that a sintering temperature of 1550 °C was high enough to achieve perfect densification, and it might be possible to lower the sintering temperature below 1550 °C by increasing the pressure applied and by extending the holding time.

Figure 2 shows the microstructure of the SPS samples in the temperature range 1550–1650 °C, investigated by SEM. Fig. 2 (a), (c), and (e) are back-scattered images; Fig. 2 (b), (d), and (e) are the secondary electron images. The secondary electron images show that all the SPS samples have dense and fine textures with a grain size of about 1 μm. The AlN powder grains are initially sub-micron in size; therefore, the degree of grain growth during sintering was small. The fast heating rate and high uniaxial pressure of the SPS process may restrain significant grain growth and promote densification in the earlier stages of sintering. The grains in the samples appear angular, suggesting that liquid phases formed during sintering and helped the densification by a solution-precipitation mechanism [17]. The light spots in the back-scattered images indicate the presence of elements heavier than Al and N, suggesting that the grain boundary phases contain Ca and Y derived from the sintering additives. The XRD results show that an $Y_4Al_2O_9$ (YAM) phase and traces of a $CaYAl_3O_7$ phase were detected in all samples as grain boundary phases, similar to the results observed for the PLS samples in our previous work [8]. The liquid phase sintering process appears to be more pronounced with the sintering temperature: the light spots become more clearly defined with increasing sintering temperature, suggesting the enhancement of liquid phase formation, segregation, and crystallization for densification. The uniaxial pressure

1 applied during SPS may also promote the liquid phase extruding through grain
2 boundaries.
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6 Figure 3 shows thermal conductivities of the SPS samples, measured by a laser
7 flash method. Thermal conductivities of the SPS samples were in the range 80–90 W
8 $\text{m}^{-1} \text{K}^{-1}$, comparable to those of the SPS samples investigated by Khor et al. using a
9 Sm_2O_3 sintering additive [15] and the PLS samples in our previous work with an
10 Y_2O_3 -CaO-B additive [8]. The thermal conductivity of the SPS samples in this work
11 tended to increase with increasing sintering temperature. The thermal conductivity of
12 the AlN ceramics could be decreased by the presence of pores, excess grain boundary
13 phases with low thermal conductivities, and oxygen impurities [1] dissolved in the AlN
14 lattice. As these samples are dense ceramics without pores, grain boundary phases and
15 oxygen impurities might affect the thermal conductivity. Applying higher uniaxial
16 pressure and extending the sintering time could reduce the number of grain boundary
17 phases and help in purifying AlN grains to reduce “oxygen trapping by grain boundary
18 phase” [18,19] to improve thermal conductivities.
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40 Conclusions

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42 The use of Y_2O_3 -CaO-B sintering additives in the SPS process helps promote
43 densification of AlN ceramics at considerably lower temperatures (1550–1650 °C) and
44 shorter holding times (<10 min). The relative densities of samples became at least 99%
45 of their theoretical values; the sample textures were dense and fine. The thermal
46 conductivities were in the range 80–90 W $\text{m}^{-1} \text{K}^{-1}$ and increased with increasing
47 sintering temperature.
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Table section

Table 1 Relative densities* (%) of SPS and PLS samples.

Sintering temperature / °C	SPS		PLS	
	0.08B	0B	0.08B	0B
1550**	99.0	99.6	55.2	51.1
1600	99.6	99.6	73.9	58.8
1650	99.3	99.3	96.0	94.8

*Theoretical density of the samples is calculated to be 3.31 g cm⁻³.

** Holding time of the SPS samples was 10 min at 1550 °C and 5 min at 1600 and 1650 °C.

Figure captions

Fig. 1 Shrinkage curve of SPS samples at: (a), 1550 °C; (b), 1600 °C; and (c), 1650 °C.

Fig. 2 SEM images of SPS samples (0.08B) at: (a), (b), 1550 °C; (c), (d), 1600 °C; and (e), (f), 1650 °C.

Fig. 3 Thermal conductivity of SPS samples (0.08B).

Fig. 1 Shrinkage curve of SPS samples SPSed at: (a), 1550°C; (b), 1600°C; and (c), 1650°C.

Fig. 2 SEM images of SPS samples (0.08B) at: (a), (b), 1550°C; (c), (d), 1600°C; and (e), (f), 1650°C.

2 μm

Fig. 3 Thermal conductivity of SPS samples (0.08B) .