

Use of Post-heat Treatment to Obtain a 2H Solid Solution in Spark Plasma Sintering-Processed AlN–SiC Mixtures

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Dense aluminum nitride-silicon carbide (AIN-SiC) solid solutions with a 2H structure were fabricated by the post-heat treatment of dense AIN-SiC composites fabricated by spark plasma sintering (SPS). The changes in the relative density, microstructure, and phases present were investigated for the compositions of 25 mol% AlN-75 mol% SiC (AlN 25), 50 mol% AlN-50 mol% SiC (AIN 50), and 75 mol% AIN-25 mol% SiC (AIN 75). The AIN-SiC composites fabricated by the SPS were dense ceramics with fine microstructures and composed of 2H and 6H AIN-SiC solid solutions. The AIN 50 samples heat treated at 2200°C and the AIN 75 samples heat treated at 2100°C were also dense ceramics and composed of only the 2H AIN-SiC solid solution. In contrast, the AIN 25 samples heat treated at 2200°C were porous ceramics and composed of several AIN-SiC solid solutions (2H, 4H, 6H, and 15R), and the AlN 75 samples heat treated at 2200°C were decomposed into an Al melt. Dense AIN-SiC solid solutions composed of only the 2H phase can be obtained by controlling the heat-treatment temperatures, except for the AIN 25 sample.

I. Introduction

S ILICON carbide (SiC) has excellent mechanical properties and oxidation and corrosion resistance at high temperatures. This implies that the SiC ceramics can be used for hightemperature structural applications. In addition, SiC is a semiconductor with a very wide bandgap (3.2 eV, which is three times that of silicon). Therefore, SiC has a great potential in high-performance semiconductor devices used in power electronics. Aluminum nitride (AlN) has an excellent thermal conductivity (320 W/mK for a single crystal, which is comparable to that of Al) and excellent electrical insulation.^{1,2} Therefore, AlN has been used as a substrate material in power electronics. AlN is also used for manufacturing semiconductors because of its high resistance to halogens and plasma.³

In 1978, Cutler *et al.*⁴ reported that AlN and SiC form a 2H solid solution over a wide range of compositions. Rafaniello *et al.*⁵ investigated the phase stabilities of the AlN–SiC solid solutions and reported that spinodal decompositions occurred when these solid solutions were annealed at lower temperatures. Subsequently, Zangvil and Ruh⁶ presented a tentative AlN–SiC phase diagram. AlN–SiC solid solutions have potential applications as not only structural materials^{7–10} but also new functional materials.^{11–15} However, it is difficult to fabricate dense 2H AlN–SiC solid solutions due to the high covalence and low diffusion coefficients of AlN and SiC. In general, hot pressing

(HP) has been used to obtain AlN-SiC solid solutions. However, firing at a high temperature (above 2100°C) for a long time (for 4 h or more) is required to obtain dense 2H AlN-SiC solid solutions from powder mixtures of AlN and SiC with sintering additives such as Y_2O_3 .^{8,16} Rafaniello *et al.*¹¹ prepared AlN–SiC solid solutions powders using the sol-gel process and sintered them dense by HP, but these powders contained large amounts of free carbon and silica. Although we also obtained 2H AlN-SiC solid solutions at 2000°C by firing for 1 h using pressureless sintering (PLS) without sintering additives,¹⁵ dense ceramics were not obtained. Even if sintering additives such as Y2O3 were used for the densification of AlN-SiC composites by PLS, a long holding time was required to obtain AlN-SiC solid solutions.^{17,18} Furthermore, the sintering additives may affect the microstructures and intrinsic properties such as electrical conduction. It has been reported that spark plasma sintering (SPS) can shorten the sintering time and lower the sintering temperature of AlN–SiC composites with Y₂O₃ as sintering ad-ditive.¹⁹ Shirai *et al.*²⁰ carried out low-temperature sintering of SiC nanopowder with a small amount of AlN using SPS. We have also reported that the SPS can provide dense AlN-SiC composites without sintering additives, which have a fine microstructure with smaller grains but comprise several solid solution phases.²¹ According to the phase diagram of AlN-SiC,⁶ the SPSed dense AlN-SiC composites without additives should be 2H single phase by heat treatment at a higher temperature. Furthermore, the heat-treatment temperature and time are expected to be lower and shorter because a fine microstructure should result in a higher rate of mass transfer.

In this study, we fabricated dense 2H AlN–SiC solid solutions by SPS, followed by post-heat treatment. First, dense AlN–SiC composites were fabricated by the SPS at a lower temperature for a short sintering duration in order to obtain a finer microstructure. The dense 2H AlN–SiC solid solutions were then fabricated by heat treatment up to 2200°C.

II. Experimental Procedure

AlN powder synthesized by the reduction–nitridation method (Grade F, Tokuyama Corp., Tokyo, Japan, mean particle size = 0.6 µm) and α -SiC powder synthesized by the Acheson method (OY-20, Yakushima Denko Co. Ltd., Tokyo, Japan, mean particle size = 0.55 µm) were used as the starting powders. They were wet mixed in ethanol for 24 h using SiC balls and a nylon pot. The starting compositions were 25 mol% AlN–75 mol% SiC (AlN 25), 50 mol% AlN–50 mol% SiC (AlN 50), and 75 mol% AlN–25 mol% SiC (AlN 75). After drying, the mixtures were sieved using a 250-µm nylon mesh to form granules. The granules wereplaced in graphite molds (inner diameter = \emptyset 25 mm) lined with a graphite foil. SPS was performed at 2000°C for 10 min under an Ar atmosphere at 1 atm. A constant uniaxial pressure of 30 MPa was applied during the SPS. After the holding time, the power supply was shut down and the

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Fig. 1. Relative densities of the SPSed and HTed samples.

uniaxial pressure was released immediately. Using a diamond wheel and cutter, the sintered samples were cut into 3 mm \times 3 mm \times 20 mm test pieces. These test pieces were placed in a carbon crucible and molded in a packing powder with the same composition as the test piece in order to prevent a composition shift caused by evaporation or decomposition. They were heat treated at 2000°–2200°C for 3 h under an Ar flow using an induction-heating furnace to obtain the AlN–SiC solid solutions. Subsequently, the surfaces of the heat treated samples were ground to remove the adhered packing powder using a diamond buffer.

We evaluated the relative densities, compositions, microstructures, and phases present in the sintered and heat treated samples. The relative densities were measured using the Archimedes method. Determining the compositions (AlN content) of the samples, elemental analyses were carried out by X-ray fluorescent analysis (XRF). Although Al and Si were detected by XRF, the anions (C, N) and other impurities were not detected because these anions



Fig. 2. AlN contents of the SPSed and HTed samples. AlN_{init} means the initial contents of AlN in the samples.

are light elements and the starting materials have high purity. Thus, we can consider a change in the AlN content of a sample as a change in its Al content. The calibration curves for determining the Al contents of the samples were obtained using the mixtures of raw powders of AlN and SiC. Their microstructures were evaluated using a scanning electron microscope (SEM). The samples for the evaluation of the microstructures were polished with a diamond paste (2–4 μ m), and then chemically etched by boiling Murakami's reagent (10 g of K₃Fe(CN)₆, 10 g of KOH, and 100 g of water). The phases present were evaluated using an X-ray diffractometer with CuK α radiation.

III. Results

(1) Relative Densities

Figure 1 shows the relative densities of the samples. For all the compositions, the relative densities of the samples sintered at 2000° C were over 99.5% of the theoretical densities; this is the







Fig. 4. SEM images of the AlN 50 samples: (a) SPSed at 2000°C for 10 min. (b) SPS-HTed at 2200°C for 3 h.

same result as that obtained in our previous study (AlN 25: 99.8%, AlN 50: 99.2%, and AlN 75: 99.6%).²¹ The samples heat treated at 2000°C were also dense materials (AlN 25: 98.7%, AlN 50: 99.2%, and AlN 75: 99.3%). The relative densities of the samples heat treated at 2100°C decreased slightly, except for the AlN 50 samples (AlN 25: 96.6%, AlN 50: 99.2%, and AlN 75: 98.8%). After heat treatment at 2200°C, the change in the relative densities depended on the composition (AlN 25: 67.7% and AlN 50: 99.2%). Note that we could not evaluate the AlN 75 sample heat treated at 2200°C because the sample decomposed and the Al melt appeared. Although the weight loss caused by the adhesion of the packing powders was not measured, it is considered to be below 5% of that in our previous study.¹⁵

(2) Composition

Figure 2 shows the changes in the AlN contents of the samples measured by XRF. In Fig. 2, the quantity AlN/AlNinit on the y-axis denotes the ratio of the Al content of a sample after the SPS or the heat treatment process to its initial AlN content (AlN_{init}). The AlN contents of the samples sintered at 2000°C were almost the same as those in the starting compositions (AIN 25: 26.0 mol%, AlN 50: 49.4 mol%, and AlN 75: 76.0 mol%); therefore, the AlN/AlN_{init} ratios of the samples were close to 1. The AlN contents of the samples heat treated at 2000°C were also close to their starting compositions (AlN 25: 25.0 mol%, AlN 50: 51.6 mol%, and AlN 75: 76.3 mol%). Further, the AlN contents of the samples heat treated at 2100°C were also close to the starting compositions, except for the AlN 25 sample (AlN 25: 16.9 mol%, AlN 50: 51.7 mol%, and AlN 75: 75.9 mol%), and the AlN/AlNinit ratios of the AlN 25 samples decreased below 0.7. Subsequently, the AlN contents of the samples heat treated at 2200°C were significantly different from their starting compositions (AlN 25: 10.8 mol% and AlN 50: 52.3 mol%), and the AlN/AlN $_{\text{init}}$ ratios of the AlN 25 samples decreased to almost 0.4.

(3) Microstructures

Figures 3-5 present SEM images of the polished and chemically etched surfaces of the sintered and heat treated samples. Note that the SEM image of the AlN 25 sample heat treated at 2200°C was taken from the fractured surface. Although the samples sintered at 2000°C had dense textures, their grain sizes were different for different compositions. The AlN 25 and AlN 50 samples were composed of small grains (approximately 1 µm); in contrast, the AlN 75 sample was composed of larger grains (approximately 2 µm). The samples heat treated at 2000°C were dense ceramics, and the grain sizes were almost the same as those of the sintered samples. In contrast, the microstructures of the samples heat treated above 2100°C were different for different compositions. The AlN 25 and AlN 75 samples heat treated at 2100°C were dense ceramics with slightly larger grains than the samples sintered at 2000°C (AlN 25: approximately 2 µm, AlN 75: approximately 5 µm). Although the AlN 50 samples heat treated at 2200°C were also dense ceramics, the samples were composed of large grains (approximately 10 µm). The AlN 25 samples heat treated at 2200°C were porous ceramics with large grains (approximately 10 µm).

(4) Phases Present

Figures 6–8 show the phases present in the samples. The phases present in the samples sintered at 2000°C were 6H and 2H; this implied that the AlN and SiC did not form the AlN–SiC solid solutions but formed the AlN–SiC composites. The phases present in the samples heat treated at 2000°C were also 6H and 2H, and the diffraction intensity of the 6H phase was not changed. The phases present in the samples heat treated at 2100°C were



5 μm

Fig. 5. SEM images of the AIN 75 samples: (a) SPSed at 2000°C for 10 min. (b) SPS-HTed at 2100°C for 3 h.



Fig. 6. XRD patterns of the SPSed and HTed AlN 25 samples: (a) SPSed at 2000°C for 10 min. (b) SPS-HTed at 2000°C for 3 h. (c) SPS-HTed at 2100°C for 3 h. (d) SPS-HTed at 2200°C for 3.



Fig.7. XRD patterns of the SPSed and HTed AlN 50 samples: (a) SPSed at 2000°C for 10 min. (b) SPS-HTed at 2000°C for 3 h. (c) SPS-HTed at 2100°C for 3 h. (d) SPS-HTed at 2200°C for 3 h.

different for different compositions. For the AlN 25 and AlN 50 samples, the 6H and 2H phases were also found, and the diffraction intensity of the 6H phase was slightly decreased in the AlN 50 sample. In contrast, the AIN 75 sample was composed of only the 2H phase. The phases present in the samples heat treated at 2200°C changed drastically. Although the AlN 50 sample was composed of only the 2H phase similar to the AlN 75 sample heat treated at 2100°C, the AlN 25 sample was mixture of 6H, 2H, 4H, and 15R phases.

IV. Discussion

In this study, the relative densities correlated with the AlN contents. The phase stability calculations of AlN and SiC show that 14 mol% of AlN and 0.2 mol% of SiC are decomposed at 2200°C under an Ar atmosphere at 1 atm (calculated by using FACT-Web programs, online version of the FACTsage™ thermochemical software). Therefore, the decrease in the rela-



Fig. 8. XRD patterns of the SPSed and HTed AlN 75 samples: (a) SPSed at 2000°C for 10 min. (b) SPS-HTed at 2000°C for 3 h. (c) SPS-HTed at 2100°C for 3 h.

tive densities is mainly caused by the loss of AlN. Figures 1 and 2 show that the relative densities of the AlN 25 samples decreased with the loss of Al. This result indicates that the decomposition or evaporation of AlN occurs in the AlN 25 sample. On the other hand, both the relative densities and the AlN contents are substantially constant in the AlN 50 and AlN 75 samples. These results suggest that no decomposition or evaporation of AlN occurs in these samples. The slight increase in the AlN content of the AlN 50 sample is due to the incorporation of Al from packing materials.

We observed that the microstructures changed with the compositions and heat treatment temperatures. The grain sizes of the AlN 25 sample drastically increased at 2200°C, which changed inversely with a decrease in the relative density. In contrast, the grain sizes of the AlN 50 sample drastically increased at 2200°C without decreases in the relative densities. This tendency is also shown in the AlN 75 sample heat treated at 2100°C. Because the sintered samples had dense and fine textures, it is expected that the heat treated samples should also have dense textures if AlN or SiC do not decompose. The typical grain growth mechanism in the AlN 25 sample is stated as below. First, the open pores are formed by the decomposition of the AlN-SiC solid solutions and evaporation of AlN from the sample. Next, the evaporated AlN is condensed on the grains of the residual AlN-SiC solid solutions. The grain sizes of the AIN 25 samples increased due to the repetition of these processes. The grain growths in the AlN 50 and AlN 75 samples might be driven not by evaporationcondensation but by solid-phase diffusion because the textures of the samples are dense at the heat treatment temperatures. As we showed in our previous study,¹⁵ the differences of the grain sizes between the AlN 50 and AlN 75 samples could be explained by the difference of the driving force in the formation of the solid solutions.

V. Summary

In this paper, we fabricated dense AlN-SiC solid solutions by the post-heat treatment of dense AlN-SiC composites and discussed the stability of AlN-SiC solid solutions. This paper can be summarized as follows:

(1) We obtained dense AlN-SiC solid solutions with fine microstructures composed of only the 2H phase, except for the AlN 25 sample.

(2) The optimum heat treatment temperatures to fabricate dense 2H AlN-SiC solid solutions are 2200° and 2100°C for the AlN 50 and AlN 75 samples, respectively.

(3) The decomposition of the heat treated samples was restrained by the dense texture of the sintered samples.

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