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Thermal conductivity of β-SiAlONs prepared by a combination of combustion synthesis and spark plasma sintering

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ABSTRACT

β-$Si_{6-z}Al_zO_zN_{8-z}$s (z = 1–3) have been synthesized by combustion synthesis (CS) and the as-received powders were densified by spark plasma sintering (SPS). The thermal properties of the dense β-SiAlONs have been investigated by the laser-flash method from room temperature to a high temperature of 800 °C. The highest thermal conductivity of 9.45 W m^{-1} K^{-1} was obtained when z = 1 at room temperature. Both thermal diffusivity and thermal conductivity decreased with an increase in the z value. In the β-$Si_{6-z}Al_zO_zN_{8-z}$, with z value increasing, more Si^{4+} and N^{3-} ions get replaced by Al^{3+} and O^{2-} ions, thereby more lattice defects are formed. These defects cause phonon scattering, accordingly reduce the thermal conductivity.

1. Introduction

β-SiAlON, a solid solution of β-Si_3N_4 in which part of Si–N has been replaced by Al–O, is most commonly described by the general formula β-$Si_{6-z}Al_zO_zN_{8-z}$ (z = 0–4.2) [1,2]. Ever since it was discovered in the early 1970s [3], β-SiAlON materials have been attracting considerable attention on account of their being suitable for high-temperature applications owing to their excellent mechanical and thermal properties.

In our previous researches, we have synthesized β-SiAlONs (z = 1–3) by a very simple method of combustion synthesis and have obtained dense products by spark plasma sintering method [4], and we have also measured their mechanical properties and corrosion behavior in different conditions [5–7].

Lots of reports concern the thermal properties for they are the very important property for many kinds of materials [8,9], in which many studies have been focused on the thermal conductivity of Si_3N_4 [10–17]. Watari et al. reported that the thermal conductivity at room temperatures of sintered β-Si_3N_4 was 80 W m^{-1} K^{-1} in the direction parallel to the hot pressing direction, where the materials were hot-pressed at 1800 °C and further hot-isostatic pressing to 2400 °C [11]. It has also been reported that when alumina was added to silicon nitride, it resulted in reduction of thermal conductivity to only 30 W m^{-1} K^{-1} [10]. It represents that the substitution of aluminum and oxygen into silicon and nitrogen sites in the β-Si_3N_4 structure increase the crystal defects, thereby decrease the thermal conductivity. In addition, the small grain size and intergranular phases also cause loss in thermal conductivity in SiAlON ceramics. Thermal conductivity of β-SiAlON at room temperature has been reported to be 12.44 W m^{-1} K^{-1} by Liu et al. [18]. The maximum thermal conductivity was reported around 17 W m^{-1} K^{-1} for β-SiAlON at ambient temperature by Joshi et al., which was prepared by hot pressing under 1850 °C for 1 h with 2 wt.% Y_2O_3 addition [19].

In our previous study, thermal conductivities of spark plasma sintered β-SiAlONs ($Si_3Al_3O_3N_5$) procured from combustion synthesis (CS) with no sintering additive were measured by the laser flash method at room temperature [20]. The results showed that thermal conductivity values increased with sintering temperature and attained a maximum of 5.49 W m^{-1} K^{-1} for fully densified β-SiAlONs sintered at 1700 °C for 10 min. However, no measurement has been performed on the thermal conductivity of CS-SPSed β-SiAlONs (z = 1–3) as a function of temperature. Therefore, the purpose of this study was to obtain the thermal conductivity of CS-SPSed β-SiAlONs (z = 1–3) as a function of temperature.

2. Experiments

2.1. Sample preparation

The synthesis method has been described in detail elsewhere [21]. Here we only repeated the preparation method briefly.

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Table 1
Characteristics of the CS-SPSed β-SiAlONs used in this study.

Samples	Phase compositions from XRD	Bulk density (g/cm^3)	Theoretical density[a] (g/cm^3)	Relative density (%)
Z1 (z = 1)	β-Si_5AlON_7	3.13	3.168	98.8
Z2 (z = 2)	β-$Si_4Al_2O_2N_6$	3.12	3.122	99.9
Z3 (z = 3)	β-$Si_3Al_3O_3N_5$	3.073	3.082	99.7

[a] See Ref. [22].

Commercially available powders of Si (98% purity, 1–2 μm in size), Al (99.9% purity, 3 μm in size), and SiO_2 (99.9% purity, 0.8 μm in size) were used as starting materials. β-SiAlON powders (CSed product, unknown purity, 0.5 μm in size) were added as the diluent. The chemical reaction for the synthesis of β-SiAlON from the abovementioned starting materials can be shown as follows:

$$(6-1.5z)Si+zAl+0.5zSiO_2+(4-0.5z)N_2 \rightarrow \beta - Si_{6-z}Al_zO_zN_{8-z} \quad (1)$$

where z takes values of 1–3. The mass percent of the diluent was determined according to our preliminary experiment.

The CSed powder was first subjected to planetary ball milling for 60 min, then was compacted into a carbon die of 10 mm in inner diameter and sintered using a SPS system (Sumitomo Coal Mining Co. Ltd., Tokyo, Japan) under vacuum of lower than 4 Pa at a compressive stress of 50 MPa. The resulting compacts were heated from room temperature to 600 °C in 5 min, and then were heated to 1600 °C at a rate of 30 °C/min. The compacts were maintained at this temperature for 10 min before the power was turned off. The phases of the CS-SPSed products were analyzed using an X-ray diffraction (XRD) (Mini Flex, Rigaku Corporation, Tokyo, Japan). The morphology was examined by scanning electron microscopy (SEM) (FE-SEM JSM-7400F, JEOL, Tokyo, Japan).

2.2. Thermal properties measurements

Specimens with a dimension of 10 mm in diameter and 2–3 mm in thickness were cut from the spark-plasma-sintered discs, and were polished using emery paper until to No. 1200. Prior to measurement, a thick layer of colloidal graphite was sputter-coated to the surface of the specimen to enhance absorption of the flash energy. The thermal diffusivity and specific heat capacity were measured by the laser-flash method (TC-7000, ULVAC Sinku Riko Co., Yokohama, Japan) from room temperature to 800 °C. The thermal diffusivity was analyzed with the $t_{1/2}$ method. The bulk density was measured according to the Archimedean principle, using distilled water as the medium. All the experiments were carried out under a flowing argon gas atmosphere. The thermal conductivity (K) of β-SiAlONs was determined by following equation:

$$K = \rho C_p \alpha \quad (2)$$

where ρ represents the bulk density, C_p is the specific heat capacity and α is the thermal diffusivity.

3. Results

3.1. Microstructure of the CS-SPSed samples

Table 1 shows the characteristics of the CS-SPSed β-SiAlONs (z = 1, z = 2, and z = 3). The bulk density decreases from 3.13 to 3.073 g/cm^3 with an increase in z value, and all of the relative densities of the as-received samples are higher than 98.8% theoretical density. Fig. 1 gives the XRD patterns of β-SiAlONs (z = 1, z = 2, and z = 3) before and after SPS. The XRD patterns of CSed products before SPS show a little un-reacted Si except β-SiAlON peaks; after SPS, only peaks due to β-SiAlONs are observed.

Fig. 2 shows the SEM images of the as-received β-SiAlONs (z = 1, z = 2, and z = 3) after combustion synthesis and also the images after spark plasma sintering. For the CSed powders, the primary microstructure is rod-like crystal with an average diameter of ~500 nm and a length of one to several micrometers. Some particles and whiskers can also be found in the microstructure. After SPS process, the product looks dense solid, and the grain size increases clearly with an increase in the z value.

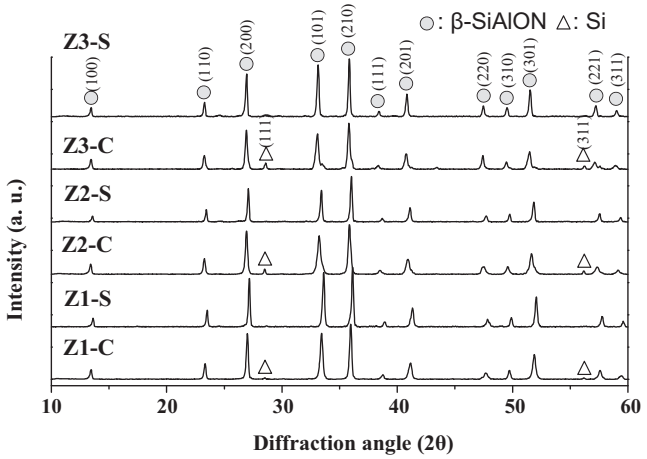

Fig. 1. XRD patterns of β-SiAlONs (Z1, Z2, and Z3). "C" means after combustion synthesis (CS) and before spark plasma sintering (SPS); "S" means after SPS.

3.2. Thermal properties

Table 2 gives the thermal properties of β-SiAlONs and β-Si_3N_4 at room temperature. β-Si_3N_4 sintered at 1900 °C for 36 h and subsequent annealed at 1700 °C for 100 h shows very high thermal diffusivity and thermal conductivity [14]. This was attributed to the reduction of internal defects of the β-Si_3N_4 grains with sintering and annealing time as the grains grew. In contrary, the thermal conductivity of β-SiAlONs is much less by nearly two orders of magnitude when compared to that of β-Si_3N_4. The β-SiAlON shows a little higher thermal conductivity of 12.44 W m^{-1} K^{-1} than those of our products [18]. This could also be attributed to the difference of the sintering method. In addition, we could not know the exact z value of this sample. For our products, it shows that both thermal diffusivity and thermal conductivity decrease with an increase in the z value. The highest thermal conductivity of 9.45 W m^{-1} K^{-1} was obtained when z = 1 at room temperature.

Fig. 3 represents the temperature dependence of thermal diffusivity of the β-SiAlONs from room temperature to 800 °C comparing with sintered β-SiAlON. The thermal diffusivity decreases with increasing temperature for all of the samples. And with z value increasing, the thermal diffusivity shows decreasing. The sintered β-SiAlON showed a little higher than our data, but we could not know the exact z value of their sample.

Fig. 4 shows the temperature dependence of heat capacity of the β-SiAlONs from room temperature to 800 °C comparing with sintered β-SiAlON. Our data shows higher than that of sintered β-SiAlON. For the CSed beta-SiAlON, Z2 shows the highest heat capacity, and Z3 shows the lowest data.