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Thermal conductivity of combustion synthesized β-sialons

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Abstract

To the first time, 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. A full densification occurred when these materials were sintered at 1600 °C with a simultaneous pressure of 50 MPa. XRD analyses indicated that single phase β-sialons were formed after SPS though the combustion synthesized β-sialon powders had considerable amounts of silicon impurities. 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.

Keywords: A. Milling; A. Sintering; C. Thermal conductivity; D. Sialon; Combustion synthesis

1. Introduction

β-Sialon, a derivative of β-Si_3N_4 is formed due to simultaneous replacement of Al and O with Si and N elements with similar hexagonal structure. β-Sialons are represented by a general formula of $Si_{6-z}Al_zO_zN_{8-z}$, where z varies from 0 to 4.2. These materials researched for more than three decades are of great technological interest due to their excellent mechanical and thermal properties possessing thermo-chemical corrosion and thermal shock resistances [1–3]. β-Sialon powders have been extensively synthesized by a solid-state high temperature reaction sintering, which is comparatively expensive as it involves increased energies and processing time. In recent years, combustion synthesis (CS) also referred as self propagating high temperature synthesis (SHS) has stimulated a growing interest because it has been shown to be a promising and cost effective technique utilized for synthesizing various ceramic materials including β-sialon powders. In this technique, a high exothermic heat is generated and sustained during reaction between reactants after external ignition. In particular, highly active and pure powders can be synthesized by this effective CS despite the impure starting materials. In our previous papers, β-sialon powders of z values ranging from 1 to 4 were successfully combustion synthesized to the first time without any diluents addition under a low nitrogen pressure of 1 MPa [4,5].

It is widely accepted that monophasic β-sialon powders are very difficult to sinter to theoretical densities without sintering additives due to lack of vitreous grain boundary phase. With an addition of some oxides such as yttria as sintering additives, the densification increases dramatically and it is possible to sinter β-sialons by pressureless sintering. However, it is necessary to develop a product without a foreign phase that has the tendency to leave a residual glassy phase during sintering and lead a detrimental effect in their high temperature and corrosion properties [6]. Thus, pressure assisted sintering techniques such as hot-pressing, hot-isostatic pressing and SPS have been applied to densify β-sialon powders. Among these aforementioned sintering methods, SPS, otherwise called as pulse electric current sintering (PECS) is a rapid densification method that promotes the neck growth between particles, thereby efficiently increasing the sinterability of particles [7].

To the best of our knowledge, no sintering work through SPS has been performed for combustion-synthesized β-sialon powders without any sintering additives. In addition, up to now, the mechanical properties of β-sialons with high aspect ratio grain structure have been extensively studied due to their high fracture toughness, flexure strength and favorable high temperature creep resistance. However, less emphasis was placed

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on their thermal properties. Hence our prime objective in this study is to perform SPS of combustion synthesized β-sialon powders without sintering aid additions and to investigate the thermal conductivities at room temperatures.

2. Experimental

2.1. β-Sialon powder synthesis

The β-sialon powders were obtained from the mixture of starting materials, silicon (Soekawa Chemicals Co., Ltd., Tokyo, Japan; 98% purity, 5 μm), aluminium (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan; 99.9% purity, 3 μm) and α-alumina (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan; 99.9% purity, 1 μm) as a source of oxygen. The starting powder mixture with nominal composition of $Si_3Al_3O_3N_5$ ($z = 3$) was planetary milled for 18 min and combustion synthesized under low nitrogen pressure of 1 MPa [4]. The resulting β-sialon powders after CS were taken in this study. The experimental setup with the optimization of planetary milling time and starting material selection to obtain pure products are described in detail elsewhere [4,5].

2.2. Sintering

The β-sialon powders after CS were planetary milled for an hour prior to sintering. The milled powders were then compacted in a carbon dye with a 10 mm inner diameter and sintered using a spark plasma sintering system (Sumitomo Coal Mining Co. Ltd., Tokyo, Japan) under vacuum condition with a compressive stress of 50 MPa. The compacts were sintered at different temperatures ranging from 1400 °C to 1700 °C with a heating rate of 250 °C/min and a soaking time of 10 min at the maximum temperature. An optical pyrometer focused on the surface of the graphite dye, was used to monitor the temperatures above 600 °C.

2.3. Characterization

The phase analysis of combustion synthesized powders and sintered samples were determined using X-ray analyser (Mini Flex, Rigaku Corporation, Tokyo, Japan). Particle size distributions of the synthesized β-sialon powders before and after milling were determined by particle size analyser (Partica LA-950, Horiba Ltd., Kyoto, Japan), where the particle sizes are measured by laser scattering method. The bulk densities (ρ) of consolidated specimens by SPS were measured by Archimedes displacement method, using distilled water as the medium. The grain morphologies of combustion synthesized β-sialon powders and fractured surfaces after SPS were examined by a high resolution field emission scanning electron microscopy (FE-SEM; JSM-7000F, JEOL, Tokyo, Japan). The thermal diffusivity and specific heat capacity measurements were performed using a standard laser flash thermal constant analyser (TC-7000, ULVAC Sinku Riko Co., Yokohama, Japan) at room temperatures [8]. This thermal analyser has normal oscillation type glass laser and is capable of measuring from room temperature to a high temperature of 1500 °C. The sample sizes used for diffusivity and specific heat capacity measurements were in the form of thin disks of diameter 10 mm and thickness of 2 mm.

The thermal conductivity (K) of β-sialons was determined by following equation:

$$K = \rho C_p \alpha$$

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

3. Results and discussion

After CS, the mechanically activated raw material mixtures were subjected to phase analysis and the X-ray diffraction patterns confirmed β-sialons of desired z value ($z = 3$) [5]. However, there were particle agglomerates present after CS due to the fusion of particles at high temperatures during synthesis. Thus, the powders were planetary milled for an hour to reduce the particle sizes that promotes the sintering ability of starting materials and also lowers the densification temperatures when compared to as-received agglomerated powders after CS. Fig. 1 shows the particle size distribution before and after planetary milling of combustion synthesized powders. A bi-modal particle size distribution was present before milling with an average particle size of 41.5 μm. As expected, with the milling time of 30 min, a narrow distribution was observed with a drastic reduction in particle size. Further milling up to 60 min led to the reduction of particle size markedly to 3.2 μm. Thus, it is inferred that the planetary milling has a prominent impact for the milling of powders. The FE-SEM images of synthesized β-sialon powders before and after planetary milling are given in Fig. 2. From the figure, it is obvious that the particle sizes have been considerably reduced after 60 min of planetary milling with uniformity which is in good agreement with the particle size analyses results.

The powders planetary milled to 60 min were spark plasma sintered at different sintering temperatures ranging from

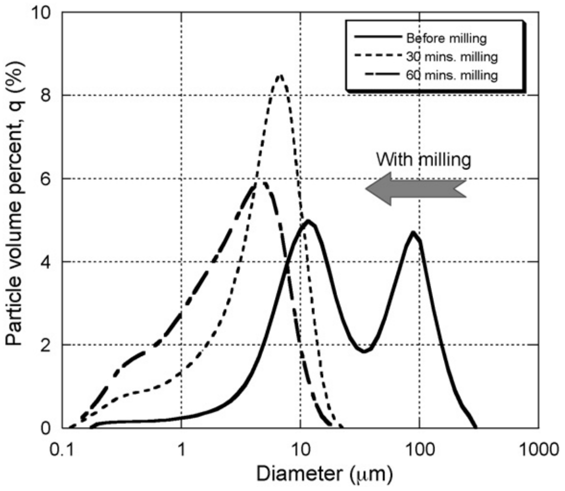

Fig. 1. Particle size distributions of combustion synthesized $Si_3Al_3O_3N_5$ ceramic powders before and after planetary milling to 30 min and 60 min.

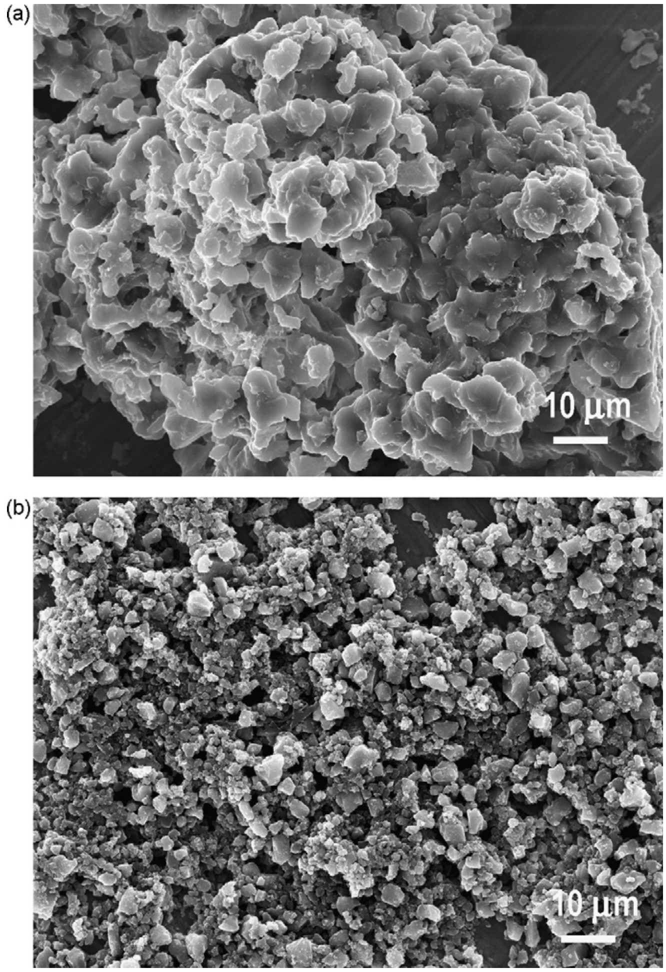

Fig. 2. A typical FE-SEM image of combustion synthesized powders (a) before and (b) after planetary milling to 60 min.

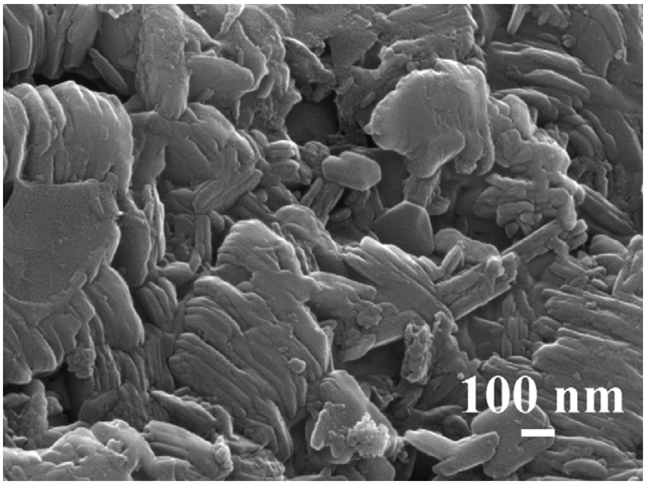

Fig. 4. A micrograph depicting the fracture surface of fully densified Si$_3$Al$_3$O$_3$N$_5$ ceramics by spark plasma sintering at 1600 °C.

1400 °C to 1700 °C in steps of 100 °C and the temperature dependence with bulk densities as well as calculated relative densities obtained from Archimedes displacement method are presented in Fig. 3. The theoretical density of β-sialons ($z = 3$) was considered as 3082 kg m^{-3} to calculate their respective relative densities at different sintering temperatures [4]. The relative density results revealed that the value was quite low at 1400 °C (83%), where there was a steep increase to 99% when sintered to 1500 °C for 10 min. Thus, it can be attributed that the degree of densification was accelerated considerably when sintered at 1500 °C and further increase in sintering temperatures to 1600 °C resulted full densification to theoretical densities. Fig. 4 presents the SEM micrograph of the fractured area of fully densified β-sialon (1600 °C) after SPS. From the micrograph it is evident that β-sialon were formed with elongated grain structures. The X-ray diffraction patterns of plasma sintered β-sialon samples at various sintering temperatures are shown as in Fig. 5. One notable feature is that, the X-ray analyses indicated that no other phases than Si$_3$Al$_3$O$_3$N$_5$ were formed after SPS when sintered up to 1700 °C. In our earlier detailed studies [4,5] of CS, it was found that along with a high concentration of β-sialon contents (83 mass%) of a $z = 3$

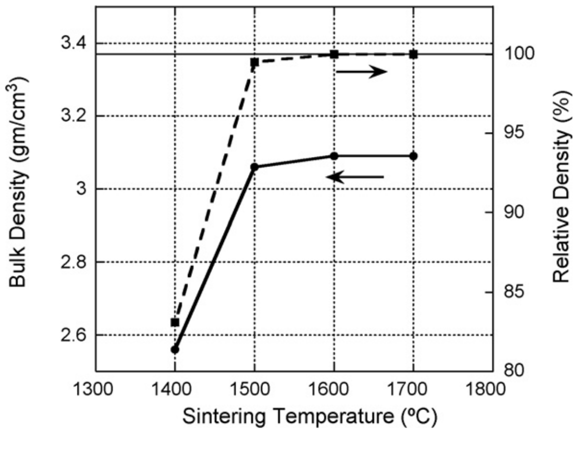

Fig. 3. Variation of bulk densities as well as relative theoretical densities with respect to sintering temperatures ranging from 1400 °C to 1700 °C in steps of 100 °C.

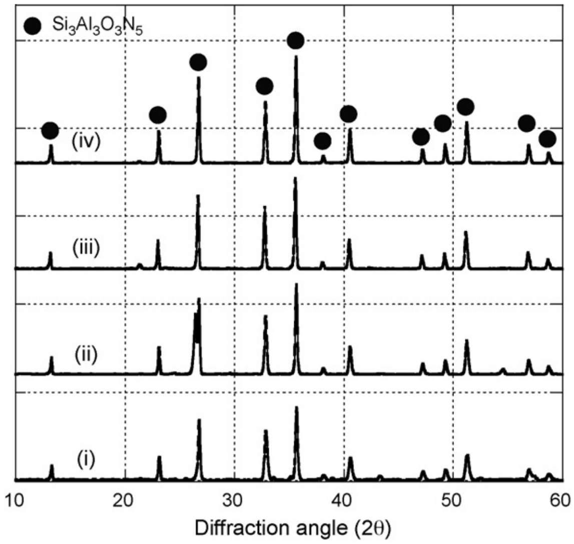

Fig. 5. X-ray diffraction patterns of spark plasma sintered samples at different sintering temperatures from 1400 °C to 1700 °C.

Table 1
Process condition, bulk density, thermal diffusivity, specific heat capacity and thermal conductivity of $Si_3Al_3O_3N_5$ ceramics consolidated by spark plasma sintering

Process condition (°C/50 MPa/10 min)	Bulk density ($\times 10^3$ kg m^{-3})	Thermal diffusivity[a] ($\times 10^{-6}$ m^2 s^{-1})	Specific heat capacity[b] (kJ kg^{-1} K^{-1})	Thermal conductivity (W m^{-1} K^{-1}) at 25 °C
1400	2.56	1.83	0.6876	3.21
1500	3.06	2.44	0.7084	5.28
1600	3.08	2.41	0.7199	5.35
1700	3.08	2.45	0.7255	5.49

[a] S.D.: <0.2%.

[b] S.D.: <1.5%.

value, a minor amount of un-reacted Si by-product phases was still present. This un-reacted Si occurrence is thought to have resulted from a too short reaction time during CS, thus not possessing a full conversion of Si to β-sialon product. However, XRD patterns showed that there were no Si peaks present after compaction into pellets through SPS. One possible explanation of this absence of Si after plasma sintering is that the un-reacted Si either evaporated or dissolved in the form of a solid solution during plasma sintering under simultaneous high pressures and temperatures. To elucidate the mechanism of Si non-existence after sintering, further investigation is required in detail. This present finding demonstrates that although un-reacted Si by-products are formed after CS, pure β-sialons are obtained after sintering, which can be useful in application standpoint.

The calculated thermal conductivity values at room temperature are summarized in Table 1 which indicates that the thermal conductivity increases with the sintering temperatures. A significant increase of conductivity from 1400 °C to 1500 °C can be explained by the dependence of sintering during the consolidation by spark plasma sintering. At a sintering temperature of 1500 °C, the samples densified to almost theoretical density. With a further increase in sintering temperature, a slight improvement of conductivity was observed and attained a maximum of 5.49 W m^{-1} K^{-1} at 1700 °C. This value is much less by nearly two orders of magnitude when compared to that of β-Si_3N_4. Watari et al. [9,10] reported that the thermal conductivity at room temperatures of sintered β-Si_3N_4 was 102 W m^{-1} K^{-1} in the direction perpendicular to the hot-pressing direction, where the materials were hot-pressed at 1800 °C and further hot-isostatic pressing to 2400 °C. Their results revealed that the thermal conductivity at room temperature is independent of grain size, but the internal defect in β-Si_3N_4 grains such as point defects and dislocations are the significant factors that affect the conductivity values. In addition, Brito and co-workers [10] observed the internal structure of β-Si_3N_4 grains with Y_2O_3 added and demonstrated that smaller grains had higher defect density, suggesting that thermal conductivity is less for smaller grains and increase in conductivity (122 W m^{-1} K^{-1}) is not because of increase of grain size, but due to the removal of crystal defects. Similarly, in our study of β-sialons, the solid solution of β-Si_3N_4, where Al^{3+} and O^{2-} ions gets replaced by Si^{4+} and N^{3-} ions turn out to be substitutional impurities in the crystal. The vacancies formed in the lattices and the mass difference due to substitution act as the phonon scattering sites, thereby reducing the thermal conductivities. It is worth noting that when alumina is added to silicon nitride, it resulted in reduction of thermal conductivity to only 30 W m^{-1} K^{-1} [11]. Also, it has been reported that the thermal conductivity decreases with the increase of alumina content in β-sialon ceramics [12].

Another possibility of decreased conductivity in our study is with regard to the sintering rate and sintering time at maximum temperature (250 °C/min and 10 min), respectively. It is well known that the grain sizes after SPS sintering will be smaller when compared to other conventional sintering techniques due to short sintering time at elevated temperatures. From the above discussion, a hypothesis is suggested that the smaller grain sizes of sintered β-sialons by SPS will have extensive internal crystal defects as observed in case of β-Si_3N_4 contributing to the reduction of thermal conductivities that has to be clarified. The thermal conductivity at room temperature of nearly theoretical densified β-sialon (Si_5AlON_7) materials containing less alumina content were reported to be 12.44 W m^{-1} K^{-1} by Liu et al. [13] An increased thermal conductivity than our value (5.49 W m^{-1} K^{-1}) might be mainly attributed to the Y_2O_3 addition as a sintering aid and long sintering time (2 h) at high temperatures of 1800 °C that produces large grains, in turn possess less crystal defects and decrease phonon scatterings. In addition, conductivities also depend on the density values as well as on alumina content [13] in β-sialons. The density of Si_5AlON_7 is slightly high (3160 kg m^{-3}) when compared to that of our sintered $Si_3Al_3O_3N_5$ ceramics (3080 kg m^{-3}), and the alumina content in Si_5AlON_7 is comparatively less that in turn have increased thermal conductivities.

4. Conclusion

For the first time, β-sialon ($Si_3Al_3O_3N_5$) ceramics obtained through CS were fully densified by SPS technique at 1600 °C without any sintering additive and their thermal conductivity was measured at room temperatures by the laser flash method. Though silicon impurities were considerably present after the powder synthesis, pure β-sialon phases were obtained after SPS which might be attributed to evaporation of silicon or dissolution in solid solution at a simultaneous high temperature and pressures during plasma sintering. The measured conductivity values increased with the sintering temperatures and had a maximum value of 5.49 W m^{-1} K^{-1}, when the samples were sintered at 1700 °C for 10 min. The nearly two order decrease in thermal conductivity values for β-sialons when compared to recently reported β-Si_3N_4 ceramics is attributed to the replacement of Si^{4+} and N^{3-} ions by Al^{3+} and O^{2-} ions that create substitutional impurities/defects in the grains and as well as the scattering of phonons at partly occupied interstitial sites, respectively.

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