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Original Papers

Combustion Synthesis and Sintering of β-Sialon Ceramics ($z = 2$) †

by

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Single-phase (β-SiAlON ($Si_4Al_2O_2N_6$, $z = 2$) powder has been prepared by the combustion synthesis method. The raw materials (Si, Al and SiO_2) were combusted with different ratios of (β-SiAlON ($z = 1$) diluent (0, 10, 20, 30, 40, 50 wt%) in 1 MPa of N_2 pressure. Without diluent, the reaction temperature was very high (> 2000℃) and the product contained metal Si residue besides (β-SiAlON product. Both the reaction temperature and amount of residual Si decreased gradually with the increase of diluent content up to 50 wt%. At 50 wt% dilution, the combustion temperature was 1859℃ and the XRD analysis showed complete conversion to pure (β-SiAlON ($z = 2$). The individual peaks of (β-SiAlON ($z = 1$) diluent were also detected in the XRD patterns and disappeared after using the product itself as a diluent five time repeats of combustion at which single-phase (β-SiAlON ($z = 2$) was produced. The sinterability of the best synthesized powder was further studied by spark plasma sintering (SPS) with 5 wt% Y_2O_3 as a sintering aid. High densification (~97.3%) was obtained after sintering at 1600℃ for 5 min under 30 MPa pressure with heating and cooling rates of 100℃/min. The Vickers hardness and fracture toughness of the sintered SiAlON were 14.8GPa and 4.4 $MPam^{1/2}$, respectively.

Key words : *β-sialon, z value, SHS, Combustion synthesis, SPS*

1 Introduction

Nitrogen ceramics are used for numerous engineering applications, especially silicon nitride and sialon which possess excellent mechanical properties, such as high strength, thermal shock and wear resistance, and good chemical inertness.[1] β-SiAlON ceramics are solid solutions formed by the simultaneous substitution of Al and O for Si and N, respectively, in β-Si_3N_4. The phase composition is expressed by the formula $Si_{6-z}Al_zO_zN_{8-z}$, where z represents the number of Al-O pairs substituting for the Si-N pairs in β-Si_3N_4 and can be varied in the range of $0 < z < 4.2$.[2] Therefore, β-SiAlON ceramics have combined properties of both silicon nitride (high strength, hardness, fracture toughness, and low thermal expansion) and aluminum oxide (corrosion resistance, chemical inertness, high temperature capabilities, and oxidation resistance).[2,3] They become ideal candidates for several applications such as cutting tips, manufacture of automotive valves, welding applications, in aerospace and automotive industry, handling of molten metals and non-ferrous alloys, and as gas filter for high temperatures and corrosive environments.[1)~5)]

Sialons components are produced exclusively by the reaction sintering method since the synthesis of sialon powders by conventional methods such as carbothermal reduction was costly and limited.[6] The combustion synthesis (CS) method (also called the self-propagating high-temperature synthesis or SHS) has a large potential as a cost-efficient process in the production of many advanced ceramics. It utilizes the heat generated by an exothermic reaction between reactants to sustain the reaction to completion very quickly so that no extra energy is needed except the small amount used for the initiating the reaction. High conversions can be attained by careful selection of the combustion parameters such as charge composition, nitrogen pressure, amount and type of diluent, etc. The main advantages are high energy-savings, rapid synthesis, and high purity of products. The previous reports showed that low-cost β-sialon powders can be prepared by CS,[7)~10)] nevertheless, less effort has been focused on the composition control of produced β-sialon powder due to complexity of the formation in such a multicomponent system. Recently, the production of β-sialons powder with $z = 1$ have been reported and the properties of its sintered materials have been thoroughly studied.[11] In this paper, the synthesis of single-phase β-sialon powder with $z = 2$ by CS process is demonstrated. The sinterability of the synthesized powder was also studied by the spark plasma sintering (SPS). The SPS is a powerful sintering technique which enables nearly full densification of materials in a period of several minutes.[12)~14)]

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2 Experimental Procedure

The raw materials used in this study were silicon metal (99.5% Si, 3μm), silica (10μm), aluminium metal (99.5% Al, 22μm) and β-sialon powders ($z = 1$, 7.5μm, as a diluent). The starting composition used to synthesize β-SiAlON ($z = 2$) phase was calculated based on the following equation :

$$(6-1.5z)\mathrm{Si} + z\mathrm{Al} + (0.5z)\mathrm{SiO_2} + (4-0.5z)\mathrm{N_2} = \beta - \mathrm{Si_{(6-z)}Al_zO_zN_{(8-z)}} \quad (1)$$

The experimental procedure is illustrated in Fig. 1. The reactants (according to above equation) were thoroughly mixed with different ratios (0, 10, 20, 30, 40, 50 wt%) of diluent powder (β-SiAlON, $z = 1$). The diluent was used to control the combustion temperature of the reaction. The charges (about 50 g) were loosely packed into a cylindrical porous graphite crucible (42 mmϕ × 90 mm H). The crucible was placed into a conventional SHS autoclave (180 mm inner diameter, 300 mm inner height and volume of 7.6 (10^2 cm^3).

The combustion reaction was performed under low nitrogen gas pressure of 1 MPa (99.99% purity). It was initiated from the bottom using 2 g ignition agent (Al/AlN pellet) placed beneath the charge, by passing a current of 60 A × 20 V for 10 s through a carbon ribbon heater under the pellet. A W-Re thermocouple was used to record the temperature-time patterns of reaction during the combustion at the center of the charge. After cooling, the products were roughly crushed and screened through a 220μm sieve. After controlling the reaction temperature using β-SiAlON ($z = 1$) as diluent and obtaining silicon-free sialon product, we used the product itself as a diluent. After five repeats of the combustion using the product of one experiment as a diluent (also 50 wt% ratio) in the next one, a single-phase β-SiAlON ($z = 2$) was obtained.

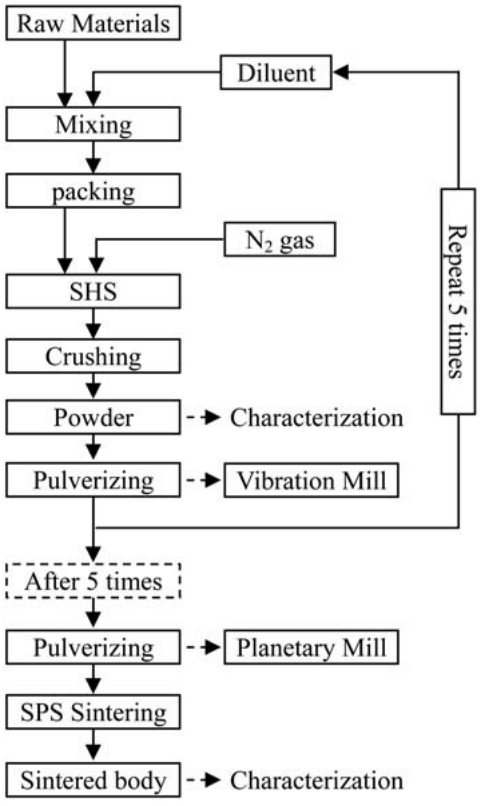

Fig. 1 Flow chart of experimental procedure.

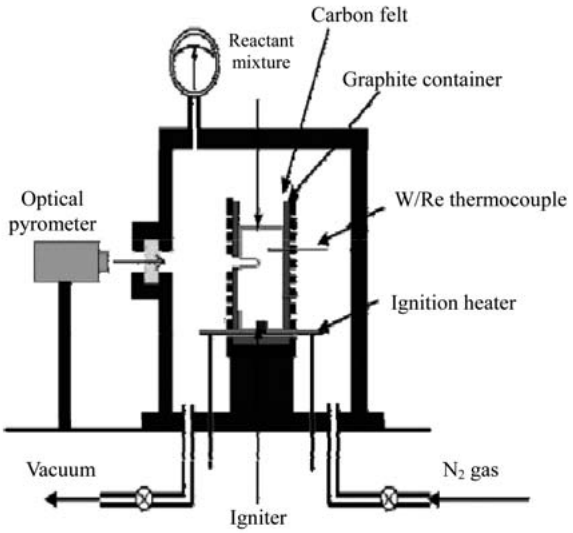

Fig. 2 A schematic diagram of combustion reactor.

The combusted products were analyzed by the x-ray diffraction analysis (JEOL, JDX-3530, Japan). The z value of β-sialon phases was determined by calculating its lattice parameters according to the XRD results with extra added pure Si as an internal standard. The morphology of products was observed by using field-emission scanning electron microscope (FE-SEM ; ERA-8800, ELIONIX, Tokyo, Japan).

The sinterability of the synthesized sialon powder was studied using the spark plasma sintering (SPS). The as-synthesized powder was crushed and screened using a 220μm sieve and then wet-milled by planetary mill in 2-propanol medium using Al_2O_3 balls. The amount of alumina contaminated from milling media was very small and not taken into account. A 5-wt % yttria powder was added to pulverized powder as a sintering aid. The powder mixture was placed inside 10 mm diameter graphite die and then sintered using Dr. Sinter® Model 1050 SPS apparatus (Sumitomo Coal Mining Company, Ltd., Japan). The schematic diagram of SPS system is shown in Fig. 3. The sintering was performed at 1600℃ for 5 min under 30 MPa pressure in vacuum atmosphere. The heating and cooling rates were 100℃/min. The temperature was measured by means of an optical pyrometer focused on a hole on the die surface centered on the sintering sample. The Vickers hardness was measured for polished specimen using an indenter with an indentation load of 1 kgf (9.81 N) for 15 s (Akashi MVK-G3 Hardness tester), and the indentation fracture toughness, K_{IC}, was determined

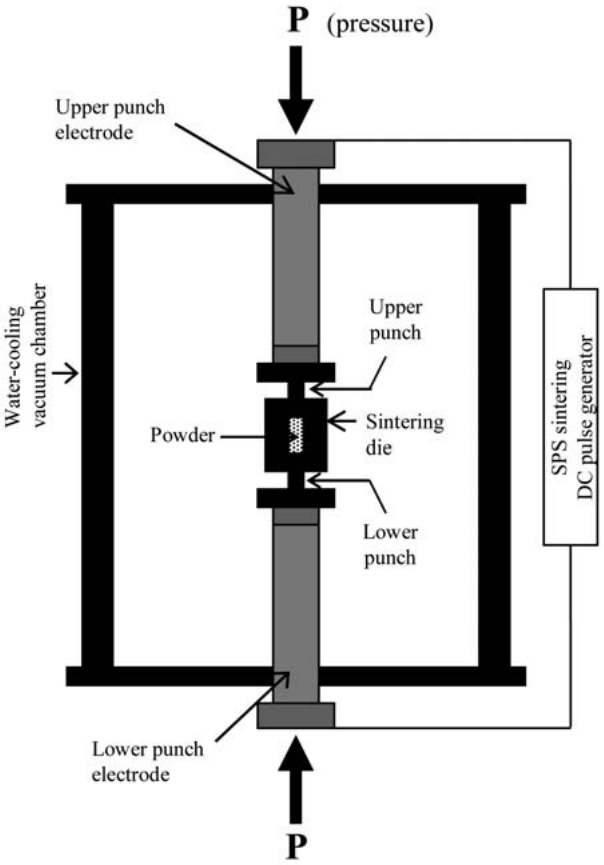

Fig. 3 A schematic diagram of SPS apparatus.

using the following equation[15]:

$$\left(\frac{K_{IC}\phi}{H_v a^{1/2}}\right)\left(\frac{H_v}{E\phi}\right)^{2/5} = 0.129\left(\frac{c}{a}\right)^{-3/2} \quad for\ \frac{c}{a} \geq 2.5 \qquad (2)$$

where H_v Vickers hardness, E Young's modulus, c radius of the surface crack, a half-diagonal of the Vickers indent, l parameter defined as c-a, and ϕ a constant taken as 3. The microstructure of fractured surfaces of sintered samples was observed by FE-SEM.

3 Results and Discussion

3. 1 Combustion synthesis of single-phase β-SiAlON (z = 2) powder

All charges with different diluent contents were combusted in 1 MPa N_2 pressure. Without diluent, the reaction temperature was very high (> 2000℃) and the thermocouple was melted. The XRD analysis of the product showed large amount of elemental Si residue besides (β-SiAlON phase (Fig. 4). With the addition of diluent (z = 1), both the combustion temperature and remained metal silicon decreased gradually with the increase of diluent content up to 50 wt%. At this value, the combustion temperature was about 1859℃ as seen in Fig. 5. After 50 wt% diluent addition, silicon-free sialon product was obtained and the complete conversion to (β-SiAlON was achieved. However, some peaks corresponding to (β-SiAlON diluent (z = 1) was present besides the peaks of z = 2 phase (as seen in Fig. 4), that was confirmed by results of internal standard method. When the combustion product itself was used as a diluent, and after 5 time repeats of combustion using the product of one experiment as a diluent (also 50 wt% ratio) in the next one, the peaks of z = 1 phase disappeared and only single-phase sialon powder of z = 2 ($Si_4Al_2O_2O_6$) was obtained as seen in Fig. 6.

Figure 7 gives the morphology of the as-synthesized product. The sialon particles had irregular shapes with average particle size of ~ 3μm.

3. 2 Spark plasma sintering of combustion synthesized β-SiAlON powder

The synthesized β-SiAlON powder (z = 2) was crushed, and wet-milled by a planetary mill to about 0.5μm particle size. The particle size distribution of the milled powder is shown in Fig. 8. The sintering was performed using spark plasma sintering system in graphite dies at 1600°C for 5

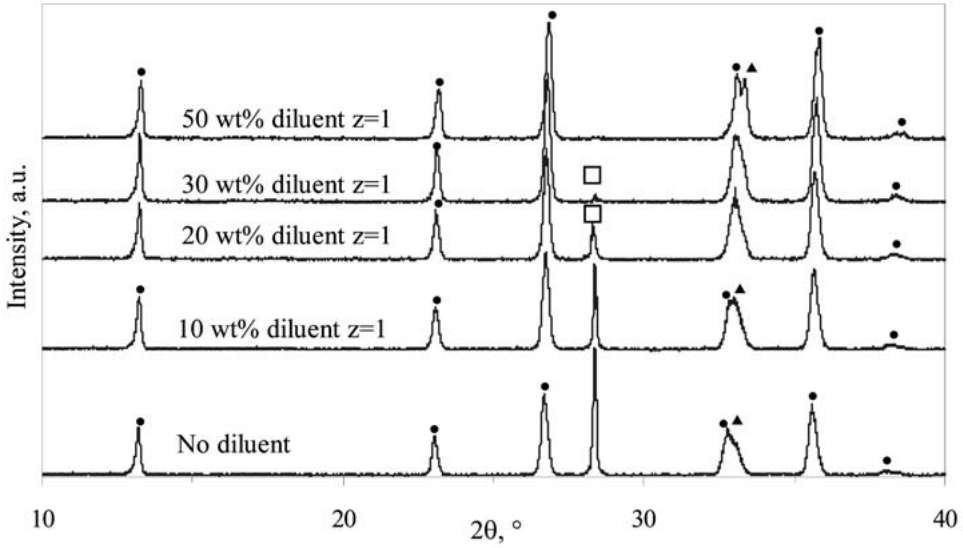

Fig. 4 X-ray diffraction patterns of synthesized SiAlON powders at various diluents amounts.
(* $Si_4Al_2O_2N_6$, ▲ Si_5AlON_7, □ Si)

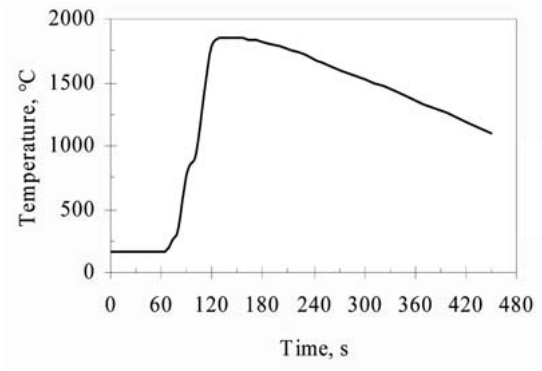

Fig. 5 The combustion thermogram after the reaction using 50wt% diluent. (z = 1)

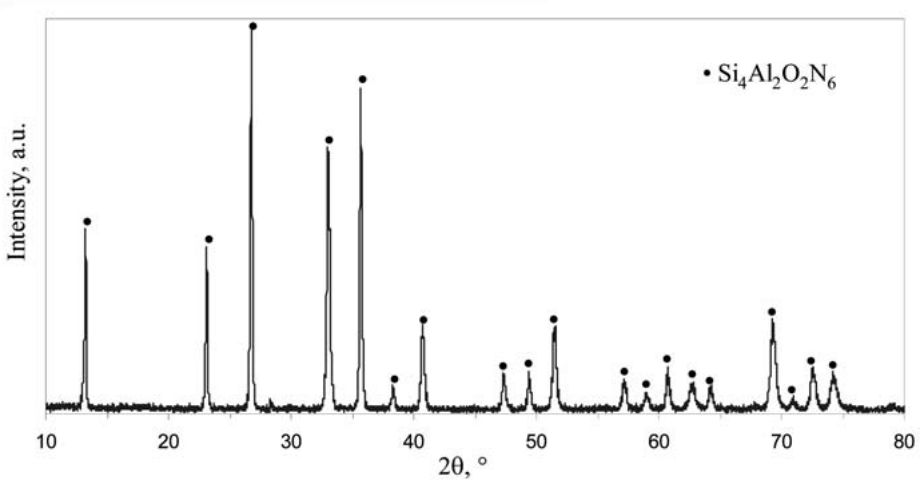

Fig. 6 X-ray diffraction patterns of as-synthesized SiAlON powder at optimum condition. (When the product was used as a diluent and the combustion was repeated five times)

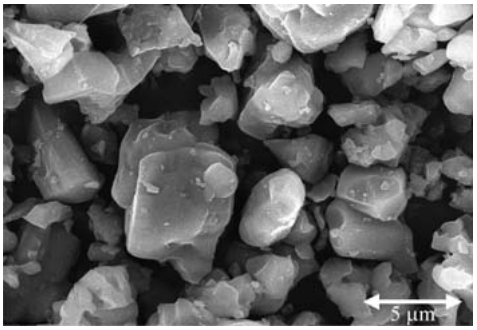

Fig. 7 FE-SEM image of as-synthesized single-phase β-SiAlON (z = 2)

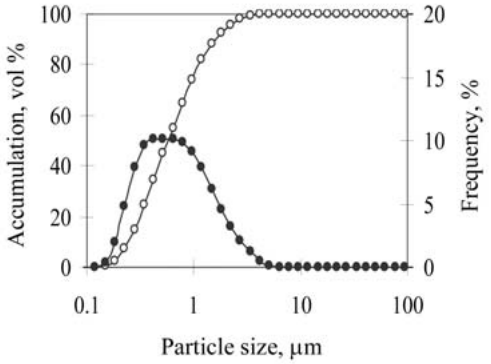

Fig. 8 Praticle size profile of pulverized β-SiAlON (z = 2), D50 = 0.5μm.

Table 1 Properties of sintered $Si_4Al_2O_2N_6$ (z = 2).

Density, %	97.3
Vickers hardness, GPa	14.8
Fracture toughness, $MPam^{1/2}$	4.4

minutes under 30 MPa pressure in the presence of 5 wt% Y_2O_3 as a sintering aid. The β-SiAlON (z = 2) was sintered well. The properties of density, hardness and fracture toughness of the dense sialon specimen are listed in Table 1. A SEM image of its fractured surface is shown in Fig. 9. Both transgranular and intergranular fractures were observed. The average grain size was 3μm.

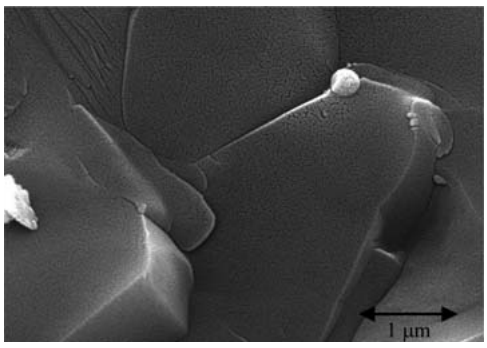

Fig. 9 Fractured surface of β-SiAlON (z = 2) sintered at 1600℃ for 5min by SPS.

4 Summary

Single-phase β-SiAlON (z = 2, $Si_4Al_2O_2O_6$) powder was successfully prepared from the stoichiometric mixture of reactants by the combustion synthesis method under low nitrogen pressure of 1 MPa. The combustion temperature of the reaction was controlled using commercial sialon powder of z = 1 as a diluent. The single-phase (β-SiAlON (z = 2) was obtained by using the product itself as a diluent after 5 times repeats of combustion. Highly-dense β-SiAlON (z = 2) compact was prepared by SPS and showed good hardness of 14.8 GPa and fracture toughness of 4.4 $MPam^{1/2}$.

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