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Combustion synthesis of single-phase β-sialons ($z = 2$–4)

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Abstract

Single-phase β-sialon powders ($z = 2$–4) have been prepared with homogeneous compositions by the combustion synthesis. The raw materials (Si, Al and SiO_2) were combusted under N_2 pressure of 1 MPa. Without using a diluent, the reaction temperatures were very high (>2000 °C) and the combustion products contained Si and Al residues. With addition of commercial β-sialon ($z = 1$) as a diluent (up to 50 wt%), both the reaction temperatures and amount of residual Si and Al significantly decreased. The combustion reactions completed at 50 wt% dilution, and pure β-sialon phases were synthesized. When the combustion product itself is used instead of the commercial diluent, the phase content of desired z value increased with the repetition times until a single-phase powder is produced. The sinterability of the synthesized powders was then tested using 5 wt% Y_2O_3 as a sintering aid by the spark plasma sintering (SPS).

Keywords: β-Sialon; z value; Combustion synthesis; Sintering

1. Introduction

Combustion synthesis (CS), or self-propagating high-temperature synthesis (SHS), is a unique process in which the raw materials could be converted to products using the strong exothermicity of the reaction except a small amount used to initiate the reaction at the beginning. High conversion rates can be attained by a careful selection of the combustion parameters such as the charge composition, nitrogen pressure, amount and type of diluent.

Silicon nitride and sialons as its derivatives are attractive nonoxide ceramics for many engineering applications, due to the excellent mechanical properties including high strength, thermal shock, and wear resistance with good chemical inertness.[1] β-Sialon ceramics are isostructural substitutional solid solutions of Al and O for Si and N, respectively in the parent hexagonal β-Si_3N_4 phase. The composition is expressed by the formula $Si_{6-z}Al_zO_zN_{8-z}$, where z represents the number of Al–O pairs replacing Si–N pairs in β-Si_3N_4 and can be varied in the range of $0 < z < 4.2$.[2] However, β-sialon structure provides a good combination in properties of both silicon nitride (high strength, hardness, fracture toughness, and low thermal expansion) and aluminum oxide (corrosion resistance, chemically inert, high-temperature oxidation resistance).[2,3] It is considered as an engineering material 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]

Sialon components are usually fabricated through reaction sintering, meanwhile the sialon powders are mostly produced by the carbothermal reduction process.[6,7] The CS method is proved to be a potential alternative to produce β-sialon powders at low energy consumption in a short reaction period. The previous reports showed that β-sialon powders can be successfully prepared by CS,[8–11] nevertheless, little effort has been devoted on the composition control of produced β-sialon powder which can be attributed to the complexity of the formation reactions in such a multicomponent system especially when z value increases. Recently, the production of pure β-sialon powder with precise $z = 1$ by CS has been developed to a commercial phase.[12]

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In this study, the combustion synthesis of single-phases β-sialon powders with $z=2$–4 was investigated under a low nitrogen pressure. The combustion was controlled by using commercial sialon powders with $z=1$ as a diluent to reduce the maximum combustion temperature. In our previous study, the details of CS of a single-phase β-sialon with $z=2$ was explained.[13] Here, the effect of z value on the combustion temperature, products composition, and resultant powder morphology was addressed. Then, the sinterability of synthesized powders was tested by spark plasma sintering (SPS). The SPS is a powerful sintering technique which enables the fast densification of powders in a period of several minutes.[14–16]

2. Experimental procedure

Synthesis of β-sialon phases ($z=2$–4) can be expressed by the following equation:

$$(6-1.5z)\mathrm{Si}+z\mathrm{Al}+(0.5z)\mathrm{SiO_2}+(4-0.5z)\mathrm{N_2} = \beta\text{-}\mathrm{Si}_{(6-z)}\mathrm{Al}_z\mathrm{O}_z\mathrm{N}_{(8-z)} \quad (1)$$

The starting materials used were: silicon metal (99.5% purity, 3 μm in average particle size), silica (10 μm), aluminium metal (99.5%, 22 μm), and β-sialon powders ($z=1$, 7.5 μm, as a diluent) supplied by Ismanj®. The diluent was used to control the combustion temperature of the reaction and to avoid coagulation of the low-melting combustible elements (Si, Al) and the high-temperature dissociation of the products. The reactants (according to above equation) were thoroughly mixed with different ratios (up to 50 wt%) of diluent powder (β-sialon, $z=1$). A charge (about 50 g) was loosely packed into a cylindrical porous graphite crucible (42 mm $\phi \times 90$ mm H) to provide a good access of the N_2 gas to the raw materials. The reaction crucible was placed into an SHS autoclave (180 mm inner diameter, 300 mm inner height and volume of 7.6×10^2 cm^3) as shown in the schematic configuration of Fig. 1. The combustion was performed under the constant nitrogen gas pressure of 1 MPa (99.99% purity). The reaction was initiated from the bottom using 2 g ignition agent (Al/AlN pellet) placed beneath the charge, by passing a small current of 60 A × 20 V for 10 s through a carbon ribbon heater under the pellet. The temperature profile and the average combustion temperature, $T_{\max}$, of the reaction were recorded by using a W-5%Re/W-26%Re thermocouple placed in the middle of the reaction burden. After cooling to room temperature, the products were roughly crushed and screened through a 220 μm sieve. Single-phases β-sialon powders with the defined z value were obtained by using the product itself as a diluent instead of initially used $z=1$ powder and repeating this combustion cycle for a few times.

The combusted products were analyzed by the X-ray diffraction analysis (JEOL, JDX-3530, Japan). The z values of β-sialon phases were determined by calculating the lattice parameter a from the XRD peaks (3 1 0), (3 2 0), (4 1 0) and (3 3 0) of β-sialon phases, according to Ref. 2 using pure Si added as an internal standard. The morphology of products was observed by the field-emission scanning electron microscope (FE-SEM; ERA-8800, ELIONIX, Tokyo, Japan).

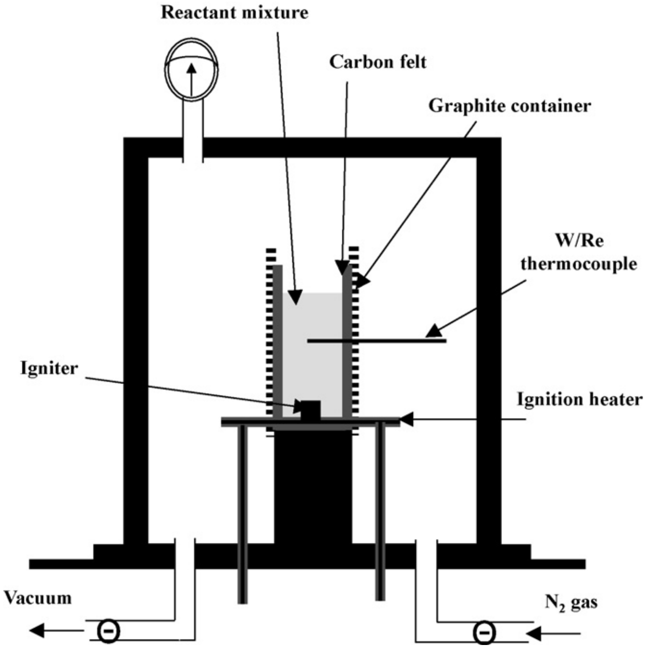

Fig. 1. A schematic diagram of combustion reactor.

The sinterability of the synthesized sialon powders was then tested by using the spark plasma sintering (SPS). The as-synthesized powders were crushed and screened using a 220 μm sieve and then wet-milled by planetary mill in 2-propanol medium using Al_2O_3 balls until an average particle (or agglomerate) size of about 0.5 μm (determined by a laser light scattering, model SALD-7000 Shimadzu Corporation Kyoto, Japan). The amount of alumina contaminated from the milling media was very small and not taken into account. A 5 wt% yttria powder was used as a sintering aid. The powder mixture was placed inside a graphite die with an inner diameter of 10 mm and then sintered using Dr. Sinter® Model 1050 SPS apparatus (Sumitomo Coal Mining Company, Ltd., Japan). The sintering was performed in a vacuum at 1600 °C for 5 min under 30 MPa pressure applied from the beginning to the end of the sintering. The heating and cooling rates were 100 °C/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 relative density of sintered pellets was determined in a deionized water by Archimedes method. The theoretical densities were calculated from the JCPDS diffraction data considering the amount of yttria added (theoretical density of yttria, β-sialons with $z=2$ and 3 were 5.03, 3.147 and 3.095 g cm^{-3}, respectively). Vickers hardness was measured on polished surfaces of dense specimens using a diamond indenter (Akashi MVK-G3 Hardness tester) with an indentation load of 1 kgf (9.81 N) for 15 s. The indentation fracture toughness, KIC, was determined from the Vickers indentations according to the method by Niihara et al. in Ref. 17. The microstructure of fractured surfaces of sintered samples was also observed by FE-SEM.

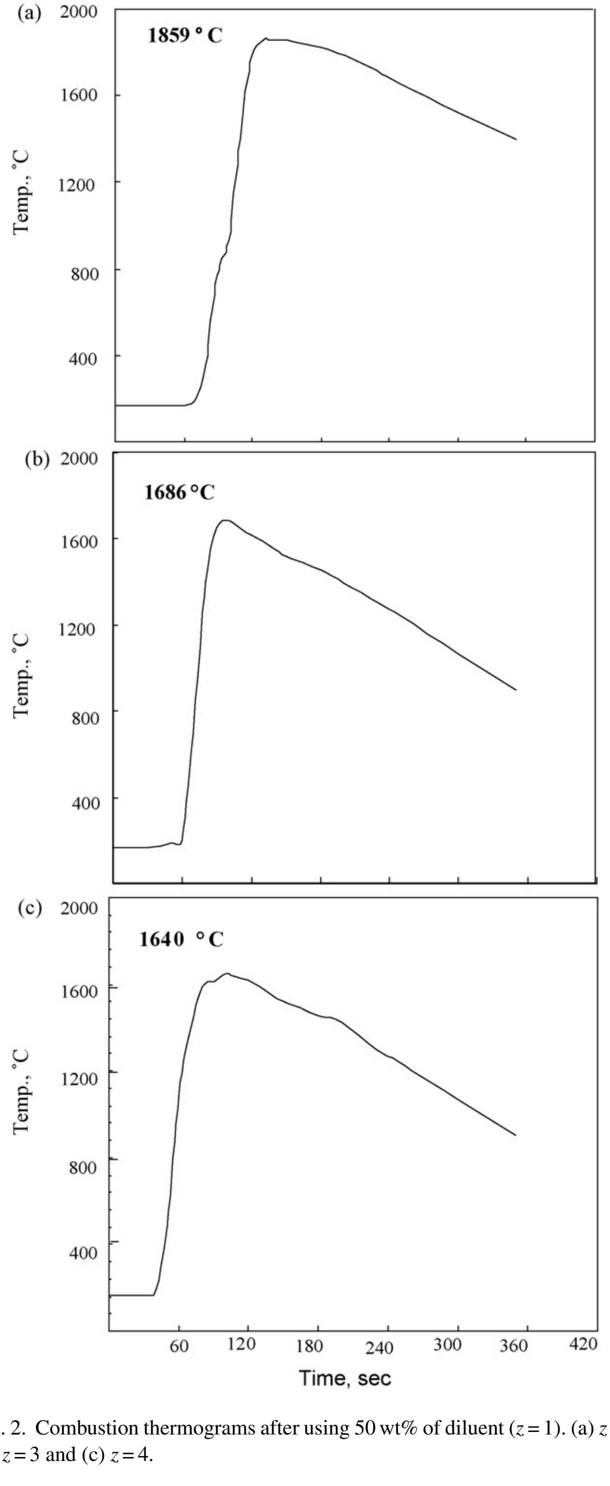

Fig. 2. Combustion thermograms after using 50 wt% of diluent ($z = 1$). (a) $z = 2$, (b) $z = 3$ and (c) $z = 4$.

3. Results and discussion

3.1. Controlling the reaction temperature and synthesis of Si free products

The combustion reaction temperatures without diluent additions were very high (>2000 °C) and the thermocouple melted. With the 50 wt% diluent addition, the combustion temperatures were significantly reduced to about 1859, 1686 and 1640 °C for $z = 2$–4, respectively, as shown in Fig. 2. It can be seen that as the reactions temperature began to go up to its maximum quickly and the reaction completed within a few minutes which reflects the very fast feature of CS. The decrease in the maximum reaction temperature with increasing the z values is in close agreement with the decrease in the adiabatic temperature (theoretical combustion temperature calculated from thermodynamics data, T_{ad}) of the combustion reactions with increasing the z values as reported by Aoyagi et al.[18]

The effect of the diluent on the phase compositions of the combusted products at different z values is shown in corresponding XRD patterns given in Fig. 3. In case of $z = 2$, large amounts of residual Si appeared besides β-sialon phases when the diluent was not used. At higher z values (3 and 4), some Al and Si_3N_4 also appeared beside Si in the combusted products. The presence of Si and Al residues can be attributed to the melting and subsequent coagulation of the metals caused by the extremely high reaction temperature and the high reaction rate of the nitridation combustion reactions, which retards the good access of reactant N_2 gas and interrupt the completion of their nitridation. It can be seen that the addition of the diluent was necessary to reduce the Si and Al residues and improve the reaction conversion. For all z values, the 50 wt% diluent addition was sufficient to produce pure sialon phases. However, the diluent phase ($z = 1$) still exists along with newly synthesized z value products as is clear in Fig. 3. It indicates that the diluent is not involved in the

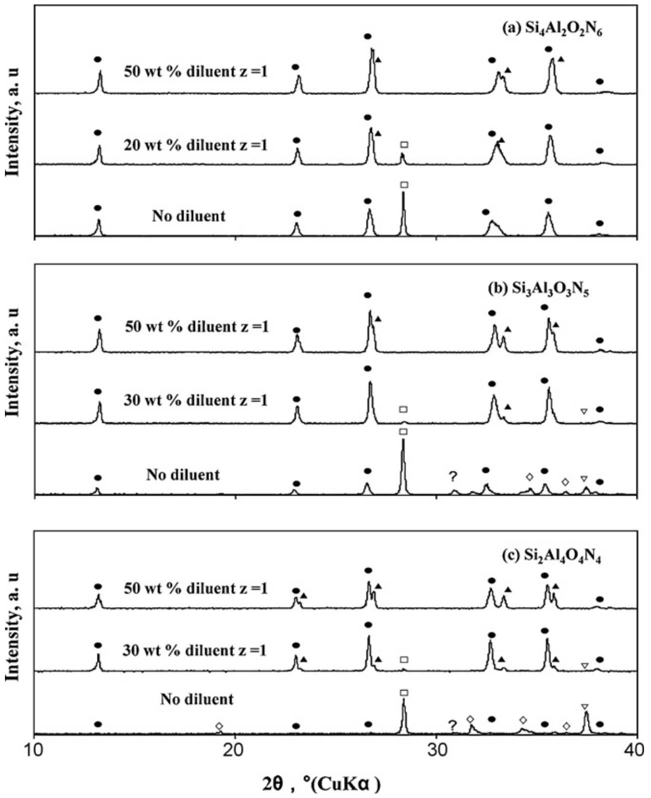

Fig. 3. XRD patterns of synthesized sialon powders at various diluents ($z = 1$) amounts. (a) β-sialon $z = 2$, (b) β-sialon $z = 3$ and (c) β-sialon $z = 4$. ((●) $Si_{(6-z)}Al_zO_zN_{(8-z)}$, (▲) Si_5AlON_7, (□) Si, (◊) Si_3N_4 and (▽)Al).

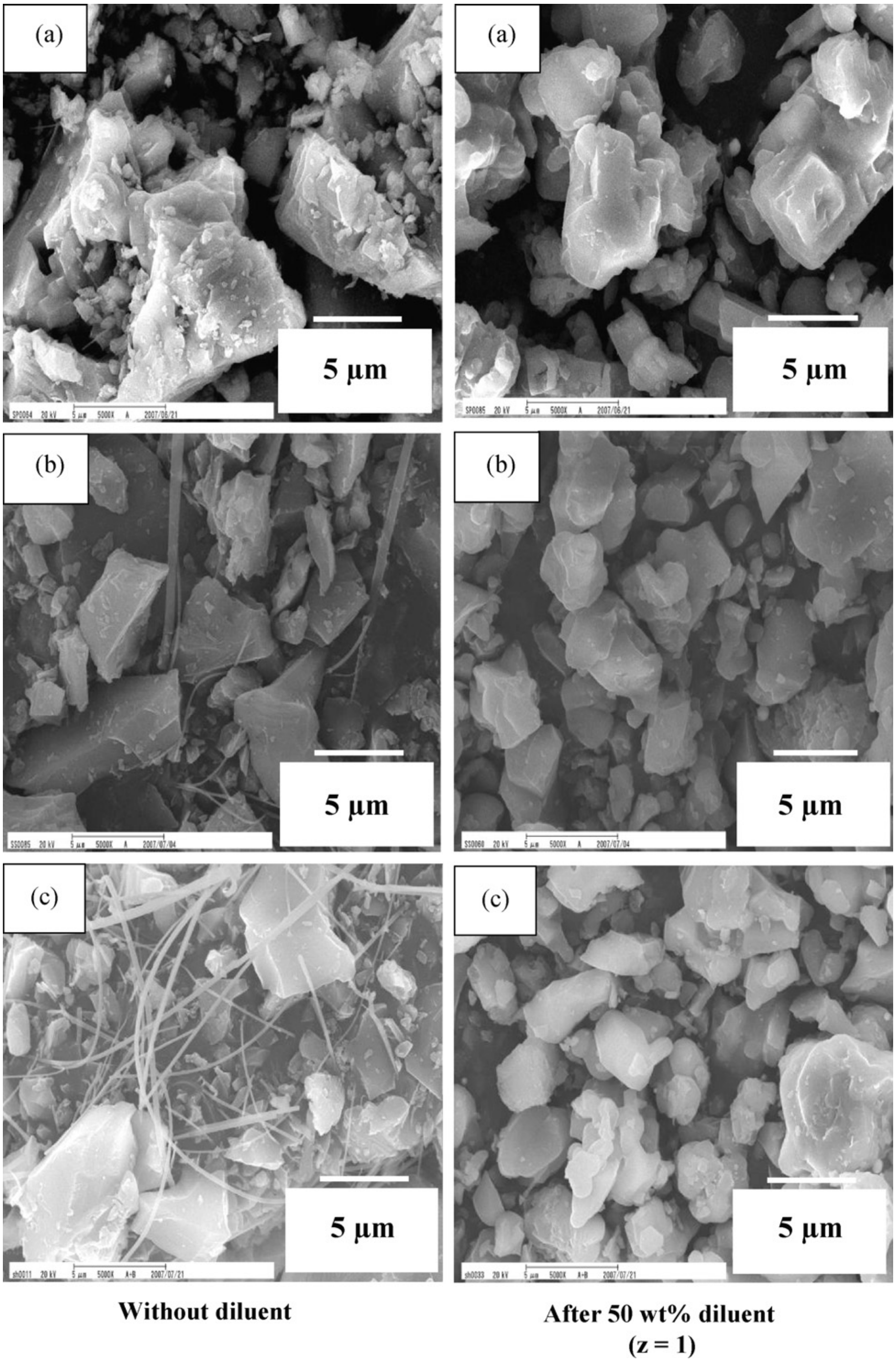

Fig. 4. FE-SEM micrographs of as-synthesized β-sialon products without diluent addition and after addition 50 wt% of diluent ($z = 1$). (a) $z = 2$, (b) $z = 3$ and (c) $z = 4$.

synthesis reaction of desired z value products. It mostly plays a passive role during the combustion and mainly reduces the combustion temperature. The product consequently consists of two phases (diluent and the synthesized phases) and not one phase with a lower z value.

One of the advantages in this study is the use of commercial β-sialon powder with $z = 1$ as a diluent which could significantly reduce the combustion temperature and result in the synthesis of pure β-sialon powders compared to other pervious reports.[10,18–20]

Fig. 4 gives the morphology of combusted products with $z = 2$–4 both without diluent and after using 50 wt% diluent. Without a diluent addition, the particles morphology was inhomogeneous with large agglomerations and the extent of inhomogeneity increased with the z value favoring the formation of long rods and fibers. This can be attributed to the very high combustion temperature and the increase of volatile species as Al with z value. With 50 wt% diluent addition, the morphologies of all combusted products were clearly uniform showing agglomerates of well-crystallized sialon particles. It can be seen

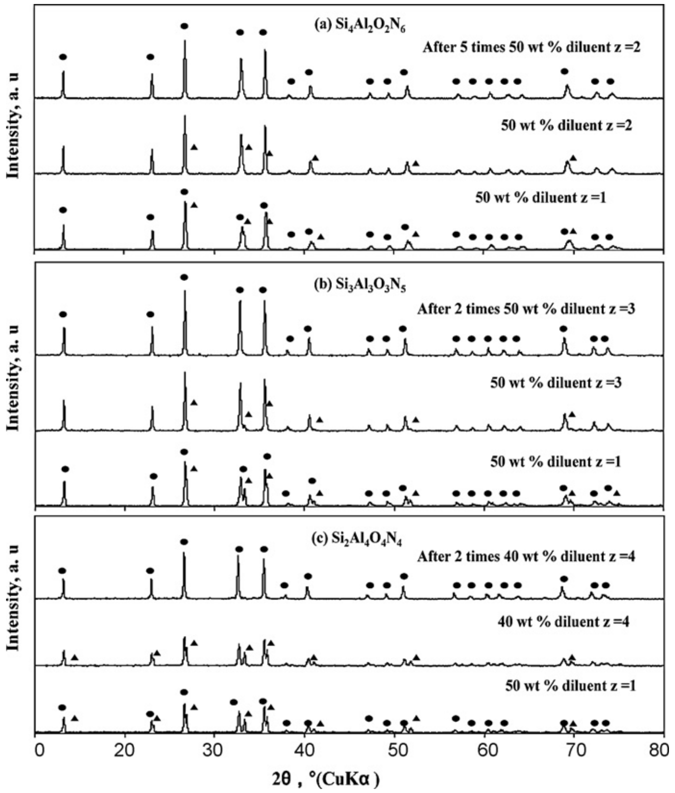

Fig. 5. XRD patterns of synthesized single sialon phases after using the products as diluents. (a) β-sialon $z=2$, (b) β-sialon $z=3$ and (c) β-sialon $z=4$. ((●) $Si_{(6-z)}Al_zO_zN_{(8-z)}$ and (▲) Si_5AlON_7).

that with the increase of z value, the average size of agglomerates decreases which is in agreement with the reduction trend in the combustion temperature with the z value.

3.2. Synthesis of β-sialon single phases

Pure single-phase β-sialon powders were further obtained by using the combusted products themselves as diluents instead of the initial diluent powder of $z=1$ and repeating this cycle for few times. Fig. 5 gives the XRD patterns of final products and shows the absence of $z=1$ diluent phase. It worth to be mentioned that for $z=2$ and 3 the product addition as a diluent in each subsequent combustion was 50 wt%, while for $z=4$ the optimum amount was only 40 wt%. Above 40 wt% addition, the combustion reaction did not propagate. In case of $z=2$, the single-phase powder could be obtained after 5 times combustion repetitions. In case of $z=3$ and 4, the single phases of $z=3$ and 4 were easily noticed after 2 repetitions.

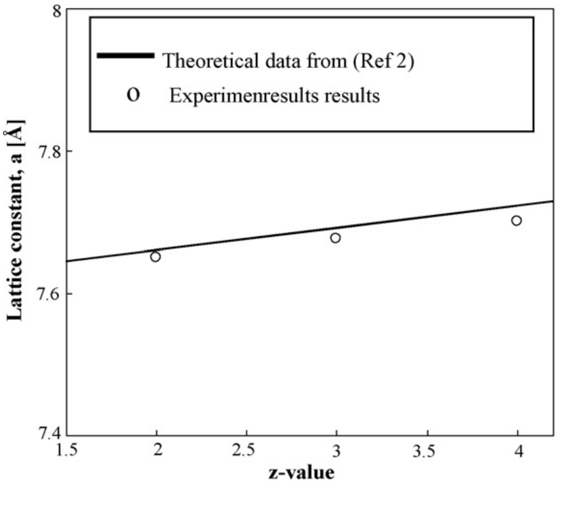

Fig. 6. Lattice constant, a, of the combustion-synthesized β-sialons according to its z value.

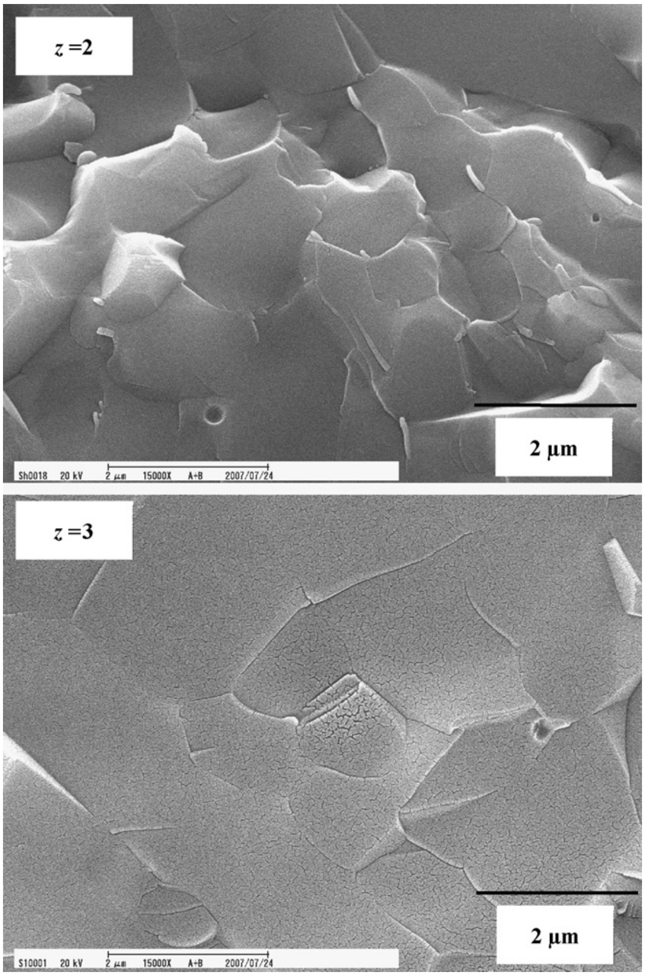

Fig. 7. Fracture surfaces of β-sialons SPS sintered at 1600 °C for 5 min.

Fig. 6 shows a good agreement between the experimental results of the lattice parameter a and z values (as determined from XRD analyses) and the theoretical data reported in Ref. 2.

3.3. Spark plasma sintering of combustion synthesized β-sialon powders

The sinterability of the final single-phases β-sialon powders with $z=2$ and 3 were tested in a vacuum at 1600 °C for 5 min under 30 MPa pressure by the SPS method. Table 1 summarizes the results of relative density, Vickers hardness, and fracture toughness of the sintered sialon compacts. It shows that the synthesized sialon powders were densified successfully to about 97% of theoretical density. The Vickers hardness

Table 1
Properties of sintered samples.

Properties	$z = 2$	$z = 3$
Relative density (%)	97.3	97.5
Vickers hardness (GPa)	14.8	17.9
Fracture toughness (MPa m$^{1/2}$)	4.4	4.8

was about 14.8 GPa and the fracture toughness was relatively good as 4.5 MPa m$^{1/2}$, which is in good agreement with the results reported in the literature through different processing methods.[21–24] The microstructures of fractured surface of dense samples are shown in Fig. 7. There are very low porosity contents and uniform microstructure consisting of small aggregates (of approximately 3 μm) of ultrafine sialon grains. Both transgranular and intergranular fractures modes could be observed. The phase composition of sintered samples was analyzed by XRD and showed no phase change due to the SPS sintering.

4. Conclusion

Pure β-sialon powders with the controlled z values ($z = 2$–4) were successfully prepared from stoichiometric mixtures of constituent elements under a nitrogen pressure of 1 MPa by the CS method. The combustion temperatures of nitridation reactions were controlled by using a commercial sialon powder of $z = 1$ as a diluent. Single-phase β-sialon powders were obtained by using the products as diluents and repeating the combustion for few times. The sinterability of the synthesized powders was evaluated by the SPS and dense β-sialon compacts were produced with relatively good values of hardness and fracture toughness.

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References

1. Frank RL. Silicon nitride and related materials. *J Am Ceram Soc* 2000;**83**(2):245–65.
2. Jack KH. Sialons and related nitrogen ceramics – review. *J Mater Sci* 1976;**11**:1135–58.
3. Ekström T, Nygren M. SiAlON ceramics. *J Am Ceram Soc* 1992;**75**(2):259–76.
4. Benco L, Hafner J, Lenčéš Z, Šajgalík P. Electronic structure and bulk properties of β-SiAlONs. *J Am Ceram Soc* 2003;**86**(7):1162–7.
5. Yang J-F, Beppu Y, Zhang G-J, Ohji T, Kanzaki S. Synthesis and properties of porous single-phase β-SiAlON ceramics. *J Am Ceram Soc* 2002;**85**(7):1879–81.
6. Alcala MD, Criado JM, Gotor FJ, Real C. β-SiALON obtained from carbothermal reduction of kaolinite employing sample controlled reaction temperature (SCRT). *J Mater Sci* 2006;**41**:1933–8.
7. Liu X-J, Sun XW, Zhang JJ, Pu XP, Ge QM, Huang LP. Fabrication of β-SiAlON powder from kaolin. *Mater Res Bull* 2003;**38**:1939–48.
8. Zeng J, Miyamoto Y, Yamada O. Combustion synthesis of sialon powders ($Si_{6-z}Al_zO_zN_{8-z}$ $z = 0.3, 0.6$). *J Am Ceram Soc* 1990;**73**(12):3700–2.
9. Miyamoto Y, Kanehira S, Radwan M. Recycling of industrial and natural wastes to Sialons. *Refract Appl News* 2004;**7**(1):14–7.
10. Aoyagi K, Hiraki T, Sivakumar R, Watanabe T, Akiyama T. Mechanically activated combustion synthesis of β-$Si_{6-z}Al_zO_zN_{8-z}$ ($z = 1$–4). *J Am Ceram Soc* 2007;**90**(2):626–8.
11. Miyamoto Y, Li Z, Tanihata K. Recycling processes of Si waste to advanced ceramics using SHS reaction. *Ann Chim France* 1995;**20**:197–203.
12. http://www.ismanj.com/index.html.
13. Shahien M, Radwan M, Kirihara S, Miyamoto Y, Sakurai T. Combustion synthesis and sintering of β-sialon ceramics ($z = 2$). *J Soc Mater Sci Jpn* 2008;**57**(12):1248–52.
14. Xu X, Nishimura T, Hirosaki N, Xie R-J, Yamamoto Y, Tanaka H. Fabrication of β-sialon nanoceramics by high-energy mechanical milling and spark plasma sintering. *Nanotechnology* 2005;**16**:1569–73.
15. Shen Z, Nygren M. Kinetic aspects of superfast consolidation of silicon nitride based ceramics by spark plasma sintering. *J Mater Chem* 2001;**11**:204–7.
16. Xu X, Nishimura T, Hirosaki N, Xie R-J, Zhu Y, Yamamoto Y, et al. New strategies for preparing nanosized silicon nitride ceramics. *J Am Ceram Soc* 2005;**88**(4):934–7.
17. Niihara K, Morena R, Hasselman DPH. Evaluation of K_{Ic} of brittle solids by the indentation method with low crack-to-indent ratios. *J Mater Sci Lett* 1982;**1**:13–6.
18. Aoyagi K, Hiraki T, Sivakumar R, Watanabe T, Akiyama T. A new route to synthesize β-$Si_{6-z}Al_zO_zN_{8-z}$ powders. *J Alloys Compd* 2007;**441**:236–40.
19. Sivakumar R, Aoyagi K, Akiyama T. Effect of mechanically activated raw materials on β-sialon formation by combustion synthesis. *J Mater Res* 2007;**22**(10):2863–7.
20. Lis J, Majorowski S, Puszynski JA, Hlavacek V. Dense β- and α/β-SiAlON materials by pressureless sintering of combustion-synthesized powders. *J Am Bull* 1991;**70**(10):1658–64.
21. Ekström T, Olsson P-O. β-sialon ceramics prepared at 1700 °C by hot isostatic pressing. *J Am Ceram Soc* 1989;**72**(9):1722–4.
22. Kawano S, Takahashi J, Shimada S. The preparation and spark plasma sintering of silcon nitride-based materials coated with nano-sized TiN. *J Eur Ceram Soc* 2004;**24**:309–12.
23. Kudyba-Jansen AA, Hintzen HT, Metselaar R. The influence of green processing on the sintering and mechanical properties of β-Sialon. *J Eur Ceram Soc* 2001;**21**:2153–60.
24. Hirano S-I, Hayashi T, Nakashima T. Sintering of β-Sialon with 5 mol% Y_2O_3–ZrO_2 additives. *J Mater Sci* 1989;**24**:3712–6.