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Fabrication of dense β-SiAlON by a combination of combustion synthesis (CS) and spark plasma sintering (SPS)

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Abstract

First, β-SiAlON (z = 1, 2, 3, and 4) powders were combustion-synthesized from well-mixed powders of Si, Al, and SiO_2 under a low nitrogen pressure of 1 MPa using β-SiAlON (calculated z = 1.14) as the diluent. Then, the synthesized powders were subjected to spark-plasma-sintering (SPS) in vacuum for 12 min under a stress of 50 MPa and a temperature of 1600 °C, without any sintering additives. X-ray diffraction (XRD) analysis revealed that a small amount of unreacted phase was found in the combustion-synthesized powders; however, pure β-SiAlON compacts were successfully obtained after SPS. The relative density of the products obtained by subjecting the combustion-synthesized powders to SPS was more than 99% of theoretical density.

Keywords: A. Silicides, various; C. Reaction synthesis; Sintering; F. Diffraction (electron, neutron and X-ray); Electron microscope, scanning.

1. Introduction

β-SiAlON is the solid solution of β-Si_3N_4 in which Si-N has been substituted with an equivalent amount of Al-O. β-SiAlON is most commonly described by the general formula β-$Si_{6-z}Al_zO_zN_{8-z}$, where z takes the values from 0 to ~4.2 [1,2]. Ever since it was discovered in the early 1970s [3,4], β-SiAlON has been actively developed. 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, superior chemical stability, and a conspicuous thermal-shock resistance. Consequently, they are being extensively used as high-temperature engineering ceramics in cutting tools and abrasive materials [5]. Recently, the use of Eu^{2+}-doped β-SiAlON phosphors for down-conversion luminescent materials in white-light-emitting diodes (LEDs) has been reported [6,7]. These observations indicate that β-SiAlON-based materials have a potential for use as functional materials in numerous fields.

Combustion synthesis (CS), also known as self-propagating high-temperature synthesis (SHS), has been attracting growing interest on account of its capacity for energy conservation, short reaction time, and an ability to afford high purity products [8]. It has been proven to be an efficient technique for the synthesis of a variety of materials such as nitrides [9,10], hydrides [11], oxides [12,13], and many intermetallics [14–17]. The CS of β-SiAlON powders is usually performed in a high-pressure N_2 atmosphere under a pressure ranging from 2 to several tens of MPa [18–21]. However, as part of our previous research [22–24], β-SiAlON powders (z = 1 to 4) were successfully combustion synthesized for the first time without the addition of any diluent at the relatively low nitrogen pressure of 1 MPa. In addition, the effect of selecting different raw material oxides on the CS of β-SiAlON was investigated. The results of the investigation indicated that SiO_2 was a better source of oxygen under low pressure, than Al_2O_3, for the production of β-SiAlON powders with z values ranging from 1 to 4. However, the purity of the β-SiAlON powders obtained by using SiO_2, was low due to the existence of an unreacted Si residue. The presence of the unreacted Si was attributed to the melting and subsequent conglomeration caused by the extremely high reaction temperature and the high reaction rate of the combustion synthesis. The use of diluents such as α/β-Si_3N_4 or β-SiAlON would help lower the combustion temperature as well as decrease the velocity of the combustion front. This would also improve the conversion rate of reactants and increase the purity of the β-SiAlON products.

Sintering methods such as pressureless sintering [19], hot isostatic pressing [2], and spark plasma sintering (SPS) [25] have been previously used to produce dense β-SiAlON. Among these aforementioned methods, SPS is regarded as a rapid and effective densification technique for ceramics as well as other hard materials.

However, to the best of our knowledge, SPS of combustion-synthesized β-SiAlON powders without sintering additives has not been previously reported, despite its genuine significance from an engineering point of view. Therefore, the purpose of this study is to synthesize high-purity β-SiAlON (z = 1 to 4) powders by combustion synthesis at a low nitrogen pressure using β-SiAlON as a diluent, and to densify the combustion-synthesized β-SiAlON powders through the SPS technique. Our eventual aim is to obtain dense β-SiAlON (z = 1 to 4) products by SPS of combustion-synthesized powders.

2. Experimental procedure

2.1 Synthesis of β-SiAlON powder

In this study, commercially available powders of Si (Soekawa Chemicals Co., Ltd., Tokyo, Japan; 98% purity; 1–2 μm); Al (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan; 99.9% purity, 3 μm); SiO_2 (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan; 99.9% purity, 0.8 μm) were used as starting materials. β-SiAlON (calculated $z = 1.14$) (ISMANJ Corporation, Kawasaki, Japan; 0.5 μm) was added as the diluent. The chemical reaction for the synthesis of β-SiAlON from the abovementioned starting materials can be represented as follows:

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

where, $z = 0–4.2$. The ratio in which the starting materials were used was precisely adjusted to compensate for the lack of Al and O in the diluent used for the synthesis of β-SiAlON ($z = 2–4$). The schemata for the step-wise synthesis is shown in Fig.1. The mixture of the starting materials was first subjected to dry planetary milling for 18 min to enhance the activity of the powder; subsequently, the powder was subjected to CS at a low nitrogen pressure of 1 MPa (nitrogen purity: 99.999%). The conditions necessary for planetary milling and the equipment required for CS have been described in detail elsewhere [22,23].

The starting powder mixture, after milling, was loosely charged into a cylindrical graphite crucible (diameter: 40 mm; length: 65 mm) with several vents both on the surface and bottom for infiltrating nitrogen into all areas of the raw materials. The raw materials were usually processed in batches of ~30 g. The combustion reaction was ignited by passing a current of 60 A at 35 V for approximately 10 s through a carbon foil, which helped burn a small quantity of the Al powder placed on top of the raw material mixture.

2.2 Sintering

Due to the low purity of the combustion-synthesized β-SiAlON powder ($z = 4$), only those β-SiAlON powders with $z = 1$, 2, and 3 were utilized for the sintering experiments. The combustion-synthesized powders were first subjected to planetary ball milling for 60 min to eliminate the agglomerates formed during the CS process, and to enhance the sinterability of the powders. Then, the milled powder was compacted into a carbon die (inner diameter: 10 mm) and sintered using a spark plasma sintering system (Sumitomo Coal Mining Co. Ltd., Tokyo, Japan) under vacuum conditions of lower than 4 Pa at a compressive stress of 50 MPa. A piece of carbon foil (thickness: 0.2 mm) was put between the powder and carbon die to avoid the reaction of them during sintering at high temperature, as well as to get the sample out of the carbon die easily after sintering. 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 12 min before the power was turned off. Temperature monitoring during sintering between 600 °C and 1600 °C was carried out using an optical pyrometer, focused on a hole on the surface of the carbon die.

2.3 Characterization

The phases of combustion-synthesized powders and the spark-plasma-sintered fractured surfaces were analyzed using an X-ray diffraction (XRD) analyzer (Mini Flex, Rigaku Corporation, Tokyo, Japan). The morphology of the reaction products was examined by scanning electron microscopy (SEM) (FE-SEM JSM-7400F, JEOL, Tokyo, Japan). The lattice parameters of the hexagonal β-SiAlON phase were calculated from the XRD peaks of the products by employing the least-squares method. The lattice parameter a was calculated from (100), (110), (200), (210), (300), and (310) peaks of β-SiAlON, and the lattice parameter c was calculated from the (101) peak using the calculated a value. The bulk density of the spark-plasma-sintered specimens was measured according to the Archimedean principle, using distilled water as the medium.

3. Results and discussion

Powders of overall compositions β-$Si_{6–z}Al_zO_zN_{8–z}$, z = 1 to 4, prepared from carefully balanced powder mixtures with different mass ratios of the diluent added, were combustion-synthesized under a nitrogen pressure of 1 MPa.

The optimum mass% of the diluent and the corresponding β-SiAlON content with z = 1 to 4 are listed in Table 1. The relative β-SiAlON content was approximately estimated from the β-SiAlON/(β-SiAlON + Si) ratio on the basis of the heights of the (200) and (101) diffraction peaks of β-SiAlON and the (111) and (220) diffraction peaks of Si. In our experiment, we found that the CS reactions did not propagate when the quantity of diluent exceeded the optimum quantity. Munir [8] had published the following empirical rule for the CS reaction: The CS reaction can self-propagate only if the adiabatic temperature (T_{ad}) ≥ 1800 K. In addition, Holt [26] had validated T_{ad} would decrease gradually with an increase in diluent additives. Owing to lack of thermodynamic data on β-SiAlON, we could not calculate the exact value of T_{ad} in our experiment. However, we speculated that, since in our experiment, the addition of excessive diluent lowered T_{ad} to less than 1800 K, the CS reaction could not self-sustain, and thus was terminated.

Fig. 2 shows the XRD patterns of the combustion-synthesized products with optimum diluent additives for z = 1 to 4. While trace amounts of unreacted Si could be detected in all of the products with different z values, in the product with z = 4, the presence of Al_2O_3 was detected. According to Dickon H.L. Ng et al. [27], Si_3N_4, AlN, and Al_2O_3 are the intermediate solid phases that are simultaneously consumed during the formation of β-SiAlON. Among these, the formation of Si_3N_4 would be most important, because it can act as a crystal seed for the formation of β-SiAlON. From equation (1), we can see that an increase in the *z* value of β-SiAlON translates to an increase in the Al and SiO_2 contents of the raw materials, and a decrease in the Si content. Thus, we can predict that for higher *z* values, the formation of Si_3N_4 involves a two-step process. First, Si is deoxidized from SiO_2 by Al, and then, the deoxidized Si is made to react with N_2. The CS process is very rapid; hence, it would culminate before some of this Si can react with N_2 to form Si_3N_4. Thus, at higher *z* values, both Si, and Al_2O_3, will be left behind as residues in the product.

Fig. 3 displays the SEM images of the combustion synthesized β-SiAlON ($z = 1{\sim}4$) powders. From this figure, it can be seen there are some different shapes of β-SiAlON crystals, rod-like morphology, tiny particles, and some whiskers. Because the combustion synthesis process normally completes in only several or tens of seconds, it is difficult to perform in situ observations. The growth of rod-like crystals and whiskers has been reported in a VLS (vapor–liquid–solid) mechanism [28].

In our CSed products, the typical rod-like morphology of β-SiAlON can be clearly seen when $z = 1$, and with increasing *z* value the thin and long rod-like crystals seem getting thicker and shorter, and simultaneously the size gets larger, which should be attributed to the expansion of crystal lattice due to more Si–N bonds replaced by Al–O bonds at higher *z* values. We can also see from this figure, the whiskers increased with increasing *z* value, which should be ascribed when to synthesize β-SiAlON with higher *z* values, more Al powders are needed in the raw materials. As we know, combustion synthesis of β-SiAlON is an exothermic reaction with high temperature, during combustion process of β-SiAlON with higher *z* values, more amounts of Al and Si evaporate. Meanwhile, SiO_2 decomposes and evaporates in the form of SiO, or is deoxidized by Al. The exist vapor of Si, Al, SiO/AlO, etc, and N_2 give an attribute for the growth of whiskers.

The shrinkage curves of the combustion-synthesized powders during the SPS process are plotted in Fig. 4. In the initial stage, shrinkage rate slightly decreased owing to the thermal expansion of the samples and the carbon die and punches, while a dramatic shrinkage was observed from 1350 °C, 1290 °C, and 1260 °C for the β-SiAlON powders with $z = 1$, 2, and 3, respectively. Near-complete densification was achieved at 1600 °C for $z = 1$ and at 1560 °C for $z = 2$ and 3 within 5 min. The dramatic shrinkage presented at around 1300 °C for the specimens should be attributed to the plastic deformation of β-SiAlON crystals. Meanwhile, the residual Si (theoretical melting point: 1414 °C) started to melt and partially evaporate due to high stress pressure (50 MPa) and the effective ball milling resulting in very small size particles before the powders being submitted to SPS. The shrinkage starting temperature and densification sintering temperature decreased with increasing z value could be ascribed to the decreasing of the melting point of β-SiAlON and the increasing amount of Si residual in the as-sintered powders.

From the XRD patterns of plasma-sintered β-SiAlON samples shown in Fig. 5, it can be seen that the Si peaks disappeared and only peaks due to β-SiAlON are observed. One possible reason for the disappearance of Si after SPS is the vaporization or dissolution of Si into the solid during the high-temperature and high-pressure sintering process. Further detailed investigation is required to elucidate the non-existence of Si after sintering.

Fig. 6 shows the SEM images of fracture surfaces of the spark-plasma-sintered β-SiAlON ($z = 1$, 2, and 3). From the figure we can see the SPSed products were dense solid and the grain size increased obviously with increasing z value.

The characteristics of the spark-plasma-sintered β-SiAlON products are summarized in Table 2. Pure β-SiAlONs were obtained through SPS, though the combustion-synthesized powders were not pure β-SiAlON products. The bulk density was measured by the Archimedes principle, while theoretical density values were obtained from literature [29]. The relative densities of the spark-plasma-sintereded β-SiAlON with $z = 1$ to 3 were more than 99% of the corresponding theoretical density.

Table 3 lists the lattice parameters and the calculated z values of β-SiAlON before and after SPS. Ekstrom [2] studied the lattice parameters of β-SiAlON as a function of composition and proposed the following equations:

$$a = 0.7603 + 0.00296z \text{ (nm)} \tag{2}$$

$$c = 0.2907 + 0.00255z \text{ (nm)} \tag{3}$$

In our study, the lattice parameters a and c were calculated from the XRD data while z was calculated by using the lattice parameter a. Evidently, the calculated z values were in agreement with the expected z values in the raw mixture, except for the product with $z = 4$. Unfortunately, the z value did not increase to 4 even after the combustion-synthesized β-SiAlON with $z = 3$ was used as a diluent to synthesize β-SiAlON with $z = 4$. From these observations, it could be inferred that the stoichiometic range of combustion-synthesized β-SiAlON would become narrow when the nitrogen pressure is decreased. In other words, β-SiAlON with higher z values cannot be combustion synthesized under low nitrogen pressures. The *z* values calculated after SPS showed a slight variation when compared to the previous values. This could probably be attributed to the dissolution of unreacted Si into the solid and the rearrangement of the elements during sintering. Moreover, the *z* value of the diluent β-SiAlON (calculated z = 1.14) has also been confirmed to affect the final *z* values of spark-plasma-sintered β-SiAlON.

4. Conclusions

From this study, the following conclusions could be drawn:

(i) β-SiAlON (z = 1, 2, and 3) were combustion-synthesized with β-SiAlON (calculated z = 1.14) as a diluent at a low N_2 pressure of 1 MPa, and a purity of more than 86% was achieved. However, the purity of the combustion-synthesized powder with z = 4 was only 76%, and the calculated z value was only 3.34.

(ii) Pure and dense β-SiAlON (z = 1, 2, and 3) were obtained through SPS of CSed powder, carried out under a stress of 50 MPa at 1600 °C for 12 min without any sintering additives.

(iii) β-SiAlON products with relative densities greater than 99% of the theoretical density were obtained after SPS.

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Figure captions

Fig. 1. Flow chart of the experimental procedure for synthesizing β-$Si_{6-z}Al_zO_zN_{8-z}$ (z = 1, 2, 3, 4).

Fig. 2. XRD patterns of combustion-synthesized β-SiAlON powders with β-SiAlON (calculated *z* = 1.14) as diluent [Z1: *z* = 1 (45 mass% diluent); Z2: *z* = 2 (40 mass% diluent); Z3: *z* = 3 (35 mass% diluent); Z4: *z* = 4 (30 mass% diluent)].

Fig. 3. SEM images of combustion-synthesized β-SiAlON powders (a) Z1 (b) Z2 (c) Z3 (d) Z4.

Fig. 4. Shrinkage curves of combustion-synthesized β-SiAlON powders spark-plasma-sintered at 1600 °C for 12 min under a stress of 50 MPa.

Fig. 5. XRD patterns of spark-plasma-sintered β-SiAlON [S1: *z* = 1; S2: *z* = 2; S3: *z* = 3].

Fig. 6. SEM images of fracture surfaces of the spark-plasma-sintered β-SiAlON (a) S1 (b) S2 (c) S3.

Table captions

Table 1

Characterization of combustion-synthesized β-SiAlON obtained using β-SiAlON (calculated $z = 1.14$) as the diluent under a N_2 pressure of 1 MPa.

Table 2

Characteristics of spark-plasma-sintered β-SiAlON at 1600 °C for 12 min under a stress of 50 MPa.

Table 3

The lattice parameters and calculated z values of β-SiAlON before and after spark plasma sintering.

Table 1

Aimed *z* value	Optimum diluent (mass%)	Phase composition from XRD	β-SiAlON content (mass%)
1	45	β-SiAlON, Si	90
2	40	β-SiAlON, Si	86
3	35	β-SiAlON, Si	86
4	30	β-SiAlON, Si, Al_2O_3	76

Table 2

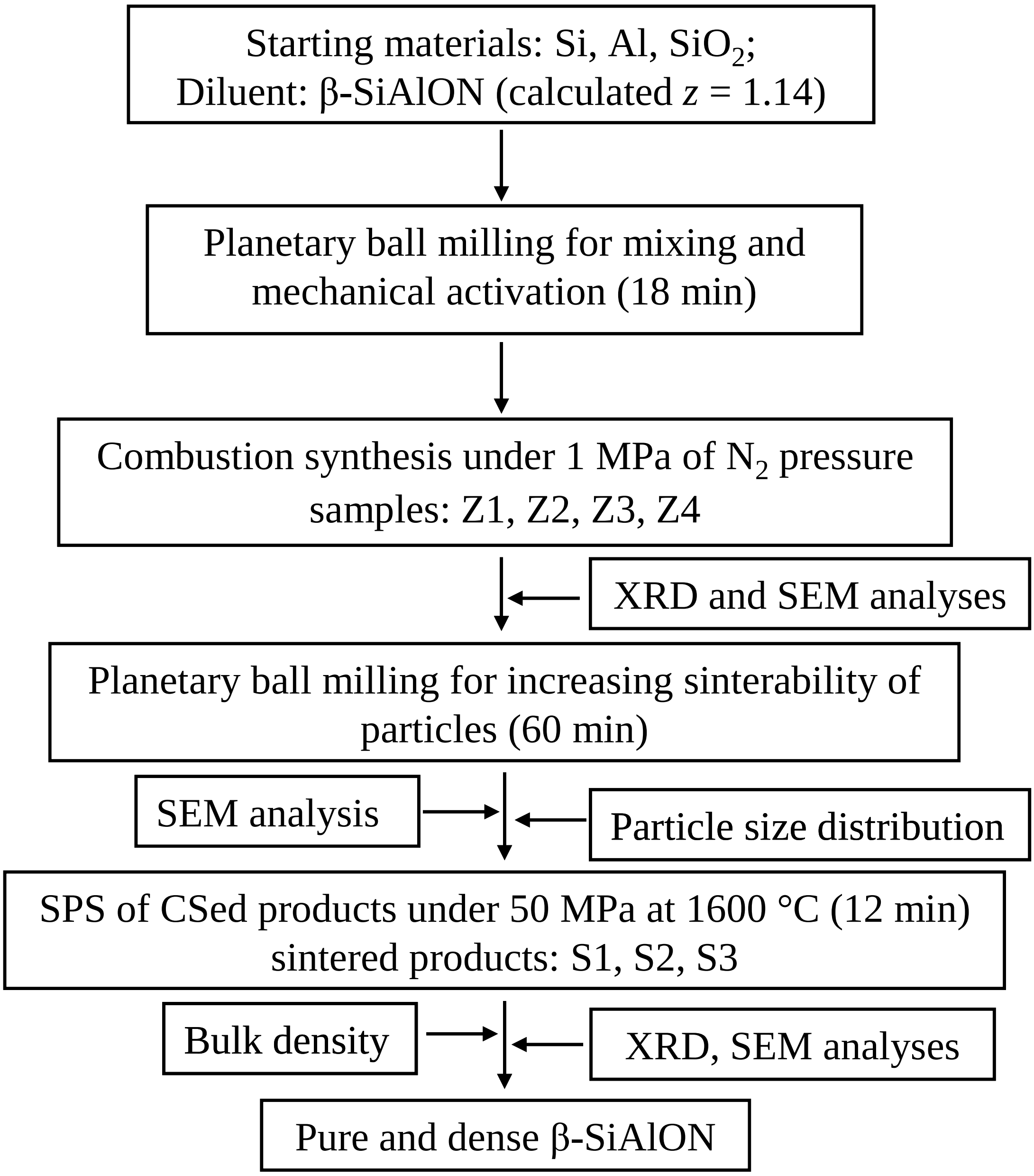
Aimed z value	Phase composition from XRD	Bulk density (g/cm^3)	Theoretical density* (g/cm^3)	Relative density (%)
1	β-SiAlON	3.146	3.168	99.3
2	β-SiAlON	3.113	3.122	99.7
3	β-SiAlON	3.067	3.082	99.5

* See Ref [29].

Table 3

Aimed z value	Before SPS			After SPS		
	Lattice parameter (Å)		Calculated	Lattice parameter (Å)		Calculated
	a	c	z*	a	c	z*
1	7.6355	2.9201	1.10	7.6373	2.9099	1.14
2	7.6628	2.9384	2.02	7.6617	2.9303	1.98
3	7.6916	2.9673	2.99	7.6889	2.9759	2.90
4	7.7021	2.9939	3.34	-	-	-

* The value was calculated from lattice parameter *a* according to Ref [2].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Diluent: β-SiAlON (calculated $z = 1.14$)
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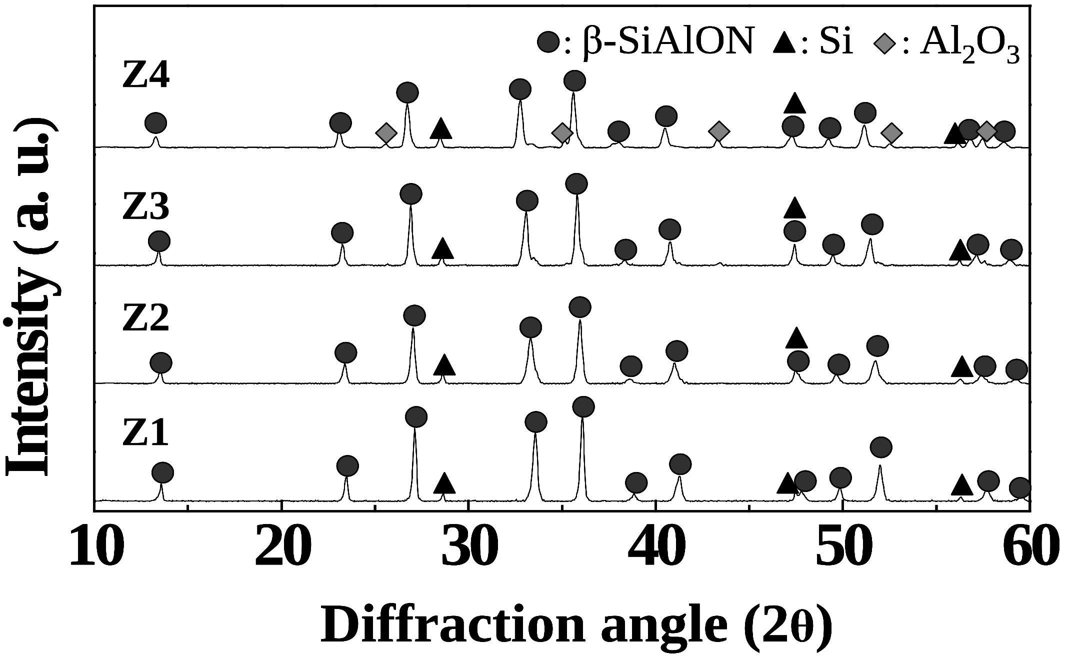
XRD and SEM analyses
Planetary ball milling for increasing sinterability of particles (60 min)
SEM analysis
Particle size distribution
SPS of CSed products under 50 MPa at 1600 °C (12 min) sintered products: S1, S2, S3
Bulk density
XRD, SEM analyses
Pure and dense β-SiAlON

Fig. 1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Z3
Z2
Z1
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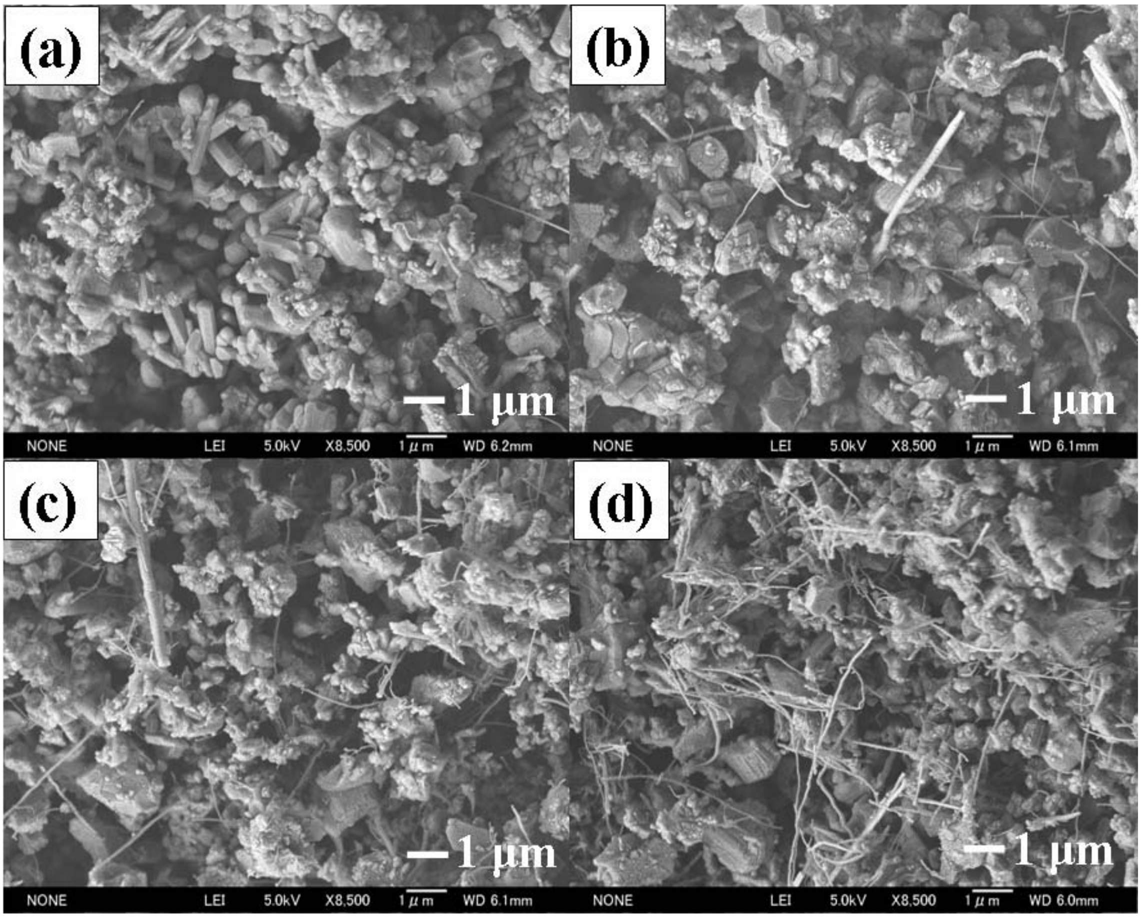
Diffraction angle (2θ)

Fig. 2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(b)
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(c)
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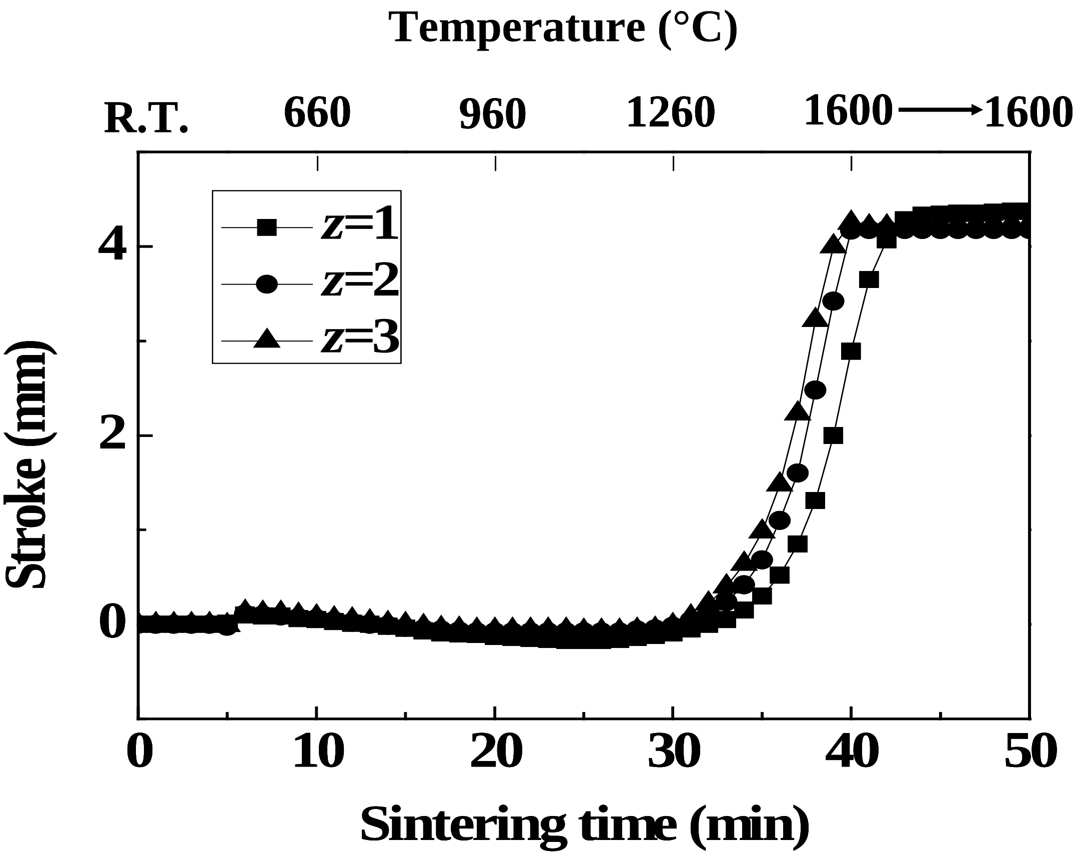
Fig. 3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R.T.
660
960
1260
1600 → 1600
Stroke (mm)
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2
0
z=1
z=2
z=3
0
10
20
30
40
50
Sintering time (min)

Fig. 4

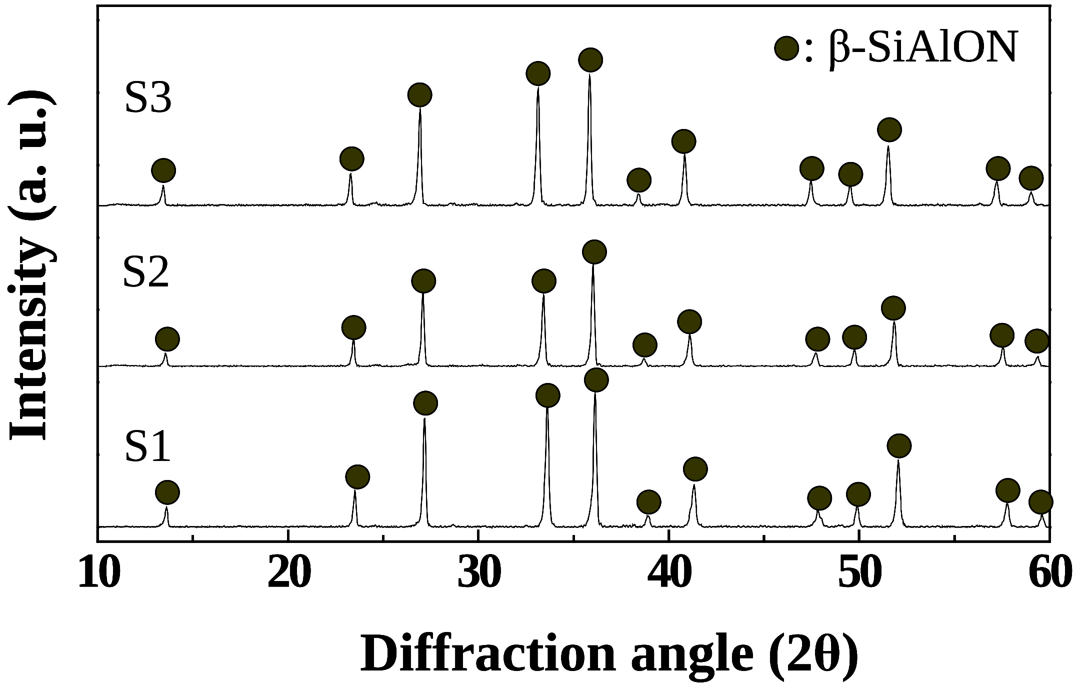
●: β-SiAlON
S3
S2
S1
Intensity (a. u.)
10
20
30
40
50
60
Diffraction angle (2θ)

Fig. 5

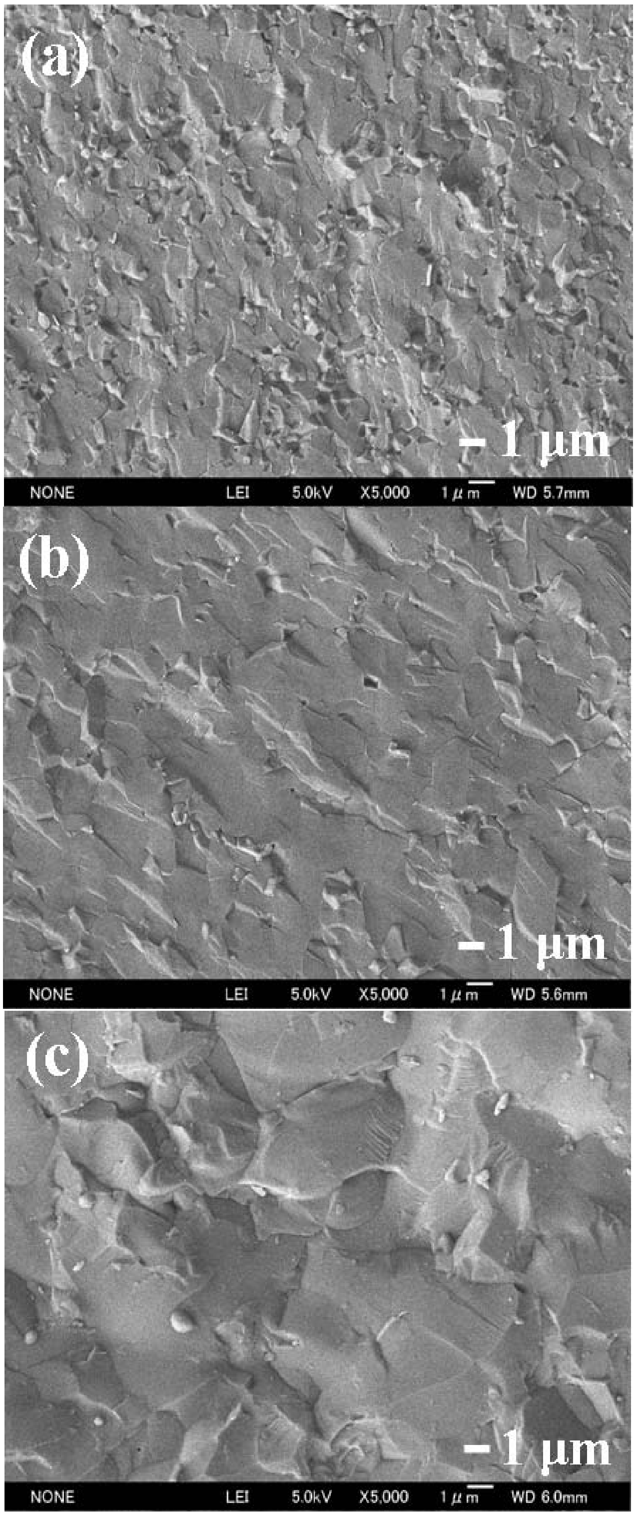
(a)
1 μm
NONE LEI 5.0kV X5,000 1 μm WD 5.7mm
(b)
1 μm
NONE LEI 5.0kV X5,000 1 μm WD 5.6mm
(c)
1 μm
NONE LEI 5.0kV X5,000 1 μm WD 6.0mm

Fig. 6