

## Fabrication of $\beta$ -SiAlONs by a Reaction-Bonding Process Followed by Post-Sintering

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### ABSTRACT

A cost-effective route to synthesize  $\beta$ -SiAlONs from Si mixtures by reaction bonding followed by post-sintering was investigated. Three different  $z$  values, 0.45, 0.92 and 1.87, in  $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$  without excess liquid phase were selected to elucidate the mechanism of SiAlON formation and densification. For RBSN (reaction-bonded silicon nitride) specimens prior to post-sintering, nitridation rates of more than 90% were achieved by multistep heating to 1400°C in flowing 5% $\text{H}_2$ /95% $\text{N}_2$ ; residual Si was not detected by XRD analysis. An increase in density was acquired with increasing  $z$  values in post-sintered specimens, and this tendency was explained by the presence of higher amounts of transient liquid phase at larger  $z$  values. Measured  $z$  values from the synthesized  $\beta$ -SiAlONs were similar to the values calculated for the starting compositions. Slight deviations in  $z$  values between measurements and calculations were rationalized by a reasonable application of the characteristics of the nitriding and post-sintering processes.

**Key words :** SiAlON, Silicon nitride, Reaction-bonding, Nitriding, Post-sintering

### 1. Introduction

An intergranular grain boundary phase (IGP) is the main cause of thermomechanical property degradation in  $\text{Si}_3\text{N}_4$  ceramics at high temperatures.<sup>1)</sup> Several successful efforts to crystallize IGP were devised by controlling the cooling schedule or using a post-heat treatment.<sup>2,3)</sup> A spotlight on SiAlONs has developed because, in a SiAlON system, much less IGP remains due to the transient nature of the liquid phase.<sup>4,6)</sup>

The  $\alpha$ - and  $\beta$ -SiAlON ceramics are modifications of  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  ceramics, respectively. Therefore, their intrinsic characteristics, including the hardness and grain morphology, have succeeded from  $\text{Si}_3\text{N}_4$  to SiAlON ceramics. A  $\alpha$ -SiAlON ceramic can accommodate additional cations into its interstitial structure, which suggests at least two promising advantages over  $\beta$ -SiAlONs, specifically increased hardness and the possibility of producing a single-phase ceramic with a minimum of grain boundary phases. However, the equiaxed nature of  $\alpha$ -SiAlON grains results in poor toughness compared with  $\beta$ -SiAlONs, which possess a high degree of toughness through self-reinforcement with elongated grains.<sup>7)</sup>  $\alpha/\beta$ -SiAlON composites have been studied extensively as these materials combine the advantages of both systems.<sup>8,9)</sup> However, the sensational discovery of  $\alpha$ -SiAlONs with improved fracture toughness through nucleation control suggests that the toughness problem may be overcome.<sup>10)</sup> In fact, tough,

coarse, and elongated  $\alpha$ -SiAlON microstructures have been detected during the past decade.<sup>10-12)</sup>

An obstacle to a wider use of both  $\text{Si}_3\text{N}_4$  and SiAlON ceramics is the relatively high production cost compared to similar metallic parts.  $\text{Si}_3\text{N}_4$  raw materials are expensive, and a RBSN (reaction-bonded silicon nitride) has drawn attention due to increased cost-effectiveness through the use of a substantially cheaper raw material, Si.<sup>13,14)</sup> However, the mechanical properties of RBSNs may not meet the high reliability and performance specifications required for advanced engineering applications due to the existence of pores and residual silicon. Recently, RBSNs have been revisited as the removal of the above mentioned defects has been made possible by a post-sintering process.<sup>15-17)</sup> Although SiAlONs can be fabricated by a reaction bonding process and subsequent post-sintering method, few reports have been published.<sup>18)</sup> Currently, the commercialization of SiAlONs is not widespread.

The purpose of the present research is to investigate the feasibility of SiAlON synthesis using a reaction bonding and post-sintering procedure. For simplicity of characterization and ease of refining, the fabrication of  $\beta$ -SiAlONs was investigated. Future studies will be undertaken on the more promising  $\alpha$ -SiAlONs.

### 2. Experimental Procedures

The raw materials used for the synthesis of  $\beta$ -SiAlONs in this study were Si (Sicomill<sup>®</sup> grade 4; Vesta Ceramics, Ljungavärk, Sweden), AlN (Grade B; H. C. Stark, Goslar, Germany) and  $\text{Al}_2\text{O}_3$  (AKP-30; Sumitomo, Tokyo, Japan). The surface oxygen content in Si and AlN was not considered

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**Table 1.** Composition of Si Mixture with Various  $z$  Values

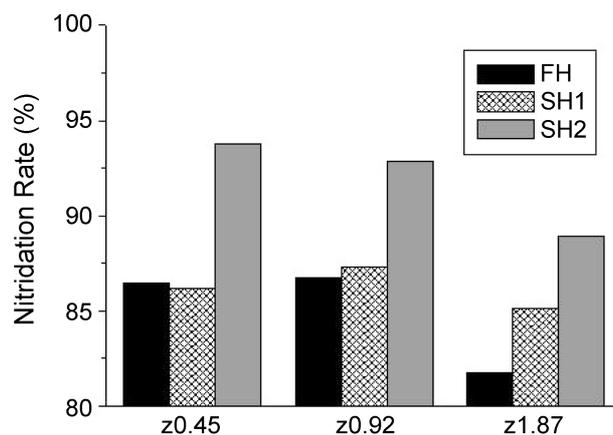
$z$	unit : gram			
	Si	AlN	Al <sub>2</sub> O <sub>3</sub>	Si <sub>3</sub> N <sub>4</sub>
0.45	55.4	2.2	5.6	92.3
0.92	50.7	4.5	11.1	84.4
1.87	41.1	9.0	22.5	68.5

\*Maximum oxygen content of Si and AlN is 1.0 and 1.5 wt%, respectively

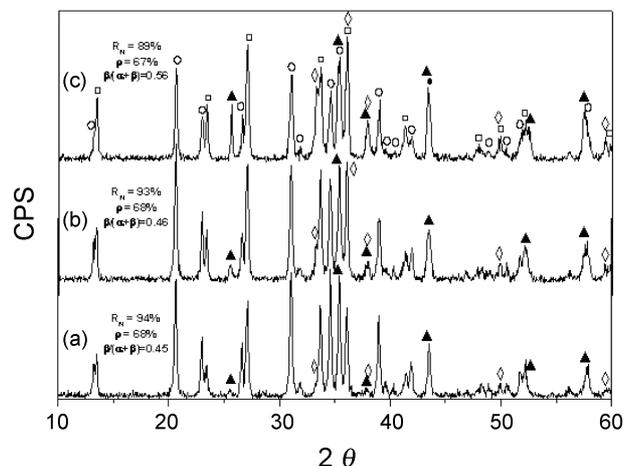
owing to the difficulty of an assessment of its loss during the nitriding process. Compositions with three different  $z$  values ranging from 0.45 to 1.87 were prepared (Table 1). Upon the completion of the nitriding reaction, the expected amount of converted Si<sub>3</sub>N<sub>4</sub> was equal to 1.665 times the raw Si, and the content of the transient liquid phase during the post-sintering increases with the  $z$  values. The powder combinations were mixed for 4 h by planetary milling with Si<sub>3</sub>N<sub>4</sub> balls using ethanol as a milling media. They were then dried using a rotating evaporator and sieved to a particle size of <150  $\mu$ m. The resulting powder mixture was uniaxially pressed into square pellets (10 mm  $\times$  10 mm  $\times$  2 mm) and subsequently cold isostatically pressed at 200 MPa. After shaping, the samples were heated in a 95% N<sub>2</sub>/5% H<sub>2</sub> flowing atmosphere in a horizontal tube furnace. Various heating schedules were investigated to identify appropriate nitriding conditions: fast heating at 300°C/h to a temperature of 1350°C (FH); and two slow heating processes at 30°C/h, the first to 1350°C (SH1) and the second to 1400°C (SH2). The specimens were kept upright on their edges and were fitted into a small hole on a graphite plate to reduce the probability of contamination and minimize the temperature gradient within the specimens. The nitridation percentage was calculated from the weight gain before and after the nitriding process. As preparation for the post-sintering of the as-nitrided specimens, samples were removed from the nitriding furnace and placed in a graphite crucible embedded in a mixture of Si<sub>3</sub>N<sub>4</sub>-BN packing powders. Post-sintering was carried out in a graphite resistance furnace at 1600°C, 1700°C, and 1800°C for 3 h under a static nitrogen gas pressure of 0.1 MPa. X-ray diffraction (XRD) (D/Max 2200; Rigaku, Tokyo, Japan) was performed for phase identification. Pure Si was mixed as a standard to the synthesized b-SiAlONs to refine the  $z$  value.

### 3. Results and Discussion

Nitridation rates ( $R_N$ ) were plotted for the three different heating schedules (Fig. 1). A value of  $R_N > 90\%$  was achieved under SH2 conditions (i.e., slow heating to 1400°C) for the three different  $z$  value compositions. Fig. 1 shows a decrease in  $R_N$  with an increasing  $z$  value, which is related to the smaller amount of Si in the mixture. Thus, the same amount of Si loss during the nitriding process would result in a greater drop in  $R_N$  in the specimen with the higher  $z$  value. Fig. 2 shows the phase analysis of specimens nitrided



**Fig. 1.** Measurement of nitridation rate ( $R_N$ ) for fast heating (FH) and for slow heating (SH1, SH2).



**Fig. 2.** XRD analysis of RBSN specimens by SH2 condition (a)  $z=0.45$ , (b)  $z=0.92$ , (c)  $z=1.87$  (○  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, □  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, ▲ Al<sub>2</sub>O<sub>3</sub>, ◇ AlN).

in the SH2 condition. The nitridation rate ( $R_N$ ), density ( $\rho$ ) and phase distribution ( $\beta$  fraction) are specified in the graph inset. The XRD pattern for the SH2 condition did not indicate any residual Si, which was observed in both FH and SH1 conditions in mixtures showing lower nitridation rates. It has been reported that if the nitridation rate exceeds 90%, Si peaks are not detected by XRD and the reaction bonding may be considered to be nearly complete.<sup>17</sup> A peak analysis indicated that both  $\alpha$ - and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> were formed and that unreacted AlN and Al<sub>2</sub>O<sub>3</sub> were detected. The reaction products were solely from the Si<sub>3</sub>N<sub>4</sub> phase, as SiAlON formation only takes place above 1500°C.<sup>9,19,20</sup> It is interesting to note that the  $\beta$ -fraction reached 46%~56%, which is substantially higher than that usually observed during the nitriding of a Si compact.<sup>21</sup>  $\beta$ -Si<sub>3</sub>N<sub>4</sub> is formed through a solution-reprecipitation mechanism; therefore, the highest  $\beta$  fraction observed in the  $z=1.87$  composition is ascribed to the highest transient liquid phase content.

Percentage theoretical densities (%TD) of post-sintered specimens are plotted in Fig. 3 for three different sintering temperatures. An increase in the density with both the  $z$  value and the

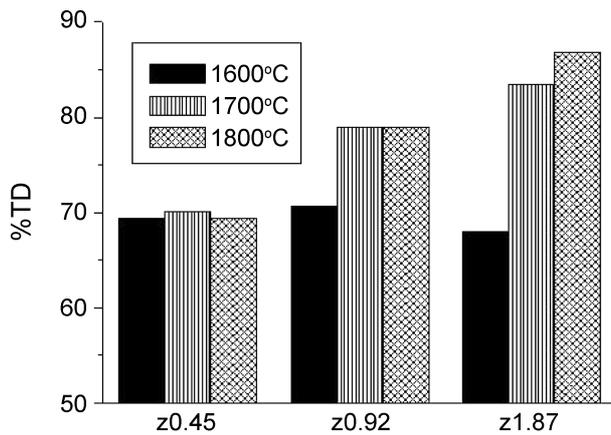


Fig. 3. Densification of  $\beta$ -SiAlONs without excess liquid phase by the pressureless sintering in the temperature range of 1600~1800°C.

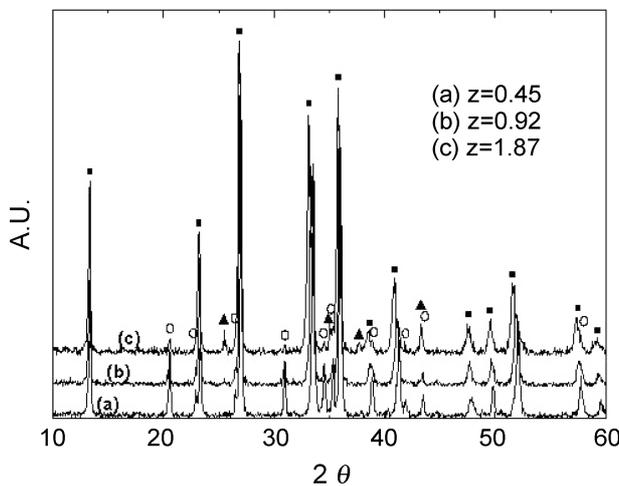


Fig. 4. XRD analysis of post-sintered specimens at 1600°C ( $\circ$   $\alpha$ - $\text{Si}_3\text{N}_4$ ,  $\blacksquare$   $\beta$ -SiAlON,  $\blacktriangle$   $\text{Al}_2\text{O}_3$ ).

sintering temperature is indicative of the typical behavior of liquid phase sintering (LPS). Observation of poor densification from the pressureless sintering in this study is natural due to the absence of an excess liquid phase. Special sintering techniques, such as hot press (HP) or spark plasma sintering (SPS), are needed to densify stoichiometric compositions.<sup>22)</sup>

Fig. 4 illustrates the phase analysis of specimens post-sintered at 1600°C.  $\beta$ -SiAlONs were the predominant phases over the range of  $z$  values tested, while both  $\alpha$ - $\text{Si}_3\text{N}_4$  and unreacted  $\text{Al}_2\text{O}_3$  remained present as a minor phase. The formation mechanism of SiAlONs is reported to be heterogeneous nucleation on existing  $\text{Si}_3\text{N}_4$  particles,<sup>23,24)</sup> and TEM research has revealed the growth of  $\alpha$ -SiAlON on the nucleus of  $\alpha$ - $\text{Si}_3\text{N}_4$ .<sup>23)</sup> The formation of  $\beta$ -SiAlONs in the present study resulted from the solution of  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  and subsequent precipitation on the  $\beta$ - $\text{Si}_3\text{N}_4$  nuclei. The higher peak intensity of the residual  $\alpha$ - $\text{Si}_3\text{N}_4$  in the mixtures with low  $z$  values (i.e., the less liquid phase) supports the nucleation formation reasoning.  $\alpha$ - $\text{Si}_3\text{N}_4$  phases disappeared in the specimens post-sintered at temperatures in excess of 1700°C.

Slow scanning between 25° and 35° of two theta regions

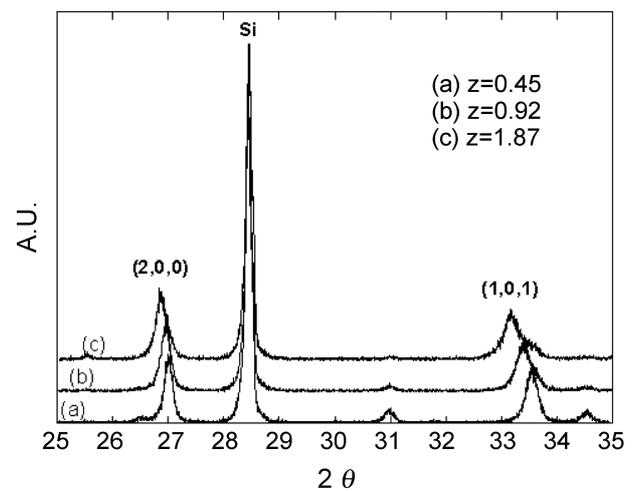


Fig. 5. Measurement of shift in two theta for the post-sintered specimens at 1600°C. Pure Si as a standard was mixed with grinded specimen.

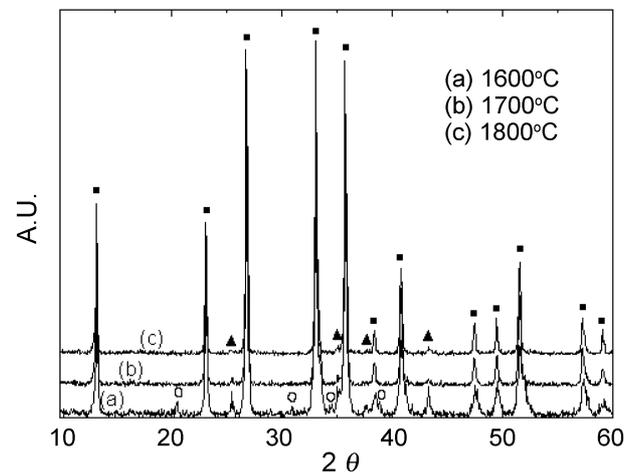


Fig. 6. XRD patterns of  $z=2.0$  post-sintered at 1600~1800°C.

with the Si standard was conducted to refine the  $z$  values by the measurement of the peak shift. The  $z$  values were calculated using the following  $a$  and  $c$  parameter equations:<sup>25)</sup>

$$a_0(\text{\AA}) = 7.603 + 0.0297z_a$$

$$c_0(\text{\AA}) = 2.907 + 0.0255z_c$$

Here, the lattice parameters  $a_0$  and  $c_0$  were induced by the peak position of the (2,0,0) and (1,0,1) planes. The mean of  $z_a$  and  $z_b$  was accepted as the measured  $z$  value. The refined  $z$  values were then 0.47, 0.95, and 1.82 for the original design values of 0.45, 0.92, and 1.87, respectively. For  $z$  values of 0.45 and 0.92, slightly higher refined  $z$  values were measured. These increases may be the result of a loss of reactant Si during the nitriding process by evaporation or a loss of product  $\text{Si}_3\text{N}_4$  during post-sintering in the form of a liquid phase. On the other hand, a lower  $z$  value was measured for  $z=1.87$ . By reasoning similar to that pertaining to the increase in the  $z$  values, the loss of AlN and  $\text{Al}_2\text{O}_3$  in the form of a glassy phase between grains may contribute to a

decreased  $z$  value. Nonetheless, the results verify that the synthesis of  $\beta$ -SiAlONs with a specific composition is possible through nitriding and post-sintering of a Si mixture.

Nearly identical  $z$  values were obtained for specimens synthesized at different temperatures (1600~1800°C). The results for a  $z$  value of 1.87 are presented in Fig. 6. It has been reported that the amount of incorporated Al and O, i.e., the  $z$  value, increases with the temperature.<sup>4)</sup> Therefore, the observation of the same degree of solid solubility with various temperatures in Fig. 6 indicates that the solubility limit of  $\beta$ -SiAlON at 1600°C exceeds 1.87. This is supported by the observation that stable  $\beta$ -SiAlON with  $z=3.0$  was formed at a temperature of 1650°C.<sup>26)</sup>

#### 4. Conclusions

Bulk  $\beta$ -SiAlON bodies were successfully fabricated by the nitriding and post-sintering of Si mixtures. A nitriding schedule appropriate for a SiAlON composition was developed. The schedule is different from that for  $\text{Si}_3\text{N}_4$  ceramics, which contain fewer additives that may act as a liquid phase source. The equilibrium phase of  $\beta$ -SiAlON was obtained by the post-sintering of nitrified specimens that included significant amounts of  $\alpha$ - $\text{Si}_3\text{N}_4$ . The refinement of synthesized  $\beta$ -SiAlONs opens the possibility of fabricating ceramics with specific compositions. A detailed analysis of the grain boundary phase is needed to verify the cause(s) of the slight differences between the refined and designed  $z$  values. The results of this study elucidate a cost-effective route for synthesizing stoichiometrically designed  $\beta$ -SiAlONs by a reaction bonding process.

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