

# Synthesis of $\beta$ -SiAlON powder by carbothermal reduction–nitridation of zeolites with different compositions

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## Abstract

$\beta$ -SiAlON was synthesized from select zeolite Y compositions with different Si/Al ratios by carbothermal reduction–nitridation (CRN), and the correlation between the starting compositions and products was investigated. The carbon content in all of the zeolite samples was fixed at 1.2 times the required stoichiometric value. Zeolite–carbon mixtures were placed in a carbon boat and fired in a furnace at 1300 °C for 0 min, and 1450 °C for 0, 120 min in a N<sub>2</sub> flow of 0.5 l/min. The main phase in each of the samples fired at 1450 °C for 120 min was determined from XRD results as  $\beta$ -SiAlON. It was also found that the ratio of  $\beta$ -SiAlON to minor phases such as  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and Si<sub>2</sub>N<sub>2</sub>O is typically higher in samples prepared from zeolites rather than from silica–alumina mixtures of the same compositions. This indicates that zeolites are ideal raw materials for the CRN synthesis of high purity  $\beta$ -SiAlONs by CRN with various  $z$  values.

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**Keywords:** SiAlON; Zeolite; Milling; Carbon; Grain size

## 1. Introduction

The  $\alpha$ - and  $\beta$ -SiAlONs are solid solutions of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> that have had some of their Si and N atoms replaced by Al and O, respectively. Furthermore, in the large interstitial sites of  $\alpha$ -SiAlON, certain metal cations, such as Li<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Y<sup>3+</sup> and the rare-earth ions, are included to balance the charge neutrality.<sup>1</sup> These solid solutions have the formulae M<sub>x</sub>Si<sub>12-m-n</sub>Al<sub>m+n</sub>O<sub>n</sub>N<sub>16-n</sub> ( $\alpha$ -SiAlON,  $x = m/v$ ,  $v$ : cation charge) and Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub> ( $\beta$ -SiAlON,  $0 < z \leq 4.2$ ), respectively. SiAlON ceramics exhibit high strength and hardness, and are highly resistant to oxidation and corrosion. SiAlON ceramics is typically produced via the high-temperature liquid phase sintering of either a powdered mixture of Si<sub>3</sub>N<sub>4</sub>–AlN–M<sub>x</sub>O<sub>y</sub>, where M is a metal such as Li, Mg, Ca and rare earth element, or Si<sub>3</sub>N<sub>4</sub>–AlN–Al<sub>2</sub>O<sub>3</sub>.<sup>2,3</sup> The corrosion resistances and high-temperature strength of these materials are known to decrease with the formation of a glassy phase in the sintered body.<sup>4</sup> Since it is difficult to fabricate SiAlON ceramics by liquid phase sintering without producing a glassy phase in the grain

boundary, the preparation of SiAlON powders<sup>5</sup> and their sintering by different method such as spark plasma sintering (SPS), has received considerable attention.<sup>6</sup> The development of high-quality SiAlON powders is essential if the structural reliability of the corresponding ceramics is to be improved.  $\alpha$ - and  $\beta$ -SiAlON powders have been largely synthesized through carbothermal reduction–nitridation (CRN) of silicate-based oxides. There are several reports describing the synthesis of  $\alpha$ -SiAlON by heating carbon-containing powder mixtures of SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–CaCO<sub>3</sub>,<sup>7</sup> SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–metal (Ca or Y),<sup>8,9</sup> clay–metal compounds<sup>10</sup> and talc (Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>)-halloysite clay minerals.<sup>11,12</sup> Additional reports have also shown that  $\beta$ -SiAlON can be synthesized from mixed powders of kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>),<sup>13</sup> powder mixture of SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O,<sup>14</sup> powder mixtures of SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>,<sup>15</sup> an alkoxide-derived SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> co-precipitate,<sup>16</sup> and SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> gel,<sup>17</sup> all in the presence of carbon in flowing N<sub>2</sub> gas. In this study, we focus our attention on using zeolites as the prime source for preparing  $\beta$ -SiAlON.

Zeolites are hydrated, crystalline tectoaluminosilicates constructed from TO<sub>4</sub> tetrahedra (T = tetrahedral atom, e.g. Si and Al),<sup>18–20</sup> and comprise a uniform number of Si and Al atoms within their structures. It is possible to synthesize zeolites with various Si/Al ratios (from 1 to infinity). Due to the similarity

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of compositions and local structures, zeolites are useful starting materials for the fabrication of SiAlON powders. Sugahara et al. focused on zeolites and polyacrylonitrile (PAN) compounds as synthetic precursors for the carbothermal reduction–nitridation (CRN) synthesis of  $\beta$ -SiAlON<sup>21</sup> by CRN. They demonstrated that zeolites were highly suited as raw materials for the synthesis of  $\beta$ -SiAlON; however, the purity of the resulting product was not high. On the other hand, we have recently shown that pure  $\beta$ -SiAlON can be synthesized from a zeolite–carbon black mixture by CRN.<sup>22</sup> In this study, we describe the synthesis of  $\beta$ -SiAlON from various zeolite Y compositions via CRN, and investigate the correlation between the starting compositions and the products.

## 2. Experimental

The characteristics of the raw materials (Zeolite Y: 330HUA, 360HUA, 371NHA Tosoh Co., Japan) are shown in Table 1, and a framework structure of zeolite Y and its XRD pattern are shown in Fig. 1a and b. Samples z-1 and z-2 were used as is, while sample z-3 was calcined at 500 °C for 6 h prior to CRN in order to remove  $\text{NH}_3$  ( $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$ )<sup>23</sup> from the zeolite, and to obtain  $\text{H}^+$ -zeolite Y. These zeolites were then mixed with carbon (650B, Mitsubishi Chemical Co., Ltd.), where the carbon content in all samples was fixed at 1.2 times the required stoichiometric value. The mixtures were dry mixed using SiAlON ball for 36 h, and then subsequently passed through a sieve with 50-mesh holes. The 1.0 g of powder mixture was then placed in a carbon boat and fired in a furnace at 1300 °C for 0 min and 1450 °C for 0 and 120 min in a  $\text{N}_2$  flow of 0.5 l/min, with a heating rate of approximately 12 °C/min. The residual car-

bon was removed by burning the resultant powders at 700 °C for 120 min in atmospheric conditions. The resulting materials were characterized by X-ray diffractometry (XRD, Rigaku, Multiflex), scanning electron microscopy (SEM, JEOL JSM-5200), and transmission electron microscopy (TEM, HITACHI H-800). Furthermore, mixtures of  $\text{SiO}_2$  (SO-C2, Admatechs Co., Ltd.),  $\text{Al}_2\text{O}_3$  (AO-502 Admatechs Co., Ltd.) and carbon black, with the same compositions as samples z-1, z-2 and z-3, were nitrated in the same way as the zeolites, and designated as samples m-1, m-2 and m-3, respectively.

## 3. Results and discussion

Fig. 2a–c show the XRD patterns obtained for the products formed by firing samples z-1, z-2 and z-3 at 1300 °C (0 min), 1450 °C (0 min) and 1450 °C (120 min), in flowing  $\text{N}_2$ . For comparison, Fig. 2d shows XRD patterns for the fired products formed from a mixture of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and carbon black, fired at 1450 °C for 120 min in a  $\text{N}_2$  flow. From a comparison of Figs. 1b and 2a, it was found that all of the zeolites were converted into an amorphous phase below 1300 °C. This is supported by the fact the framework structure of zeolite Y is known to collapse around 1000 °C.<sup>18,19</sup> It was determined from XRD analysis (Fig. 2a) that both samples z-1 and z-2 form mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) after being fired at 1300 °C for 0 min. On the other hand, for sample z-3 (the highest Si/Al ratio of the three raw zeolites), no mullite was observed after being fired under the same conditions (1300 °C for 0 min). Previous reports have shown that mullite is formed when crystalline aluminosilicates such as kaolinite<sup>24</sup> and zeolite are fired over 1000 °C.<sup>25</sup> It seems that the formation of mullite is highly dependent on the Si/Al ratio, where zeolites

Table 1  
Compositions of raw materials

	Type	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Grain size ( $\mu\text{m}$ )	Cation	z-Value	
					Prospected <sup>a</sup>	Product <sup>b</sup>
Sample z-1	330HUA	6.0	0.3	$\text{H}^+$	1.5	1.6
Sample z-2	360HUA	14.0	0.4	$\text{H}^+$	0.7	0.8
Sample z-3	371NHA	27.0	0.6	$\text{NH}_4^+ \rightarrow \text{H}^{+c}$	0.4	0.6

<sup>a</sup> Prospected: z-values after the ideal nitridation to form  $\beta$ -SiAlON.

<sup>b</sup> Product: z-values calculated from XRD patterns<sup>27</sup>  $z_a = (a - 0.7603)/0.00296$ ;  $z_c = (c - 0.2907)/0.00255$ .

<sup>c</sup> Calcined at 500 °C for 6 h to form  $\text{H}^+$  type FAU.

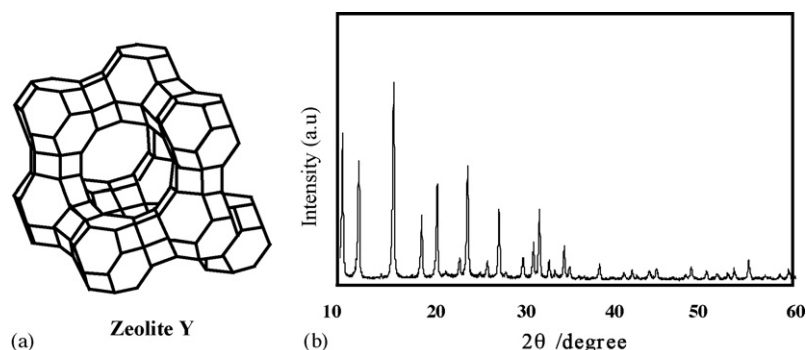


Fig. 1. (a) Structure and (b) XRD pattern of zeolite Y.

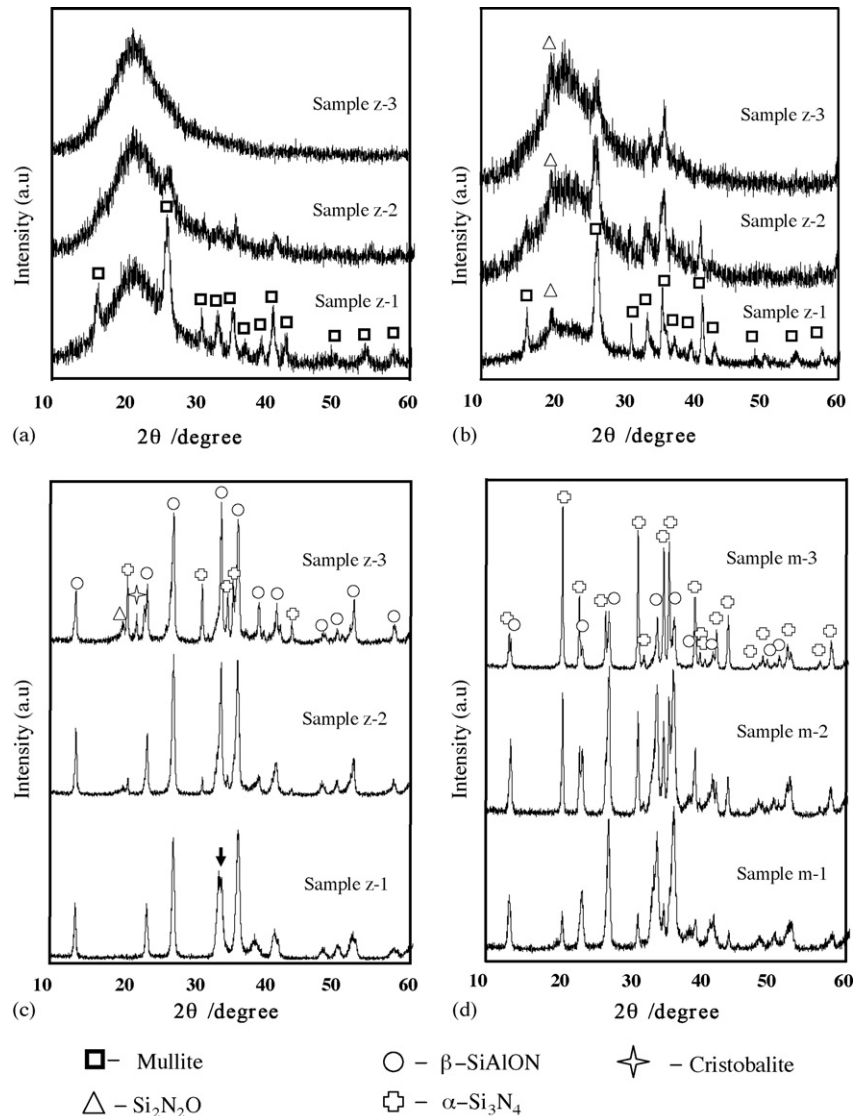
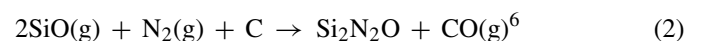
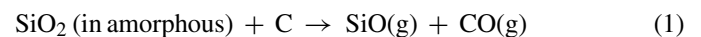


Fig. 2. (a–c) XRD patterns of the products formed using zeolites as raw materials fired at (a) 1300 °C for 0 min, (b) 1450 °C for 0 min, (c) 1450 °C for 120 min. (d) XRD pattern of the product formed using a silica–lumina mixture as the raw material fired at 1450 °C for 120 min.

with a lower Si/Al ratio (sample z-1 < sample z-2 < sample z-3) form greater quantities of mullite. Since the Si/Al ratio in mullite (=1/3) is lower than in all the raw zeolites used in this study, it is thought that a Si-rich amorphous phase and Al-rich mullite phase are formed in each of these samples by way of firing. The SEM micrographs of three raw powders and their resulting products are shown in Figs. 3–5, respectively. As shown in Figs. 3b, 4b and 5b, it is found that the particle morphology of samples z-1, z-2 and z-3 (all fired at 1300 °C for 0 min) is nearly the same as for the raw zeolites (Figs. 3a, 4a and 5a), respectively. Therefore, it appears that both amorphous and mullite phases co-exist in each of the fired particles.

For the zeolite samples fired at 1450 °C for 0 min, it was observed that a small amount of Si<sub>2</sub>N<sub>2</sub>O was formed, as confirmed by XRD shown in Fig. 2b; indicating that nitridation of the samples occurred under these conditions, and that the Si-rich amorphous phases in each sample were nitrided prior to the mullite phases. By comparing this evidence with the obtained XRD

(Fig. 2b) and SEM (Figs. 3c, 4c and 5c) results, it is thought that the fibrous material observed in samples z-1, z-2 and z-3 (both fired at 1450 °C for 0 min) is Si<sub>2</sub>N<sub>2</sub>O, since no fibrous material is evident in Figs. 3b, 4b and 5b fired at 1300 °C (0 min). The SEM micrographs (Figs. 3c, 4c and 5c) also show that the particle morphology of the zeolites fired at 1450 °C for 0 min is still maintained, although the fibrous structure of Si<sub>2</sub>N<sub>2</sub>O is only partly formed. Typically, Si<sub>2</sub>N<sub>2</sub>O is formed by the reaction of N<sub>2</sub> and as-generated SiO in the presence of carbon, as indicated in the following equation:



The peak intensity of mullite in sample z-2 (fired at 1450 °C for 0 min) is considerably stronger than that observed for the same sample fired at 1300 °C for 0 min, while in sample z-3 fired at 1450 °C for 0 min, the formation of mullite was confirmed

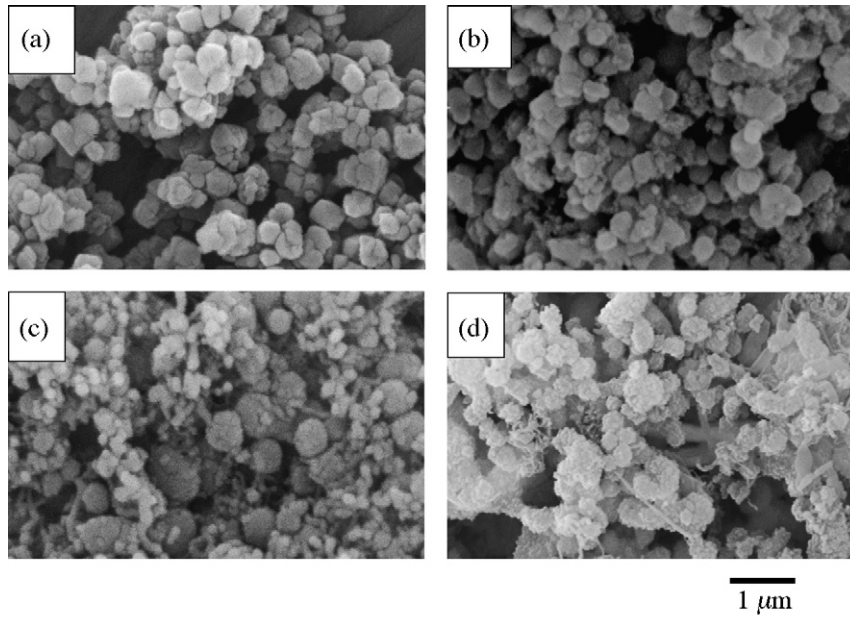


Fig. 3. SEM micrographs of sample z-1 and the products fired at different temperatures and holding times: (a) ambient temperature, (b) 1300 °C for 0 min, (c) 1450 °C for 0 min and (d) 1450 °C for 120 min.

(shown in Figs. 2a and b). Since the Si/Al ratios of samples z-2 and z-3 are higher than that in sample z-1, it appears that higher temperatures and longer firing times are needed for the formation of mullite.

It was found that the main phase formed in each zeolite sample fired at 1450 °C for 120 min is  $\beta$ -SiAlON (Fig. 2c). In particular, samples z-1 and z-2 both demonstrated the successful synthesis of highly pure  $\beta$ -SiAlON. The formation of  $\alpha$ - $\text{Si}_3\text{N}_4$  (samples z-2 and z-3),  $\text{Si}_2\text{N}_2\text{O}$  (samples z-2 and z-3) and cristobalite (sample z-3), are also confirmed as minor phases in each case. It is noteworthy that the XRD peak corresponding

to  $\beta$ -SiAlON is particularly broad (as indicated by the arrow in Fig. 2c); suggesting that  $\beta$ -SiAlON has a large distribution of  $z$  values. This is due to the formation of both Si-rich amorphous and Al-rich mullite phases in each particle during firing, and the subsequent conversion of these two phases into  $\beta$ -SiAlON. The SEM micrographs in Figs. 4d and 5d show the formation of  $\beta$ -SiAlON aggregates and fibrous materials, especially in sample z-3. The fibrous products are thought to be  $\text{Si}_2\text{N}_2\text{O}$ , since their morphology is similar to that observed in Fig. 5c. The TEM images of the products fired at 1450 °C for 120 min are shown in Fig. 6. Here, a number of aggregates are observed, and these are

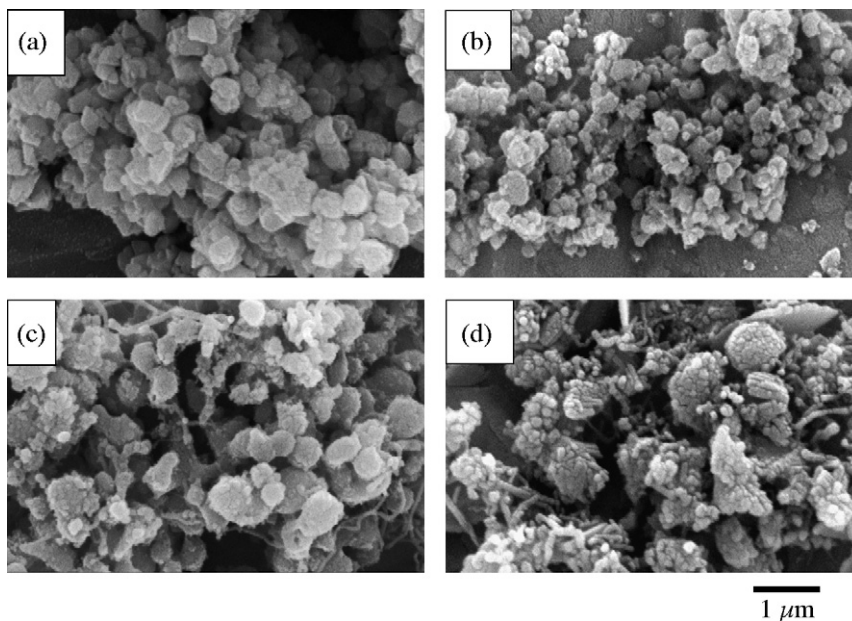


Fig. 4. SEM micrographs of sample z-2 and the corresponding products fired at different temperatures and holding times: (a) ambient temperature, (b) 1300 °C for 0 min, (c) 1450 °C for 0 min and (d) 1450 °C for 120 min.

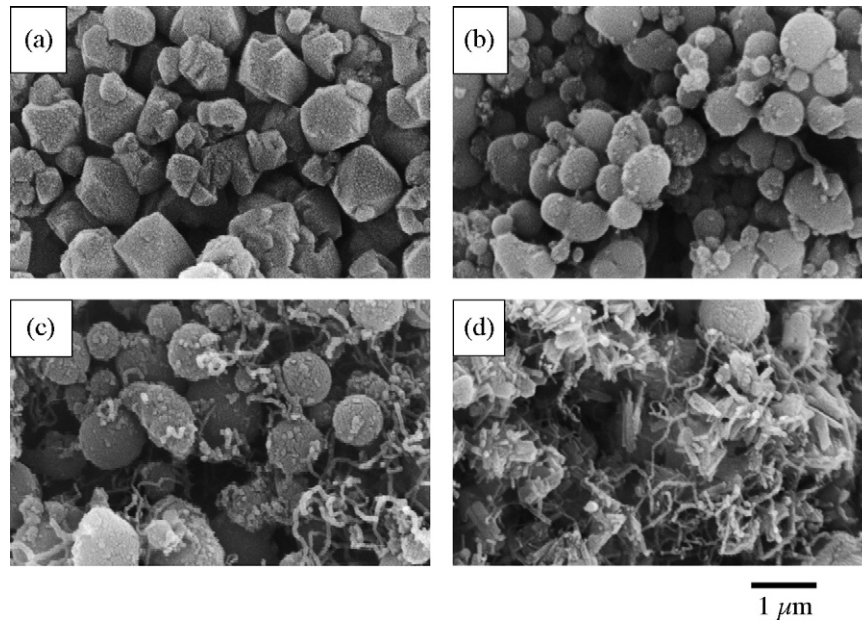


Fig. 5. SEM micrographs of sample z-3 and the corresponding products fired at different temperatures and holding times: (a) ambient temperature, (b) 1300 °C for 0 min, (c) 1450 °C for 0 min and (d) 1450 °C for 120 min.

composed of  $\beta$ -SiAlON nanoparticles with sizes of ca. 50 nm, as shown in Fig. 6a. It is interesting that these aggregates are of a similar size to those of the raw materials; indicating that the zeolite particles are converted into  $\beta$ -SiAlON, while maintaining approximate morphologies. In addition to the aggregates and fibrous materials observed in samples z-2 and z-3 (both fired at 1450 °C for 120 min), columnar grains are also evident (Fig. 6b and c). These columnar grains are thought to be  $\alpha$ - $\text{Si}_3\text{N}_4$  formed by the reaction between SiO and  $\text{N}_2$  in the presence of carbon,

as indicated in the following equation:

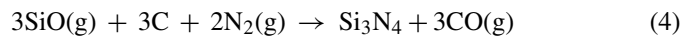
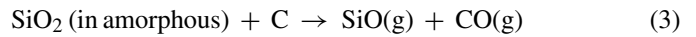


Fig. 2d shows XRD patterns of the products formed from the firing of a mixture of carbon black, silica and alumina at 1450 °C for 120 min. From a comparison with Fig. 2c, it was found that the ratios of  $\beta$ -SiAlON to  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\text{Si}_2\text{N}_2\text{O}$  are obviously

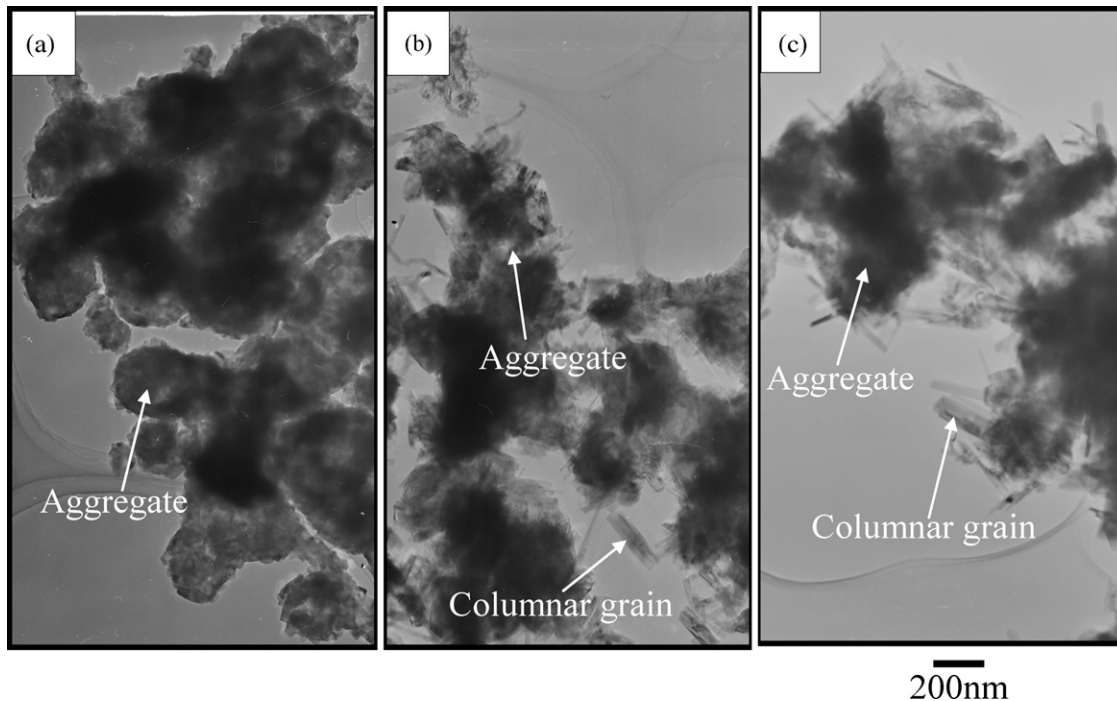


Fig. 6. TEM images of the corresponding products fired at 1450 °C for 120 min: (a) sample z-1, (b) sample z-2 and (c) sample z-3.

higher in the samples prepared from zeolites than those prepared from silica–alumina mixtures. It is known that SiO gas is generated by firing a silica–alumina mixture under a reducing atmosphere at 1450 °C, although AlO systems do not generate any gases. Since the Si and Al atoms in the silica–alumina mixture are not distributed uniformly on an atomic scale, SiO gas ( $\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}$ ) is formed easily, and this reacts with  $\text{N}_2$  to generate a large volume of  $\alpha\text{-Si}_3\text{N}_4$ .<sup>26</sup> On the other hand, since the Si and Al atoms in zeolites are mixed uniformly on an atomic scale, it is thought that the well-dispersed Al atoms in both the amorphous and mullite phases in each particle prevents the formation of SiO gas, and hence the formation of  $\alpha\text{-Si}_3\text{N}_4$  is suppressed. As shown in Table 1, it was confirmed that  $z$ -values prospected from raw materials and calculated from XRD patterns<sup>27</sup> are close to each other; indicating that the formation of SiO gas is suppressed, that is, zeolites are ideal raw material for the synthesis of  $\beta\text{-SiAlONs}$  with controlled compositions.

#### 4. Conclusions

$\beta\text{-SiAlON}$  was synthesized from zeolite Y with different Si/Al ratios by carbothermal reduction–nitridation (CRN), and the correlation between the starting compositions and products was investigated. It was found that  $\beta\text{-SiAlON}$  is the main phase formed in each sample fired at 1450 °C for 120 min. Especially, highly pure  $\beta\text{-SiAlON}$  was successfully synthesized from lower Si/Al zeolites. It was also found that the ratio of  $\beta\text{-SiAlON}$  is obviously higher in the samples prepared from zeolites rather than prepared from silica–alumina mixtures; indicating that zeolites are ideal raw materials for the CRN synthesis of high purity  $\beta\text{-SiAlONs}$  with various  $z$ .

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