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Mechanical-activated, combustion synthesis of β-SiAlON

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ABSTRACT

This paper describes the synthesis of β-$Si_{6-z}Al_zO_zN_{8-z}$ ($z = 1$) powder via combustion synthesis (CS) assisted with mechanical activation by a high-energy planetary ball milling under various nitrogen pressures (0.7, 1.0, 1.5, and 2.5 MPa). Here, we did not examine only the effect of ball milling time and nitrogen pressure on the reaction rate and microstructure of CSed products using XRD and SEM, but also the effect on the nitrogen pressure required for CS of β-SiAlON. The results show that prolonged milling time was quite effective for enhancing the reactivity of raw materials and also for promoting the conversion rate of β-SiAlON. The mechanical activation minimized the required nitrogen pressure for combustion synthesizing β-SiAlON, which the reaction can self-propagate at only 0.7 MPa in nitrogen pressure. Significantly, SEM observation revealed that the rod-like crystals agglomerated together with increasing ball milling time, and became longer and thicker with increasing nitrogen pressure.

1. Introduction

The β-SiAlON, being most commonly described as β-$Si_{6-z}Al_zO_zN_{8-z}$, is the solid solution of β-Si_3N_4 in which Si–N has been substituted with an equivalent amount of Al–O, in which z takes the values from 0 to ~4.2 [1,2]. 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. Recently, the report of use of Eu^{2+}-doped β-SiAlON phosphors for down-conversion luminescent materials in white-light-emitting diodes (LEDs) indicates that β-SiAlON-based materials have more extensive application potential in many fields as functional materials [3,4]. However, additional applications can be explored, if the cost could be significantly reduced.

Combustion synthesis (CS), known as self-propagating high-temperature synthesis (SHS), has been proven to be a cost-effective and energy-saving technology for the synthesis of a variety of materials such as nitrides [5], hydrides [6], and oxides [7]. For combustion synthesis of β-SiAlON, the presence of the un-reacted 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 β-SiAlON could help to lower the combustion temperature as well as improve the conversion degree of reactants accordingly. However, the mass ratio of diluents was often as high as 40% of raw materials [8,9]. This actually results in the increase of the material cost. Thus, we need search for a method which could reduce the mass ratio of diluents additives and also improve the conversion degree of reactants.

Mechanically activated (or assisted) SHS (MASHS) is currently a subject of extensive experimental investigation and has been applied in a number of systems [10,11]. It has been observed in many systems that preliminary MA of reactants brought about a decrease in both the ignition and combustion temperatures and an increase in the conversion degree [12–17]. The mechanical activation has also been reported responsible for the reduction of the minimum nitrogen pressure required for the CS of Si_3N_4 [18]. As part of our previous research [19–21], β-SiAlON powders ($z = 1$–4) were successfully combustion synthesized at the relatively low nitrogen pressure of 1 MPa assisted with mechanical activation. In this study, our purpose was to combustion synthesize β-SiAlON powders under various nitrogen pressures assisted with different duration mechanical activation. Then we would investigate the effect of mechanical activation and nitrogen pressure on reaction conversion rate and microstructure of CS of β-SiAlON, and we also presented the effect of mechanical activation on the minimum nitrogen pressure required for CS of β-SiAlON. We hope that new findings will pave the way for practically using β-SiAlON with many benefits of minimizing input energy, shortening operating time, suppressing carbon-dioxide emission and reasonable productive price.

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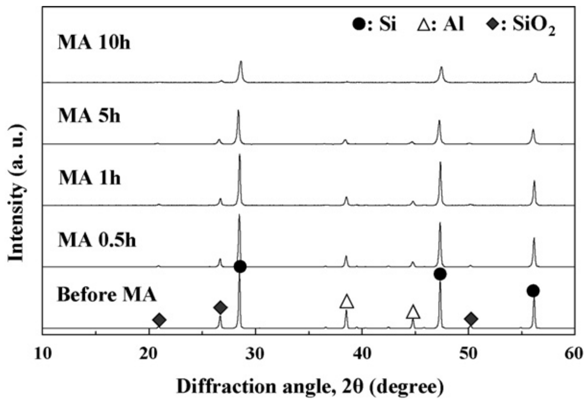

Fig. 1. XRD patterns of raw materials with and without mechanical activation.

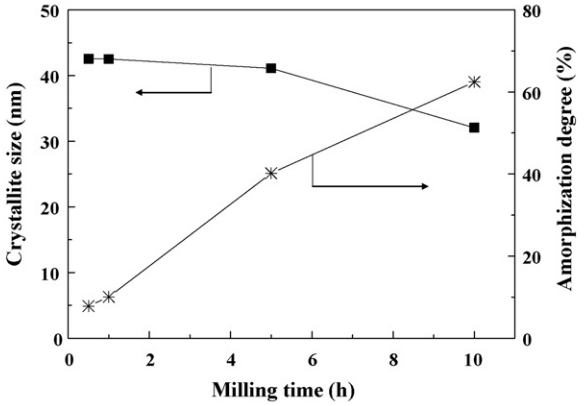

Fig. 2. Amorphization degree and crystallite size of Si in raw mixtures with different duration of mechanical activation.

2. Experimental procedure

In this study, commercially available powders of Si (98% purity; 1–2 μm in size); Al (99.9% purity, 3 μm in size); SiO_2 (99.9% purity, 0.8 μm in size) were used as starting materials. The chemical reaction for the synthesis of β-SiAlON from the abovementioned starting materials can be represented as follows, where in this study $z = 1$ was taken.

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

The mixtures of the starting materials were mechanically milled by a planetary ball milling for various durations of time in a steel container with a volume of 250 ml. Steel balls with the diameter of ⌀ 10 mm were used as the milling media. The ball-to-sample weight ratio was taken as 10:1. The ball milling was processed at 300 rpm. To avoid high-temperature generated during long time milling, the process paused for 10 min at every 15 min to cool the steel container naturally. The activated powders were subjected to CS under the applied nitrogen pressures (nitrogen purity: 99.999%). The conditions necessary for CS have been described in detail elsewhere [20,21]. The phase of the reaction products was identified by X-Ray diffraction (XRD) (Cu Kα-radiation). The microstructure was also examined by scanning electron microscopy (SEM).

3. Results and discussion

β-SiAlON powder was combustion synthesized, assisted with various duration mechanical activation in pressurized nitrogen ranging from 0.7 to 2.5 MPa. Fig. 1 shows the XRD patterns of the raw mixtures milled to different periods. Note that the intensities of all the peaks decreased significantly with increasing milling time, while the broadening increased synchronously, which can be attributed to the amorphization of the raw powders. The peaks of Al and SiO_2 disappeared almost after milling to 10 h. Because the amount of Si took up more than half of the total mass in raw materials, here only the amorphization degree and the crystallite size of Si were calculated. The amorphization degree was calculated according to $(1 - I/I_0) \times 100\%$, in which, I is the intensity of the $\mathrm{Si}_{(1\,1\,1)}$ peak in the mill-treated reactants, and I_0 is the intensity of the un-milled $\mathrm{Si}_{(1\,1\,1)}$ peak. The crystallite size was estimated using Scherrer formula:

$$L = \frac{0.89\lambda}{\beta \cos\theta} \quad (2)$$

Here, L is the crystallite size (nm), β is the full width at half-maximum (FWHM) of the diffraction peak that appeared at Bragg angle 2θ (nm), and λ is the corresponding wavelength of the X-ray radiation (nm). In this equation, the broadening of diffraction peaks by the internal stress is not considered. The variation of the amorphization degree and crystallite size of Si in the milled mixtures as a function of milling time is presented in Fig. 2. The amorphization degree increased and the crystallite size decreased with an increase in milling time. When the raw reactants were milled to 10 h, the amorphization degree increased to 62%, while the crystallite size decreased to the value of 32 nm. The reduced particles can also be seen from the SEM micrographs shown in Fig. 3. Their size reduced significantly after 10 h ball milling, and they cohered together due to high specific surface area. Besides the reduced particle size, it is believed that various defects can be formed during mechanical activation, and the high defect concentration plays a significant role during the combustion synthesis.

Fig. 4 shows the XRD patterns of CSed products with different ball milling time under the nitrogen pressure of 1 MPa. All of the products consisted of β-SiAlON and un-reacted Si. According to the relative intensity ratio of the maximum peaks for the two compositions, the content of un-reacted Si decreased gradually with the increase of milling time. One reason is that the reactivity and the storage energy in the raw mixtures were promoted by the effective mechanical activation. In addition, it has been proven that heat release in mechanically activated samples begins and proceeds in several stages, such as melting and eutectic reaction, at lower tem-

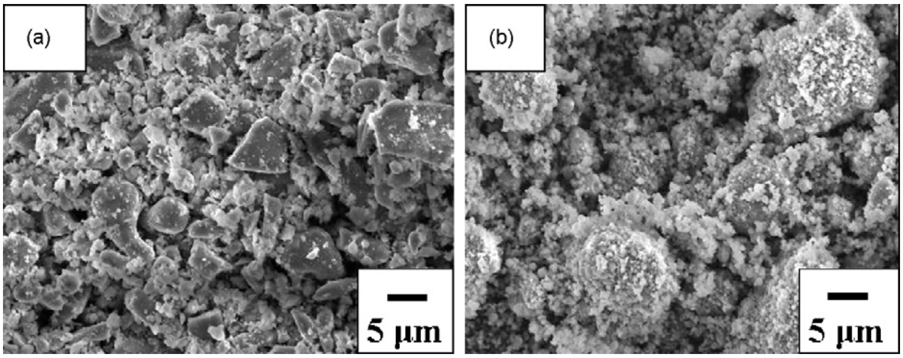

Fig. 3. SEM micrographs of raw mixtures (a) before mechanical activation and (b) mechanically activated to 10 h.

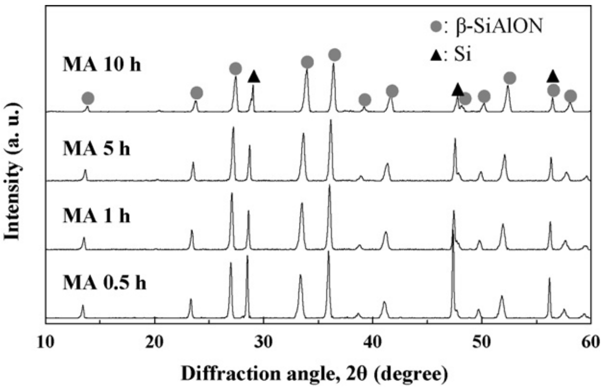

Fig. 4. XRD patterns of powders combustion synthesized under 1 MPa nitrogen pressure from raw mixtures milled to different duration time.

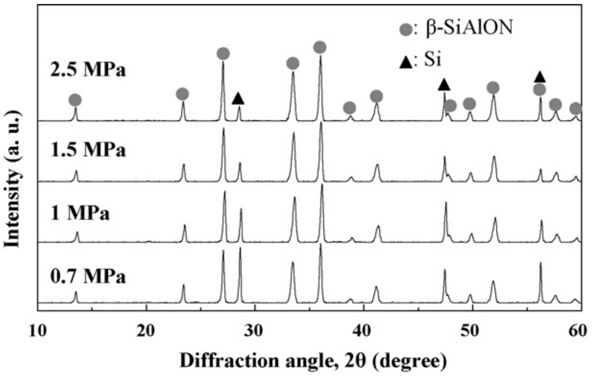

Fig. 5. XRD patterns of powders combustion synthesized under various nitrogen pressures from raw mixtures milled to 5 h.

peratures than in the un-activated powder mixtures [14]. This can be regarded as another reason that both the ignition temperature and the highest combustion temperature lowered down with the ball milling and the melting of Si was prevented, then the reaction conversion rate was enhanced. However, overlong ball milling caused too low ignition and combustion temperature that combustion process could not self-propagate, which can be attributed to Munir's empirical rule [22] for the CS reaction: the CS reaction can self-propagate only if the adiabatic temperature (T_{ad}) ≥ 1800 K.

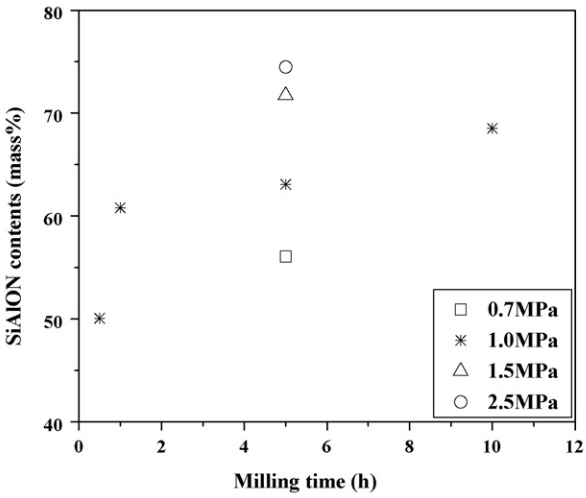

Fig. 6. β-SiAlON contents of products combustion synthesized under various pressures with various duration of mechanical activation.

Fig. 5 shows the XRD patterns of CSed products under 0.7–2.5 MPa nitrogen pressures from the raw materials milled to 5 h. The content of β-SiAlON increased with the increase in nitrogen pressure. It is generally considered, high pressure is responsible for promoting the N_2 infiltration into the mixtures, then conferring a large reaction interfacial area between raw mixtures and N_2. On the contrary, the low nitrogen pressure results in less reaction interfacial area between reactants and N_2, which makes it difficult to ignite the reactants. As we aforementioned, the reaction interfacial area between reactants and N_2 can be enhanced due to the significant reduced grain size of the raw mixtures by ball milling. Therefore, the CS process can propagate under lower pressure assist with effective mechanical activation. In our study, the mechanical activation showed helpful on self-propagation under the nitrogen pressure as low as only 0.7 MPa, but no propagation occurred under 0.5 MPa, even though the mixtures were milled for up to more than 10 h.

The relative β-SiAlON contents are shown in Fig. 6. They were approximately estimated from the β-SiAlON/(β-SiAlON + Si) ratio on the basis of the heights of the (2 0 0) and (1 0 1) diffraction peaks

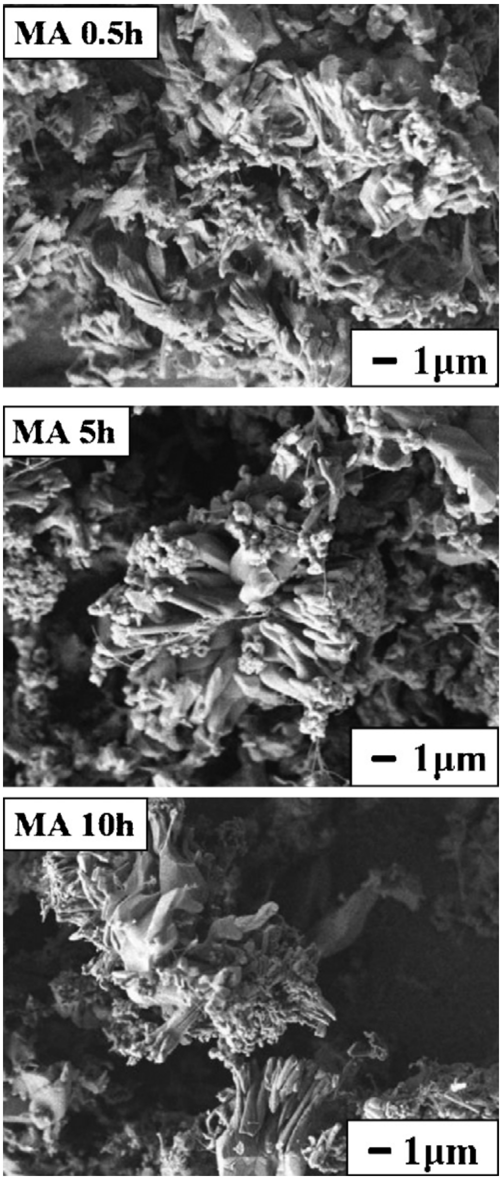

Fig. 7. SEM micrographs of powders combustion synthesized at 1 MPa pressure from different duration ball-milled mixtures.

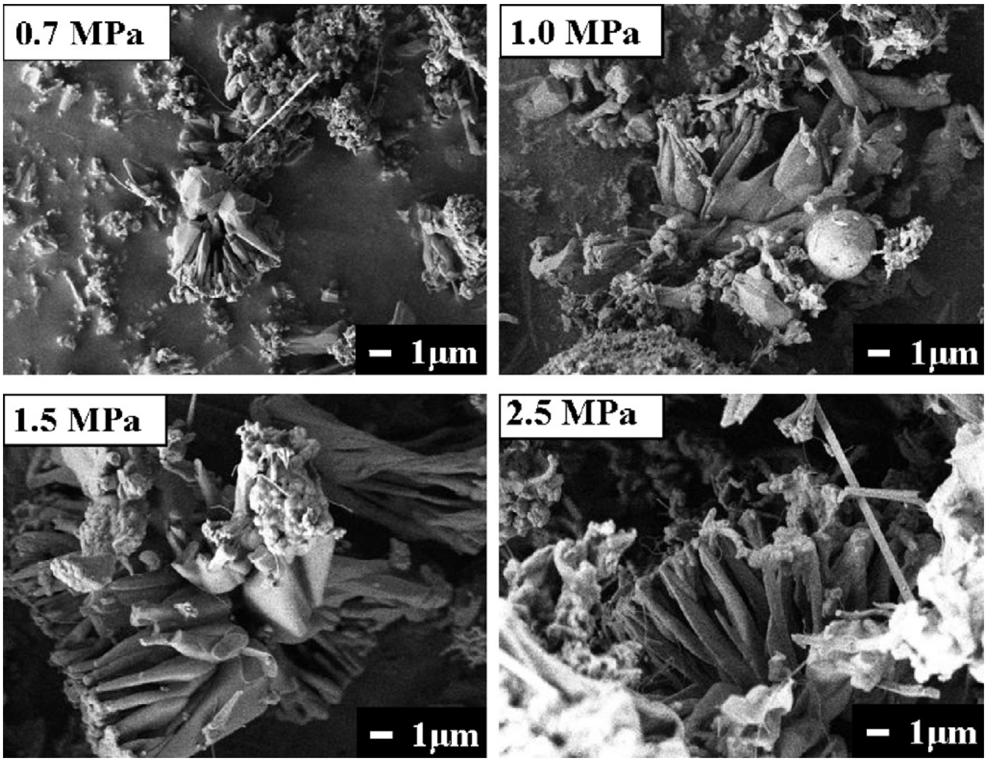

Fig. 8. SEM micrographs of powders combustion synthesized under various pressures from 5 h ball-milled mixtures.

of β-SiAlON and the (1 1 1) and (2 2 0) diffraction peaks of Si. The relative β-SiAlON contents increased gradually with the increase in ball milling time and also in the nitrogen pressure. Though the increase in nitrogen pressure can decrease the un-reacted Si consequently increase the purity of the product, an ultrahigh nitrogen pressure is not desirable from the viewpoint of either safety or decreasing the facility cost. The CS process could not self-propagate under the pressure lower than 0.7 MPa or from overlong milled raw mixtures.

Fig. 7 shows the SEM micrographs of CSed β-SiAlON products synthesized under 1 MPa pressure from different duration ball-milled mixtures. Some different shapes of β-SiAlON crystals, such as rod-like morphology, tiny particles, and thin whiskers can be seen. There are droplets on all the tops of the rod-like crystals, which indicate that the growth of the rod-like crystals should be in a VLS (vapor–liquid–solid) mechanism that has also been reported in reference [23]. With the increase of ball milling time, the products agglomerated together and showed a shape like flower due to the cohered particles by long ball milling shown in aforementioned Fig. 3.

The effect of N_2 pressure on the microstructure of CSed β-SiAlON is shown in Fig. 8. When the pressure increased from 0.7 to 1.5 MPa, the rod-like crystals became longer and thicker. For the product synthesized under 2.5 MPa, the rod-like crystals did not show clearly growth comparing with those synthesized under 1.5 MPa, but they showed more uniform in the length and thickness.

4. Conclusions

β-$Si_{6-z}Al_zO_zN_{8-z}$ ($z = 1$) powder was successfully combustion synthesized under various nitrogen pressures, assisted with different durations of mechanical activation. The following results were obtained:

(1) The conversion rate of β-SiAlON increased with increasing ball milling time. But overlong ball milling caused too low combustion temperature that combustion process could not self-propagate.
(2) The mechanical activation showed responsible for the reduction of the minimum nitrogen pressure required for the CS of β-SiAlON, which the reaction self-propagated under a low nitrogen pressure as only 0.7 MPa.
(3) The rod-like crystals agglomerated together with increasing ball milling, and became longer and thicker with increasing nitrogen pressure, according to SEM observations.

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