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Combustion Synthesis of High-Purity β-SiAlON Fine Powders using Natural Kaolin

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Significance

Single-phase β-SiAlON particles with submicron size were prepared via combustion synthesis (CS) using natural kaolin, Si, and Al as raw materials under a nitrogen atmosphere of 1 MPa. Kaolin could not only act as the raw material to provide the source of oxygen, but also act as the diluent to reduce the reaction temperature by eliminating the structural water during reaction process.

Keywords: β-SiAlON, combustion synthesis, Kaolin, submicron

Introduction

Beta-SiAlONs are nonstoichiometric compounds, which derived from the β-Si_3N_4 structure by the equivalent substitution of Si—N with Al-O. They have a hexagonal crystal structure with a general formula of $Si_{6-z}Al_zO_zN_{8-z}$ $(0 < z \leq 4.2)$. β-SiAlON is one of the most promising ceramic materials for high-temperature engineering applications due to its excellent properties, such as high strength and hardness, good thermal and chemical stability, superior wear resistance, and superior thermal shock resistance.[1–3] Moreover, the Eu^{2+}-doped β-SiAlON is now considered as a candidate for application in white light-emitting diodes (LEDs) that have the characteristics of a green-emitting phosphor.[4,5]

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an economical, effective, and energy-saving process for synthesizing industrial materials,[6–9] especially ceramics. This process uses the heat generated during a strong exothermic reaction in order to sustain the combustion process. No external energy is needed except for the ignition energy. CS has many advantages, including a low-energy input, a short reaction time, simple equipment, and a high-purity product. In conventional CS for preparing β-SiAlON, it is difficult to obtain pure single-phase products except by adding a large amount of diluents to the reactants, such as β-SiAlON,[10–12] or α/β-Si_3N_4.[13–15] This is due to that the combustion temperature is extremely high and silicon particles melt in the combustion front and coalesce during the reaction, which inhibits the complete nitridation of Si particles.[16,17] Diluent plays a role of enthalpy absorber, which decreases the combustion temperature and simultaneously slows down the reaction speed to improve the reaction efficiency. However, the simple use of the diluent is an inefficient process by using a part of the product as the starting reactant. In fact, as much as 50% of diluent β-SiAlON must be added to obtain a pure product. Furthermore, it is still a challenge to obtain fine or submicron size particle product directly. In this letter, we report a novel, more economical combustion synthesis process that using natural kaolin as raw material to produce β-SiAlON.

Experimental Procedure

The raw materials used in this work included the commercially available powders of Si (Soekawa Chemicals Co., Ltd., Tokyo, Japan; 99.9% purity; 1-2 μm) and Al (Kojundo

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Additional Supporting Information can be found in the online version of this article.

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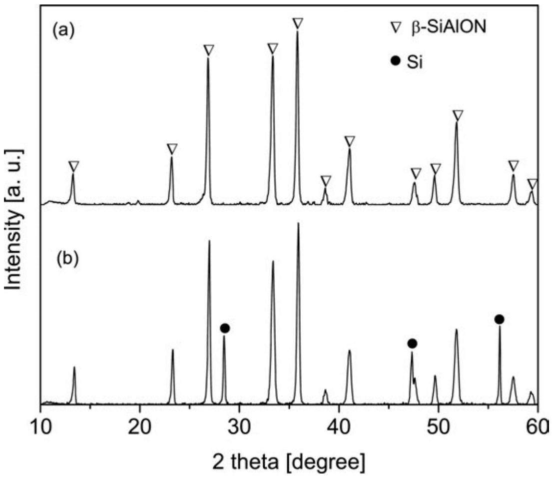

Figure 1. XRD patterns for the CSed β-Si_5AlON_7 powders obtained at nitrogen pressure of 1 MPa using kaolin as raw material, (a) using kaolin with structural water, (b) using kaolin without structural water.

Chemical Laboratory Co., Ltd., Saitama, Japan; 99.9% purity; 3 μm) and natural kaolin. The kaolin clay was supplied by W. A. Kaolin Holdings Pty., Ltd. (LOT 3 Ward Rd, East Rockingham, WA). The chemical composition, pretreatment process and characterization of the kaolin were described in supplementary materials.

The reactions for the combustion synthesis of β-Si_5AlON_7 (β-$Si_{6\text{-}z}Al_zO_zN_{8\text{-}z}$, z = 1) using kaolin with and without dehydration treatment can be described by the following equations

$$\frac{33}{7}\mathrm{Si}+\frac{5}{7}\mathrm{Al}+\frac{1}{7}(\mathrm{Al_2O_3}\cdot 2\mathrm{SiO_2}\cdot 2\mathrm{H_2O})+\frac{7}{2}\mathrm{N_2} \rightarrow \beta\text{-}\mathrm{Si_5AlON_7}+\frac{2}{7}\mathrm{H_2O(g)} \quad (1)$$

$$\frac{33}{7}\mathrm{Si}+\frac{5}{7}\mathrm{Al}+\frac{1}{7}(\mathrm{Al_2O_3}\cdot 2\mathrm{SiO_2})+\frac{7}{2}\mathrm{N_2} \rightarrow \beta\text{-}\mathrm{Si_5AlON_7} \quad (2)$$

All reactants were weighed according to the stoichiometric ratio. The reactants were mixed and mechanically activated by a planetary ball milling using zirconia balls in a zirconia pot at a ball to sample mass ratio of 10:1. The activated mixture was subsequently charged into a cylindrical carbon crucible with vents, which were used for the intrusion of the nitrogen gas. Ignition agent of the Al powders was placed on the top of the mixture. The combustion reaction was carried out at a nitrogen pressure of 1 MPa (purity: 99.999%) by passing a current of 60 A for 10 s through a carbon foil. The conditions for the planetary milling and the equipment for combustion synthesis have been described in detail elsewhere.[16]

Results and Discussion

The XRD patterns of the products are presented in Figure 1. It can be clearly observed that no other phase was identified, except β-Si_5AlON_7; the diffraction pattern is in agreement with the JCPDS card (no. 48-1615). However, strong Si peaks were detected as an impurity in the product when using dehydrated kaolin as raw material. This can be explained by that Si particles were fused and subsequently hardened under the fast reaction with a high-reaction temperature, which caused the remaining of Si in the product.

The energy dispersive X-ray spectrometry (EDS) analysis shows identified elements of Si, Al, O, and N; no impurities were detected in the product. This is because of the extremely high reaction temperature resulted in the evaporation of the minor impurities in kaolin. ICP was used for the analysis of metal impurities in the SiAlON product. The result was listed in Table 1. According to Table 1, the content of each metal element is lower than 0.3%, which suggests that the SiAlON prepared in this work is qualified for its application as engineering materials.

The SEM images of the CSed β-Si_5AlON_7 powders from kaolin are shown in Figure 2. The β-Si_5AlON_7 product consisted of fine particles with diameter of around 500 nm as well as a small amount of irregular elongated particles. However, for the particles obtained using dehydrated kaolin, they exhibited a rodlike shape which were significantly agglomerated, with only very few tiny particles. Furthermore, large bulk morphologies with lengths between 4 and 6 μm were found in this product. This difference is owing to the untreated Si, as confirmed by the differences between the XRD patterns in Figure 1.

To obtain a precise estimation of the particle size and particle-size distribution, particle-size distribution measurement were performed by laser particle-size analyzer. Before particle-size analysis, the sample suspension was deagglomerated by ultrasonic treatment for 5 min. Particle-size distribution graph of β-SiAlON powders are given in Figure 3. The results are in fairly good in agreement with the direct observation by SEM. The β-SiAlON powder was composed of particles with size ranging from 300 nm to 700 nm.

The lattice parameters of the hexagonal β-Si_5AlON_7 phase were calculated from the XRD peaks, with the values of 7.631 Å for *a* and 2.937 Å for *c*. According to *a* and *c*, the calculated z value was 0.94 by the equations in the reference,[2] which was in agreement with the expected value of 1 for the raw mixture.

Single-phase β-SiAlON was obtained when use kaolin without dehydration treatment; therefore, it can be deduced that the structural water of kaolin plays a significant role in the synthesis process. The reaction for the dehydroxylation which occurred within the temperature range of 350–830°C can be described by the following equation

$$\mathrm{Al_2O_3}\cdot 2\mathrm{SiO_2}\cdot 2\mathrm{H_2O}=\mathrm{Al_2O_3}\cdot 2\mathrm{SiO_2}(\text{metakaolinite}) + 2\mathrm{H_2O(g)}(\Delta H^0_{298K}=294.76\ \mathrm{kJ\ mol^{-1}}) \quad (3)$$

By this endothermic reaction, the adiabatic temperature (T_{ad}) of the combustion synthesis reaction using kaolin as a raw material was lowered by 350°C compared with the T_{ad}

Table 1. ICP Analysis for the Metal Impurities of the Combustion Synthesized β -Si_5AlON_7 Powders at Nitrogen Pressure of 1 MPa Using Kaolin Without Dehydration Treatment

Constituent	Ca	Fe	K	Mg	Ti
Content (mass %)	0.006	0.062	0.14	0.019	0.038

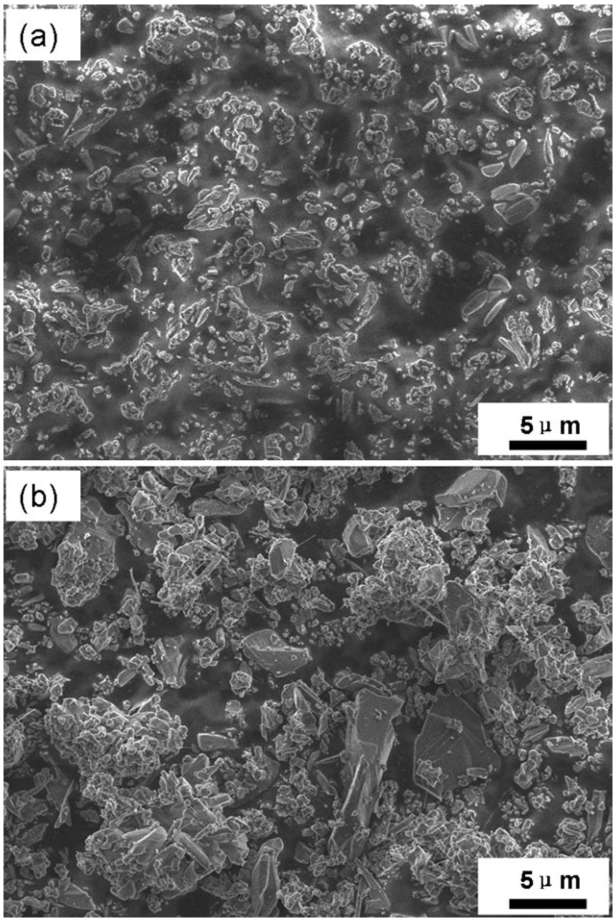

Figure 2. SEM images for the CSed β-Si_5AlON_7 powders obtained at nitrogen pressure of 1 MPa using kaolin as raw material, (a) using kaolin with structural water, and (b) using kaolin without structural water.

needed when using $Al_2O_3{\cdot}2SiO_2$ as a raw material. The method for the calculation of T_{ad} has been described in detail elsewhere.[16]

According to the result confirmed above, it is clearly known that the structural water in kaolin is the key factor in the formation of single-phase β-SiAlON. In the conventional synthesis process of β-SiAlON using Si, Al, and SiO_2 or Al_2O_3 as raw materials, at the preflame stage, a part of Al first react with N_2 to form AlN; the remaining Al reacted with SiO_2 to form Al_2O_3 and Si; simultaneously, these two exothermic reactions release large amounts of heat.[18,19] With the huge amount of reaction heat generated instantaneously, silicon particles melt at the surface quickly, which makes it difficult for the diffusion of the N_2 gas into the cores of powders through the liquid obstacle layer; consequently, unreacted Si remain in the product within the very short reaction time of the whole combustion synthesis process. However, when kaolin ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) was used as the raw material in this study to substitute the use of pure SiO_2 or Al_2O_3, the eliminating of structural water absorbed part of the released heat at the preflame stage; this reduced the temperature of the preflame and alleviated the melting of Si. Subsequently, the metakaolin ($Al_2O_3{\cdot}2SiO_2$) transformed $Al_2O_3{\cdot}3SiO_2$ and SiO_2 (amorphous), then the amorphous SiO_2 reacted with Al to form Al_2O_3 and Si, accompanied by a mass of heat release, the temperature reached the ignition point of the Si—N_2 reaction, Si particles react with N_2 to form Si_3N_4 crystals on Si surface. Simultaneously, by the dissolution, mass transportation, and precipitation processed occurred between Si_3N_4, AlN, and Al_2O_3, β-SiAlON particles were formed.[20] Moreover, with the loss of hydroxyl groups in kaolin during dehydration, a lot of pores formed which also enhanced the nitridation process to make a complete conversion to β-SiAlON.

The microstructure of the product was also affected by the reaction temperature.[21] In the case of using kaolin as the raw material, the reaction temperature was lowered attribute to the evaporation of structural water in kaolin. At low-reaction temperature, high-viscosity phase reduced the mass transport during the solution-reprecipitation process.[22] As a result, the agglomeration for β-SiAlON particles was limited, which showed small particles. On contrast, the high-reaction temperature accelerated the mass transport during the reaction, hence, the β-SiAlON nuclei grew into elongated grains when using kaolin without structural water as raw material.

This new preparative process is of great importance for energy saving in fabricating β-SiAlON ceramics. Kaolin acts as a diluent to absorb the reaction enthalpy, and it thereby maintains a relatively low-overall reaction temperature. In addition, the dehydration process requires significant amounts of heat from the CS of β-SiAlON to eliminate the structural water. Consequently, the Si can be fully nitridated to form β-SiAlON. In any case, by the loss of hydroxyl groups in kaolin, the pores that are formed in the structure further enhance the nitridation process. Moreover, in our previous research,[23] experiments were carried out with Al_2O_3 as one of the sources of oxygen, instead of SiO_2. The results showed that the reaction did not propagate to the synthesis of β-SiAlON owing to the low-calorific values of the raw materials. In contrast with these results, kaolin, as the source of the oxygen, appropriately regulated the calorific values, and therefore, played an important role in the better control of the conversion of reactants to products and the production of a single-phase β-SiAlON.

In summary, single-phase, submicron sized β-SiAlON particles were fabricated directly from natural kaolin by CS at nitrogen pressure of 1 MPa without adding any diluent. The use of kaolin in this new preparative process has several notable advantages: it can produce pure products without

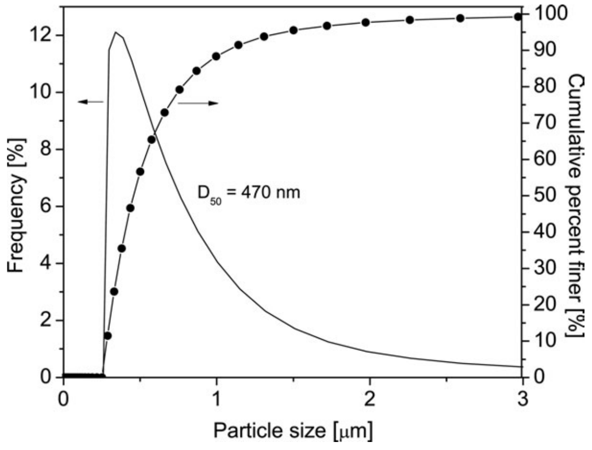

Figure 3. Particle-size distribution of the CSed β-Si_5AlON_7 powders obtained at nitrogen pressure of 1 MPa using natural kaolin as raw material.

requiring the addition of any diluent; the large-scale use of this material can greatly reduce the cost of the β-SiAlON production; provides fine particles with median diameter of about 470 nm. The major parameter affecting the process is the structure water in kaolin, which lowered the T_{ad} by 350°C. Future work is planned to verify the benefits between using kaolin as the raw material in comparison to conventional combustion synthesis method by analyzing the energy, exergy-based life cycle assessment (LCA).

Literature Cited

1. Jack KH. Review Sialons and related nitrogen ceramics. *J Mater Sci*. 1976;11:1135–58.
2. Ekström T, Käll PO, Nygren M, Olssen PO. Dense single-phase β-sialon ceramics by glass-encapsulated hot isostatic pressing. *J Mater Sci*. 1989;24:1853–61.
3. Ekström T, Nygren M. SiAlON ceramics. *J Am Ceram Soc*. 1992;75[2]:259–76.
4. Ho Ryu J, Park Y-G, Sik Won H, Hyun Kim S, Suzuki H, Yoon C. Luminescence properties of Eu^{2+}-doped β-$Si_{6-z}Al_zO_zN_{8-z}$ microcrystals fabricated by gas pressured reaction. *J Crystal Growth*. 2009;311(3):878–82.
5. Zhu XW, Masubuchi Y, Motohashi T, Kikkawa S. The z value dependence of photoluminescence in Eu^{2+}-doped β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$) with $1 \leq z \leq 4$. *J Alloys Compd*. 2010;489(1):157–61.
6. Parkin IP, Elwin G, Barquin LF, Bui QT, Pankhurst QA, Komarov AV et al. Self-propagating high temperature synthesis of hexagonal ferrites $MFe_{12}O_{19}$ (M = Sr, Ba). *Adv Mater*. 1997;9(8):643–45.
7. Munir ZA, Anselmi-Tamburini U. Self-propagating exothermic reactions: The synthesis of high-temperature materials by combustion. *Mater Sci R*. 1989;3(7–8):277–365.
8. Martirosyan KS, Luss D. Carbon combustion synthesis of complex oxides: Process demonstration and features. *AIChE J*. 2005;51(10):2801–10.
9. Locci AM, Licheri R, Orrù R, Cincotti A, Cao G, De Wilde J et al. Low-gravity combustion synthesis: Theoretical analysis of experimental evidences. *AIChE J*. 2006;52(11):3744–61.
10. Xuemei Y, Kotaro W, Tomohiro A. Fabrication of dense β-SiAlON by a combination of combustion synthesis (CS) and spark plasma sintering (SPS). *Intermetallics*. 2010;18(4):536–41.
11. Aoyagi K, Sivakumar R, Yi X, Watanabe T, Akiyama T. effect of diluents on high purity beta-SiAlONs by mechanically activated combustion synthesis. *J Ceram Soc Jap*. 2009;117(6):777–79.
12. Shahien M, Radwan M, Kirihara S, Miyamoto Y, Sakurai T. Combustion synthesis of single-phase β-sialons (z = 2-4). *J Euro Ceram Soc*. 2010;30(9):1925–30.
13. 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]:3700–02.
14. Wu Y, Zhuang H, Wu F. Mechanism of the formation of β-Sialon by self-propagating high-temperature synthesis. *J Mater Res*. 1998;13(1):166–72.
15. Lis J, Majorowski S, Puszynski JA, Hlavacek V. Dense β- and α/β-SiAlON materials by pressureless sintering of combustion-synthesized powders. *Am Ceram Soc Bull*. 1991;70(10):1658–64.
16. 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):626–28.
17. Yi X, Akiyama T. Mechanical-activated, combustion synthesis of β-SiAlON. *J Alloys Compd*. 2010;495(1):144–48.
18. Li J, Wang J, Chen H, Sun B, Jia J. Synthesis of β-SiAlON—AlN-polytyppoid ceramics from aluminium dross. *Mater Trans*. 2010;51(5):844–48.
19. Ng DHL, Cheung TLY, Kwong FL, Li Y-F, Yang R. Fabrication of single crystalline β’-SiAlON nanowires. *Mater Lett*. 2008;62(8–9):1349–52.
20. 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.
21. Madras G, McCoy BJ. Temperature effects for crystal growth: a distribution kinetics approach. *Acta Mater*. 2003;51(7):2031–40.
22. He E, Yue J, Fan L, Wang C, Wang H. Synthesis of single phase β-SiAlON ceramics by reaction-bonded sintering using Si and Al_2O_3 as raw materials. *Scripta Mater*. 2011;65(2):155–58.
23. 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(1–2):236–40.

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