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Short communication

Preparation of single phase nano-sized β-SiAlON powders by nitridation of silica–alumina gel in ammonia

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Abstract

β-SiAlON powder was prepared from silica–alumina gel and by heat-treatment in ammonia. Element analysis, X-ray diffraction, magic-angle spinning nuclear magnetic resonance, scanning electron microscopy and transmission electron microscopy were used to characterize the powder. It was found that nitridation reactions took place at 1100 °C and β-SiAlON began to crystallize at 1300 °C with mullite, O-SiAlON and χ-SiAlON as the intermediate phases. Nano-sized single phase β-SiAlON powder was obtained after heating at 1350 °C for 3 h.

Keywords: A. Sol–gel processes; D. Sialon; Powders; Ammonia

1. Introduction

β-SiAlON is a series of solid solution compounds of β-Si_3N_4. The formula of β-SiAlON is generally written as $Si_{6-z}Al_zO_zN_{8-z}$ ($0<z<4.2$), in which the Si–N bonds are replaced by Al–O bonds in the number of z [1]. Because of their excellent mechanical and thermal stable properties, β-SiAlONs have been recognized as the candidates for applications in cutting tools, wear components, metal forming tools, and other high temperature structural parts [2]. Recently, β-SiAlONs doped with rare-earth as well as other oxynitride materials show attractive optical properties [3], and have been reported as promising host materials for luminescent phosphor applied in white light emitting diodes [4].

Generally, β-SiAlONs are prepared by solid-state reactions of AlN–Si_3N_4–Al_2O_3 at >1500 °C. However, it is difficult to obtain the single phase material [5], and the β-SiAlON grains grow inevitably during the high temperature processing. Carbothermal reduction and the nitridation method (CRN) is economical process, the starting raw material can be natural clay minerals (such as kaolinite [6], halloysite [7]) or waste materials like fly-ash [8], but normally the products contain a mixture of α-SiAlON, mullite, α-Al_2O_3 and other compounds [6–9]. Furthermore, the residual carbon and the SiC by-product are disadvantageous when the SiAlONs are used as phosphors in optical applications [10].

Recently, nitridation of oxide precursor by ammonia has attracted attention to prepare nitride and oxynitride powders [10–13]. Owing to the high reactivity of ammonia, (oxy)nitride could be formed at lower temperature, thus the agglomeration of powder decreases accordingly. Another benefit is that the post treatment of carbon residue could be avoided. Fine α-SiAlON powders have been successfully prepared by this method at 1400–1500 °C [10,13]. Synthesis of Eu-doped β-SiAlON powders have also been reported by the ammonia nitridation of Si_3N_4 powder dispersed in aluminum glycine gel; however, both α-SiAlON and 15R-SiAlON exist as impurities in the product [14].

Sol–gel process is a relatively easy and economical method to synthesize uniform and high-quality precursor, which has been used extensively in preparation of ultra-fine oxide ceramic powders. However, few studies concerned about synthesis of oxynitride by combination of the sol–gel process and ammonia nitridation. In this work, we report the ammonia reduction nitridation synthesis of β-SiAlON powders from a

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silica–alumina gel precursor. A simple route to obtain single phase nano-sized β-SiAlON powders is provided.

2. Experimental

2.1. Preparation procedures

The raw materials for SiAlON precursor were water soluble alumina sol and silica sol. Alumina sol was prepared in laboratory by refluxing aluminum metal powder and crystalline aluminum chloride hydrated ($AlCl_3 \cdot 6H_2O$) water solution. The alumina content in the as-prepared sol was 20 wt%, Al/Cl = 1.8/1 (molar ratio), and the colloidal particle size was 2–5 nm (by TEM observation, not shown). Commercial silica sol (SW30, Foshan Zhongfa Sodium Silicate Company, Foshan, China) was used as silica source. The SiO_2 content was 30 wt%, and the colloidal size was ~20 nm. 40 g silica sol and 10.2 g alumina sol was stirred magnetically in a 250 ml beaker for 30 min, then transferred to 80 °C oven to evaporate water for 24 h. The β-SiAlON precursor powder (Si/Al = 5/1) was obtained by crushing the silica–alumina gel and passing through 200-mesh sieve.

For nitridation, ~1.5 g gel powder was placed in an alumina boat (150 mm × 30 mm × 10 mm), and heated in a 1250 mm length alumina tube furnace with 50 mm inner diameter (Luoyang Shenjia Kiln Corporation., Ltd.). Flowing NH_3 (99.999%, 0.40 L/min) was used as the nitridation gas. Before heating, the furnace tube was evacuated and flushed with nitrogen gas repeatedly. The heating rate was 5 °C/min and the holding time at the set temperature was 3 h. The pyrolysis temperatures were from 1100 °C to 1400 °C.

2.2. Characterization

Phase analysis was carried out by X-ray diffraction (XRD, X'Pert PRO, PANalytical, Almelo, Netherlands) with CuK_a radiation. The lattice parameters of the β-SiAlON phase were calculated with a least-squares program from a great number of diffraction positions, which was calibrated with Si. The average size was determined from the full width at half maximum (FWHM) of the X-ray diffraction peaks using Scherrer's equation, $D = K\lambda/(B \cos\theta)$, where D was the crystallite size, K was a constant with a value of 0.9, λ was the X-ray wavelength with a value of 0.154 nm, B was the FWHM of a diffraction peak, and θ was the diffraction angle. Field emission scanning electron microscopy (FE-SEM, LEO 1530 Gemini, Zeiss, Oberkochen, Germany) and transmission electron microscopy (TEM, JEM 2100, JEOL, Tokyo, Japan) were used for exploring the powder morphology and microstructure. Nitrogen and oxygen content were determined using Oxygen/Nitrogen Analyzer (EMGA-620W, Horiba, Kyoto, Japan). The Si/Al molar ratio was analyzed by energy dispersive X-ray spectroscopy (EDX) equipped on the SEM. The ^{27}Al and ^{29}Si MAS NMR spectra were acquired at 7.05 T using a Bruker Avance 300 MHz spectrometer (Bruker, Switzerland) and a 4 mm ZrO_2 rotor spun at 5 kHz. The ^{27}Al and ^{29}Si spectra were referenced to $AlCl_3 \cdot 6H_2O$ and tetramethylsilane (TMS), respectively.

3. Results and discussion

Table 1 summarizes the chemical compositions of the powders prepared at various temperatures. At 1100 °C, nitrogen of 5.14 wt% has been incorporated, indicating relatively high reactivity of the gel powders. The rapid nitridation reaction takes place between 1300 °C and 1350 °C, and the nitrogen content increases from 8.16 wt% to 36.5 wt% accordingly, very close to the theoretical value (34.8%) of $Si_{6-z}Al_zO_zN_{8-z}$ ($z = 1$). Commonly, a high temperature above 1400 °C is required in the carbothermal reduction–nitridation process (CRN) [6–9]. In this attempt, complete transformation to β-SiAlON is achieved at 1350 °C for 3 h. To our knowledge, this is the most moderate condition to obtain β-SiAlON. It is ascribed to the high reactivity of Si–Al precursor gel, in which both the colloidal particle size are in nanometers (< 20 nm) and homogeneously mixed. A treatment at 1400 °C leads to over nitridation, and the resultant nitrogen is 37.9 wt%. Moreover, EDX analysis shows slight increase of Al/Si molar ratio, implying loss of SiO gas in flowing ammonia.

XRD patterns of the products after nitridation for 3 h are shown in Fig. 1. No crystalline phase is detected at 1100 °C, the broad hump at $2\theta \sim 22°$ suggests a large part of SiO_2 is still unreacted and in amorphous state, in consistent with the low nitridation extent. At 1200 °C, several diffraction peaks corresponding to mullite are observed on the amorphous background. The standard Gibbs free energy of formation of mullite (reaction 1) is more negative than that of the (oxy)nitrides (reactions 2 and 3) at low temperature, so solid state reaction of the Si–Al oxides competes with nitridation reaction. However, the diffraction intensity of mullite decreases at 1300 °C, and both O-SiAlON ($Si_{1.8}Al_{0.2}O_{1.2}N_{1.8}$) and χ-SiAlON ($Si_{12}Al_{18}O_{39}N_8$) are identified as the major crystalline phases. Moreover, β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$) phase (2θ at about 35.9°) is also detected. This suggests that nitridation reactions (4, 5 and 6) become dominant at higher temperature and the formation of mullite is suppressed. After firing at 1350 °C, the amorphous hump completely disappears and the only crystalline phase is β-SiAlON. The disappearance of intermediate SiAlON phases (O and χ) suggests that beta phase can be formed by further nitridation of them, as shown in reactions 7 and 8. Lattice constants refinement of the 1350 °C sample shows that $a = 0.7630$ nm and $c = 0.2930$ nm, and the corresponding z value estimated using the equation of Ekström [15] is 0.9,

Table 1
Compositions of SiAlON powders.

Temperature (°C)	Nitrogen (wt%)	Oxygen (wt%)	Al/Si [a]
1100	5.14	35.10	0.194
1200	4.24	35.21	0.204
1300	8.16	29.91	0.207
1350	36.58	7.46	0.205
1400	37.89	7.3	0.212

[a]analyzed by EDX.

close to the designed formula $AlSi_5ON_7$ ($z=1$). Crystallite size calculated from the diffraction line broadening is 40–50 nm, indicating the as prepared β-SiAlON is nano-sized. β-SiAlON prepared at 1400 °C is Si-rich, confirmed by the lower z value (~0.8). At the same time, the total Al/Si of the sample is enhanced, implying the existence of Al-rich phase. However, besides β-SiAlON, no other crystalline phase is identified by XRD, probably because diffraction lines are obscured by overlapping and/or the content is quite low in the product.

$$3Al_2O_3(s)+2SiO_2(s)\rightarrow 3Al_2O_3\bullet 2SiO_2(s) \quad (1)$$

$$Al_2O_3(s)+2NH_3(g)\rightarrow 2AlN(s)+3H_2O(g) \quad (2)$$

$$2SiO_2(s)+2NH_3(g)\rightarrow Si_2N_2O(s)+3H_2O(g) \quad (3)$$

$$9Al_2O_3(s)+12SiO_2(s)+8NH_3(g)\rightarrow Si_{12}Al_{18}O_{39}N_8(s)+12H_2O(g) \quad (4)$$

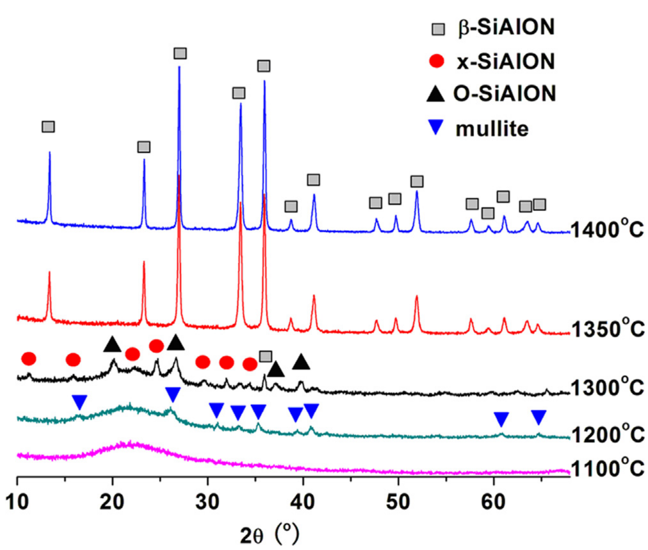

Fig. 1. XRD patterns of powders synthesized at 1100–1400 °C. β-SiAlON: Si_5AlON_7; χ-SiAlON: $Si_{12}Al_{18}O_{39}N_8$; O-SiAlON: $Si_{1.8}Al_{0.2}O_{1.2}N_{1.8}$; mullite: $Al_6Si_2O_{13}$.

$$0.1Al_2O_3(s)+1.8SiO_2(s)+1.8NH_3(g)\rightarrow Si_{1.8}Al_{0.2}O_{1.2}N_{1.8}(s)+2.7H_2O(g) \quad (5)$$

$$Al_2O_3(s)+10SiO_2(s)+14NH_3(g)\rightarrow 2Si_5AlON_7(s)+21H_2O(g) \quad (6)$$

$$Si_{12}Al_{18}O_{39}N_8(s)+78SiO_2+118NH_3(g)\rightarrow 18Si_5AlON_7(s)+177H_2O(g) \quad (7)$$

$$2.5Si_{1.6}Al_{0.4}O_{1.4}N_{1.6}(s)+SiO_2+3NH_3(g)\rightarrow Si_5AlON_7(s)+4.5H_2O(g) \quad (8)$$

^{27}Al MAS NMR spectra are shown in Fig. 2a. Gel precursor shows the presence of resonances at ~0 and ~60 ppm, corresponding to AlO_6 octahedron and AlO_4 tetrahedron, respectively. At 1200 °C, octahedral peak reduces, and the tetrahedral peak becomes broad due to formation of 5-coordinated sites (~45 ppm), which is characteristic of mullite [7]. A new intense peak (~110 ppm) appears at 1350 °C, corresponding to Al–N resonance in β-SiAlON [9,16]. At the same time the resonances of AlO_6 reduces dramatically and could hardly be identified. Although oxygen is present in the 1350 °C sample, the mixed type of coordinations AlO_xN_{4-x} ($1\le x<4$) such as AlN_3O is not observed for the quadrupolar broadening [16].

Fig. 2b shows the ^{29}Si MAS NMR spectra. A board resonance centered at -110 ppm is observed in gel precursor, which is characteristic of SiO_4 tetrahedron in silica. At 1100 °C, a new resonance at -90 ppm corresponding to $SiNO_3$ [7] appears, indicating that nitrogen has been incorporated in the Si–O network. The resonance of mullite at -94 ppm [7] appears at 1200 °C, coinciding with the XRD result. At 1300 °C, both of SiN_3O (-60 ppm) [7] and SiN_4 (-46 ppm) [7] appear, confirming the further nitridation of silicon oxynitride. Besides SiN_4, other $Si(O,N)_4$ signals could hardly be detected at 1350 °C, especially uncombined silica or silica-rich glass (-106 to -116 ppm) is absent, implying the complete transformation to crystalline SiAlON. The ^{27}Al and ^{29}Si MAS NMR spectra reveal that the nitridation stops at 1350 °C, in consistent with the results of XRD and nitrogen content.

Morphology of the powders after nitridation is shown in Fig. 3. After 1200 °C (Fig. 3a), it is easy to identify the mullite crystals from the amorphous matrix, as shown by the arrow.

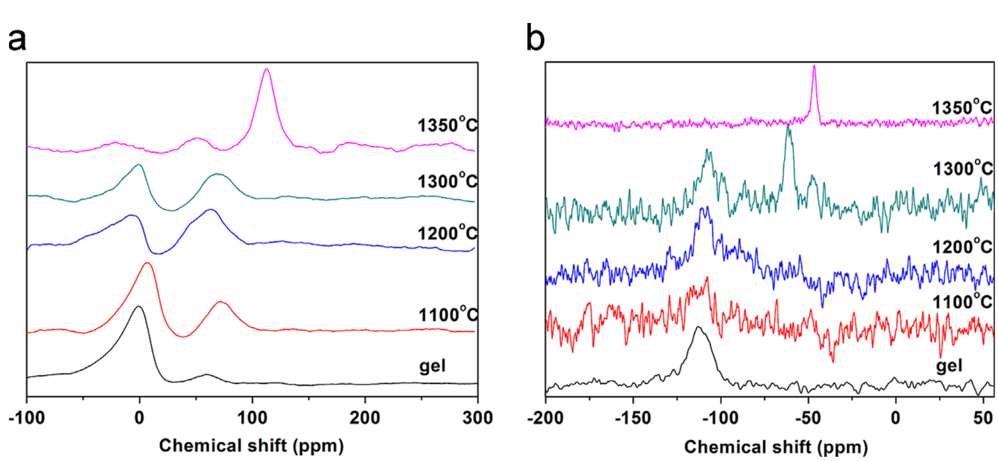

Fig. 2. MAS NMR spectra of the synthesized powders. (a) ^{27}Al and (b) ^{29}Si.

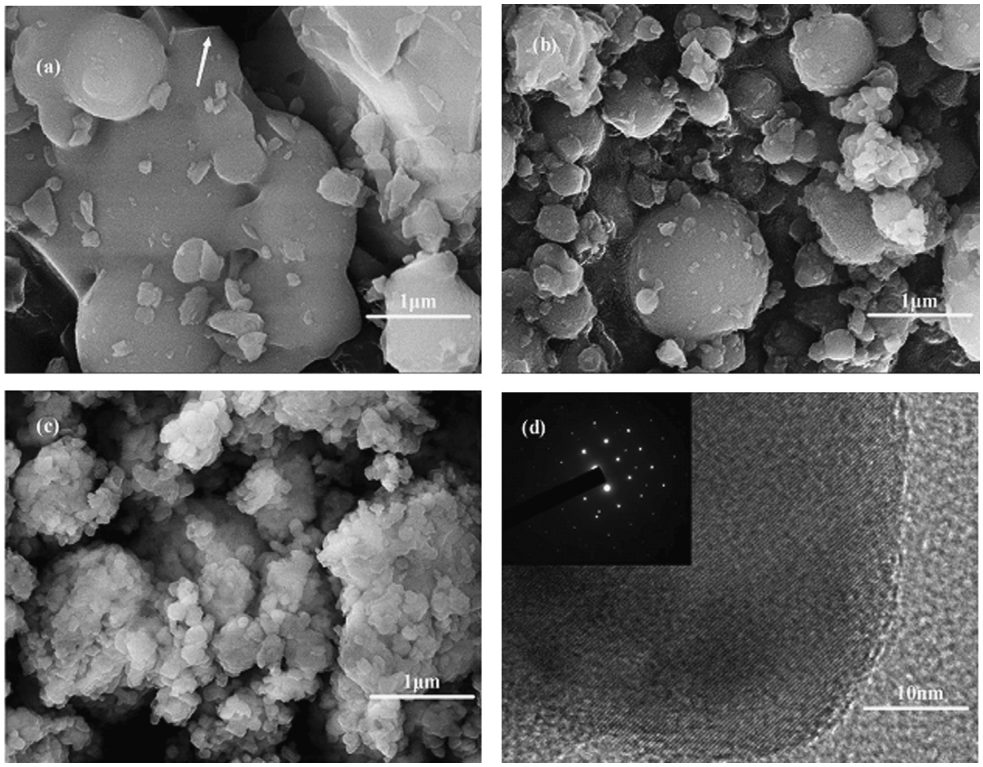

Fig. 3. SEM micrographs of powders synthesized at (a) 1200 °C, (b) 1300 °C, (c) 1350 °C and (d) TEM micrographs of powders synthesized at 1350 °C.

More SiAlONs crystallize with the elevated temperature (Fig. 3b). The 1350 °C sample (Fig. 3c) is totally composed of nano-sized particles. Selected area diffraction (SAD) confirms its high crystallinity, and high resolution TEM (Fig. 3d) shows glass phase is absent from the sphere particle, coinciding with the XRD result. Generally, the glass-free nano-sized β-SiAlON powder prepared by this method is beneficial for applications of SiAlON as the phosphors and the raw material for structural ceramics.

4. Conclusions

In this work, β-SiAlON powder was synthesized using silica-alumina gel as the raw materials and by reduction nitridation in ammonia. The gel experienced phase change during heating from amorphous, mullite to intermediate SiAlON phases (O- and χ-), and finally transformed to β-SiAlON. Nano-sized β-SiAlON powder with high purity was obtained at 1350 °C for 3 h.

Acknowledgments

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