Effect of NH₄Cl addition on the morphology of β-SiAlON powders prepared by salt-assisted nitridation

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1. Introduction

β-SiAlON is one type of solid solution formed via Al and O dissolution in β-Si₃N₄, represented by the formula Si₆₋zAl₂O₃N₈₋z (0 < z ≤ 4.2), where z denotes the number of Si atoms replaced by Al in β-Si₃N₄. β-SiAlON solid solution retains the hexagonal structure of the β-Si₃N₄ system. However, β-SiAlON ceramic shows better sinter-ability, high-temperature properties, and oxidation resistance than pure Si₃N₄ ceramic.² It is considered one of the most promising high-temperature structural materials because of its high strength and hardness, good thermal properties, superior wear properties, chemical stability, and thermal shock resistance.³

In addition, β-SiAlON has broad applications to cutting tools because of its abrasion resistance. Thus, many scholars have conducted extensive and in-depth research. At present, various synthetic methods have been developed to fabricate β-SiAlON products, including (1) high-temperature solid state reaction,⁴-⁶ which is a complex, high-cost process that is not suitable for application to refractory production; (2) carbothermal reduction nitridation (CRN),⁷-¹⁰ which requires a high reaction temperature and a short reaction time and leads to low-purity products; and (3) combustion synthesis (CS),¹¹,¹² which usually requires a very short reaction time and an extremely high combustion temperature, so the purity of the products is always low. In order to obtain high-purity products, the synthesis method must decrease the reaction temperature as well as prolong the reaction time. During the last decade, molten salt synthesis has been widely used for the preparation of carbide and nitride.¹³-¹⁷ Molten salt synthesis has proven to be an effective, energy-saving method for the synthesis of a variety of advanced materials. It has many advantages over the other methods, such as a relatively low synthesis temperature, higher utilization, simple equipment, and high-purity products. At present, some nitrides have been fabricated by salt-assisted nitridation, including β-SiAlON⁸,¹⁰ and β-Si₃N₄.²⁰

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In this work, β-SiAlON powders were synthesized via salt-assisted nitridation of a powder mixture by using Si, Al, and SiO₂ as the main starting materials and NaCl and NaF as the molten salt medium. The influence of processing factors such as the NH₄Cl content and the reaction temperature on the synthesis of β-SiAlON was studied. The introduction of NaCl and NaF to the raw materials as the molten salt medium was beneficial because they offer protection against the melting of Si. Because the melting points of NaCl (801°C) and NaF (993°C) are lower than that of Si (1410°C), the product can be obtained in this system. The morphologies of β-SiAlON in the presence of NaCl and NaF were determined by evaluating the reacted products.

2. Experimental procedure

Si (purity ≥99.9%, 9 μm), Al (purity ≥99.0%, 0.05 mm), and SiO₂ (purity ≥99.0%, 15 μm) powders were used as the raw materials. NaCl (purity ≥99.0%) and NaF (purity ≥98.0%) were used to form the molten salt, and NH₄Cl (purity ≥98.0%) was used as the auxiliary nitrogen source. All materials were mixed to synthesize β-SiAlON (Si₆₋zAl₂O₃N₈₋z) with z = 2 because β-SiAlON (z = 2) has excellent slag erosion resistance compared to β-SiAlON with other z values. The nitridation synthesis of β-SiAlON can be expressed by the following reaction (1):

\[ 2Al(s) + 3Si(s) + SiO_2(s) + 3N_2(g) = Si_6Al_2O_2N_8(s) \] (1)

Different contents of NH₄Cl were added with 65 wt% NaCl, 3 wt% NaF, 10 wt% Al powder, 7 wt% Si powder, and 15 wt% SiO₂. The molar ratio of Si:Al:O:N was 5:3:7:5 (2.4, 3.2, 4.8) in raw materials with different contents of NH₄Cl. The powders were fully mixed, fired from room temperature to 1250–1450°C at a rate of 5°C min⁻¹, and held for 3 h under a nitrogen flow of 90 ml/min (nitrogen purity: 99.99%). In this system, NH₄Cl as the auxiliary nitrogen source, the N₂ can be generated inside the raw material and promote progress of the nitridation reaction. Then the samples were repeatedly washed with distilled water using ultrasonic equipment until the salt was completely dissolved. A product consisting of β-SiAlON was successfully
obtained after drying.

Phase analysis of the products was performed using X-ray diffraction (XRD, Philips, X’Pert Pro). The morphology of the products was observed by scanning electron microscopy (SEM, Nova NanoSEM400, FEI Company), and the crystal structure of the products was observed by transmission electron microscopy (TEM, JEOL, JEM2000F).

3. Results and discussion

3.1 Phase composition of the products

Figure 1 shows the XRD patterns of the powders synthesized with different initial compositions after nitridation sintering at 1350°C and holding for 3 h. β-SiAlON, Si, and α-Al2O3 were the main crystalline phases in the powders. However, the z values of β-SiAlON varied, where one powder had a z-value of 3 and the other had a z-value of 2. Insufficient nitrogen was available to form β-SiAlON (z = 3) when the NH4Cl content was low. As well known, NH4Cl decomposed easily at the temperature as low as 385°C in the air. Therefore, it inferred that the a few reactions might take place in molten salt system of Si/Al/SiO2/N2 in the decomposition of NH4Cl process. The reaction was as follows:21)

\[
\begin{align*}
\text{NH}_4\text{Cl} & = \text{NH}_3(g) + \text{HCl}(g) \\
\text{Si}(s) + 4\text{HCl}(g) & = \text{SiCl}_4(s) + 2\text{H}_2(g) \\
\text{SiO}_2(s) + 4\text{HCl}(g) & = \text{SiCl}_4(s) + 2\text{H}_2\text{O}(g) \\
\text{Al}(s) + \text{NH}_3(g) & = \text{AlN}(s) + 1.5\text{H}_2(g) \\
\text{Al}(s) + 3\text{HCl}(g) & = \text{AlCl}_3(s) + 1.5\text{H}_2(g) \\
\text{AlCl}_3(s) + \text{NH}_3(g) & = \text{AlN}(s) + 3\text{HCl}(g) \\
3\text{SiCl}_4(s) + 6\text{H}_2(g) + 2\text{N}_2(g) & = \text{Si}_3\text{N}_4(s) + 12\text{HCl}(g) \\
3\text{SiCl}_4(s) + 4\text{NH}_3(g) & = \text{Si}_3\text{N}_4(s) + 12\text{HCl}(g) \\
\text{Si}_3\text{N}_4(s) + \text{SiO}_2(s) + 2\text{AlN}(s) & = \text{Si}_4\text{Al}_2\text{O}_2\text{N}_6(s)
\end{align*}
\]

To investigate the effect of the nitridation temperature, the powders were synthesized at temperatures ranging from 1250 to 1450°C for 3 h with the addition of 20 wt% NH4Cl, and their XRD patterns are given in Fig. 2. As shown in Fig. 2, β-SiAlON (z = 2) was already formed at 1250°C, and the amount of β-SiAlON increased with an increase in temperature. Compared with Fig. 1, the products were β-SiAlON (z = 2), indicating that 20 wt% NH4Cl provided a sufficient nitrogen source. In addition, in Figs. 1 and 2, the α-Al2O3, Si, and Si3N4O phases were present in the samples because of reactions (11) and (13). The Si phase was present because the partial melting of Si powder could not be reacted completely, resulting in residual Si powder. However, the Si phase disappeared at 1450°C in Fig. 2, and more β-SiAlON (z = 2) crystals were formed by reaction (12).

\[
\begin{align*}
4\text{Al}(l) + 3\text{SiO}_2(s) & = 2\text{Al}_2\text{O}_3(s) + 3\text{Si}(l) \\
\frac{7}{2}\text{Al}_2\text{O}_3(s) + (6 - z)\text{Si}(l) + \left(\frac{8 - z}{2}\right)\text{N}_2(g) & = \text{Si}_{6-z}\text{Al}_z\text{O}_2\text{N}_{8-z}(s) + \frac{3}{4}2\text{O}_2(g) \\
\text{Si}_{z}(s) & = \text{Si}_{z}\text{N}_2\text{O}(s) + \frac{3}{2}2\text{O}_2(g)
\end{align*}
\]

3.2 Morphology of the products

Figure 3 shows the morphology of the powders that were synthesized at 1350°C with different contents of NH4Cl. In Fig. 3, when the NH4Cl content was 10 wt% (a) or 15 wt% (b), the β-SiAlON crystals were rod-like with smooth tops. However, at 20 wt% NH4Cl (c), the β-SiAlON crystals were rod-like with conical tops. Although the sizes of the β-SiAlON crystals were approximately 1–3 μm, the number of β-SiAlON crystals increased when 20 wt% NH4Cl was added by semi-quantitative analysis in Table 1. Thus, the morphology of β-SiAlON depended on the NH4Cl content. β-SiAlON, α-Al2O3, Si, and Si3N4O appear in Fig. 1, but NaCl, NaF, and NH4Cl did not exist in the powders, which indicates that nitrogen from NH4Cl may have been involved in the synthesis of β-SiAlON. Therefore, it is inferred that a NH4Cl content of 20 wt% could provide more nitrogen, and a large number of β-SiAlON crystals were formed. However, while some NH4Cl acted as a nitrogen source, the rest was volatilized. Thus, the amount of β-SiAlON crystals was greater when the NH4Cl content was 20 wt%.

The morphology of the β-SiAlON crystals depended on the temperature. Figure 4 shows the morphology of the powders synthesized at 1450°C with 10 wt% (a), 15 wt% (b), and 20 wt% (c) NH4Cl and the EDS (d) pattern of the rod-like crystals. The shapes of the β-SiAlON crystals have distinctive features when different NH4Cl contents were added. As shown in the image, the β-SiAlON crystals were rod-like with smooth tops, and the size...
distribution of the $\beta$-SiAlON crystals was uniform. However, with 20 wt % NH$_4$Cl, the amount of $\beta$-SiAlON crystals increased, and the crystals were smaller than those synthesized with 10 and 15 wt % NH$_4$Cl.

Therefore, the Si powder was in the liquid phase at 1450°C and evenly dispersed between the SiO$_2$ and Al powders. Reaction (1) occurred to completion. In addition, 20 wt % NH$_4$Cl could provide a sufficient nitrogen source and thus produced more $\beta$-SiAlON crystals. Lower NH$_4$Cl contents could not provide sufficient nitrogen, and thus the amount of $\beta$-SiAlON crystals was lower. The $\beta$-SiAlON crystals had a hexagonal, short, columnar crystal structure when different NH$_4$Cl contents were added. The $\beta$-SiAlON crystals also agglomerated together, which indicates that the salt-assisted nitridation synthesis method provided a good environment for $\beta$-SiAlON growth. The growth mechanism of $\beta$-SiAlON was vapor–liquid–solid (VLS) mechanism at 1450°C and vapor–solid (VS) mechanism at 1350°C.\textsuperscript{22)}
Further detailed understanding of the crystal structure and morphology of the β-SiAlON powders is provided by TEM, high-resolution TEM (HRTEM), and selected-area electron diffraction (SAED) investigations. Figures 5(a) and 5(b) shows the typical rod-like morphology of the product, and the inset in Fig. 5(a) shows the presence of Si, Al, O, and N elements in the product. Thus, the product was β-SiAlON crystal according to the phase analysis in Fig. 2. Compared to Fig. 5(a), Fig. 5(b) shows the size of the β-SiAlON crystals, which were on the micrometer scale (2–4 μm). In Fig. 5(c), the HRTEM lattice image demonstrated that the β-SiAlON crystals possessed a perfect crystal structure, and the corresponding SAED pattern further verified their rod-like hexagonal structure, as shown in Fig. 5(d). The marked lattice fringe d-spacing of 0.66 nm corresponds to the (101) plane of β-SiAlON. The lattice fringe, along with the SEAD pattern, indicates that the growth direction of the β-SiAlON powder was [010].

4. Conclusion

A convenient method to obtain β-SiAlON products was developed. When different NH₄Cl contents were added at 1350°C, the morphologies of the β-SiAlON crystals showed significant changes, including rod-like crystals with smooth tops and tapered tips. At 1450°C, the β-SiAlON crystals were rod-like crystals with smooth tops and numbers of β-SiAlON crystals was greater. Thus, NH₄Cl provided a nitrogen source in the reaction, which promoted the complete nitridation of Si to generate β-SiAlON crystals and the size of the β-SiAlON crystals changed when different NH₄Cl contents were added.

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