Research Article

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The effects of $\beta$-$\text{Si}_3\text{N}_4$ on the formation and oxidation of $\beta$-$\text{SiAlON}$

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Abstract: The influence of the additive $\beta$-$\text{Si}_3\text{N}_4$ on the formation and oxidation of $\text{Si}_3\text{Al}_2\text{O}_6\text{N}_6$ during the sintering of $\text{Al}$, $\text{Si}$, and $\text{Al}_2\text{O}_3$ powders under flowing nitrogen atmosphere was examined. An increasing molar percentage of $\beta$-$\text{Si}_3\text{N}_4$ was shown to alter the morphology of $\text{Si}_3\text{Al}_2\text{O}_6\text{N}_6$ from a fiber-like to a rod-like structure and also shortened the time needed to form a dense, continuous oxide layer, which served as a barrier to the diffusion of $\text{O}_2$. An optimal molar percentage of $\beta$-$\text{Si}_3\text{N}_4$ of 29.9 mol% was discovered, at which the grain growth was enhanced, and the surface area was, in turn, reduced, yielding superior resistance to oxidation. Our results provided a theoretical basis for the formation of $\beta$-$\text{SiAlON}$ and demonstrated the potential of its use in high-temperature oxidizing environments.

Keywords: $\beta$-$\text{SiAlON}$, $\beta$-$\text{Si}_3\text{N}_4$, microstructure, oxidation

1 Introduction

$\beta$-$\text{Si}_3\text{N}_4$ has a hexagonal close-packed crystal structure, which is composed of covalently bonded [$\text{Si}_3\text{N}_4$] tetrahedral subunits. The Si–N bond length in the crystal is 1.74 Å, which is similar to that of the Al–O bond in crystalline $\text{Al}_2\text{O}_3$ ($d = 1.75$ Å). Although an $\text{Al}_2\text{O}_3$ crystal typically comprises octahedral [$\text{Al}_2\text{O}_6$] subunits, Al–O bonds can substitute Si–N bonds in tetrahedral [$\text{Si}_3\text{N}_4$] subunits of $\beta$-$\text{Si}_3\text{N}_4$ to yield $\text{Si}_{6-x}\text{Al}_x\text{O}_{6}\text{N}_{8-x}$ ($\beta$-$\text{SiAlON}$), where $0 < x \leq 4.2$. $\beta$-$\text{SiAlON}$ is a substitutional solid solution [1–4], in which the Al–O bond is approximately 50% stronger than that in $\text{Al}_2\text{O}_3$. $\beta$-$\text{SiAlON}$ is therefore more resistant to decomposition at high temperatures than $\text{Si}_3\text{N}_4$ due to its lower vapor pressure and higher thermodynamic stability [5–7]. $\beta$-$\text{SiAlON}$ exhibits the properties of both $\text{Si}_3\text{N}_4$ and $\text{Al}_2\text{O}_3$, such as excellent thermal shock resistance and mechanical properties and resistance to molten slag corrosion [8–10].

The influence of $\beta$-$\text{Si}_3\text{N}_4$ on the formation and properties of $\text{Si}_3\text{N}_4$-based ceramics has been widely studied. Yu et al. prepared graded $\text{Si}_3\text{N}_4$ ceramics with superior wear resistance and a low wear rate by combining two-step sintering and $\beta$-$\text{Si}_3\text{N}_4$ seeds [11]. Meanwhile, Lukianova et al. reported that the electrical resistivity of $\text{Si}_3\text{N}_4$ ceramics was linearly dependent on the content of $\beta$-$\text{Si}_3\text{N}_4$ in the precursor [12]. Guo et al. studied the effects of $\beta$-$\text{Si}_3\text{N}_4$ seeds on the nucleation and growth of $\text{Lu}_2\text{O}_3$-doped $\text{Si}_3\text{N}_4$ ceramics and showed that seeds with a smaller diameter and a lower aspect ratio induced a finer self-reinforced microstructure, and, in turn, an improved fracture toughness [13]. A similar observation was made by Acikbas et al., but the resulting $\alpha$-$\beta$-$\text{SiAlON}$ displayed a poor oxidation resistance due to its inherent thermodynamic instability in an oxidizing environment [14]. It is generally accepted that a pure, dense $\text{Si}_3\text{N}_4$ phase exhibits superior oxidation resistance to $\text{SiAlON}$-based ceramics [15].

The effect of additives on the oxidation resistance of $\text{SiAlON}$ has also been widely explored. Li et al. found that $\beta$-$\text{SiAlON}$ powder prepared using a combustion method displayed a weaker oxidation resistance with an increasing addition of diluents, which was attributed to a decrease in particle size [16]. Li et al. used a mixture of $\text{NH}_4\text{F}$ and $\text{NH}_4\text{Cl}$ additives to promote the growth of a $\text{Ca}$-$\alpha$-$\text{SiAlON}$ crystal with improved oxidation resistance [17]. The oxidation resistance was related to both the crystal phase and the microstructure and was optimized by adjusting the composition. Finally, Shan et al. reported that the oxidation resistance of $\text{Y}_n\text{SiAlON}$ was improved by increasing the nitrogen content ($n = 1$) and decreasing the Y/Si ratio (0.04) [18].

In this study, to the best of our knowledge, the effects of different $\beta$-$\text{Si}_3\text{N}_4$ additions on the oxidation behavior...
of Si₄Al₂O₂N₆ were explored for the first time. Si₄Al₂O₂N₆ was prepared via high-temperature nitridation in the presence of various molar ratios of the additive β-Si₃N₄. The oxidation resistance was assessed using a non-isothermal oxidation test between room temperature and 1,500°C to determine the oxidation onset temperature. Meanwhile, the underlying oxidation mechanism was studied using an isothermal oxidation test between 1,200 and 1,400°C for 2 h. The study showed that the improvement in the oxidation resistance of Si₄Al₂O₂N₆ by the addition of β-Si₃N₄ will promote its further use in high-temperature industrial applications.

2 Experimental

Si₄Al₂O₂N₆ was synthesized according to the compositions outlined in Table 1. α-Al₂O₃ powder (99.7% purity, ≤75 µm), metal aluminum powder (99.0% purity, ≤75 µm), silica powder (99.0% purity, ≤75 µm), and β-Si₃N₄ (99.9%, 1.25 µm) were used as raw materials. The microstructure of β-Si₃N₄ characterized by scanning electron microscopy (SEM) is shown in Figure 1. 3 wt% Y₂O₃ (98.0% purity, chemically pure) was added as a sintering accelerator and 2 wt% phenolic resin was added as a binder at room temperature. Samples with a molar percentage of 0 mol% (control), 21.4, 25.4, and 29.9 mol% were denoted 1, 2, 3, and 4, respectively. The fine powders were wet-milled at the appropriate proportions for 6 h. After wet-milling, slurries were dried and then pressed into ∅20 mm × 15 mm cylinders at a pressure of 15 MPa. After drying at 190°C, the samples were sintered in a nitriding furnace (GWDL-1KY; China) at 1,550°C for 3 h at a heating rate of 2.5°C/min with N₂ gas (N₂ ≥ 99.9%, O₂ ≤ 0.005%) flowing at a rate of 1 L/min.

Before and after the oxidation experiment, phase identification was performed with powder X-ray diffraction analysis (XRD; X’Pert Powder, PANalytical, the Netherlands).

Table 1: Initial composition of different samples

| Specimen no. | Compositions (mol) | Molar percentage of Si₃N₄ |
|--------------|--------------------|--------------------------|
|              | Si | Si₃N₄ | Al | Al₂O₃ | Si₃N₄ |
| 1#           | 4  | 0     | 0.67 | 0.67 | 0     |
| 2#           | 1.6 | 0.8  | 0.67 | 0.67 | 21.4  |
| 3#           | 1.3 | 0.9  | 0.67 | 0.67 | 25.4  |
| 4#           | 1  | 1     | 0.67 | 0.67 | 29.9  |

Figure 1: The SEM photograph of the β-Si₃N₄ powder.

The microstructure of the fractured surfaces was characterized with SEM (Sigma HD, Zeiss, Germany), equipped with an X-ray energy-dispersive spectroscopy (EDS; IE250X-Max50, Oxford, UK). Isothermal and non-isothermal oxidations of the Si₄Al₂O₂N₆ powder were conducted on NETZSCH instrument (Setsys Evolution, STA 449 F3; NETZSCH Scientific Instruments Trading Co. Ltd, Germany). For the non-isothermal oxidation experiment, O₂ was injected into the furnace at a flow rate of 80 mL/min, and the Si₄Al₂O₂N₆ powder was heated at a rate of 10°C/min from room temperature to 1,500°C. Based on the results of non-isothermal oxidation, 1,200, 1,300, and 1,400°C were chosen as isothermal oxidation temperatures. Initially, Ar was pumped through the vacuum, then the furnace was heated to the required temperature for 2 h, with a heating rate of 10°C/min. O₂ was injected at a flow rate of 80 mL/min; after completion of the study, the isothermal oxidation was terminated by purging the furnace of O₂ with Ar. Si₄Al₂O₂N₆ grain sizes were assessed by SEM images using “Nano Measurer” software (Fudan University, Shanghai, China). At least 300 grains were counted to obtain average values and size distributions. The specific surface area and pore size distribution were tested using Brunner-Emmet-Teller (BET, ASIQMUTV00U 000-6, Quantachrome, USA) method.

3 Results and discussion

Initially, the thermodynamics of the reactions in the Si−Al−O−N system were briefly examined to delineate the formation of the Si₄Al₂O₂N₆ phase [19,20]. To achieve this, overlapped phase stability diagram of Si−O−N and Al−O−N systems at 1,623 and 1,823 K, respectively, were
constructed using the thermodynamics of the reactions in the Si–Al–O–N system, which is shown in Figure 2. The phase diagram revealed a stable region of SiAlON, where the high-temperature region was larger. The values of \( \log(p_{\text{N}_2}/p^0) \) (points 1 and 2 in all figures) and \( \log(p_{\text{O}_2}/p^0) \) (lines A and B in all figures) at 1,673 K were lower than the value obtained at 1,823 K. Although the formation of \( \text{Si}_4\text{Al}_2\text{O}_2\text{N}_6 \) from \( \alpha\text{-Al}_2\text{O}_3 \) Al and Si powders is spontaneous, higher temperatures were used to drive the reaction.

Figure 2: Overlapped phase stability diagram of Si–O–N and Al–O–N systems at (a) \( T = 1,673 \text{ K} \) and (b) \( T = 1,823 \text{ K} \).

Figure 3 shows the XRD spectra of the \( \text{Si}_4\text{Al}_2\text{O}_2\text{N}_6 \) powder with different molar percentages of Si\( \text{N}_4 \) (0, 21.4, 25.4, and 29.9 mol%). The diffraction peaks of hexagonal \( \text{Si}_4\text{Al}_2\text{O}_2\text{N}_6 \) (•, PDF#01-076-0599) are indicated by vertical lines for comparison. No other peaks were detected, which suggested that no other crystalline phase remained after synthesis. In the present \( \text{Al}_2\text{O}_3\text{–Al–Si–N}_2 \) system, Si and Al reacted with \( \text{N}_2 \) to form \( \text{Si}_3\text{N}_4 \) and AlN, thereby nitrogen was introduced into the structure, and \( \text{Al}_2\text{O}_3 \) provided Al–O units for the formation of \( \beta\text{-SiAlON} \).

Figure 3: XRD patterns the \( \text{Si}_4\text{Al}_2\text{O}_2\text{N}_6 \) powders with 2\( \theta \) range of (a) 10°–80°, (b) 26.5°–27°, (c) 33°–33.5° and (d) 35.5°–36°.
No residual Si was identified, confirming the complete nitridation of Si powder to Si$_3$N$_4$. Detailed variations in the diffraction peaks of phases are highlighted in Figure 3(b–d), where the dashed lines are the diffraction pattern fitted by XPS software [21]. The intensities of the peaks indexed to (200), (101), and (210) planes of Si$_4$Al$_2$O$_2$N$_6$ were obtained by measuring the peak area and denoted as $I_{200}^{Si4Al2O2N6}$, $I_{101}^{Si4Al2O2N6}$, and $I_{210}^{Si4Al2O2N6}$. All peak areas of Si$_4$Al$_2$O$_2$N$_6$ increased as the initial β-Si$_3$N$_4$ molar percentage increased. Both β-Si$_3$N$_4$ and β-SiAlON have a hexagonal crystal structure. However, due to the inclusion of Al and O in β-SiAlON, the peaks indexed to the (210) plane were shifted to lower diffraction angles with increasing β-Si$_3$N$_4$ molar percentage. This was attributed to an increase in substitution of Si–N bonds with moderately longer Al–O bonds, which increased $d$ spacings of individual lattice planes and ultimately resulted in an increase in lattice parameters. It is known that the formation and mechanical properties of SiAlON ceramics is enhanced with an increasing molar content of β-Si$_3$N$_4$ in the precursor [22]. Our results confirmed that the same effect was observed specifically for the formation of the β-SiAlON form.

However, there existed remarkable differences in the crystal morphology of samples with the increase in the molar percentage of β-Si$_3$N$_4$. The SEM micrographs of

![Figure 4: The SEM photographs of β-SiAlON ceramics: (a) 1#, (b) 2#, (c) 3#, (d) 4#, and (e) and (f) the enlarged morphology and EDS analysis of 1# and 2#.](image)
β-SiAlON with different molar percentages of β-Si₃N₄ are shown in Figure 4. SEM analysis showed that the β-SiAlON crystal morphology changed from fiber-like crystals in sample 1 to a rod-like morphology in sample 2, as the molar percentage of β-Si₃N₄ in the precursor increased (Figure 4a–d). EDS analysis of samples 1 and 2 showed that the N to O ratio increased from 2.33 to 2.99 when β-Si₃N₄ was added to the precursor (Figure 4e and f). The N content of sample 2 was 42.59%, which corresponded to a stoichiometry of Si₄Al₂O₂N₆.

Figure 5 shows that the particle size distribution of the β-SiAlON powder increased as the molar percentage of β-Si₃N₄ in the precursor increased. For example, the radial size of individual particles in sample 1 was within the range 0.15–0.35 µm, while the radial particle sizes in samples 3 and 4 were larger, in the range 0.4–0.8 µm. The structural and size distribution data showed that β-Si₃N₄ served as a nucleating agent, which increased the rate of non-spontaneous nucleation [23]. Hence, the addition of β-Si₃N₄ also facilitated the nitridation process, caused increased crystal growth and larger individual grain sizes.

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The non-isothermal oxidation behavior of the Si₄Al₂O₂N₆ powder is characterized in Figure 6. The oxidation reaction began at approximately 1,200°C. The weight gain rate increased rapidly between 1,200 and 1,500°C, after which the run was terminated. The degree of oxidation of Si₄Al₂O₂N₆ was calculated from the weight gain according to the following reaction:

$$\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6 + 6\text{O}_2 \rightarrow 4\text{SiO}_2 + 2\text{Al}_2\text{O}_3 + 3\text{N}_2$$

The mass of the Si₄Al₂O₂N₆ powder was 32.1% higher than the original mass when fully oxidized (i.e., 100% oxidized). The total mass change of samples 1, 2, 3, and 4 were 9.93%, 8.89%, 7.19%, and 6.39%, respectively, which corresponded to oxidation degrees of 30.9%, 27.7%, 22.4%, and 19.9%, respectively. This suggested that a higher β-Si₃N₄ content in the precursor made the product Si₄Al₂O₂N₆ more oxidation resistant.

The specific weight gain due to the oxidation of Si₄Al₂O₂N₆ was then examined as a function of oxidation time between 1,200 and 1,400°C, as shown in Figure 7. The weight gain was higher at 1,400°C than at 1,200°C or 1,300°C, and the specific weight gain for sample 4 was
lower than for all other samples. The specific weight increased linearly with temperature in the early stage of oxidation (within 0.5 h) from 1,200 to 1,400°C. However, after 0.5 h, the specific weight increased according to a parabolic curve relationship, which suggested a change in the oxidation mechanism. During the initial stage, Si₄Al₂O₄N₆ reacted with O₂ at the surface, after which O₂ diffused through the oxide layer into the inside of the material and N₂ produced during the oxidation diffused out. The dense oxide layer was either incomplete or too thin to prevent O₂ diffusion into the matrix, thus the oxidation rate was controlled by the rate of reaction at the Si₄Al₂O₄N₆ surface. At extended oxidation times, the specific weight gain increased, while the degree of weight gain decreased, indicating that the oxide layer formed after 0.5 h was complete or sufficiently thick to prevent O₂ diffusion into the matrix interior. In this regime, the oxidation rate was controlled by the rate of diffusion of O₂. The parabolic oxidation kinetic curves of Si₄Al₂O₄N₆ powder showed a close fit to the Arrhenius parabolic equation [24]:

\[ W^2 = K_p t + C, \]  

where \( W^2 \) represented the square of the weight gain per unit area; \( K_p \) was an oxidation rate constant, which was calculated from the slope; \( t \) was the oxidation time; and \( C \) was constant, which was the intercept and ideally zero. Overall, the \( W^2 \) vs. \( t \) plots obtained from sample 4 when oxidized at 1,200–1,400°C showed the closest fit to the Arrhenius parabolic model (Figure 8). The calculated oxidation rate constants, \( K_p \), for samples 1–4 oxidized between 1,200 and 1,400°C are listed in Table 2. As the molar content of \( \beta \)-Si₃N₄ increased, the obtained \( K_p \) values decreased, which meant that the dense, continuous oxide layer formed quicker and the oxidation resistance increased.

According to the non-isothermal oxidation results, samples 1 and 4 displayed the highest and lowest

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**Figure 7:** Specific weight gains as a function of oxidation time for Si₄Al₂O₄N₆ powder oxidized at different temperatures.
degrees of oxidation. The XRD analysis of the oxidized products of 1 and 4 indicated that Si₄Al₂O₂N₆ was the major product phase, and Al₂O₃ was the main oxidation product, shown in Figure 9. The relative intensity of peaks indexed to Al₂O₃ compared to that indexed to Si₄Al₂O₂N₆ changed with both oxidation temperature and β-Si₃N₄ molar content. For sample 1, the relative intensity of Al₂O₃ peaks increased with oxidation temperature, which indicated an increase in the oxidation degree in sample 1. In contrast, the relative intensities of Al₂O₃ and Si₄Al₂O₂N₆ from sample 4 changed negligibly as the oxidation temperature increased, which indicated that the oxidation resistance of β-SiAlON was improved with the addition of β-Si₃N₄.

The pore size distribution and nitrogen absorption–desorption isotherm of samples 1, 2, 3, and 4 after nitridation at 1,550°C were then analyzed (Figure 10). A pore size distribution with a maximum 3 nm was observed, which suggested that the material had a mesoporous structure. However, the specific surface area of samples 1, 2, 3, and 4 was 0.888, 0.879, 0.807, and 0.741 m² g⁻¹, respectively, which suggested that an increase in the grain size, as observed by SEM (Figure 5), leads to a decrease in the specific surface area. The variance in microstructure and oxide layer density across samples leading to different behaviors during oxidation suggested that the efficiency of the oxidation reaction may be dependent on exposed surface area. For instance, samples with larger particle size and larger surface areas, such as sample 4, exhibited the strongest oxidation resistance compared with those with small particle sizes, such as sample 1.

Table 2: Calculated oxidation rate constant ($K_o$) for Si₄Al₂O₂N₆ powder oxidized at 1,200–1,400°C mg² cm⁻⁴ s⁻¹

| Specimen no. | 1,200°C | 1,300°C | 1,400°C |
|-------------|---------|---------|---------|
| 1           | 2.74 × 10⁻² | 7.30 × 10⁻² | 9.38 × 10⁻² |
| 2           | 2.39 × 10⁻² | 6.43 × 10⁻² | 7.35 × 10⁻² |
| 3           | 0.87 × 10⁻² | 3.19 × 10⁻² | 4.29 × 10⁻² |
| 4           | 0.6 × 10⁻² | 2.21 × 10⁻² | 2.41 × 10⁻² |

Figure 8: Square of specific weight gains as a function of oxidation time for Si₄Al₂O₂N₆ powder oxidized at different temperatures: (a) 1,200°C, (b) 1,300°C, and (c) 1,400°C.
Conclusions

Si$_4$Al$_2$O$_2$N$_6$ was prepared via high-temperature nitridation of a mixture of α-Al$_2$O$_3$, metal Al, and Si powders and β-Si$_3$N$_4$ as an additive. As the content of β-Si$_3$N$_4$ increased, the morphology of individual Si$_4$Al$_2$O$_2$N$_6$ crystallites varied from a fiber-like to a rod-like structure. The addition of β-Si$_3$N$_4$ facilitated the grain growth, which leads to a reduction in surface area and in turn a superior resistance to oxidation. Precursor samples containing 29.9 mol% of β-Si$_3$N$_4$ required the shortest time to form a dense, continuous oxide layer, which prevented the diffusion of O$_2$ into the inside of material and therefore exhibited the higher oxidation resistance.

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