Research Article

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The effects of β - Si_3N_4 on the formation and oxidation of β -SiAlON

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Abstract: The influence of the additive β - Si_3N_4 on the formation and oxidation of $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ during the sintering of Al, Si, and Al_2O_3 powders under flowing nitrogen atmosphere was examined. An increasing molar percentage of β - Si_3N_4 was shown to alter the morphology of $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ 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 O_2 . An optimal molar percentage of β - Si_3N_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 β -SiAlON and demonstrated the potential of its use in high-temperature oxidizing environments.

Keywords: β -SiAlON, β - Si_3N_4 , microstructure, oxidation

1 Introduction

β - Si_3N_4 has a hexagonal close-packed crystal structure, which is composed of covalently bonded $[\text{SiN}_4]$ 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 Al_2O_3 ($d = 1.75$ Å). Although an Al_2O_3 crystal typically comprises octahedral $[\text{AlO}_6]$ subunits, Al–O bonds can substitute Si–N bonds in tetrahedral $[\text{SiN}_4]$ subunits of β - Si_3N_4 to yield $\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$ (β -SiAlON), where $0 < x \leq 4.2$. β -SiAlON is a substitutional solid

solution [1–4], in which the Al–O bond is approximately 50% stronger than that in Al_2O_3 . β -SiAlON is therefore more resistant to decomposition at high temperatures than Si_3N_4 due to its lower vapor pressure and higher thermodynamic stability [5–7]. β -SiAlON exhibits the properties of both Si_3N_4 and Al_2O_3 , such as excellent thermal shock resistance and mechanical properties and resistance to molten slag corrosion [8–10].

The influence of β - Si_3N_4 on the formation and properties of Si_3N_4 -based ceramics has been widely studied. Yu et al. prepared graded Si_3N_4 ceramics with superior wear resistance and a low wear rate by combining two-step sintering and β - Si_3N_4 seeds [11]. Meanwhile, Lukianova et al. reported that the electrical resistivity of Si_3N_4 ceramics was linearly dependent on the content of β - Si_3N_4 in the precursor [12]. Guo et al. studied the effects of β - Si_3N_4 seeds on the nucleation and growth of Lu_2O_3 -doped Si_3N_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 α/β -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 Si_3N_4 phase exhibits superior oxidation resistance to SiAlON-based ceramics [15].

The effect of additives on the oxidation resistance of SiAlON has also been widely explored. Li et al. found that β -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 NH_4F and NH_4Cl additives to promote the growth of a Ca- α -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 Y- α -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 β - Si_3N_4 additions on the oxidation behavior

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of $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ were explored for the first time. $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ was prepared via high-temperature nitridation in the presence of various molar ratios of the additive $\beta\text{-Si}_3\text{N}_4$. 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 $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ by the addition of $\beta\text{-Si}_3\text{N}_4$ will promote its further use in high-temperature industrial applications.

Figure 1: The SEM photograph of the $\beta\text{-Si}_3\text{N}_4$ powder.

2 Experimental

$\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ was synthesized according to the compositions outlined in Table 1. $\alpha\text{-Al}_2\text{O}_3$ powder (99.7% purity, $\leq 75\ \mu\text{m}$), metal aluminum powder (99.0% purity, $\leq 75\ \mu\text{m}$), silica powder (99.0% purity, $\leq 75\ \mu\text{m}$), and $\beta\text{-Si}_3\text{N}_4$ (99.9%, $1.25\ \mu\text{m}$) were used as raw materials. The microstructure of $\beta\text{-Si}_3\text{N}_4$ characterized by scanning electron microscopy (SEM) is shown in Figure 1. 3 wt% Y_2O_3 (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 $\beta\text{-Si}_3\text{N}_4$ 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 $\varnothing\ 20\ \text{mm} \times 15\ \text{mm}$ 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 N_2 gas ($\text{N}_2 \geq 99.9\%$, $\text{O}_2 \leq 0.005\%$) 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).

The microstructure of the fractured surfaces was characterized with SEM (Sigma HD, Zeiss, Germany), equipped with an X-ray energy-dispersive spectroscope (EDS; IE250X-Max50, Oxford, UK). Isothermal and non-isothermal oxidations of the $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ powder were conducted on NETZSCH instrument (Setsys Evolution, STA 449 F3; NETZSCH Scientific Instruments Trading Co. Ltd, Germany). For the non-isothermal oxidation experiment, O_2 was injected into the furnace at a flow rate of 80 mL/min, and the $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ 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. O_2 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 O_2 with Ar. $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ 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.

Table 1: Initial composition of different samples

Specimen no.	Compositions (mol)				Molar percentage of Si_3N_4
	Si	Si_3N_4	Al	Al_2O_3	
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

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 $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ 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

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

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 $\lg(P_{\text{N}_2}/P^0)$ (points 1 and 2 in all figures) and $\lg(P_{\text{O}_2}/P^0)$ (lines A and B in all figures) at $1,673 \text{ K}$ were lower than the value obtained at $1,823 \text{ K}$. Although the formation of $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ from α - Al_2O_3 Al and Si powders is spontaneous, higher temperatures were used to drive the reaction.

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_3N_4 (0, 21.4, 25.4, and 29.9 mol%). The diffraction peaks of hexagonal $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ ($\bullet$, 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 Al_2O_3 -Al-Si- N_2 system, Si and Al reacted with N_2 to form Si_3N_4 and AlN, thereby nitrogen was introduced in to the structure, and Al_2O_3 provided Al-O units for the formation of β - SiAlON .

Figure 3: XRD patterns the $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ powders with 2θ range of (a) 10° – 80° , (b) 26.5° – 27° , (c) 33.0° – 33.5° and (d) 35.5° – 36.0° .

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[#].

No residual Si was identified, confirming the complete nitridation of Si powder to Si_3N_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 $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ were obtained by measuring the peak area and denoted as $I_{\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6}^{(200)}$, $I_{\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6}^{(101)}$, and $I_{\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6}^{(210)}$. All peak areas of $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ increased as the initial β - Si_3N_4 molar percentage increased. Both β - Si_3N_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_3N_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_3N_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_3N_4 . The SEM micrographs of

Figure 5: Grain size distribution of Si₄Al₂O₂N₆ ceramics.

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 μ m, while the radial particle sizes in samples 3 and 4 were larger, in the range 0.4–0.8 μ m. 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.

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:

Figure 6: Non-isothermal oxidation curves of Si₄Al₂O₂N₆ powder.

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

Figure 7: Specific weight gains as a function of oxidation time for $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ powder oxidized at different temperatures.

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, $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ reacted with O_2 at the surface, after which O_2 diffused through the oxide layer into the inside of the material and N_2 produced during the oxidation diffused out. The dense oxide layer was either incomplete or too thin to prevent O_2 diffusion into the matrix, thus the oxidation rate was controlled by the rate of reaction at the $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ 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 O_2 diffusion into the matrix interior. In this regime, the oxidation rate was controlled by the rate of diffusion of O_2 . The parabolic oxidation kinetic curves of

$\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ powder showed a close fit to the Arrhenius parabolic equation [24]:

$$W^2 = K_p t + C, \quad (2)$$

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 are listed in Table 2. As the molar content of $\beta\text{-Si}_3\text{N}_4$ 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

Figure 8: Square of specific weight gains as a function of oxidation time for Si₄Al₂O₂N₆ powder oxidized at different temperatures: (a) 1200°C, (b) 1300°C, and (c) 1400°C.

Table 2: Calculated oxidation rate constant (K_p) 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}

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**.

Figure 9: XRD patterns of the samples oxidized under different temperatures for (a) specimen 1# and (b) specimen 4#.

Figure 10: Pore size distribution and nitrogen absorption-desorption isotherm of samples.

4 Conclusions

$\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ was prepared via high-temperature nitridation of a mixture of $\alpha\text{-Al}_2\text{O}_3$, metal Al, and Si powders and $\beta\text{-Si}_3\text{N}_4$ as an additive. As the content of $\beta\text{-Si}_3\text{N}_4$ increased, the morphology of individual $\text{Si}_4\text{Al}_2\text{O}_2\text{N}_6$ crystallites varied from a fiber-like to a rod-like structure. The addition of $\beta\text{-Si}_3\text{N}_4$ 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 $\beta\text{-Si}_3\text{N}_4$ 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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