Preparation of Si_2N_2O from Flashing Combustion Synthesized Si_3N_4 and Silica Fume

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Abstract. Using flashing combustion synthesized Si_3N_4 and silica fume as raw materials, the effects of firing temperature (1300°C, 1400°C, 1500°C, and 1600°C) and duration (3h, 6h, and 9h) on the synthesis of Si_2N_2O were studied. The results show that the main mechanism of the reaction is Si_3N_4 and silica fume react to form Si_2N_2O through solid-solid reaction or solid-liquid reaction. After heat treatment at 1300°C, there is a small amount of melting liquid in the system, with a trace of Si_2N_2O formed. After heat treatment at 1400°C, 1500°C, and 1600°C, there is a large amount of melting liquid in the system, accelerating the formation of Si_2N_2O slightly. The duration has very little effect on the synthesis reaction. When Si_2N_2O forms, the oxygen content in the melting liquid decreases, viscosity of the liquid increases, the diffusion of ions in the melting liquid slows, hindering the continuous crystallization of Si_2N_2O. Thus, a fusing agent or hot pressing is re-quired to introduce more low viscosity liquid for the continuous crystallization of Si_2N_2O. In addition, silica fume crystallizes obviously at 1300°C and 1400°C.

Introduction

Si_2N_2O is a ceramic material with high refractoriness featured with high thermodynamic stable temperature[7], excellent thermal shock resistance[9], good oxidation resistance, high hot strength, and good resistance to nonferrous metals melts[1], *etc*. Compared with Si_3N_4 ceramics it has better oxidation resistance at elevated temperatures, i.e. good oxidation resistance at 1600°C in air and high modulus of rupture at 1400°C[6]. Therefore, Si_2N_2O is a promising high temperature structural material used in high temperature oxidization condition.

Si_2N_2O can be obtained by two approaches. The first one, use metal silicon and SiO_2 as starting materials, utilize the heat released by the SHS process to synthesize Si_2N_2O in nitrogen atmosphere at high temperatures[10]. The second one, use SiO_2 and Si_3N_4 as the starting materials to synthesize Si_2N_2O[8]. Si_2N_2O mainly forms from nitrogen containing liquid[3]. In the second approach, the suitable liquid to produce Si_2N_2O is the key point. What's more, the reaction rate is very low. Thus, the preparation of Si_2N_2O in China mainly adopts the first one and most of them are in lab-scale.

The efficiency of synthesis Si_2N_2O from metal silicon is high, but the synthesis is directly influenced by factors such as the diffusion depth of nitrogen in the reaction system and the diffusion efficiency. In addition, the structure of the as-prepared products is hard to control. So this method is more suitable to synthesize Si_2N_2O raw material. The preparation of Si_2N_2O products requires methods such as hot pressed sintering based on the pre-synthesized starting materials[4].

As for the mass produced large sized products such as refractories, the SHS process of metal silicon greatly restrains the production of Si_2N_2O-related refractories. Take the penetration depth of nitrogen into the product bodies for example, commonly, the penetration depth of nitrogen in refractories is 3－4cm, too shallow for the blocks with thickness of dozens of centimeters. Besides, the process shall proceed in conditions of high temperature, high pressure and nitrogen atmosphere, which is hard to realize the industrialization.

Thus, in this work, Si_2N_2O was prepared with silica fume and Si_3N_4 as raw materials sintered under normal pressure in hot carbon reduced air atmosphere, which is easy to industrialize. The silica fume was from the ferroalloy industry and has a high specific surface area and a high activity.

The Si_3N_4 was prepared by flashing combustion method. The feasibility to industrialize this simple process was discussed. The effects of reaction temperature and duration on the synthesis of Si_2N_2O from silica fume and Si_3N_4 were studied.

Experiment

The flashing combustion synthesized β-Si_3N_4 fines with d_{50} of 45μm, and the silica fume with a SiO_2 content over 90% and d_{50} of 0.85μm were adopted as the raw materials. Mixture with a Si_3N_4 : SiO_2 mass ratio of 50% : 50% was ball mixed in a ball mill for 4h, adding with 0.2% sodium hexametahposphate. After drying, the ball-milled mixture was added with a temporary binder and pressed into specimens with sizes of Φ25×20mm under 6MPa.

As seen in the S-C-N-O system state diagram (Fig. 1), the dashed line corresponds to the hot carbon reduced air atmosphere. It is found that the stable phase at the temperature range of 1250－1700°C is Si_2N_2O, indicating this atmosphere is favorable to the formation of Si_2N_2O.
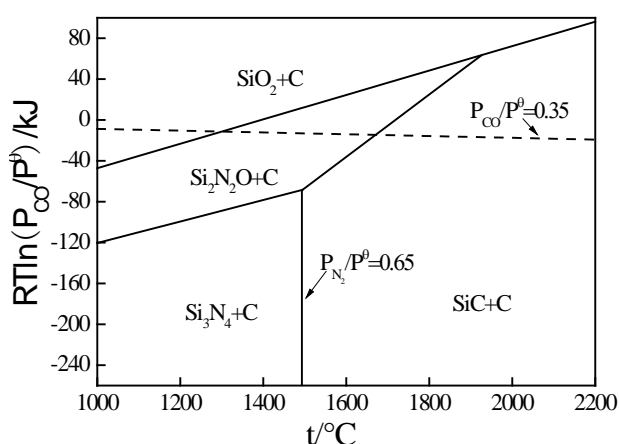

Figure 1. State diagram of S-C-N-O system

This work adopted the hot carbon reduced air atmosphere mentioned in Fig. 1. Blow the air slowly into a high temperature atmosphere furnace through a hot carbon net of 1500°C. Then, raise the temperature slowly to 1300°C, 1400°C, 1500°C, and 1600°C for duration of 3h, 6h, and 9h, respectively. Sample from the inside of the specimen and analyze with XRD (X' pert PRO MPD, Philips, Netherlands), SEM (FEI Nova 230 Nano SEM, FEI Company, USA), and EDS (Inca Energy, Oxford, UK) to investigate the phase composition, microstructure, and element distribution of the specimens.

Results and discussion

1.1 *Experiment results*
(1)SEM analysis of raw materials
As can be seen in Fig. 2(a), the particles of silica fume from the ferroalloys industry are small, ranging from dozens to hundreds of nanometers. The flashing combustion synthesized silica nitride particles develop well with prismatic shapes. And the crystals interlock with each other with diameters of micrometers and length of dozens of micrometers.
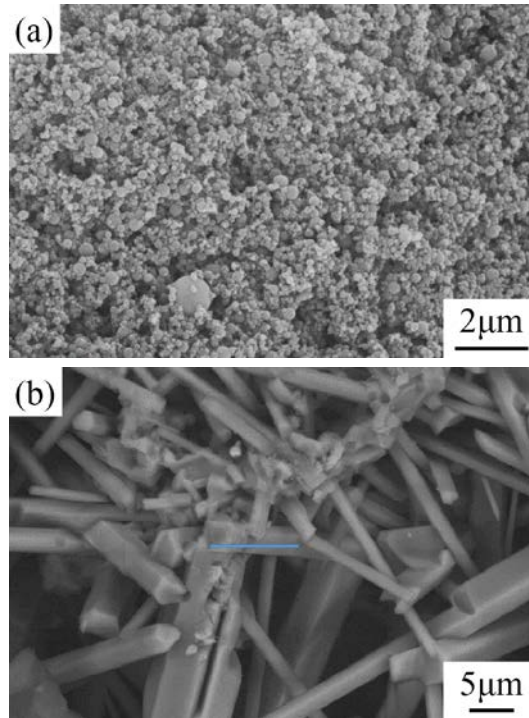
Figure 2. SEM photographs of silica fume and flashing combustion synthesized β-Si_3N_4 :(a) silica fume, (b) β-Si_3N_4.

(2)Analysis of specimens with different firing temperatures and different duration

① XRD analysis of specimens fired at 1300°C, 1400°C, 1500°C and 1600°C for 3h

As shown in Fig. 3, after firing at 1300°C, the peaks of Si_2N_2O are observed, indicating that Si_2N_2O forms at this temperature. As firing temperature rises, the peaks get stronger. After firing at 1600°C, the peaks of Si_2N_2O are very obvious. But in general, with the duration of 3h, the effect of firing temperature on the peaks is not obvious: the peak intensity gets stronger mildly as temperature rises. β-Si_3N_4 is still the main phase, meanwhile, SiO_2 is also a main phase, and the peaks of SiO_2 tend to be stronger at 1300～1400°C, after 1500°C the SiO_2 peaks weaken greatly, which means that the silica fume crystallizes intensely at 1300－1400°C. After 1500°C, the peaks get lower, and amorphous peaks appear at low angles in XRD patterns.
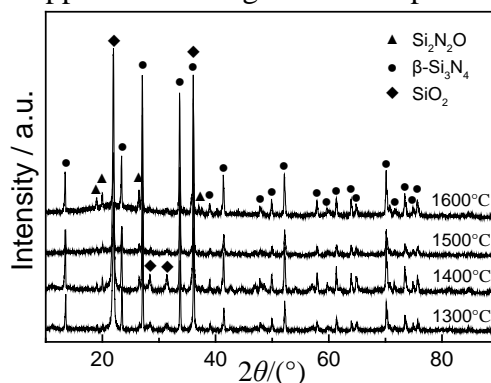

Figure 3. XRD patterns of specimens fired at 1300°C, 1400°C, 1500°C and 1600°C for 3h

② XRD analysis of specimens fired at 1300°C, 1400°C, 1500°C and 1600°C for 3h, 6h and 9h, respectively

As shown in Fig. 4, at firing temperature of 1300°C, the duration of 3h, 6h, 9h has no obvious influence on the peak intensity of Si_2N_2O. The peak intensities at firing temperature of 1400°C, 1500°C and 1600°C are stronger than that at 1300°C. However, at different temperatures, the duration has no influence on the crystallization of the Si_2N_2O. It is noted that the system has strong

SiO$_2$ peaks at 1300°C and 1400°C, which means that the crystallization force of the silica fume is very strong at the temperatures. At 1500°C and 1600°C, the peak intensity of SiO$_2$ decreases greatly and the XRD results show the appearance of amorphous phases, indicating that silica fume is in melting state. Peak intensity of β-Si$_3$N$_4$ varies slightly at different tempeartures, meaning that the content of β-Si$_3$N$_4$ merely changes and proving it is stable in the system.
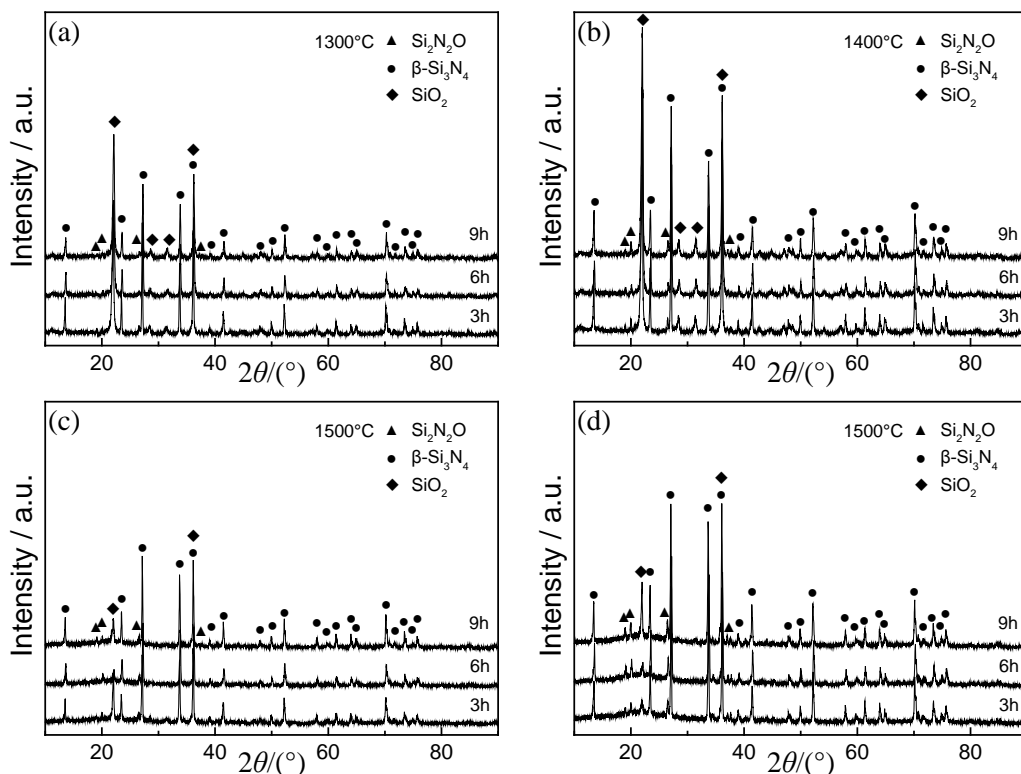

Fig. 4 XRD pattern of specimens fired at different sintering temperatures for different duration: (a) 1300°C; (b) 1400°C; (c) 1500°C; (d) 1600°C.

(3)SEM analysis of specimens fired at different temperatures for 6h

SEM photographs of specimens fired at different temperatures for 6h are shown in Fig.5. Combined with the XRD results, it is concluded that at 1300°C, only a small amount of melting phase forms in the system, and the Si$_2$N$_2$O formation is very little. Since there are some impurities existing in silica fume, a trace of melting liquid forms, resulting in some local closure and separation in the system. At 1300°C, most Si$_3$N$_4$ particles are loose and insolated. Small and uniform pores distributes among the particles. At 1400°C, the Si$_3$N$_4$ particles are still insolated, but some liquid phases appear in the system. Although the bonding is not strong, obvious packing and cementation exist. At 1500°C and 1600°C, the system is almost in melting state, with a totally closed state. Most Si$_3$N$_4$ particles are bonded together, few Si$_3$N$_4$ particles are insolated. Melting phases pack the Si$_3$N$_4$ particles tightly. With tempreture increasing, the pores are becoming more and more and the pore volume increases. The whole system presents a cemented network structure.
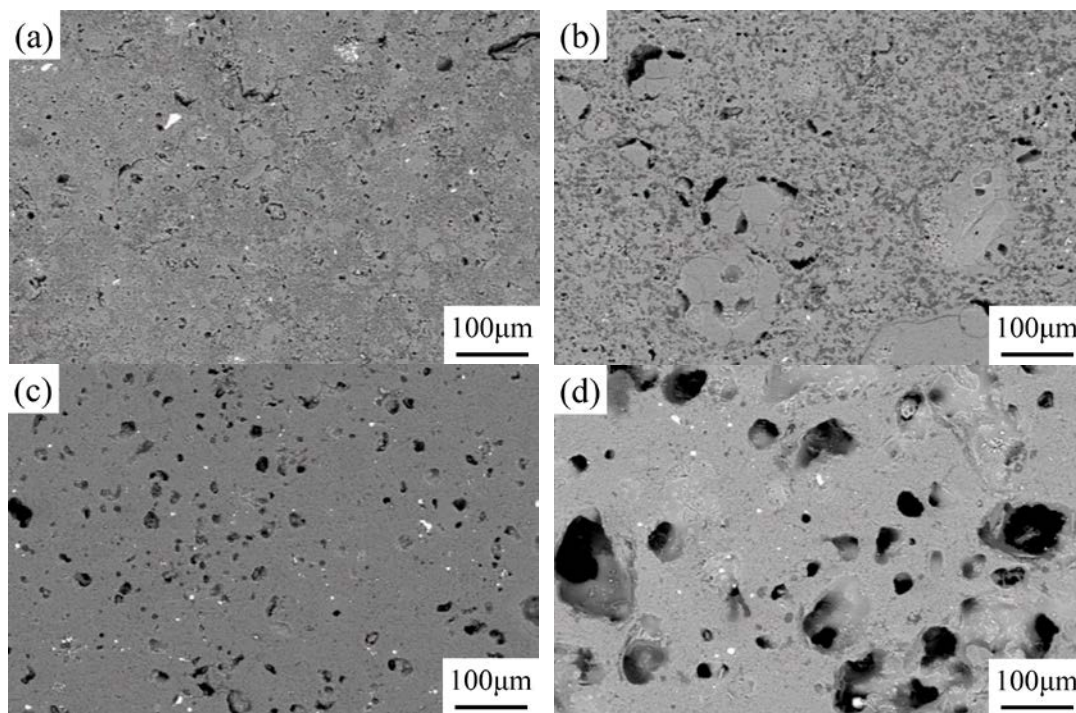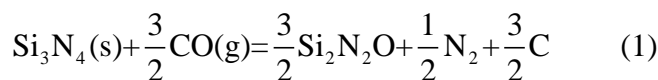
Figure 5. SEM photographs of specimens fired at different sintering temperatures for 6h
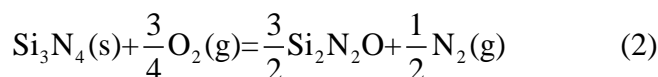(a) 1300°C; (b) 1400°C; (c) 1500°C; (d) 1600

1.2 *Analysis and discussion*

(1) Thermodynamics analysis of Si_3N_4—silica fume system

In this system, the formed Si_2N_2O is mainly from the following reactions.

$$Si_3N_4(s) + \frac{3}{2}CO(g) = \frac{3}{2}Si_2N_2O + \frac{1}{2}N_2 + \frac{3}{2}C \qquad (1)$$

$$\Delta_r G^\theta = -381420.75 + 159.50T(J \cdot mol^{-1})$$

$$Si_3N_4(s) + \frac{3}{4}O_2(g) = \frac{3}{2}Si_2N_2O + \frac{1}{2}N_2(g) \qquad (2)$$

$$\Delta_r G^\theta = -553023.50 + 30.85T(J \cdot mol^{-1})$$

$$Si_3N_4(s) + SiO_2(s) = 2Si_2N_2O(s) \qquad (3)$$

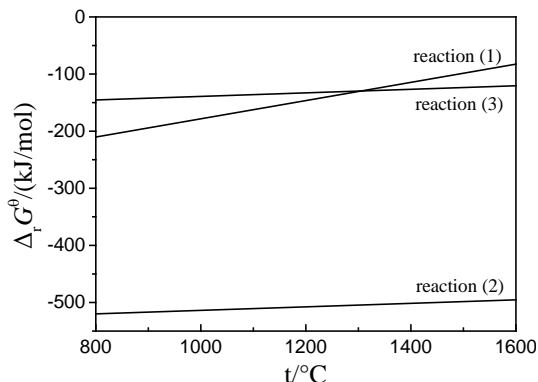$$\Delta_r G^\theta = -178770.00 + 31.10T(J \cdot mol^{-1})$$

Figure 6. $\Delta_r G^\theta$ of reactions at different temperatures

As shown in Fig. 6, in normal conditions, reactions (1)—(3) can happen. Reaction (2) has the lowest $\Delta_r G^\theta$, making it the easiest one to happen. However, after 1400°C, the impurities in the silica fume form phases with low melting temperatures, blocking the pores and hindering the penetration of O_2 and CO, making the gas reactions hard to proceed in the system. Thus, the formation of

Si_2N_2O at different temperatures is based on the reaction between Si_3N_4 and silica fume. Reactions (1) and (2) are restrained in this system, therefore, the forming speed of Si_2N_2O depends on the speed of solid-solid reactions or solid-liquid reactions[2].

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(2) Effect of temperature on Si_2N_2O crystallization

Diffusion between solid SiO_2 and Si_3N_4 is slow. If only relying on the contact diffusion between the two solids, there will be only very a small amount of Si_2N_2O forming. The growth of Si_2N_2O crystals just likes the synthesis of Sialon: as the appearance of liquid, Si_2N_2O crystallizes from the liquid, and grows bigger. So the liquid in the system is a key factor to make the Si_2N_2O crystals nucleate and grow. Therefore, a large amount of Si-N-O-X silicate melting phase is the necessary condition to form Si_2N_2O.

After firing at 1300°C, only a trace of melting liquid forms in the system (Fig. 5(a)), Si_2N_2O can only be formed by the diffusion or through the very limited liquid, so very little Si_2N_2O forms. As temperature rises, the liquid is becoming more and more: liquid is not obvious at 1300°C, but obvious at 1400°C; at 1500°C and 1600°C, the system melts completely. However, as temperature increases, the Si_2N_2O peaks tend to be obvious, but the increase is slight, and there is no large amount of Si_2N_2O formed. The increase of temperature enhances the liquid content of the system but only slightly improves the crystallization of Si_2N_2O.

(3) Effect of duration on Si_2N_2O crystallization

The XRD patterns of specimens fired at one temperature for different duration (Fig. 4) show that at 1300°C, 1400°C, 1500°C, and 1600°C, with duration increasing from 3h to 9h, the diffraction peaks of Si_2N_2O do not increase obviously, indicating the system does not have a large amount of Si_2N_2O formed. At 1500°C and 1600°C, the melting liquid content in the system is relatively high. In this condition, prolonging the duration has no accelerating effect on Si_2N_2O crystallization.

(4) Analysis on Si_2N_2O crystallization mechanism in Si_3N_4－silica fume system

At 1300°C and 1400°C, strong silica fume crystallization appears in the system. The structure of short-range order and long-range disorder has turned into long-range order structure. Some Si-Si and O-O bonds break, forming a stable tetrahedral structure with Si-O bonds. At 1500°C and 1600°C, silica fume melts, providing the precursor for the growth of Si_2N_2O crystals.

When solid or melting SiO_2 contacts with the surface of Si_3N_4 crystals, some [Si-N] tetrahedrons or groups leave the surface of Si_3N_4 crystals and diffuse into the melt. [Si-N] tetrahedrons or groups react with O^{2-} or [Si-O] tetrahedrons from the melt, breaking Si-N bonds and establishing new Si-O bonds, so Si_2N_2O crystallizes. Once Si_2N_2O crystals form, the oxygen content in the melt declines and the liquid viscosity increases, making ions in the melt hard to diffuse and thus hindering the continuous crystallization of Si_2N_2O, Therefore, for the continuous crystallization of Si_2N_2O, a fusing agent or hot pressing is required[1, 5], because this will introduce more low viscosity liquid for the mass crystallization of Si_2N_2O.

Conclusions

(1) In reduction atmosphere, Si_2N_2O was synthesized using flashing combustion synthesized Si_3N_4 and silica fume as raw materials. Because of the self-close effect of silica fume, the Si_2N_2O phase is the direct reaction product of Si_3N_4 and silica fume.

(2) After heat treatment at 1300°C, there is a small amount of melting liquid in the system, with a trace Si_2N_2O formed. After heat treatment at 1400°C, 1500°C, and 1600°C, there is a large amount of melting liquid in the system, accelerating the formation of Si_2N_2O slightly. The temperature

rising can enhance the melt content of the system, but only slightly improves the Si_2N_2O crystallization. The prolonging of duration has very little effect on the Si_2N_2O crystallization.

(3) The system show strong silica fume crystallization at 1300°C and 1400°C. At 1500°C and 1600°C, the silica fume is melting and amorphous.

(4) When Si_2N_2O crystals form, the oxygen content in the melting liquid decreases, liquid viscosity increases as well, so the diffusion of ions in the melt becomes difficult, hindering the continuous crystallization of Si_2N_2O. Thus, fusing agent or hot press is required to introduce more low viscosity liquid for the continuous crystallization of Si_2N_2O.

Acknowledgments

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