SYNTHESIS OF α-Si_3N_4 POWDER BY MOLTEN SALT CATALYTIC NITRIDATION

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ABSTRACT

In this paper, it was intended that reducing the cost of Si_3N_4 powder according to the application prospect of Si_3N_4 ceramic. Using Fe micro powder as catalyst, the α-Si_3N_4 powder was prepared by molten salt catalytic nitridation in the NaCl-NaF molten salt media. Effects of nitridation temperatures on nitridation of Si powder were investigated. Moreover, composition and microstructure of samples were characterized by XRD, SEM and TEM. The results shows that addition of 2 wt% Fe powder, the nitridation of Si powder was completed after 5 h nitridation at 1350 °C in the NaCl-NaF eutectic salts. The crystal morphologies of as-prepared α-Si_3N_4 were in the presentation of anomalous and short rod-like in the samples.

KEYWORDS:

- Molten salt catalytic nitridation
- Metal catalyst
- α-Si_3N_4 powder
- Microstructure

INTRODUCTION

Silicon nitride ceramics possess chemical stability, excellent mechanical properties and good oxidation resistance at room temperature and high temperature[1], and it has been widely used in steel, aerospace, chemical and electronics and other fields[2]. However, silicon nitride foam ceramic has not been effectively used, the reason is the high preparation cost of Si_3N_4 powder and high performance requirements of Si_3N_4 powder[3]. Therefore, it is researchers' aim that improving performance and reducing preparation cost of Si_3N_4 powder.

At present, several methods have been applied for preparation of Si_3N_4 powder, such as direct nitridation of silicon powder, carbothermal reduction nitridation (CRN) of silica and high temperature self-propagating combustion method[4-6]. However, the above methods have some disadvantages, such as long production time, high production cost and complex production process. To some extent, production and application of Si_3N_4 foam ceramics have been limited. In recent years, the molten salt method has attracted much attention, because of the advantages of simple operation, low synthesis temperature and controllable chemical composition. To date, many oxidations were prepared by molten salt method. However, the reports that the nitrides were synthesized by molten salt method are not systematic. In our pervious study[7], TiN whiskers have been successfully prepared on the graphite surface by molten salt nitridation method. To improve nitridation rate of Si powder, researchers have tried to add metal nitrates and oxides to promote nitridation of silicon[8]. In this research group, Si_3N_4 powder was prepared by molten salt nitridation method using metal cobalt and nickel as catalyst[9,10]. Therefore, in this paper, Fe powder was used as catalyst, Si_3N_4 powder was prepared by molten salt nitridation method. Effects of nitride temperature, catalyst content and hold time on synthesis of Si_3N_4 powder were studied in NaCl-NaF molten salt.

EXPERIMENTAL

Firstly, 35 wt% silicon powder (purity ≥ 99.96 wt%, particle size ≤ 44 μm) and 65 wt% analytically pure grade salts (95 wt% NaCl and 5 wt% NaF) were mixed for 30 min in corundum mortar, and then adding different amounts of Fe powder (purity ≥ 99.9 wt%, particle size ≤ 2 μm) continue dry mixing for 30 min. Secondly, 5 g mixture was loaded in an alumina crucible and placed at into an electric furnace, flowing of N_2 gas (purity ≥ 99.999%) several times to clear air in the furnace. Then, The furnace was heated from room temperature at 5 °C·min^{-1} to 1150 °C held for 1h, continue heating to 1250 °C or 1350 °C maintain 1-7 h before cooling to room temperature. Lastly, samples were washed with distilled water several times to remove residual salts, and washed samples were dried at 110 °C for 12 h in the oven. Composition and structure of samples were characterized by XRD, SEM and TEM combined with EDS.

RESULTS AND DISCUSSION

Fig.1 shows XRD patterns of samples with 2 wt% Fe powder after 5 h nitridation at different temperatures and curves of relative contents of phases. It is found that XRD pattern of sample heated at 1050 °C is mainly unreacted Si peaks and weak $FeSi_2$ peaks, as showed in Fig. 1(a). When nitride temperature is 1150 °C, α-Si_3N_4 and Si_2N_2O phases are

detected in the XRD pattern, while intensity of Si peaks decreases and $FeSi_2$ peak disappears, indicating that reaction of Si powder and N_2 begin to occur and form α-Si_3N_4 phase. Formation of Si_2N_2O has two main factors. On the one hand, Si powder surface is oxidized to form a trace of SiO_2 in the process of preservation; On the other hand, O_2 impurity of N_2 gas reacts with Si form SiO. At 1250 °C, intensity of α-Si_3N_4 peaks is obviously enhanced and intensity of Si_2N_2O peaks decreases. At 1350 °C, the Si peak disappears, indicating that conversion rate of Si powder increases to 100%. Relative content of phases in the samples was calculated by Rietveld fine method. As showed in Fig. 1(b), Si content decreases and content of α-Si_3N_4 increases with the increase of nitridation temperature. At 1350 °C, content of α-Si_3N_4 reaches 94 wt% in the samples. XRD results show that α-Si_3N_4 is formed at 1050-1150 °C in the samples with 2 wt% Fe catalyst by molten salt nitridation method. While nitridation temperature is 1350 °C, Si powder in the samples is all nitrided.

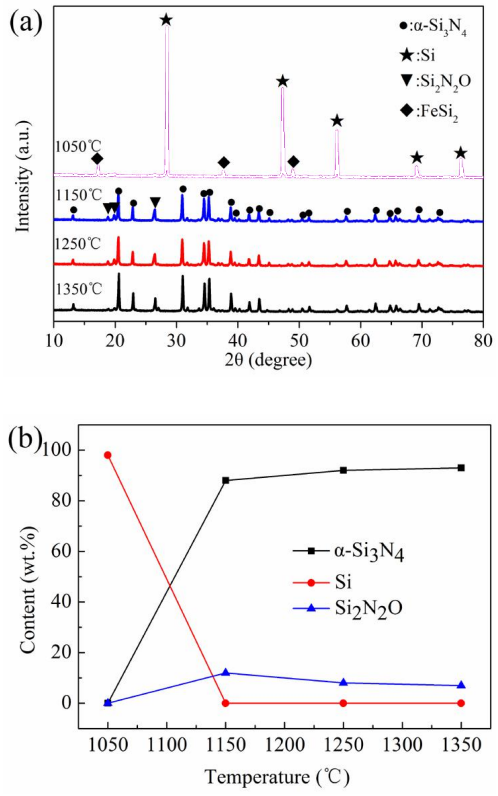

Fig. 1 (a): XRD patterns of samples with 2 wt% Fe catalyst nitrided at various temperatures for 5h, (b): the graph of relative content of crystalline phase

Fig. 2 shows SEM images of samples with 2 wt% Fe catalyst nitrided at 1150 °C, 1250 °C and 1350 °C for 5 h, respectively, in NaCl-NaF molten salt system. As shown in Fig. 2(a), when nitridation temperature is 1150 °C, there are a large number of irregular particles in the sample, which are arranged in a staggered arrangement to form a bigger particle. EDS results indicate that irregular particles consist of Si and N elements, as showed in Fig. 2(a) illustrations, combining with XRD results, irregular particles can be confirmed as α-Si_3N_4. Morphology of α-Si_3N_4 exhibits irregular and short rod-like with temperature increased, where the irregular particle size is too small, short rod-like particles intersperses among the particles. 1350 °C, α-Si_3N_4 particle size increased significantly.

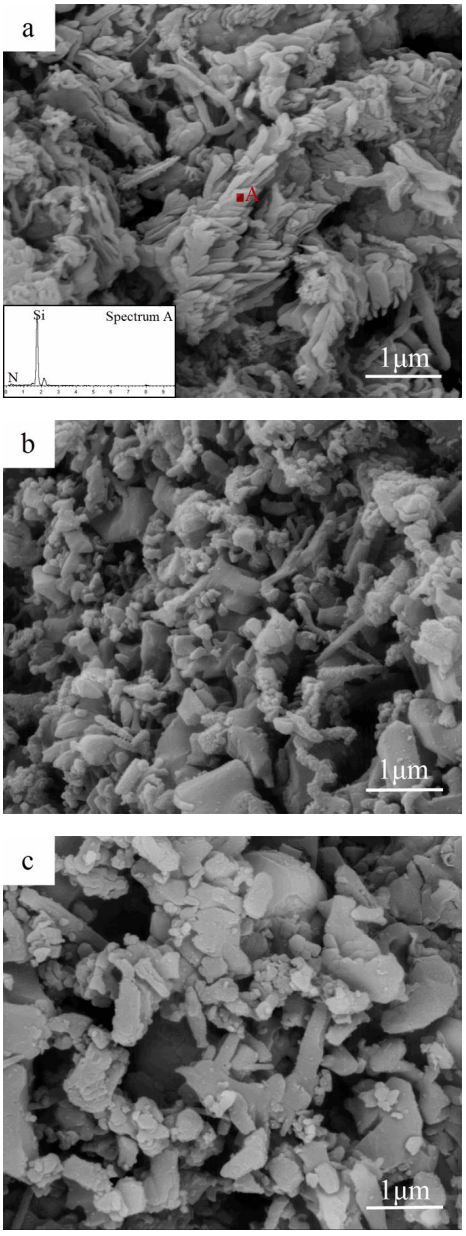

Fig. 2 SEM images of samples nitrided at different temperatures for 5h with 2 wt% Fe catalyst. (a): 1150 °C, (b): 1250 °C, (c): 1350 °C

Fig. 3 shows TEM images of samples 2 wt% Fe as catalyst after 1350 °C held for 5 h. As shown in Fig. 3(a), there are

many irregular α-Si_3N_4 particles in the sample, corresponds to SEM result of sample (Fig. 2(b)). It could be clearly seen that main elements are Si and N in irregular particles from the EDS pattern in Fig. 3(a), combining with XRD results, confirming that irregular particles are α-Si_3N_4. Fig. 3(b, c) shows SAED pattern and HR-TEM image of region A in Fig. 3(a), respectively. Fig. 3(b) shows that irregular particles are single-crystal structure. Moreover, lattice spacings of 0.431 nm and 0.288 nm correspond with (101) and (201) crystal planes of α-Si_3N_4, as shown in Fig. 3(c).

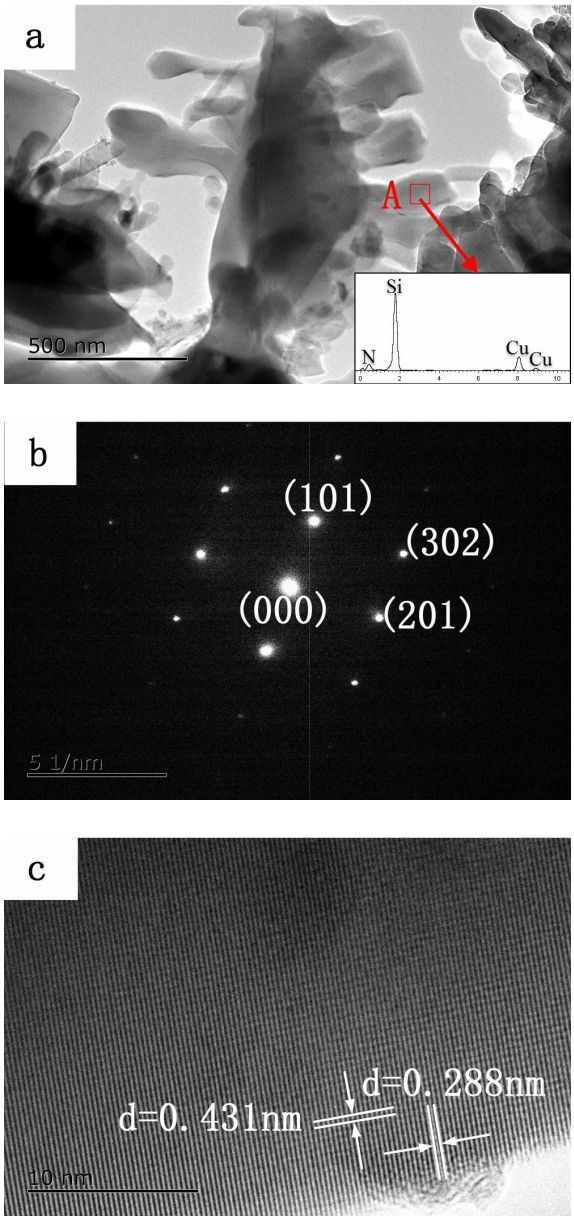

Fig. 3 TEM, SAED and HR-TEM images of sample containing 2 wt% Fe powder nitrided at 1350 °C held for 5h. (a): a typical TEM image, (b): SAED pattern of area A in Fig. 3(a), (c): HR-TEM image of areas A in (a)

CONCLUSIONS

In this work, α-Si_3N_4 was synthesized at 1050-1150 °C in samples with 2 wt% Fe in the NaCl-NaF molten salt medium. Conversion rate of Si powder in the sample increases with the increase of nitridation temperatures. At 1350 °C, relative content of α-Si_3N_4 reaches to 94 wt%. When Fe is used as catalyst, there are lots of irregular α-Si_3N_4 particles in samples by molten salt nitridation method.

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