Original Research Paper

Ni-catalyzed synthesis of hexagonal plate-like alpha silicon nitride from nitridation of Si powder in molten salt media

Zhinan Chai, Jun Ding *, Chengji Deng, Hongxi Zhu, Guangqiang Li, Chao Yu

The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, PR China

A B S T R A C T

The catalytic effects of Ni during the nitridation of Si from a molten salt and the morphologies of the nitridation products were investigated. The phase composition, particle size, and morphological structure of the α-Si$_3$N$_4$ powder were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and a Brunauer–Emmett–Teller (BET) specific-surface-area analysis. The results showed that Ni significantly accelerated Si nitridation and the formation of the hexagonal plate-like α-Si$_3$N$_4$ phase by the formation of Ni–Si in the eutectic salt at 1050–1350 °C. Further, the nitridation rate of the Si powder was increased to 93% after 5 h at 1250 °C with 2-wt% Ni used as the catalyst. The specific surface area of the α-Si$_3$N$_4$ synthesized powder was 5.70–10 m^2/g, exceeding that of 1.70 m^2/g of the Si powder.

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1. Introduction

Si$_3$N$_4$ possesses many excellent properties, including a high strength and fracture toughness, chemical stability, superior thermal shock resistance, and excellent sintering ability, even in high-temperature condition. Thus, Si$_3$N$_4$ ceramics are commonly used in metallurgy, glasses, mechanical engineering, and biotechnology for heat exchangers, gas turbines, bone substitutes, and cutting tools [1–5]. Si$_3$N$_4$/SiC materials are also widely used as lining materials for metallurgical blast furnaces, catalyst carriers, hot-gas filters, and bioreactors because of the properties offered by the combined Si$_3$N$_4$ and SiC [6–8]. However, the Si$_3$N$_4$ powder typically restricts the application of both Si$_3$N$_4$ ceramics and Si$_3$N$_4$/SiC materials.

In general, Si$_3$N$_4$ powders are traditionally prepared by methods including the direct nitridation of Si, microwave carbothermal reduction and nitridation [9,10], self-propagating high-temperature synthesis [11], vapor-phase reaction [12], and the Sol–Gel method [13]. However, these methods have the disadvantages of high manufacturing cost, high synthesis temperature, and severe energy losses. A simple and facile molten-salt synthesis (MSS) method has drawn the attention of many researchers because it is a high adaptable, simple operation with no special equipment, a significantly reduced synthesis temperature, and a shorter reaction time compared with those of other modern synthesis methods. It provides a liquid environment for the synthesis reaction, resulting from acceleration of the mass transfer of reactants. The composition, morphology, and particle size of the resulting powders can be effectively controlled with this method. Most importantly, the purity of the product is improved significantly relative to that obtained using other methods. In previous studies, MMS has been utilized to prepare NiWO$_4$ powders, NbC powders, MgAl$_2$O$_4$ microplatelets, porous TiC/C ceramics, and SiC nanowires [14–21]. In a previous work, TiN whiskers were successfully obtained by MSS in a N$_2$ atmosphere [22].

In this study, a α-Si$_3$N$_4$ powder was prepared by a molten-salt nitridation synthesis (MSNS). The effects of the heat-treatment temperature, amount of Ni catalyst, and holding time were systematically investigated. Elemental Ni was reported to regulate the kinetics of Si nitridation and accelerate the growth of α-Si$_3$N$_4$ nanobelts [23]. However, the addition of small amounts of Ni metal micropowder as a catalyst for the nitridation of Si powder by MSNS has not been thoroughly investigated.

We report the Ni-catalyzed synthesis of Si$_3$N$_4$ powder in a NaCl–NaF eutectic salt. The composition, morphology, and particle size of the as-prepared α-Si$_3$N$_4$ powder were characterized. Moreover, the catalytic effect of Ni and the influence of the synthesis temperature on the process of α-Si$_3$N$_4$ powder formation were investigated, and the formation mechanism of hexagonal plate-like α-Si$_3$N$_4$ was determined.

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* Corresponding author. Tel.: +86 27 68862089; fax: +86 27 68862085.
  E-mail address: dingjun@wust.edu.cn (J. Ding).

2. Experimental

Si powders ($\geqslant$99.96 wt% purity, $\leqslant$44 μm, Beijing Xing Rong Yuan Technology Co. Ltd.) were used as the starting raw material, analytical-grade (99.0-wt%) NaCl and NaF were used for the molten salts, and high-purity N_2 (purity > 99.999%) was used as the nitrogen source. Ni powders ($\geqslant$99.9-wt% purity, $\leqslant$2 μm, Beijing Xing Rong Yuan Technology Co, Ltd.) were added at levels of 0, 0.5, 1, 2, 3, and 5-wt%.

An alumina ball mill was used to dry-mix 35-wt% Si powder and 65-wt% salt (95-wt% NaCl and 5-wt% NaF) for 1 h; A mixed powder sample of 5 g was loaded in an alumina crucible and placed at the center of a long alumina tube inserted into an electric furnace. The alumina tube was initially purged with N_2 multiple times. The furnace was heated from room temperature at 3 °C min^{-1} to 1050, 1150, 1250, and 1350 °C (the melting temperature of Si powder is 1410 °C). The maximum temperature was held for 5 h in a continuous flow of N_2, at the constant pressure of $P_{total\ pressure}$ = 1 MPa (P_{N_2} = 0.99999 MPa and P_{O_2} = 10^{-5} MPa). A sample with the addition of 2-wt% Ni was heated to 1250 °C and held for 1, 3, 5, and 7 h. Si nitridation is a strongly exothermic reaction; therefore, the samples must be held for 1 h at 1150 °C before they are heated to the final temperature to prevent the melting of the Si powder from hindering further reaction. The fired samples were allowed to cool to room temperature in the furnace. The samples were repeatedly washed with distilled water using ultrasonic cleaning equipment and filtered several times to remove the residual salt.

The phase of the powders resulting from nitridation was characterized by powder X-ray diffraction (XRD, X'Pert Pro MPD) with Cu Kα radiation, and the microstructures were observed with scanning electron microscopy (SEM, Nova 400 Nano) and transmission electron microscopy (TEM, JEOL, JEM2000F). The surface elements of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600W) with Al Kα radiation. A Brunauer–Emmett–Teller (BET) specific-surface-area analysis was conducted to characterize the powders using a fully automatic surface-area and porosity analyzer (Quantachrome, Autosorb-1-MP).

3. Results and discussion

The MSNS of Si_3N_4 powder occurred during heat treatments at 1050, 1150, 1250, and 1350 °C for 5 h. Fig. 1 shows the XRD patterns of the as-prepared products obtained at different temperatures and with 2-wt% Ni. Very small peaks corresponding to the α-Si_3N_4 phase were observed in the sample heat-treated at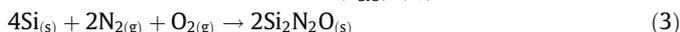 1050 °C, but peaks corresponding to unreacted Si remain strong. In addition, peaks from the (1 0 0), (2 0 0) and (1 1 1) planes of the orthorhombic Si_2N_2O phase are identified at 2θ = 18.993°, 20.002°, and 26.478° in the XRD pattern, respectively. The mechanism of formation of the Si_2N_2O phase was previously reported [24]. Mainly, a small amount of oxygen from N_2 gas and the active "SiO_2" on the Si powder surface react with Si and O_2, as summarized in (1)–(4). These reactions can occur spontaneously, according to thermodynamic calculations, indicating that Si_2N_2O is formed easily in the presence of O_2 or SiO_2 under these conditions.

$$2Si_{(s)} + O_2 \rightarrow 2SiO_{(g)} \tag{1}$$
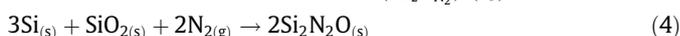$$\Delta G = -207.33 + 0.674T + RT\ln(P_{O_2})\ (kJ)$$

$$Si_{(s)} + SiO_{2(s)} \rightarrow 2SiO_{(g)} \tag{2}$$
$$\Delta G = 716.65 - 0.381T - RT\ln(P_{SiO}^2)\ (kJ)$$

$$4Si_{(s)} + 2N_{2(g)} + O_{2(g)} \rightarrow 2Si_2N_2O_{(s)} \tag{3}$$
$$\Delta G = -1903.301 - 0.581T + RT\ln(P_{O_2}P_{N_2}^2)\ (kJ)$$

$$3Si_{(s)} + SiO_{2(s)} + 2N_{2(g)} \rightarrow 2Si_2N_2O_{(s)} \tag{4}$$
$$\Delta G = -1645.684 - 0.072T + RT\ln(P_{N_2}^2)\ (kJ)$$

The α-Si_3N_4 peaks increase and the Si peaks decrease in intensity as the temperature increased. Upon increasing the heat-treatment temperature to 1350 °C, the α-Si_3N_4 peaks become obviously stronger and the weaker Si peaks disappear; however, the Si_2N_2O peaks remain unchanged, as shown in Fig. 1. The Si_2N_2O peak is identified at 2θ = 26.478° increase in intensity as the nitridation temperature increased. Some peaks overlap may occur between the α-Si_3N_4 and Si_2N_2O phases, causing this apparent increase in intensity. Furthermore, the molten NaCl–NaF salts at 681 °C caused the Si grains and N_2 gas to dissolve rapidly and diffuse into the eutectic salt, thereby increasing the rate of Si nitridation.

Fig. 2 shows the effect of the Ni content on the formation of α-Si_3N_4 in the as-synthesized products after 5 h of nitridation at 1250 °C. Weak α-Si_3N_4-phase peaks and strong Si peaks are observed for the sample without Ni. On the other hand, many α-Si_3N_4 peaks and a small number of Si_2N_2O peaks are present for the sample containing 0.5-wt% Ni. As the content of Ni is increased to 2-wt%, the α-Si_3N_4 peaks are obviously increased, and the Si and Si_2N_2O peaks are decreased. In addition, no change occurs in the Si_3N_4 peak intensities as the Ni content increased. Some of the as-prepared α-Si_3N_4 may have reacted with SiO_2 as follows:

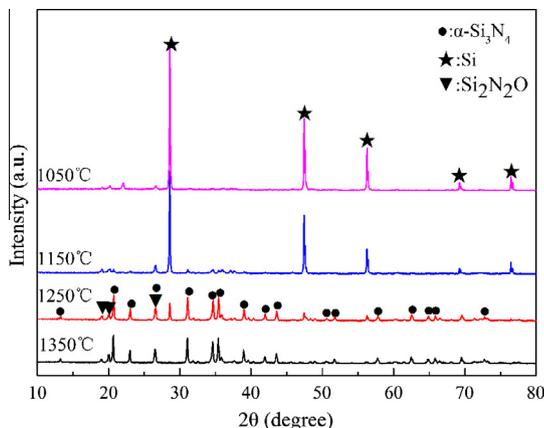$$SiO_{2(s)} + Si_3N_{4(s)} \rightarrow 2Si_2N_2O_{(s)} \tag{5}$$

Fig. 1. XRD patterns of the samples containing 2-wt% Ni heat-treated at different temperatures for 5 h.
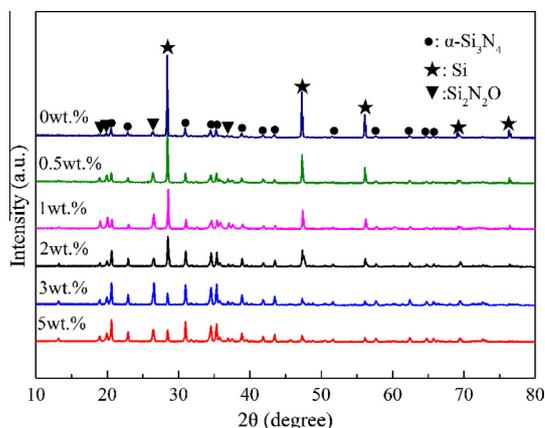
Fig. 2. XRD patterns of the samples containing various amounts of Ni after 5 h of nitridation at 1250 °C.