Synthesis of Silicon Nitride Ceramic Material using Direct Nitridation Process

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Abstract— Silicon nitride has been widely employed as one of the most important engineering ceramics for many practical applications due to their excellent properties such as high temperature resistance, low density, high corrosion resistance and other mechanical properties. In this study, silicon nitride (Si_3N_4) ceramic materials was synthesized by a direct nitridation method of amorphous silicon powder under a flow mixture of argon and nitrogen or ammonia. The amorphous silicon powder was placed in a tube furnace at the temperature of from 1300ºC to 1600ºC for 30-800 min under a flow of gases mixture. The phase compositions and morphology of the obtained Si_3N_4 powder were characterized by using X-ray diffractometry (XRD) and SEM techniques, respectively. The α-Si_3N_4 formed at temperature of 1500ºC under a mixed gases flow of 3 L/ min for 400 composed of straight rod-like fibers with a length in the range of 5 to 100 μm and diameters of about 0.3-4 μm. The effects of gas flow rate, conversion temperature, reduction time and gas compostion on the effectiveness of α-Si_3N_4 formation were investigated in detail. Effect of the auxiliary gases and synthesizing conditions for direct nitridation of Si_3N_4 on α phase content and phase transformation of α-Si_3N_4 to β-Si_3N_4 were also evaluated.

Keywords— Silicon nitride, direct nitridation, β-Si_3N_4, α-Si_3N_4.

I. INTRODUCTION

Silicon nitride have been widely used in many fields of application such as automobile and aerospace industries, high speed air turbine bearing and biotechnology industry, catalyst supports. This ceramic materials could be employed as riser tubes, thermocouple sheaths, crucibles, filters for molten metals, high temperature gas filters, cutting tools, ball bearings and heat engine parts (turbine blades, gas turbines, turbocharger rotors, cam roller, rotor blades, nozzle), etc [1-4].

To date two well-known hexagonal crystal structures of silicon nitride, which are α-Si_3N_4 and β-Si_3N_4 phases, have been extensively studied. α-Si_3N_4 with stacking sequence in structure is commonly harder than β-

Si_3N_4, however β–phase is considered to be more stable at high temperature than that of α-Si_3N_4[5].

Silicon nitride are commonly fabricated by five main methods such as carbothermal reduction and nitridation (CRN), silicon diimide process, vapor phase reaction process and plasma synthesis or direct nitridation of Si powder. In the carbonthermal reaction approach, Si_3N_4 starts forming at 1400ºC and phases are transformed from α-Si_3N_4 to β-Si_3N_4 at temperature of higher than 1600ºC [6,7].

Figure 1 shows the crystal structure of silicon nitride, where silicon atoms (black) and nitrogen (green) form hexagonal crystal structures [8].
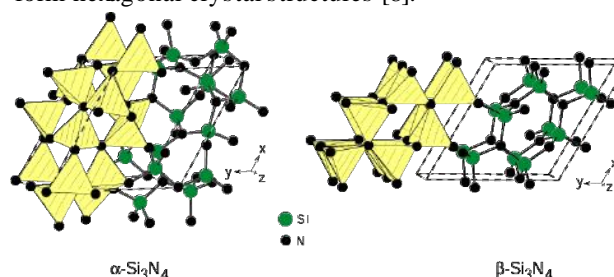

Fig.1: (a) AB layers of Si and N atoms in β-Si_3N_4 (b) CD layers of Si and N atoms in α-Si_3N_4.

In this study, silicon direct nitridation method was employed to fabricate Si_3N_4 ceramic material by placing Si powder under the gasses mixture of argon and nitrogen or ammonia [9-20]. The effect of the reaction conditions are assessed and optimized.

II. MATERIALS AND METHODS

2.1 Materials

For this study, the starting material is amorphous silicon powder which was received from Sigma-Aldrich, Inc (USA), with ammonia, nitrogen as a nitrogen gas precursor

(China Abrasive Import & Export Corp., China, 99%)

2.2 Produce the silicon nitride powder

Si_3N_4 ceramic material was fabricated by using the silicon direct nitridation method. Typically, the amorphous silicon powder was placed into a graphite crucible coated with boro nitride BN with internal diameter of ϕ100 mm ,
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The nitridation reaction were carried out in a horizontal tube furnace (Gas pressure sintering GPS, FPW 100/150-2200-100-LA, Elatec Inc., USA) under the gases flow rate of 1 to 3 L/min of nitrogen gas (99.99%, China) and ammonia gas with the mixtures gas pressure is raised from 0.2 to 1 MPa.at temperatures ranging from 1300ºC to 1600ºC for 30 to 800 min The obtained powder were then sintered using a Self-propagating high temperature synthesis SHS system (model 1050, Sumitomo Coal Mining Co., Ltd). Before heating, the furnace was purged with nitrogen or ammonia-argon mixtures to remove the remaining air in the tube. The furnace was then heated at a ramp rate of 10ºC/min to 1000ºC, and then heating continued at 5ºC/min to the final temperature. After reaching temperature, samples were held from 30 to 800 min before cooling. After the sintering process was completed, the furnace was cooled to room temperature with the cooling rate of 20ºC/min.

After cooling to room temperature, the substrates were removed from the reactor to determine the amount of Si_3N_4 deposited, and for further characterizations

2.3 Survey on properties of silicon nitride powder

The phase compositions of the silicon nitride powder were determined by X-ray diffraction (XRD; Siemens D500, Germany), using CuK_α radiation (λ=1.5406 Aº) with a step of 0.02º (2θ) and a scanning rate of 2º min^{-1}. The pattern was collected in the range from 10° to 90°.

The morphology of ceramic materials were investigated by scanning electron microscopy (SEM, FEI-Inspect F, JEOL, Japan). The operating parameters were 20kV for accelerating voltage, beam current 0.5 nA, 50 s life time and beam diameter of 1-2 μm.

The conversion of Si is determined by the formula:

$$C = \frac{Si_o - Si_c}{Si_o} x100\%$$

Where, C is the conversion percentage of Si, Si_o is initial amount of Si, Si_c is amount of Si after the reaction.

III. RESULTS AND DISCUSSION

Illustrated in Figure 2 are SEM images of Si_3N_4 ceramic materials prepared with various flow rates. It can be seen from the figure that with the gasses flow rate of 1 L/min, Si_3N_4 (mainly α-phase) is composed of dendritic fibers, while at 2 L/min is mostly composed of curvulate fibers with some anomalous particles. With the flow rate of 3 L/min the Si_3N_4 crystal is composed of straight rod-like fibers with a length in the range of 5 to 100 μm and diameters of about 0.3-4 μm. It is obvious that the completeness of Si_3N_4 crystals increases along with gas flow rates.
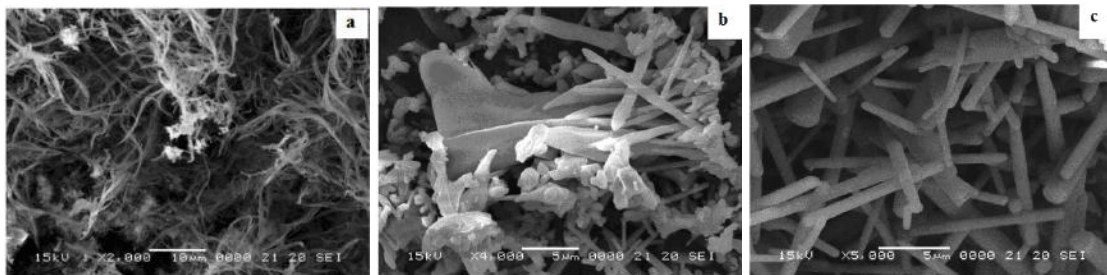

Fig.2: SEM images of Si_3N_4 formed under different flow rates: (a) 1 L/min, (b) 2 L/min, (c) 3 L/min.

The crystalline phase of Si_3N_4 at different reaction temperatures was investigated. The XRD patterns of the samples sintered at different temperatures are shown in Figure 3.
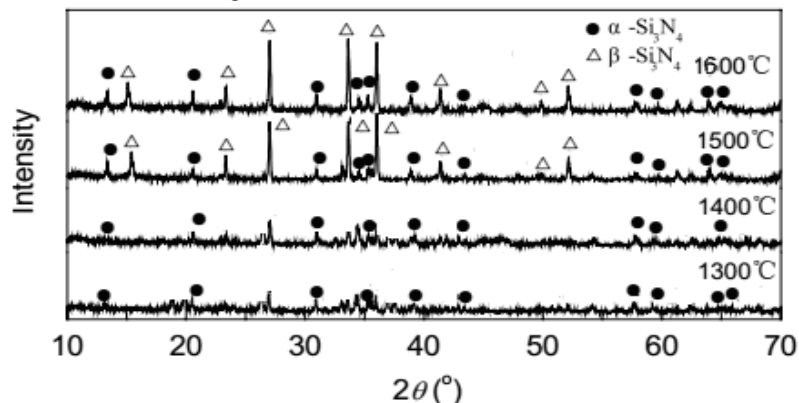

Fig.3: XRD patterns of Si_3N_4 ceramic materials prepared at different temperatures in 75 vol% N_2-25 vol% Ar mixtures with gas flow rate of 3 L/min and 0.2 MPa

It is obviously that α-Si$_3$N$_4$ was evidently detected at 1300°C, however the intensity was relatively weak. The intensity of α-Si$_3$N$_4$ peaks increased with increasing temperature. The XRD analysis showed that β-Si$_3$N$_4$ appeared at temperature of 1500°C. When the temperature increased to 1600°C, the amount of β-Si$_3$N$_4$ increased. Besides, β-Si$_3$N$_4$ appeared in the products and became the predominant crystalline phase when the synthesis temperature was above 1500°C. At 1600°C, the peak intensity of β-Si$_3$N$_4$ was higher than that obtained at 1500°C, which indicate the highly crystallinity of β-Si$_3$N$_4$ at high temperature.

Effect of reaction temperature and time on phase composition and micromorphology of silicon nitride

The effect of temperature and time on nitridation of silicon was investigated at different temperatures (1300°C, 1400°C, 1500°C and 1600°C) for 600 min in the nitrogen-argon mixtures (75 vol% N$_2$) with gas flow rate 3 L/min at 0.2 MPa. Figure 4 presents the effect of conversion effeciency of Si powder into Si$_3$N$_4$ on reaction temperature. It is obvious that the rate of Si nitridation increased when the temperature increase. The conversion of Si was 81 % in effeciency at the temperature of 1300°C. This increased to 85 % at 1400°C, 88 % at 1600°C, and reached the maximum 92 % at 1500°C after 400 min.
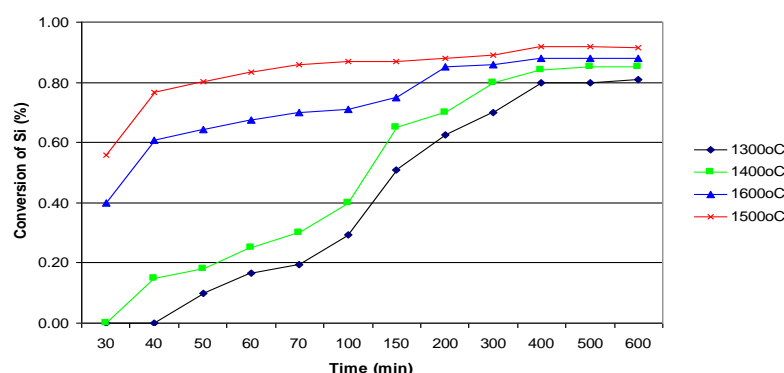

Fig.4: Effect of temperature on conversion of Si in 75 vol% N$_2$-25 vol% Ar mixtures at gas flow rate was 3 L/min and 0.2 MPa

We found that the conversion of Si decreased when the temperature increased to 1600°C. This can be explained that at 1600°C, Si can be melted, so the Si surface is covered which decrease contact between Si and N$_2$ particles.

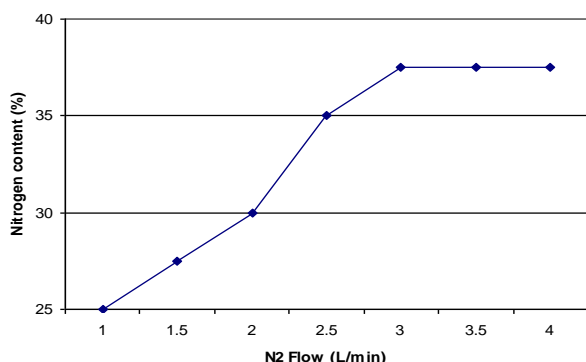**Effect of operating gas flow rates on nitridation of silicon**

Fig.5: Effect of N$_2$ flow on nitrogen content of Si$_3$N$_4$ powders in 75 vol% N$_2$-25 vol% Ar mixtures at 1300°C and 400 min.

The effect of operating gas flow rates was investigated at flow rates from 1 L/ min to 4 L/ min for 400 min in the nitrogen-argon mixtures (75 vol% N$_2$) at 1300°C. Figure 5 shows the effect of N$_2$ flow on nitrogen content of prepared Si$_3$N$_4$ materials. The nitrogen content of Si$_3$N$_4$ powder increased along with the increase of N$_2$ flow and reach a maximal of 37.5% at the flow rate of 3 L/min. When the flow rate was further increase, the content of nitrogen was almost unchanged.

Effect of ammonia and nitrogen on nitridation of silicon

The effect of ammonia and nitrogen on nitridation of silicon was investigated at different nitrogen or ammonia concentration in the mixtures with argon at temperature of 1400°C, gas flow rate 3 L/min and reaction time of 400 min (Figure 6).The figure indicates that the rate of Si nitridation increased with increasing nitrogen or ammonia concentration from 35 vol% to 95 vol%. Fig. 6a shows the rate of Si conversion under the flow of N$_2$ – Ar gasses mixture. The rate of Si nitridation reached the maximum of 92 % with the mixture ratio of 95 vol% N$_2$ – 5 vol% Ar after 400 min of reaction time. The maximum Si conversion of 92% also is reached after reaction time of

450 min, 500 min and 600 min for the mixture ratio of in 75 vol% N_2 – 25 vol% Ar, 55 vol% N_2 – 45 vol% Ar, 35 vol% N_2 – 65 vol% Ar, respectively. After the rate of Si nitridation was unchanged when time further increased.The rate of Si conversion under the flow of NH_3 – Ar mixture are shown in Figure 6b. After 350 min

reaction, Si conversion was increased from 36% in 35 vol% NH_3 – 65 vol% Ar to 47% in 55 vol% NH_3 – 45 vol% Ar, 86% in 75 vol% NH_3 – 25 vol% Ar and reached the maximum of 92 % in 95 vol% NH_3 – 5 vol% Ar mixture.
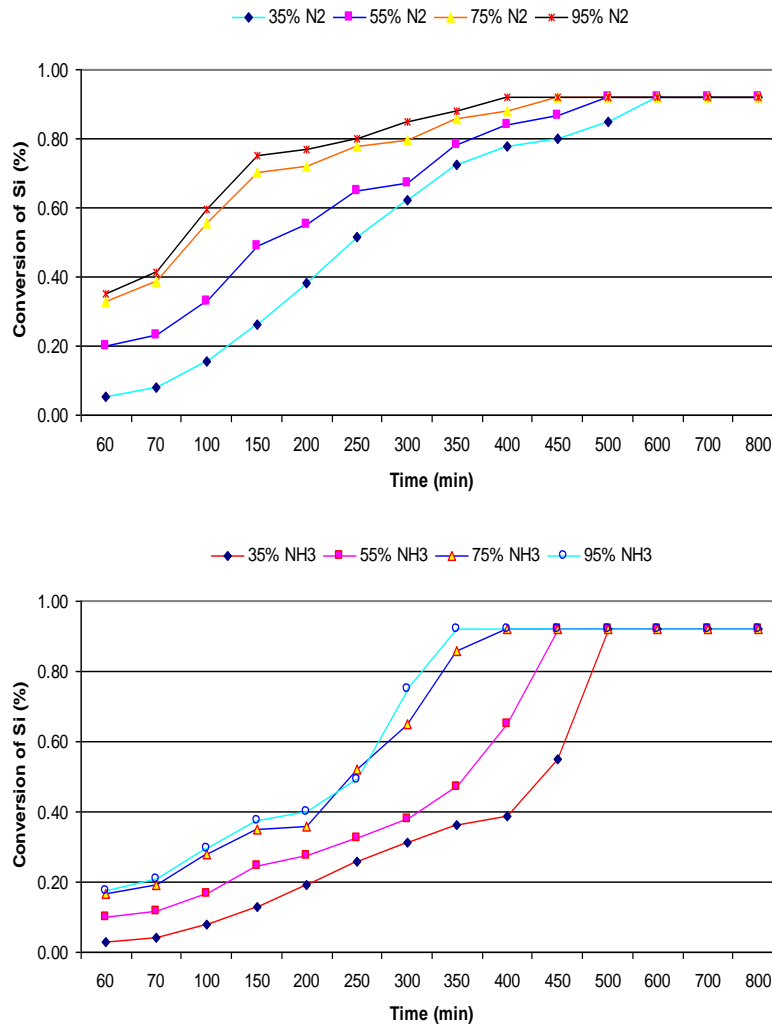

Fig.6: Effect of ammonia and nitrogen on nitridation of silicon at gas flow rate 3 L/min, 400 min and 1400°C: (a) N_2 - Ar; (b) NH_3 - Ar.

It can be found that the effectiveness of Si nitridation in 75 vol% N_2 – 25 vol% Ar is similar to the rate of Si nitridation in 95 vol% N_2 – 5 vol% Ar. Therefore, the Si nitridation in 75 vol% N_2 – 25 vol% Ar mixture instead of the Si nitridation in 95 vol% N_2 – 5 vol% Ar mixture is selected as optimized N_2 – A mixture ratio. Furthermore, the rate of Si nitridation in 75 vol% NH_3 – 25 vol% Ar is same as the rate of Si nitridation in 95 vol% NH_3 – 5 vol% Ar. As a reasult, for NH_3 – Ar mixture the optimized ratio is 75 vol% NH_3 – 25 vol% Ar mixture
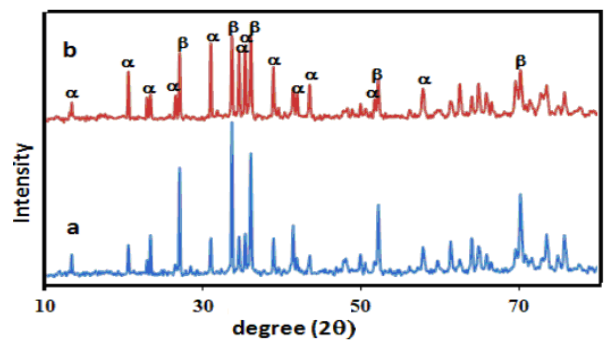

Fig.7: XRD patterns of samples after nitridation at (a) N_2-Ar; (b) NH_3-Ar.

In the first stage, the conversion of Si in the NH_3-Ar mixture is lower than the conversion of Si in the N_2-Ar mixture. This can be explained that the molar of N_2 is double in comparison with NH_3. However, the reaction between Si and NH_3 may be easier than the reaction between Si and N_2.

Figure 7 illustrates the XRD pattern of the samples after nitridation by using N_2-Ar and NH_3-Ar mixtures. It is obvious that with N_2-Ar mixture, the obtained ceramic was mainly β-Si_3N_4 some traces of α-Si_3N_4. While with NH_3-Ar mixture α-Si_3N_4 is dominant phase in the ceramic materials.

IV. CONCLUSIONS

In short, silicon nitride (Si_3N_4) ceramic materials was successfully fabricated by a direct nitridation method. In the resultant ceramic materials, although β-Si_3N_4 was detected, but α-Si_3N_4 was the main phase of silicon nitride,. Si_3N_4 ceramic materials can be obtained from amorphous silicon powder annealed at 1500^oC under 75 vol% N_2 – 25 vol% Ar or 75 vol% NH_3 – 25 vol% Ar mixture at gas flow rate was 3 L/min for 400 min. The conversion of Si was 81 % in nitridation at $1300°C$. It increased to 85 % at $1400°C$, 88 % at $1600°C$, and reached the maximum 92 % at $1500°C$ after 400 min.Percentages of α-Si_3N_4 content obtained with ammonia and argon is higher than those with nitrogen and argon.α-Si_3N_4 was detected at temperature of 1300^oC, but the intensity was very weak. β-Si_3N_4 became apparent at the temperature of $1500°C$. When the temperature increased to $1600°C$, the amount of β-Si_3N_4 increased. Besides, β-Si_3N_4 appeared in the products and became the predominant crystalline phase when the synthesis temperature was above $1500°C$. The nitrogen content of Si_3N_4 powder increased with the increase of N_2 flow and reached the maximum when the N_2 flow was 3L/ min.

REFERENCES

[1] Riley F. L, Silicon nitride and related materials, Journal of the American Ceramic Society, **83** (2010) 245-265.

[2] Hampshire, S. Silicon nitride ceramics-review of structure, processing and properties. Journal of Achievements in Materials and Manufacturing Engineering, **24** (2007) 43-50.

[3] H. Klemm, Silicon nitride for high-temperature applications, Journal of the American Ceramic Society, **93** (2010) 1501-1522.

[4] Riley Frank L. Silicon Nitride and Related Materials. Journal of the American Ceramic Society, **83** (2004) 245-265.

[5] Riley F. L. Silicon Nitrides: An Overview. Science of Ceramics, **12** (2013) 15-20.

[6] Taylor R. M., J. P. Bernero, A. A. Patel, D. S. Brodke. Silicon nitride: a new material for spinal implants. In Orthopaedic Proceedings, V**ol. 92 (**2010) 130-133.

[7] Sangster, Raymond C. Formation of Silicon Nitride: From the 19th to the 21st century. Materials Science Foundations (2005) 948.

[8] Klemm, H. Silicon nitride for high-temperature applications. J. Am. Ceram. Soc, **93** (2010) 1501-1522.

[9] Yin Shao-wu, Li Wang, Li-ge Tong, Fu-ming Yang and Yan-hui Li. Kinetic study on the direct nitridation of silicon powders diluted with α-Si_3N_4 at normal pressure. International Journal of Minerals, Metallurgy, and Materials 20, **5** (2013) 493-498.

[10] S.J.P. Durham, K. Shanker, R.A.L. Drew, Carbothermal synthesis of silicon nitride: effect of reaction conditions, Journal of the American Ceramic Society, **74** (2011) 31-37.

[11] Karaku, Nuray. Sintering behaviour of silicon nitride powders produced by carbothermal reduction and nitridation. Advanced Powder Technology, **24** (2013) 697-702.

[12] Chen, Kai, et al. Synthesis of β-Si_3N_4 powder from quartz via carbothermal reduction nitridation. Powder technology, **235** (2013) 728-734.

[13] N. Karakus, A.O. Kurt, H.O. Toplan, Synthesizing high α-Si_3N_4 powders containing sintering additives, Ceramics International, **35** (2009) 2381-2385

[14] Mitomo, M. and Uenosono, S. Microstructural development during gas-pressure sintering of α-Si_3N_4, J. Am. Ceram. Soc., **Vol.75** (2012) 103-107.

[15] Irene G. Cano and Miguel A. Rodriguez. Synthesis of α-Silicon nitride by SHS: fiber growth, Scripta Materialia, **Vol.50** (2004) 383-386.

[16] Mitomo, M., Tsutsumi, H., Tanaka, S., Uenosono, S. and Saito, F. Grain growth during gas-pressure sintering of α-silicon nitride, J. Am. Ceram. Soc., **Vol.73** (2010) 2441-2445.

[17] Zou C R, Li B. Microstructure and properties of porous silicon nitride ceramics prepared by gel-casting and gas pressure sintering. Materials and Design, **44** (2013) 114-118.

[18] George V.Bichurov, J.Intemational Journal of Self-Propagating High-Temperature Synthesis, **9** (2016) 247-253.

[19] Lee JS, Mun JH, Han BD, Kim HD, Shin BC, Kim IS. Effect of raw-Si particle size on the properties of sintered reaction-bonded silicon nitride. Ceram. Int, **30** (2004) 965 -976.

[20] Yin, S. W., Wang, Tong. Kinetic study on the direct nitridation of silicon powders diluted with α-Si_3N_4 at normal pressure. Int. J. Min. Met. Mater, **20** (2013) 493-498.