Low-Temperature Preparation of α-Si$_3$N$_4$ Powder via Combined High-Energy Ball Milling and Molten Salt Nitridation Method

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Abstract. In this work, α-Si$_3$N$_4$ powder was synthesized by a combined high-energy ball milling and molten salt nitridation method using silicon powder as raw materials, and NaCl-NaF binary molten salt as reaction medium and diluents. The effects of nitridation temperature, soaking time, and NaF content in the molten salt on the formation of α-Si$_3$N$_4$ were investigated. The results show that the nitridation of silicon powder was completed at NaF content of 10wt% in the molten salt after nitridation at 1200°C and held for 4 h. The α-Si$_3$N$_4$ content in the as-synthesized powder is 96wt%. The α-Si$_3$N$_4$ whiskers with 40-280 nm in diameter and several microns to tens of microns in length appear in the final products. The crystal growth process of α-Si$_3$N$_4$ whiskers follows vapor-crystal (VC) mechanism.

1. Introduction

Silicon nitride ceramics possess many excellent properties, including low bulk density, good thermal shock resistance, creep resistance, chemical stability, wear resistance and excellent mechanical properties even at high temperatures. Thus, silicon nitride ceramics are widely used in some important fields such as energy, electronics, metallurgy, machinery, chemical industry and military industry for heat exchangers, gas turbines, ceramic bearing balls, and cutting tools[1-4]. Silicon nitride powder is the raw materials for the fabrication of silicon nitride ceramics, and it is also one of the key factors affecting products’ performance. The preparation methods of silicon nitride powder include the direct nitridation of silicon powder [5], carbothermal reduction and nitridation [6], combustion synthesis [7], imide-decomposition [8] and gas phase reaction method [9]. However, there are still many disadvantages in these methods, such as high nitriding temperature and long nitriding cycle of direct nitridation, difficult to control the reaction temperature and high β-Si$_3$N$_4$ content in the product of combustion synthesis, and high manufacturing cost of idmie-decomposition method.

Molten salt nitridation method is a simple and facile technology to prepare nitride ceramic powder for its high adaptability, simple operation with no special equipment, significantly reduced synthesis temperature, and shorter nitriding cycle compared with those of other synthesis methods. In previous studies, molten salt nitridation has been utilized to prepare TiN powder [10], Si$_3$N$_4$ powder [11, 12], AlN powder [13], and β-Sialon powder [14]. Ding et al. [11] and Chai et al. [12] successfully prepared α-Si$_3$N$_4$ powder by molten salt nitridation, respectively. However, in their work, cobalt (Co) or nickel (Ni) need to be used as catalysts, which not only increased the preparation cost of α-Si$_3$N$_4$ powder, but
also seriously affected the purity of the powder and the performance of the product because the catalysts will react with silicon to form metal silicides which will remain in the powder as impurity after the nitridation reaction.

The high-energy ball milling is a mechanical activation technology, and the raw material powder is subjected to mechanical force during the ball milling process to obtain higher energy and generate more defects, so that the activation energy of the reaction is greatly reduced, and the reaction can occur at a relatively low temperature [15-17]. Liu et al. [17] successfully synthesized nanocrystal aluminum nitride powder by mechanical activation combined with carbothermal reduction and nitridation method. The results show that the synthesis temperature of AlN powder is reduced and the reaction time is shortened by high-energy ball milling process.

In this paper, α-Si₃N₄ powder was prepared by high-energy ball milling assisting molten salt nitridation method using silicon powder as raw materials, and NaCl-NaF binary molten salt as reaction medium and diluents. The effects of nitridation temperature, soaking time, and NaF content in the molten salt on the formation of α-Si₃N₄ were systematically investigated.

2. Experimental

Silicon powder (purity ≥ 99.9 wt%, particle size ≤ 10 μm) was used as the starting raw material, analytical-grade (99.0-wt% purity) NaCl and NaF were used as the molten salt, and high-purity N₂ (purity > 99.999 vol%) was used as the nitrogen source.

An high-energy ball mill was used to dry-mix silicon powder and inorganic salt (90-wt% NaCl and 10-wt% NaF) for 3 h; the mass ratio of silicon powder to inorganic salt was 1:2, and the ball milling speed was 600 r/min. The raw material after high-energy ball milling was loaded in a corundum crucible, and then the crucible was placed at a tubular furnace. The furnace was heated from room temperature at 3 °C/min to 1000, 1050, 1100, 1150, and 1200 °C and held at the maximum temperature for 4 h in the flowing nitrogen atmosphere. Some samples were heated to 1200 °C and held for 1, 2, 3, 4, and 5 h, respectively. Another samples with various NaF contents in molten salt at levels of 0, 5, 10, 15 wt% were heated to 1200 °C and held for 4 h. The product was washed repeatedly with deionized water and filtered to remove the residual salt, and then dried at 80 °C for 12 h to obtain the final powder.

The phase of the powder resulting from nitridation was characterized by powder X-ray diffraction (XRD, X’Pert Pro MPD) with Cu Ka radiation, and the content of crystalline phases in the samples was calculated by the Rietveld refinement method. The microstructures were observed with field emission scanning electron microscopy (FE-SEM, SU8220).

3. Results and discussion

3.1. Effect of nitridation temperature on the α-Si₃N₄ formation

Figure 1 shows the XRD patterns of the as-prepared samples nitried at different nitridation temperatures. The a-Si₃N₄ peaks increase and the Si peaks decrease in intensity as the temperature increased. When the nitriding temperature is 1000 °C, there is the Si peaks and very weak Si₂N₂O peaks, and there is no a-Si₃N₄ peaks found, which indicates a-Si₃N₄ has not yet been formed; at 1050 °C, there are some weak a-Si₃N₄ peaks, which indicates a-Si₃N₄ has been formed at the temperature; at 1150 °C, the peak intensity of a-Si₃N₄ is strong, and the peak intensity of Si is already very weak, which indicates most Si has been nitried; upon increasing the nitridation temperature to 1200 °C, the a-Si₃N₄ peaks become obviously stronger and the weak Si peaks disappear. However, theSi₂N₂O peaks remain unchanged. The mechanism of formation of the Si₂N₂O phase was previously reported [12, 18]. Mainly, a small amount of oxygen from N₂ gas and the active“SiO₂” on the Si powder surface react with Si and N₂, as summarized in the reaction (1) and (2).

\[ 4\text{Si}(s) + 2\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{Si}_2\text{N}_2\text{O}(s) \]  

(1)
Figure 1. XRD patterns of the as-prepared samples obtained from the combinations of silicon powder and NaCl-NaF molten salt, with silicon/salt mass ratio of 1:2 and NaF content in the molten salt of 10 wt%, by a 3-hour high-energy ball milling and subsequent 4-hour nitridation process differing in nitridation temperature.

Figure 2. Content of crystalline phases in the as-prepared samples obtained from the combinations of silicon powder and NaCl-NaF molten salt, with silicon/salt mass ratio of 1:2 and NaF content in the molten salt of 10 wt%, by a 3-hour high-energy ball milling and subsequent 4-hour nitridation process differing in nitridation temperature.
\[3\text{Si(s)} + \text{SiO}_2(s) + 2\text{N}_2(g) \rightarrow 2\text{Si}_2\text{N}_2\text{O}(s)\] (2)

Figure 2 shows the content of crystalline phases in the samples nitrided at different nitridation temperatures. With the increase of nitriding temperature, the content of \(\alpha\)-Si\(_3\)N\(_4\) increases, the content of residual Si decreases, and the content of Si\(_2\)N\(_2\)O remains in a certain range (4-10 wt%). When the temperature increases to 1200 °C, there is no residual Si left. The content of \(\alpha\)-Si\(_3\)N\(_4\) is 96 wt%, and the content of Si\(_2\)N\(_2\)O is 4 wt%. As well-documented in the literature, the complete nitriding temperature of silicon powder can only be decreased to 1350-1400°C via catalytic nitridation \[18,19\] or salt-assisted catalytic nitridation method \[11,12\], while the complete nitriding temperature of silicon powder is significantly decreased to 1200 °C, based on high-energy ball milling assisting molten salt nitriding method, which is 200°C lower than that of conventional direct nitridation of silicon powder or other methods mentioned above.

![Figure 2. XRD patterns of the as-prepared samples obtained from the combinations of silicon powder and NaCl-NaF molten salt, with silicon/salt mass ratio of 1:2 and NaF content in the molten salt of 10 wt%, by a 3-hour high-energy ball milling and subsequent 1200 °C nitridation process differing in soaking time.](image)

3.2. Effect of soaking time on the \(\alpha\)-Si\(_3\)N\(_4\) formation

Figure 3 shows the XRD patterns of the as-prepared products obtained for different soaking time. As expected, the \(\alpha\)-Si\(_3\)N\(_4\) peaks increase and the Si peaks decrease in intensity as the soaking time increased. For the soaking time of 1 h, the peak intensity of Si is still very strong, indicating there are still a lot of residual Si; for the soaking time of 2 h, the peak intensity of Si decreased and the peak intensity of \(\alpha\)-Si\(_3\)N\(_4\) increased; for the soaking time of 3 h, the peak intensity of \(\alpha\)-Si\(_3\)N\(_4\) has become much stronger, and the Si peaks are barely visible, which indicates the residual silicon content is already very low; upon extending the soaking time to 4 h, the \(\alpha\)-Si\(_3\)N\(_4\) peaks is still strong and the weak Si peaks disappear; the soaking time is extended to 5 h, and there is no obvious change in the peak intensity of \(\alpha\)-Si\(_3\)N\(_4\).

Figure 4 shows the content of crystalline phases in the samples nitrided for different soaking time. With the increase of soaking time, the content of \(\alpha\)-Si\(_3\)N\(_4\) increases, the content of residual Si decreases, and the content of Si\(_2\)N\(_2\)O remains in a certain range (4-10 wt%). For the soaking time of 3
h, the content of $\alpha$-Si$_3$N$_4$ in the powder is 94 wt%, and the content of residual Si is only 1 wt%. For the soaking time of 4 h, there is no residual Si left and the conversion ratio of silicon powder reached 100%, which confirms that the prolonged soaking time contributes to the formation of $\alpha$-Si$_3$N$_4$.

**Figure 4.** Content of crystalline phases in the as-prepared samples obtained from the combinations of silicon powder and NaCl-NaF molten salt, with silicon/salt mass ratio of 1:2 and NaF content in the molten salt of 10 wt%, by a 3-hour high-energy ball milling and subsequent 1200 °C nitridation process differing in soaking time.

**Figure 5.** XRD patterns of the as-prepared samples obtained from the combinations of silicon powder and NaCl-NaF molten salt, with silicon/salt mass ratio of 1:2 and various NaF contents in the molten salt, by a 3-hour high-energy ball milling and subsequent 1200 °C /4-hour nitridation process.
3.3. Effect of NaF content in the molten salt on the \( \alpha \)-Si\(_3\)N\(_4\) formation

Figure 5 shows the XRD patterns of the as-prepared products obtained with various NaF content in the molten salt. The \( \alpha \)-Si\(_3\)N\(_4\) peaks increase and the Si peaks decrease in intensity as NaF content in the molten salt increased. When NaF content is 0 wt%, that is to say, when NaF is not used as molten salt, there is mainly the Si peaks and very weak \( \alpha \)-Si\(_3\)N\(_4\) peaks; when NaF content is 5 wt%, the peak intensity of Si is obviously weakened, and the peak intensity of \( \alpha \)-Si\(_3\)N\(_4\) is obviously enhanced; when NaF content is 10 wt%, the Si peaks disappears indicating the silicon powder is completely nitrided; when NaF content is 15 wt%, there is no obvious change in the peak intensity of \( \alpha \)-Si\(_3\)N\(_4\).

Figure 6 shows the content of crystalline phases in the samples with various NaF content in the molten salt. With the increase of NaF content, the content of \( \alpha \)-Si\(_3\)N\(_4\) increases, the content of residual Si decreases, and the content of Si\(_2\)N\(_2\)O remains in a certain range (4-10 wt%). When NaF is not used as molten salt, the content of \( \alpha \)-Si\(_3\)N\(_4\) is 28 wt%, which indicates that silicon powder cannot be completely nitrided only with NaCl molten salt as reaction medium; when NaF content is 5 wt%, the content of \( \alpha \)-Si\(_3\)N\(_4\) is 78 wt%; when NaF content is 10 wt%, the conversion ratio of silicon powder has reached 100%, which indicates that the addition of NaF contributes to the nitriding of silicon powder.

D Campos-Loriz et al. [20] suggested that NaF can firstly react with Si to form SiF\(_4\) (reaction (3)), and then SiF\(_4\) reacted with Si to form SiF\(_2\) (reaction (4)); finally, SiF\(_2\) reacted with N\(_2\) to form \( \alpha \)-Si\(_3\)N\(_4\) (reaction (5)). In other words, the existence of NaF can change the gas-solid reaction between Si powder and N\(_2\) into the gas phase reaction between SiF\(_2\) and N\(_2\), thus promoting the nitriding of silicon powder.

\[
\begin{align*}
\text{Si(s) + 4NaF(l) &\rightarrow SiF}_4\text{(g) + 4Na(g)} & (3) \\
\text{SiF}_4\text{(g) + Si(s) &\rightarrow 2SiF}_2\text{(g)} & (4) \\
6\text{SiF}_2\text{(g) + 2N}_2\text{(g) &\rightarrow Si}_3\text{N}_4\text{(s) + 3SiF}_4\text{(g)} & (5)
\end{align*}
\]

**Figure 6.** Content of crystalline phases in the as-prepared samples obtained from the combinations of silicon powder and NaCl-NaF molten salt, with silicon/salt mass ratio of 1:2 and various NaF contents in the molten salt, by a 3-hour high-energy ball milling and subsequent 1200 °C /4-hour nitridation process.
3.4. Morphology and formation mechanism of α-Si₃N₄

Figure 7 shows the SEM images of the as-prepared sample nitrided at 1200 °C and held for 4 h when the content of NaF in molten salt is 10 wt%. The morphology of the as-prepared powder is irregular granular-like and a large number of whiskers appear in the final products. The diameter of the whisker is 40-280 nm, and the length of the whisker ranges from several microns to tens of microns. The reaction mechanism of the formation of α-Si₃N₄ in the present study is illustrated by the schematic in Figure 8. Granular-like α-Si₃N₄ is formed by the conventional gas-solid reaction of Si with N₂. The growth of α-Si₃N₄ whisker follows vapor-crystal (VC) mechanism [21]. The Si powder reacts with NaF to form SiF₄, and then SiF₄ reacts with N₂ to form α-Si₃N₄ crystal nuclei. Subsequently, the continuously formed α-Si₃N₄ from SiF₄ vapors through VC mechanism perpendicularly deposits onto the surfaces of the small α-Si₃N₄ nuclei, and finally grow into the α-Si₃N₄ whiskers.

![Figure 7. SEM images of the as-prepared samples obtained from the combinations of silicon powder and NaCl-NaF molten salt, with silicon/salt mass ratio of 1:2 and NaF content in the molten salt of 10 wt%, by a 3-hour high-energy ball milling and subsequent 1200 °C /4-hour nitridation process.](image)

![Figure 8. Schematic illustrating the synthesis of α-Si₃N₄ by high-energy ball milling assisting molten salt nitriding method.](image)

4. Conclusion

In this work, the powder with high content of α-Si₃N₄ is synthesized by combination of high-energy ball milling with molten salt nitridation method, using silicon powder as raw materials, and NaCl-NaF binary molten salt as reaction medium and diluents. Silicon powder could be nitrided completely at 1200°C and held for 4 h with salt/silicon mass ratio of 2:1 and NaF content in the molten salt of 10 wt%. The α-Si₃N₄ content in the as-synthesized product is 96 wt%. The morphology of the as-prepared powder is irregular granular-like. The α-Si₃N₄ whiskers with 40-280 nm in diameter and several microns to tens of microns in length appear in the final products. The growth of the α-Si₃N₄ whisker follows vapor-crystal (VC) mechanism.

References

[1] Riley F L. 2000. J. Am. Ceram. Soc. 83 245-265
[2] Klemm H 2010 *J. Am. Ceram. Soc.* 93 1501-1522
[3] Krstic Z and Krstic V D 2012 *J. Mater. Sci.* 47 535-552
[4] Zhu X and Sakka Y 2008 *Sci. Technol. Adv. Mat.* 9 033001
[5] Li Y W, Zhang X, Tian H B, Liu J H and Li N 2003 *B. Chin. Ceram. Soc.* 22 30-34
[6] Vlasova M V, Bartnitskaya T S, Sukhikh L L, Krushinskaya L A, Tomilaand T V, Artyuch S Yu 1995 *J. Mater. Sci.* 30 5263-5271
[7] Chen Y X, Li J T and Du J S 2008 *Mater. Res. Bull.* 43 1598-1606
[8] Bi Y H, Cheng F, Li J, Zhang D M and Zhang L M 2007 *J. Wuhan Univ. Technol.* 29 8-11
[9] Kijima K, Setaka N and Tanaka H 1974 *J. Cryst. Growth.* 24 183-187
[10] Ding J, Deng C, Yuan W, Zhu H and Li J 2013 *Ceram. Int.* 39 2995-3000
[11] Ding J, Zhu H, Li G, Deng C and Chai Z 2016 *Ceram. Int.* 42 2892-2898
[12] Chai Z, Ding J, Deng C, Zhu H, Li G and Yu C 2016 *Adv. Powder Technol.* 27 1637-1644
[13] Tian L, Liang F, Zhang J F, Wang J K, Tan C, Zhang H J and Zhang S W *J. Ceram. Soc.* 38 352-355
[14] Liu J, Ding J, Zhu H, Deng C and Chai Z 2017 *J. Ceram. Soc. Jpn.* 125 155-158
[15] Yoshikazu K, Masaki I, Atsuo Y and Kiyoshi O 2004 *Solid State Ionics* 172 185-190
[16] Ren K G, Chen K X, Zhou H P, Jiu H B, Zhong J D and Ning X H 2008 *Key Eng. Mater.* 368-372 862-864
[17] Liu X, Ma M 2000 *J. Chin. Ceram. Soc.* 28 468-471
[18] Huang J, Zhang S, Huang Z, Fang M, Liu Y and Chen K 2014 *Ceram. Int.* 40 11063-11070
[19] Gu Y, Lu L, Zhang H, Cao Y, Li F and Zhang S 2015 *J. Am. Ceram. Soc.* 98 1762-1768
[20] Campos-Loriz D, Howlett S P, Riley F L and Yusaf F 1979 *J. Mater. Sci.* 14 2325-2334
[21] Ge Y, Wang Q, Cui W, Zou Y, Xie Z and Chen K 2015 *J. Am. Ceram. Soc.* 98 3398-3403