1. Introduction

Silicon nitride (Si$_3$N$_4$) is considered as one of the most promising structural materials for engineering application, owing to its high thermal shock resistance, high strength retention at elevated temperature as well as high corrosion resistance and low creep properties.\(^1\)-\(^4\)

Amongst the different classes of Si$_3$N$_4$ ceramics, reaction bonded silicon nitride (RBSN) has a variety of advantages such as low sintering shrinkage, low cost and high strength retention at elevated temperature. However, the production and application of RBSN ceramics are restricted due to the high reaction nitridation temperature and long dwell time. To overcome these drawbacks, a few of catalysts for enhancing the nitridation rate of silicon powders are investigated. For example, Fe, Co, Ni, and Cr have been demonstrated to be capable of greatly accelerating Si nitridation,\(^5\)-\(^10\) which enable dissolution of N$_2$ and promote the formation of Si$_3$N$_4$. Moreover, the effects of metal oxides on the nitridation process of Si powders are also studied.\(^1\)-\(^4\)\(^5\)-\(^10\)

For example, Guo et al.\(^14\) reported that TiO$_2$ greatly enhances Si nitridation at approximately 1673 K; Hyuga et al.\(^15\) reported that CeO$_2$ and Eu$_2$O$_3$ obviously accelerate the nitridation process of Si powders; Kim et al.\(^16\) suggested that Yb$_2$O$_3$ accelerates the nitridation of Si powders by reacting with the outer SiO$_2$ layer of the raw material at 1373 K. However, the usage of conventional micro-sized metal oxides as catalyst still suffers from the drawbacks of poor activity resulted from their large particle size. Even worse, large size additive particles may act as defects in the sintered body, which is detrimental to the mechanical properties of the final product.

Lanthanum oxide (La$_2$O$_3$) nanoparticles (NPs) have been widely used as catalysts, luminescent displays, Ultra Violet shielding, etc.\(^17\),\(^18\) But little is known about their behavior and influence on the catalytic nitridation of silicon powders.\(^19\),\(^20\) Therefore, in present work, La$_2$O$_3$ NPs was used as catalyst to accelerate the nitridation of Si powders, the effects of La$_2$O$_3$ NPs amount and temperature on the nitridation of Si powders were investigated. The responsible mechanism of catalytic reaction and formation of Si$_3$N$_4$ whiskers were also proposed based on the experimental and thermodynamic calculation results.

2. Experimental

2.1 Raw materials

Si powders (≥99 wt % purity, $D_{50}=10\mu m$, Wugang Refractory Co. Ltd., Wuhan China), La(NO$_3$)$_3$·6H$_2$O (≥99 wt % purity, Sinopharm. Ltd., Shanghai China) and NH$_3$·H$_2$O (27 wt %, Dahong Chem. Co. Ltd., Wuhan China), and Poly ethylene glycol [PEG, H(CH$_2$CH$_2$O)$_n$OH, 2000, Sinopharm. Ltd., Shanghai China] were directly used as raw materials without further purification.
2.2 Preparation of La$_2$O$_3$ NPs/Si composite powders

A precipitation method was used to in-situ deposit La$_2$O$_3$ NPs onto the surface of raw Si powders. Typically, for the preparation of La(OH)$_3$/Si composite powders with 3 wt% La$_2$O$_3$ NPs, 5 g of Si powders, 0.342 g of La(NO$_3$)$_3$·6H$_2$O and 0.1 g of PEG were firstly dispersed in 250 mL distilled water and stirred for 30 min. Then an aqueous solution of NH$_3$·H$_2$O (14.29 mol/L) was added dropwise to the suspension under vigorous stirring and hold for another 10 min (pH value of the solution is 8.6). Subsequently, 14.29 mol/L NH$_3$·H$_2$O was quickly added to the suspension under stirring until pH value of the solution reached 10. The resultant La(OH)$_3$/Si composite powders were collected by filtration and dried up at 393 K (pH value of the solution is 8.6). Finally, the as-obtained La(OH)$_3$/Si composite powders were heated to 1473 K for 2 h in a corundum furnace under a flowing nitrogen atmosphere.

2.3 Characterization of the final products

Phase compositions of the as-prepared samples were identified by X-ray diffraction (XRD) analysis using a Philips X’Pert PRO diffractometer (PANanalytical, Netherland). Spectra within the range between 10 and 90° (20) were recorded at 40 mA and 40 kV using Cu K$_\alpha$ radiation ($\lambda = 0.1542$ nm). ICDD cards of No. 01-089-5012, 01-073-1210, 01-082-0697 and 01-083-1853 were respectively used for the identification of Si, α-Si$_3$N$_4$, β-Si$_3$N$_4$ and Si$_2$N$_2$O phases. The Rietveld refinement method was used to calculate the contents of crystalline phases in the final products. Morphologies, microstructures, and elemental composition of as-prepared Si$_3$N$_4$ were examined by using field-emission scanning electron microscope (Nova 400 Nano FESEM, FEI Co., USA, 15 kV) and transmission electron microscope (TEM, 2000F, Jeol Ltd., Japan, 200 kV) equipped with an energy dispersive X-ray spectroscopy (EDS, Noran 623M-3SUT, Thermo Electron Corporation, Japan).

3. Results and discussion

3.1 Thermodynamic analysis on the nitridation of Si powders

To predict the evolution of phase composition as a function of temperature in present La–O–Si–N system, thermodynamic calculations were performed by using the FactSage 6.2 software (Center for Research in Computational Thermochemistry, Montreal, Canada). Figure 1 shows the predicted phase composition at 1473 and 1773 K for the system (Si$_3$N$_2$O is not considered since there is no any thermodynamic data of Si$_3$N$_2$O crystal phase in the FactSage 6.2 software), and the phase stability could be obtained under different values of $lg(P_{O_2}/P^0)$ and $lg(P_{N_2}/P^0)$ ($P_{N_2}$, $P_{O_2}$, and $P^0$ respectively represent the pressure of N$_2$ and O$_2$ in reaction system and standard atmospheric pressure). In this experiment, the samples were fired under a N$_2$ atmosphere at a pressure of approximately 0.1 MPa [$lg(P_{N_2}/P^0) = 0$]. At 1473 K, Si(s) reacts with N$_2$ and forms Si$_3$N$_4$(s) only if $lg([p(O_2)/p^0])$ is lower than $-19.97$. LaN(s) is formed when $lg([p(O_2)/p^0]) < -25.75$. However, as $lg([p(O_2)/p^0])$ is greater than $-19.97$, Si(s) reacts with O$_2$ to forms SiO$_2$(s) [Fig. 1(a)]. As shown in Fig. 1(b), Si$_3$N$_4$ and LaN are stable at 1773 K when $lg([p(O_2)/p^0]) < -15.92$ and $< -21.75$, respectively. In a word, Fig. 1 confirms that Si$_3$N$_4$, LaN and SiO$_2$ can be synthesized at appropriate conditions in present paper, and that residual P$_2$O$_5$ is important for the formation of Si$_3$N$_4$.

Based on the result of Fig. 1 and the general knowledge of Si powder nitridation,$^{21,22}$ the main possible reactions occurred in present system could be listed as follows:

\[ 3\text{Si}(s) + 2\text{N}_2(g) = \text{Si}_3\text{N}_4(s) \]
\[ \Delta G_1^0 = -745 + 0.333T \text{ (kJ/mol)} \]  
(1)

\[ 2\text{La}_2\text{O}_3(s) + 2\text{N}_2(g) + 3\text{Si}(s) = 4\text{LaN}(s) + 3\text{SiO}_2(s) \]
\[ \Delta G_2^0 = -339 + 0.39T \text{ (kJ/mol)} \]  
(2)

\[ \text{SiO}_2(s) + \text{Si}(s) = 2\text{SiO}(g) \]
\[ \Delta G_3^0 = 695 - 0.333T \text{ (kJ/mol)} \]  
(3)

\[ 2\text{LaN}(s) + 3\text{SiO}(g) + \text{N}_2(g) = \text{La}_2\text{O}_3(s) + 3\text{SiN}_4(s) \]
\[ \Delta G_4^0 = -1621 + 0.64T \text{ (kJ/mol)} \]  
(4)

\[ 3\text{SiO}(g) + \text{N}_2(g) = \text{Si}_3\text{N}_4(s) + 2\text{O}_2(g) \]
\[ \Delta G_5^0 = -434 + 0.58T \text{ (kJ/mol)} \]  
(5)

The corresponding Gibbs free energies in standard state showed that reaction (1) and reaction (2) are thermodynamic favorable at room temperature and below 869 K.

\[ Fig. 1. \] Predominance area diagram for La–O–Si–N system at (a) 1473 K and (b) 1773 K simulated by using the FactSage 6.2 software.
respectively. However, it is difficult to recognize the occurrence of reaction (3)–(5) due to the lack of actual pressure of \( p(O_2) \) and \( p(SiO) \). \( \text{La}_2\text{O}_3 \) should be involved in the Si powder nitridation through reaction (2) and (4) based on the results of Fig. 1.

### 3.2 Nitridation of Si powders with \( \text{La}_2\text{O}_3 \) NPs as catalyst

Morphologies of as-prepared Si particles deposited with \( \text{La(OH)}_3 \) NPs were characterized by TEM (Fig. 2). It can be clearly seen that there existed numerous tiny particles with an average size of 70–80 nm on the surface of a relatively large granule [Fig. 2(a)]. The result of EDS confirmed that the large granule was Si, and those tiny particles were \( \text{La(OH)}_3 \) NPs [Fig. 2(b)]. Moreover, to further determine the distribution of \( \text{La(OH)}_3 \) NPs on Si powders, EDS mapping analysis was also carried out. The results shown in Fig. 3 further confirmed again the presence of \( \text{La(OH)}_3 \) on the surface of Si granule.

The addition amount of \( \text{La}_2\text{O}_3 \) NP catalysts was an important parameter that greatly affecting the nitridation of Si powders. XRD patterns and relative contents of crystalline phases of the samples resultant from 2 h nitridation at 1573 K are shown in Fig. 4. The XRD results [Fig. 4(a)] revealed that for the sample prepared without \( \text{La}_2\text{O}_3 \) NPs, crystalline phases of Si, \( \text{Si}_2\text{N}_2\text{O} \) and \( \alpha/\beta-\text{Si}_3\text{N}_4 \) were detected. The existence of a minor amount of \( \text{Si}_3\text{N}_2\text{O} \) in the samples was due to the residual oxygen (Nitrogen purity is about 99.999%, and \( p(O_2) \) is about 1 Pa) in \( \text{N}_2 \) as well as the existence of \( \text{SiO}_2 \) thin layer on the surface of raw Si. On increasing \( \text{La}_2\text{O}_3 \) amount to 1 wt%, \( \alpha-\text{Si}_3\text{N}_4 \) along with a small amount of \( \beta-\text{Si}_3\text{N}_4 \) was identified. However, on further increasing the \( \text{La}_2\text{O}_3 \) amount to 2–4 wt%, the intensities of Si peaks increased again, which should be attributed to the agglomeration of high amount of \( \text{La}_2\text{O}_3 \) NPs. The contents of crystalline phases in the samples containing various amounts of \( \text{La}_2\text{O}_3 \) NPs were also calculated by the Rietveld refinement method. As shown in Fig. 4(b), without using any catalyst, the content of residual Si was as high as 60 wt% at 1573 K. In contrast with the sample prepared at the identical temperature with 1 wt% \( \text{La}_2\text{O}_3 \) NP as catalysts, the content of residual Si was only 35

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**Fig. 2.** TEM image (a) and EDS spectrum (b) [the white square in Fig. 2(a)] of the \( \text{La(OH)}_3/\text{Si} \) composite powder with 1 wt% \( \text{La}_2\text{O}_3 \) before nitridation. \( \text{La(OH)}_3 \) NPs [highlighted by dotted rings in the Fig. 2(a)] attached on the surface of Si particle.

**Fig. 3.** TEM image, lanthanum, oxide and silicon elemental mapping image of the \( \text{La(OH)}_3/\text{Si} \) composite powders with 1 wt% \( \text{La}_2\text{O}_3 \) before nitridation.

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wt%. On increasing the content of La₂O₃ to 2–4 wt\%, there was no obvious change in the phase composition of final product. Thus, it can be concluded that 1 wt% was the optimal amount of La₂O₃ NP catalysts.

**Figure 5** presents typical morphology of the Si₃N₄ prepared at 1573 K for 2 h with 4 wt% La₂O₃ NPs. A number of whiskers were uniformly distributed in the samples. Most of the whiskers were about 20–300 nm in diameter and tens of micrometers in length. The EDS result of as-prepared whiskers revealed the existence of Si and N elements, and the average atomic ratio of the former to the latter was measured to be approximately 0.72, which was in a good agreement with the stoichiometric ratio of Si₃N₄.

3.3 Effect of firing temperature on the preparation of Si₃N₄ powders

The nitridation temperature was another key factor affecting the catalytic nitridation of Si powders. **Figure 6(a)** presents XRD patterns of product samples after 2 h nitridation at 1473–1623 K, using 1 wt% La₂O₃ NPs as catalysts. At 1473 K, Si remained as the main crystal phase, along with minor amounts of Si₂N₂O and Si₃N₄, indicating that nitridation was far from completion. Upon increasing nitridation temperature to 1573 K, the intensity of Si₃N₄ diffraction peaks in final product increased. On further increasing nitridation temperature to 1623 K, only α-Si₃N₄, β-Si₃N₄ and Si₂N₂O were detected in the sample,
indicating the complete nitridation was achieved. Relative contents of crystalline phases in the samples after 2 h nitridation at various temperatures were shown in Fig. 6(b). At 1473 K, 64 wt% of Si remained in the sample after 2 h nitridation. Upon increasing temperature from 1523 to 1623 K, Si contents were dramatically reduced from about 64 to 0 wt%. It was worth noting that the complete nitridation temperature (1623 K) and catalyst additions (1 wt%) are lower than that conventional catalytic nitridation method14,23–26 (Table 1). For instance, Guo et al.14 synthesized Si3N4 by the direct nitridation of Si powders using 8 wt% TiO2 as catalysts at 1673 K. In the present work, the nitridation of Si powders catalyzed by 1 wt% La2O3 NPs could be completed at 1623 K after holding for 2 h. These results indicated that La2O3 NPs exhibited a remarkable accelerating effect on the nitridation of Si powders. To the best of our knowledge, this is the first report on the catalytic nitridation of Si by using in-situ formed La2O3 NPs as catalysts.

Figure 7 presents SEM and TEM images, and selected-area electron diffraction (SAED) pattern of Si3N4 resultant from 2 h nitridation at 1623 K using 1 wt% La2O3 NP catalysts. Figure 7(a) reveals that a number of whiskers were fabricated in the final product. EDS (inset) showed that the whisker contained mainly Si and N, confirming that the whisker was Si3N4. Figure 7(b) shows the TEM image of a monodispersed whisker. High-resolution transmission electron microscopy (HRTEM) lattice image [Fig. 7(c)] corroborates that this whisker had single-crystal nature. The lattice fringe spacing was measured to be 0.431 nm, which matched well with that of the (101) planes of α-Si3N4 crystal, further confirming that the whisker was α-Si3N4. In addition, both the lattice fringes and the SAED patterns suggest that the α-Si3N4 whisker grew along [101] direction. As discussed in our previous literatures8,10 due to the (101) planes of α-Si3N4 crystal has highest surface energy, the incoming Si and N prefer to diffuse to and deposit on the high energy surfaces (101) in the length directions [101], resulting in formation of nanowhiskers. The SAED pattern [Fig. 7(d)] further verifies that the whisker was single-crystal α-Si3N4. The Si3N4 whiskers possessing a perfect crystalline structure with few defects [Fig. 7(c)] could be a promising candidate reinforcing agent for ceramics27,28.

Based on the thermodynamic calculation results in Fig. 1 and experiment results in Figs. 2–7, the possible catalyst-assisted nitridation mechanism of La2O3 NPs on Si powders was schematically illustrated in Fig. 8 and described as follows. Firstly, La2O3 NPs attached on the surface of Si powders inclined to react with Si and N2 to form LaN and SiO2 via reaction (2) [Fig. 8(a)]. As temperature increased, the resulted SiO2 could react with Si to produce gaseous SiO29 via reaction (3). Owing to the exothermal nature of the nitridation of

![Fig. 7. Characterization of Si3N4 powders resultant from 2 h nitridation at 1623 K using 1 wt% La2O3 NP catalysts. (a) SEM (EDS inset), (b) TEM, (c) HRTEM image and (d) SAED pattern of Si3N4 whisker.](image1)

![Fig. 8. The mechanism for catalytic nitridation of Si powders using La2O3 NPs as catalysts.](image2)
Si, the temperature of microzone in present system can be enough high for the occurrence of reaction (4), thus LaN and SiO were consumed and La2O3 and Si3N4 were formed under the nitrogen atmosphere. It is believed that the repeatedly transformation between La2O3 and LaN via reactions (2) and (4) facilitates the nitridation of Si powders and finally resulted in the completely nitridation of Si powders at 1623 K in present paper. As a byproduct, LaN should be formed in the nitridation process according to Zhang et al. report, but it could not be detected in the XRD patterns due to its low amount. The vapor-vapor-solid (VVS) is regarded as the dominant mass-transforming mechanism for the formation of $\alpha$-Si3N4 whisker in present paper because droplets were not observed at the tip of the as-prepared Si3N4 whiskers. Firstly, Si reacts with N2 to form $\alpha$-Si3N4 seeds which act as active centers for the formation and growth of whisker. Then SiO(g) reacts with N2 to form Si3N4 molecule and deposits on the preferential growth plane of the $\alpha$-Si3N4 whisker [Fig. 8(c)]. The whiskers grow gradually by continuously absorbed the SiO(g) and N2 [Fig. 8(d)]. Finally, the fully-nitrided products composed of $\alpha$-Si3N4 whisker are obtained [Fig. 8(e)].

4. Conclusions

In-situ formed La2O3 NPs were used as catalysts to enhance the nitridation of Si powders at relatively low temperatures. The nitridation of Si powders was completed after 2 h firing at 1623 K with 1 wt% La2O3 NPs present in raw powders. The addition of La2O3 NPs as catalysts not only decreased the nitridation temperature of Si powders but also promoted the formation of Si3N4 whiskers. A number of Si3N4 whiskers were about 20–300 nm in diameter and tens of micron in length. The growth process of the whiskers was governed by VVS mechanisms, and the effect of La2O3 NPs on the enhanced nitridation of Si powders can be ascribed to the repeatedly transformation between La2O3 and LaN.

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