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# Kinetic study on the direct nitridation of silicon powders diluted with α-$Si_3N_4$ at normal pressure

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**Abstract:** Silicon nitride ($Si_3N_4$) powders were prepared by the direct nitridation of silicon powders diluted with α-$Si_3N_4$ at normal pressure. Silicon powders of 2.2 μm in average diameter were used as the raw materials. The nitriding temperature was from 1623 to 1823 K, and the reaction time ranged from 0 to 20 min. The phase compositions and morphologies of the products were analyzed by X-ray diffraction and scanning electron microscopy, respectively. The effects of nitriding temperature and reaction time on the conversion rate of silicon were determined. Based on the shrinking core model as well as the relationship between the conversion rate of silicon and the reaction time at different temperatures, a simple model was derived to describe the reaction between silicon and nitrogen. The model revealed an asymptotic exponential trend of the silicon conversion rate with time. Three kinetic parameters of silicon nitridation at atmospheric pressure were calculated, including the pre-exponential factor (2.27 $cm\cdot s^{-1}$) in the Arrhenius equation, activation energy (114 $kJ\cdot mol^{-1}$), and effective diffusion coefficient ($6.2\times10^{-8}$ $cm^2\cdot s^{-1}$). A formula was also derived to calculate the reaction rate constant.

**Keywords:** silicon nitride; powders; nitridation; reaction kinetics; activation energy

## 1. Introduction

Silicon nitride ($Si_3N_4$) has excellent properties, such as high strength retention at high temperature, good thermal shock resistance, high temperature deformation resistance, and high corrosion resistance. Thus, $Si_3N_4$ is one of the most promising structural materials for high temperature and high mechanical stress applications. Some typical applications of $Si_3N_4$ ceramics include gas turbine components, pistons and cylinder liners, turbocharger rotors, high temperature bearings, high speed cutting tools, etc. [1-3]. One of the most common methods for preparing $Si_3N_4$ ceramics is hot press sintering, which uses $Si_3N_4$ powders mixed with a small amount of sintering additives as raw materials.

Currently, the main approaches to the preparation of $Si_3N_4$ powders include carbothermal reduction [4], gas phase reaction [5], thermal decomposition [6], and direct nitridation of silicon (Si) powders [7-8]. However, carbothermal reduction produces a large amount of silicon carbide, the gas phase reaction requires high cost materials, and the thermal decomposition process is too complex to control. In contrast to these methods, the direct nitridation of Si powders is simple, cost-effective, and suitable for industrial production. Thus, this process is becoming one of the main methods for preparing $Si_3N_4$ powders.

During the direct nitridation of Si powders, the intrinsic reaction rate can be remarkably improved by increasing the nitriding temperature. However, when the temperature exceeds the melting point of Si (i.e., 1683 K), Si powders melt and condense together, which reduces the reactive surface and hinders further reaction [9-10]. The condensation of liquid Si can be prevented by adding $Si_3N_4$ diluent in the process of self-propagating high-temperature synthesis [11].

In this work, $Si_3N_4$ powders were prepared by the direct nitridation of Si powders diluted with α-$Si_3N_4$ at

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atmospheric pressure. The phase compositions and morphologies of the products were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The effects of nitriding temperature and reaction time on the Si conversion rate were investigated. Based on the shrinking core model as well as the relationship between the Si conversion rate and reaction time at different temperatures, a simple model was derived to describe the reaction between Si and nitrogen ($N_2$).

## 2. Experimental

### 2.1. Experimental materials

Si powders (2.2 μm in average diameter and 99.9% purity) were used as the raw materials, and α-$Si_3N_4$ powders (2.2 μm in average diameter and 99.0% purity) were used as the diluent. Nitrogen (99.99% purity) was used as the reaction gas.

### 2.2. Experimental apparatus

Fig. 1 shows the schematic diagram of the experimental apparatus, which mainly consists of a resistance furnace, a reaction chamber, and a gas supply system. The resistance furnace was heated by Si molybdenum rods, which can provide the highest temperature of 1873 K as measured by an S-type thermocouple. The reaction chamber is a ceramic tube with an inner diameter of 30 mm and a length of 1000 mm. The gas supply system is composed of a $N_2$ cylinder, a reducing valve, a flowmeter, some rubber pipes, and a corundum pipe.

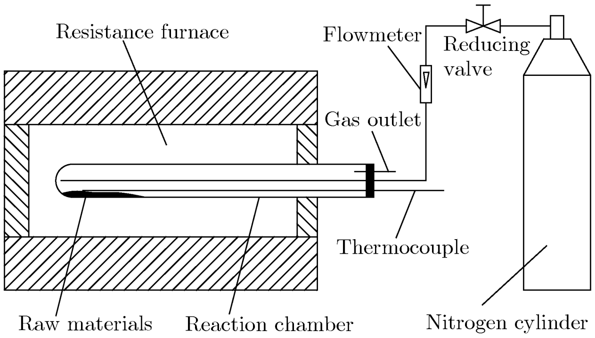


**Fig. 1. Schematic diagram of the experimental apparatus.**

### 2.3. Experimental schedule

The dried Si and α-$Si_3N_4$ powders were uniformly mixed according to a predetermined mass proportion (50wt% Si and 50wt% α-$Si_3N_4$). The mixtures were then placed at the bottom of the reaction chamber, and $N_2$ was introduced into the reaction chamber at a flow rate of 2.0 L·min$^{-1}$ to replace air in the chamber. The process of gas exchange lasted for 20 min. The reaction chamber was placed on the hearth of the furnace, which had been heated to different predetermined temperatures (1623, 1673, 1723, 1773, and 1823 K). The flow rate of $N_2$ was maintained at 400 mL·min$^{-1}$. After predetermined nitriding times (5, 10, 15, and 20 min), the chamber was removed and cooled to room temperature in air.

### 2.4. Quantitative determination

The phase content of α- and β-$Si_3N_4$ in the products was determined by a normalizing method proposed by Zhou [12], which had the advantages of eliminating the preferred orientation, good reproducibility, and small error. This quantitative determination method was adopted by Li *et al.* [13]. Once the phase content is determined, the conversion rate of Si powders can be calculated according to the following equation:

$$X_{\mathrm{Si}} = \frac{1 - \dfrac{m_{\mathrm{Si}}}{1 - m_\alpha}}{1 + \dfrac{2}{3} m_{\mathrm{Si}}} \tag{1}$$

where $X_{\mathrm{Si}}$ is the conversion rate of Si powders, $m_{\mathrm{Si}}$ the mass fraction of Si in the products, and $m_\alpha$ the mass fraction of α-$Si_3N_4$ diluent in the raw materials.

## 3. Results and discussion

### 3.1. XRD analysis

When the added proportion of α-$Si_3N_4$ is 50wt% and the nitriding time is 10 min, the XRD patterns of the experimental products at different nitriding temperatures are shown in Fig. 2. The products mainly include Si, α-$Si_3N_4$, and β-$Si_3N_4$, in which α-$Si_3N_4$ is the dominant and popular phase because of its better sintering properties. Combined with the above quantitative determination method, when the nitriding temperature increases from 1623 to 1823 K, the conversion rate of Si powders increases from 65.4% to 92.5%, the amount of β-$Si_3N_4$ in the products also increases from 10.4wt% to 28.2wt%, and the amount of unreacted Si in the products decreases from 14.2wt% to 2.8wt%. These phenomena indicate that an increased

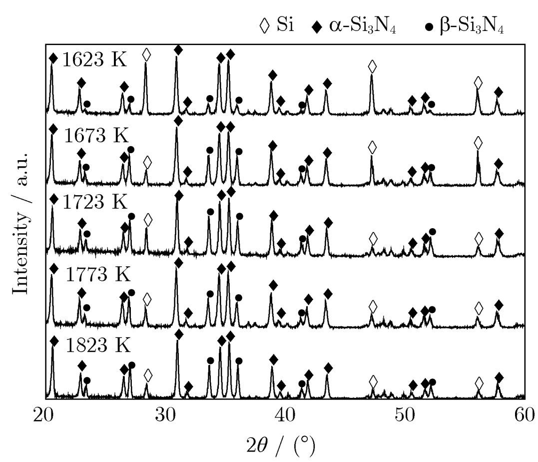


**Fig. 2. XRD patterns of the products at different nitriding temperatures (10 min, 50wt% α-$Si_3N_4$ diluent).**

nitriding temperature results in not only an increased conversion rate of Si powders but also an increased β-$Si_3N_4$ content. To decrease the β-$Si_3N_4$ content, the nitriding temperature should be properly controlled.

### 3.2. SEM analysis

When the added proportion of α-$Si_3N_4$ is 50wt% and the nitriding time is 10 min, the SEM image of the products at the nitriding temperature of 1823 K is shown in Fig. 3. Most of the products exhibit spherical morphologies, although some are columnar, whisker-shaped or cluster-shaped particles. Without the addition of α-$Si_3N_4$ diluent, liquid Si agglomerates and forms a large Si block when Si powders melt. Consequently, the reactive surface area decreases. Given that the added proportion of α-$Si_3N_4$ is high, Si powders are effectively separated. Agglomeration between the particles does not occur and the particles are uniformly dispersed.

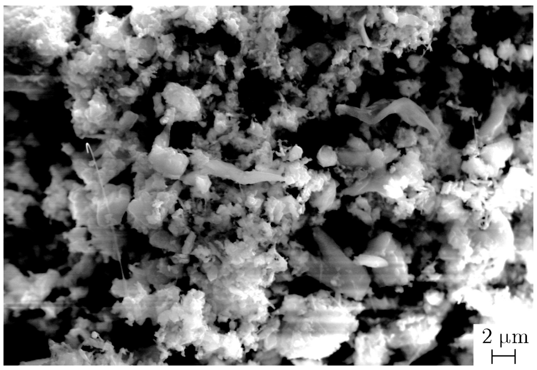


**Fig. 3. SEM image of the products (1823 K, 10 min, 50wt% α-$Si_3N_4$ diluent).**

### 3.3. Analysis of Si conversion rate

Fig. 4 shows relationships between the Si conversion rate and reaction holding time at different temperatures with 50wt% α-$Si_3N_4$ added. The conversion rate of Si powders gradually increases with the increase in nitriding time.

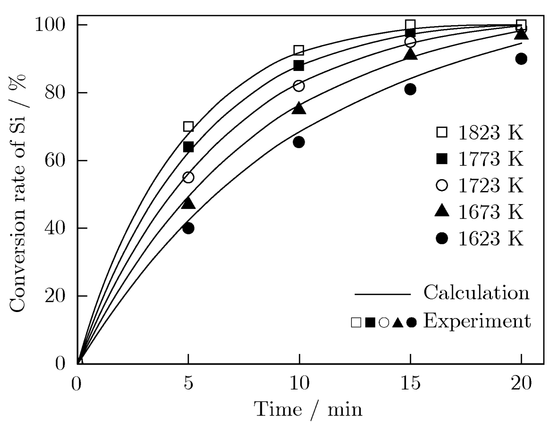


**Fig. 4. Relationships between the Si conversion rate and reaction time.**

When the temperature increases from 1623 to 1823 K at the nitriding time of 10 min, the conversion of Si powders remarkably increases from 65.4% to 92.5%. Therefore, increasing the nitriding temperature can significantly increase the nitridation rate, which is conducive to the initial stage of nitriding reaction. However, the influence of temperature on the nitridation rate is not very significant at the final stage of the reaction.

## 4. Theoretical model and calculation

### 4.1. Model of the reaction between Si and $N_2$

Different reaction conditions and the relatively unclear nitridation reaction mechanism have prompted researchers to use different kinetic methods for the Si-$N_2$ reaction. Different models have also been proposed to describe the transformation from Si powders to $Si_3N_4$ powders. Jovanovic [14] suggested that the conversion rate of Si could be fitted with the asymptotic exponential law. Yagi and Kunii [15] used the shrinking core model to study the combustion of carbon particles. Pigeon and Varma [16] investigated the nitridation of Si powders using the sharp interface model.

The following reaction between Si and $N_2$ proceeds at high temperature:

$$2N_2 + 3Si \rightarrow Si_3N_4 \tag{2}$$

When the nitriding temperature is higher than the melting point of Si (1683 K), Si particles melt and evaporate at the beginning of the nitridation reaction. The gas-liquid reaction and chemical vapor deposition reaction occur to produce $Si_3N_4$, which coats the surface of Si particles. Once the coated product layers are formed on the surface of Si particles, $N_2$ diffuses onto the surface of the unreacted Si core through the product layers. The gas-liquid reaction between $N_2$ (g) and Si (l) occurs to generate $Si_3N_4$. When the nitriding temperature is less than the melting point of Si, a gas-solid reaction between $N_2$ (g) and Si (s) occurs to produce $Si_3N_4$. For simplicity, the traditional gas-solid reaction mechanism is used to build the Si-$N_2$ reaction model. The simulation results agree with the experimental data.

In this article, the shrinking core model with constant particle size is used to create the Si-$N_2$ reaction model. This model involves three steps: gas film diffusion, solid product layer diffusion, and surface chemical reaction. Thus, three kinds of resistances are observed: gas film diffusion resistance, solid product layer diffusion resistance, and chemical kinetic resistance. The reaction rate equation for a single spherical particle is shown in Eq. (3) [17]:

$$r_A = \frac{f}{f_g + f_s + f_r} \tag{3}$$

where $r_A$ is the reaction rate, mol·s$^{-1}$; $f$ the total driving force, mol·cm$^{-3}$; $f_g$ the gas film diffusion resistance,

$s \cdot cm^{-3}$; $f_s$ the solid product layer diffusion resistance, $s \cdot cm^{-3}$; and $f_r$ the chemical kinetic resistance, $s \cdot cm^{-3}$.

The expressions of the driving force and resistance are shown in Eq. (4) [17]:

$$\begin{cases} f = c_{ag} \\ f_g = \dfrac{1}{4\pi R_p^2 k_g} \\ f_s = \dfrac{(1-X_{Si})^{-1/3}-1}{4\pi R_p D_e} \\ f_r = \dfrac{1}{4\pi R_p^2 (1-X_{Si})^{2/3} k_s} \end{cases} \quad (4)$$

where $c_{ag}$ is the concentration of $N_2$ calculated by the ideal gas equation, $mol \cdot cm^{-3}$; $R_p$ the average radius of Si particles, cm; $k_g$ the gas phase mass transfer coefficient, $cm \cdot s^{-1}$; $D_e$ the effective diffusion coefficient of $N_2$ within the solid product layer, $cm^2 \cdot s^{-1}$; and $k_s$ the reaction rate constant based on the unit reaction interface, $cm \cdot s^{-1}$.

In the present study, increasing the flow rate of $N_2$ does not change the reaction rate, so the gas film diffusion resistance $f_g$ can be ignored. Therefore, only the product layer diffusion resistance$f_s$ and chemical kinetic resistance $f_r$ are considered in the reaction rate.

### 4.2. Calculation of kinetic parameters

(1) Nitriding temperature lower than the melting point of Si

At the nitriding temperature of 1623 K (lower than the melting point of Si), the chemical reaction rate is slow, the $Si_3N_4$ product layer is thin, and the diffusion resistance in the product layer can be ignored. Thus, the reaction is a type of chemical kinetic control on the interface. The relationship between the reaction time and Si conversion rate can be determined by Eq. (5) [17]:

$$\tau = \frac{\rho_{Si} R_p}{b M_{Si} k_s c_{ag}} \left[1-(1-X_{Si})^{\frac{1}{3}}\right] \quad (5)$$

where $\tau$ is the reaction time, s; $\rho_{Si}$ the density of Si, $g \cdot cm^{-3}$; $b$ the ratio of the stoichiometric coefficients in Eq. (2), and $M_{Si}$ the molecular weight of Si, $g \cdot mol^{-1}$. The values of these variables are listed in Table 1.

**Table 1. Values of variables in Eq. (5)**

| $\rho_{Si}$ / ($g \cdot cm^{-3}$) | $R_p$ / cm | $b$ | $M_{Si}$ / ($g \cdot mol^{-1}$) | $p_{N_2}$ / Pa | $R_g$ / ($J \cdot mol^{-1} \cdot K^{-1}$) | $c_{ag}$ / ($mol \cdot cm^{-3}$) |
|---|---|---|---|---|---|---|
| 2.329 | $1.1 \times 10^{-4}$ | 1.5 | 28 | $1.01 \times 10^5$ | 8.314 | $7.5 \times 10^{-6}$ (at 1623 K) |

Note: $c_{ag} = p_{N_2}/(R_g T)$.

Values in Table 1 can be used to derive Eq. (6) from Eq. (5):

$$\tau = \frac{0.81}{k_s}\left[1-(1-X_{Si})^{\frac{1}{3}}\right] \quad (6)$$

Eq. (6) is used to fit the experimental data at 1623 K (Fig. 4), and the reaction rate constant can be calculated, i.e., $k_{s1} = 4.87 \times 10^{-4}$ $cm \cdot s^{-1}$ at 1623 K. Then $k_{s1}$ is input into Eq. (6) to calculate the Si conversion rate at 1623 K. The calculated and experimental results are consistent, and the curve is shown in Fig. 4.

(2) Nitriding temperature higher than the melting point of Si

At different nitriding temperatures of 1673, 1723, 1773, and 1823 K, given the relatively higher temperature than the melting point of Si, the reaction rate increases. The chemical kinetic resistance $f_r$ and diffusion resistance $f_s$ in the product layer cannot be ignored. Thus, the relationship between the reaction time and the Si conversion rate can be determined by Eq. (7) [17]:

$$\frac{b M_{Si} c_{ag}}{\rho_{Si} R_p}\tau = \frac{1}{k_s}\left[1-(1-X_{Si})^{\frac{1}{3}}\right] + \frac{R_p}{6D_e}\left[1-3(1-X_{Si})^{\frac{2}{3}}+2(1-X_{Si})\right] \quad (7)$$

Eq. (7) is used to fit the experimental data at 1773 K (Fig. 4), and the effective diffusion coefficient of $N_2$ and the reaction rate constant can be calculated, i.e., $D_e = 6.2 \times 10^{-8}$ $cm^2 \cdot s^{-1}$ and $k_{s2} = 9.95 \times 10^{-4}$ $cm \cdot s^{-1}$ at 1773 K. Then $k_{s2}$, $D_e$, and other data are input into Eq. (7) to calculate the Si conversion rate at 1773 K. The calculated curve at 1773 K exhibits an asymptotic exponential trend (Fig. 4), which is consistent with the finding of Jovanovic [14].

The activation energy $E$ (114 $kJ \cdot mol^{-1}$) and pre-exponential factor $k_{s0}$ (2.27 $cm \cdot s^{-1}$) are then calculated by inputting the values of $k_{s1}$ at 1623 K and $k_{s2}$ at 1773 K into the Arrhenius equation: $k_s = k_{s0}\exp(-E/RT)$.

Therefore, the reaction rate constant $k_s$ at any temperature can be calculated according to

$$k_s = 2.27\exp\left(-\frac{114000}{8.314T}\right) \quad (8)$$

Assuming that the effective diffusion coefficient of $N_2$ ($D_e$) does not change with temperature, $k_s$, $D_e$, and other data are inputted into Eq. (7) to calculate the Si conversion rate at 1673, 1723, and 1823 K. The calculated and experimental results are consistent, and the curves are shown in Fig. 4. An asymptotic exponential trend is observed, consistent with the finding of Jovanovic [14].

In the Arrhenius equation, the index factor $\exp(-E/RT)$ plays a critical role in the reaction rate constant $k_s$. The core of the index factor is the activation energy $E$, so determining the activation energy is an important step in kinetic analysis. However, since different experimental conditions and research methods are used by researchers, the obtained activation energy values are not the same. Under experimental conditions in this article, the activation energy is 114 $kJ\cdot mol^{-1}$, which is within the obtained range (54-777 $kJ\cdot mol^{-1}$) by other researchers [14, 18-20].

Yang *et al.* [21] demonstrated that the conversion rate of Si powders could be considerably improved by increasing the added proportion of α-$Si_3N_4$diluent. In particular, when the added proportion of α-$Si_3N_4$ increases from 10wt% to 50wt%, the conversion rate of Si powders increases from 38% to 92.5% and the amount of unreacted Si decreases from 45.4wt% to 2.8wt%. These phenomena indicate that α-$Si_3N_4$ can induce the separation of Si powders and reduce the condensation of liquid Si. Consequently, the reactive surface area and the Si conversion rate increase.

Therefore, the addition of α-$Si_3N_4$ can prevent the agglomeration of liquid Si and decrease the activation energy, which is conducive to the nitridation reaction, consistent with the finding of Yang *et al.* [21]. The role of the added proportion of α-$Si_3N_4$ diluent in the kinetic model and the kinetic mechanism of this diluent require further study.

## 5. Conclusions

(1) The contents of α- and β-$Si_3N_4$ products gradually increased with the nitriding temperature increasing. When the temperature increased from 1623 to 1823 K with the nitriding time of 10 min, the conversion rate of Si powders remarkably increased from 65.4% to 92.5%.

(2) Based on the shrinking core model as well as the relationship between the Si conversion rate and reaction time at different temperatures, a simple model was derived to describe the reaction between Si and $N_2$. The model revealed an asymptotic exponential trend of the silicon conversion rate with time.

(3) Some kinetic parameters of Si powders nitridation at atmospheric pressure were calculated. The parameters were the pre-exponential factor (2.27 $cm\cdot s^{-1}$) in the Arrhenius equation, activation energy (114 $kJ\cdot mol^{-1}$), and effective diffusion coefficient ($6.2\times10^{-8}$ $cm^2\cdot s^{-1}$). A formula was also derived to calculate the reaction rate constant.

(4) The addition of α-$Si_3N_4$ diluent can prevent the agglomeration of liquid Si but decrease the activation energy, which is conducive to the nitridation reaction.

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