

Synthesis of silicon nitride powder through nitrogen gas atomization

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The feasibility of synthesizing silicon nitride powder utilizing reactive atomization processing was analysed. The range of times required for the flight time of particles, the cooling rate of the silicon melt, the reaction time of silicon and nitrogen, and the diffusion of nitrogen through silicon nitride layers were obtained and compared. The results of this study indicated that the production of silicon nitride powder through the reactive atomization process would be limited by diffusion of nitrogen through the nitride (ash) layer, assuming the nitride layer was coherent and the unreacted core model was a valid representation of the liquid silicon–silicon nitride system.

Nomenclature

$k(T)$ = reaction rate constant at temperature, T (s^{-1})
 k_0 = Arrhenius coefficient
 E = activation energy (kJ mol^{-1})
 R = gas constant
 T = temperature (K)
 Φ_α = fraction of normalized conversion of α -phase in time t
 Φ_β = fraction of normalized conversion of β -phase in time t
 k_α = reaction rate constant for α -phase (s^{-1})
 k_β = reaction rate constant for β -phase (s^{-1})
 k_α^i = intrinsic first-order rate constant for α -phase (s^{-1})
 x_α = conversion fraction of α -phase in time t
 x_β = conversion fraction of β -phase in time t
 n_α = reaction order for α -phase = 1
 n_β = reaction order for β -phase = 0.5
 J = diffusion flux ($\text{mol m}^{-2} \text{s}^{-1}$)
 D = diffusivity, or diffusion coefficient ($\text{m}^2 \text{s}^{-1}$ or $\text{cm}^2 \text{s}^{-1}$)

dC = change in concentration (mol m^{-3})
 dl = change in distance, l (m)
 $A_{(g)}$ = gaseous reactant A
 B = reactant B (may be solid or liquid)
 P = solid product P
 b = stoichiometric coefficient of reactant B
 p = stoichiometric coefficient of product P
 t = time of reaction passed (s)
 τ = time for complete reaction of a particle (s)
 X_B = conversion fraction
 r_c = core radius (m)
 R_p = particle radius (m)
 ρ_B = molar density of reactant B (mol m^{-3})
 k_g = mass transfer coefficient between fluid and particle (m s^{-1})
 C_{A_g} = concentration of gaseous reactant A (mol m^{-3})
 D_e = effective diffusion coefficient of gaseous reactant in ash layer ($\text{m}^2 \text{s}^{-1}$)

1. Introduction

Silicon nitride, Si_3N_4 , is a ceramic material that possesses good mechanical properties. It is an ideal engineering material for high temperature applications with good thermal shock and oxidation resistance [1]. In applications such as turbines, turbochargers, heat exchangers and engines, where high temperature and multiple friction contacts are present, densified silicon nitride is a material of choice [1–4].

Presently, silicon nitride powder is produced from direct carbothermic reduction of silica, vapour phase reactions and nitridation of silicon powder [5]. The first method has some problems with carbon contamination. The second method can produce very fine Si_3N_4 powder, but is more expensive. The direct nitridation of silicon powder is the most common way of producing silicon nitride powder [5]. The direct ni-

tridation of silicon powder is done at elevated temperatures and sometimes under high pressure. The time required to produce silicon nitride powder from these processes ranges from 6 to 100 h [2–4, 6]. The actual time depends on the amount of silicon to be converted, the reaction temperature and the reaction pressure [6].

The reaction of silicon and nitrogen is



The product of the reaction has two possible phases, α or β . The product phase is determined by the reaction conditions; for a complete discussion of this subject please refer to refs [6] and [7].

The kinetics of the reaction between solid silicon particles and nitrogen gas has been studied in many previous works. Rossetti *et al.* [8] found that the

α -phase formation obeyed a first-order rate law, whereas the β -phase formation obeyed a phase-boundary controlled rate law; both were formed by separate and parallel reaction paths. They presented their kinetics rate equations in terms of normalized conversion, ϕ , of silicon to silicon nitride. The ϕ_α represents the conversion of silicon to α - Si_3N_4 at time t divided by the total conversion of silicon to α - Si_3N_4 , likewise for the β -phase reaction. Although their rate equations agree with other experimental observations, it is not convenient. The use of normalized conversion requires knowledge of the amount of silicon converted to silicon nitride, and that knowledge is often what is being sought. So, Varma *et al.* [1] developed rate equations which represented the conversion of silicon to Si_3N_4 at time t divided by the amount of silicon available for conversion. The rate equations of both works will be used and compared in this study.

This was a feasibility study for synthesizing silicon nitride powder through the use of gas atomization. By using the concept of "Reactive atomization" [9], combining the atomization of molten silicon and the reaction between molten silicon and nitrogen, the time required to produce Si_3N_4 powder could be drastically reduced.

The objective of this study was to pursue a theoretical analysis of the synthesis of silicon nitride powder through the use of nitrogen gas atomization. This work includes the analysis of reaction kinetics and diffusion through the Si_3N_4 layer, and the identification of the most likely product phase. The feasibility of the process depended heavily on the kinetics of the reaction, the diffusion of nitrogen through the Si_3N_4 layer, the cooling rate of molten silicon and the flight time of the atomized particles.

The process being analysed can be described as shown in Fig. 1, where:

- a. Initial reaction – reaction of molten Si with nitrogen



- b. Si_3N_4 coated droplets – reaction carried out on the surface of the droplets; Si_3N_4 crystals precipitated out when droplets were cooled to below the melting point of Si; direct reaction of the Si and N ends, when droplet surfaces were coated with Si_3N_4 ; reaction kinetics was expected to be the limiting step.

- c. Reaction continues – continuation of reaction of Si and N through the Si_3N_4 coating; diffusion of N and/or Si through the Si_3N_4 layer to the reaction sites may have been the limiting step.

2. Analytical procedure

The purpose of this work was to compare the time required for conversion of silicon metal to silicon nitride to the flight time of the molten metal powder. In the analysis, the parameters for the atomization process were assumed, because no atomizer was available for experimental analysis. The two most important parameters in the analysis of the atomization are the flight time of the powder in the atomizer and the cooling rate of the molten metal. The flight time of the powder determined the total time possible for the reaction. The cooling rate determined the time that the molten silicon would remain liquid. This was important in the reaction kinetics and the diffusion of

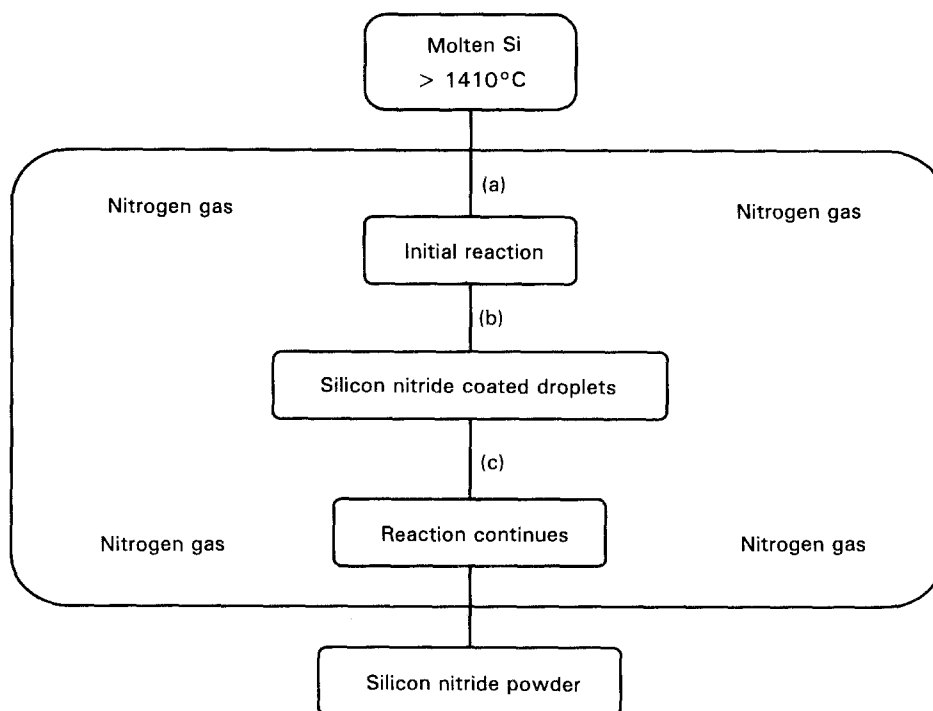


Figure 1 Generalized process description diagram for proposed atomization process to produce silicon nitride powder.

nitrogen through the silicon nitride layer. A range of values for the flight time limit could be obtained by assuming various atomizing gas velocities and various atomizer heights. The flight time was equal to the atomizer height divided by particle velocity. The cooling time was obtained by assuming a range of cooling rates and the degrees superheat above the melting point of silicon (1410 °C). The cooling time was equal to the degrees superheat divided by the cooling rate. A range of times for the molten silicon to cool to solid could be obtained for the analysis.

The analysis process included the determination of the rate limiting step for the Si₃N₄ formation using the proposed atomization process. Models of reaction kinetics and diffusion rates were developed and extreme conditions of the process investigated. In obtaining the extreme conditions of the process, the boundary values of the process became known and were used to determine the feasibility of the proposed atomization process.

The assumptions for the analysis for all of the kinetics and diffusion models were as follows, unless otherwise specified: constant particle size, 100 μm diameter; spherical particles: particle velocity equal to the atomizing gas velocity; Arrhenius coefficient for rate constant was correct; and all pressure, temperature and nitrogen concentration conditions were constant throughout the process.

2.1. Arrhenius equation

Because the rate constants from the literature were for the solid–gas reaction, it was necessary to extrapolate the constants for the liquid–gas reaction. The rate constants for the reaction of Equation 1 for solid silicon, and for α- and β-Si₃N₄, respectively, are given as [8]:

$$k_{\alpha,s} = 1.00 \times 10^{-3} \text{ s}^{-1} \text{ at } 1623 \text{ K (1350 °C)}$$

$$k_{\beta,s} = 1.68 \times 10^{-4} \text{ s}^{-1} \text{ at } 1623 \text{ K (1350 °C)}$$

Using the Arrhenius equation, the reaction rate constant as a function of temperature is

$$k(T) = k_0 \exp(-E/RT) \quad (3)$$

The activation energies for solid silicon and molten silicon reactants, respectively, are given as, [10]:

$$E(1683 \text{ K, solid}) = 652 \text{ kJ mol}^{-1}$$

$$E(1733 \text{ K, liquid}) = 460 \text{ kJ mol}^{-1}$$

The reaction rate constants for liquid silicon, assuming k_0 is independent of the Si phase (i.e. liquid or solid), can be calculated from

$$k_1(T_2) = k_0 \exp(-E_1/RT_2) \quad (4)$$

$$k_0 = k_s(T_1)/\exp(-E_s/RT_1) \quad (5)$$

and are equal to (for α- and β-Si₃N₄, respectively):

$$k_{\alpha,1} = 1.31 \times 10^4 \text{ s}^{-1} \text{ at } 1733 \text{ K (1460 °C)}$$

$$k_{\beta,1} = 2.21 \times 10^3 \text{ s}^{-1} \text{ at } 1733 \text{ K (1460 °C)}$$

2.2 Kinetic models

The following are the models developed for the ana-

lysis of the proposed atomization process. Models K1 and K2 are from previous works on the silicon to silicon nitride reaction kinetics.

2.2.1 Model K1: literature model 1 [8]

K1-A Solid silicon core.

K1-B Liquid silicon core.

$$\alpha: \frac{d\phi_\alpha}{dt} = k_\alpha(1 - \phi_\alpha) \quad (6)$$

$$\beta: \frac{d\phi_\beta}{dt} = 3k_\beta(1 - \phi_\beta)^{2/3} \quad (7)$$

$$\text{global: } \frac{d\phi}{dt} = 3[k_\alpha(1 - \phi_\alpha) + k_\beta(1 - \phi_\beta)^{2/3}] \quad (8)$$

assumptions:

1. α- and β-Si₃N₄ were formed by separate and parallel reaction paths;
2. α-Si₃N₄ formation obeyed a first-order rate law;
3. β-Si₃N₄ formation obeyed a phase boundary controlled rate law;
4. at $t = 0$, $\phi_\alpha = 0$ and $\phi_\beta = 0$.

The global equation above was obtained from the reaction of solid silicon with nitrogen gas. Because the reaction involved an interfacial reaction, the α rate equation of Equation 6 can be replaced with Equation 9 in the derivation of the global equation (Equation 8). From Rossetti *et al.* [8], the k_α^i is equal to $3k_\alpha$.

$$\alpha: \frac{d\phi_\alpha}{dt} = k_\alpha^i(1 - \phi_\alpha) = 3k_\alpha(1 - \phi_\alpha) \quad (9)$$

Because the above global equation is for solid Si particles and the atomization process under study is with molten Si, the interfacial reaction of solid and gas can be ignored, and the following equation can be used to evaluate the liquid system.

$$\text{global: } \frac{d\phi}{dt} = k_\alpha(1 - \phi_\alpha) + 3k_\beta(1 - \phi_\beta)^{2/3} \quad (10)$$

2.2.2 Model K2: literature model 2 [1]

K2-A Solid silicon core.

K2-B Liquid silicon core.

$$\alpha: \frac{dx_\alpha}{dt} = k_\alpha(1 - x_\alpha - x_\beta)^{n_\alpha} \quad (11)$$

$$\beta: \frac{dx_\beta}{dt} = k_\beta(1 - x_\alpha - x_\beta)^{n_\beta} \quad (12)$$

$$\text{global: } \frac{dx}{dt} = k_\alpha(1 - x_\alpha - x_\beta)^{n_\alpha} + k_\beta(1 - x_\alpha - x_\beta)^{n_\beta} \quad (13)$$

assumptions:

1. α- and β-Si₃N₄ were formed by separate and parallel reaction paths;

2. α -Si₃N₄ formation obeyed a first-order rate law;
3. β -Si₃N₄ formation obeyed a phase boundary controlled rate law;
4. at $t = 0$, $x_\alpha = 0$ and $x_\beta = 0$.

2.3 Diffusion models

The diffusion models D1–D4 are based on Fick's first law, see Fig. 2 [11]:

$$J = -D \frac{dC}{dl} \quad (14)$$

assumptions for models D1–D4:

1. semi-infinite slab;
2. isothermal conditions;
3. no reactions;
4. constant nitrogen concentration near surface of particle;
5. constant nitrogen pressure of 1.013×10^5 Pa;
6. spherical particles;
7. constant particle size.

All diffusion models neglect Si through Si₃N₄ diffusion because the Si is too large, relative to the N atom [7]. The diffusion coefficient for nitrogen in liquid Si was from [10]; all other D_N values were from [3].

Diffusion models D5 and D6 are based on the "unreacted core model" [12].

2.3.1. Model D1: all liquid silicon

D1-A Concentration of N at the interface of the diffusion front is zero.

D1-B Concentration of N at the interface of the diffusion front is the saturation of N in liquid Si, 0.02 mol % [7]; assumption:

1. dl is the distance of the diffusion front, starting from the surface of the particle into the particle.

$$D_{N, Si(l)} = 3.32 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \text{ at } 1683 \text{ K (1410}^\circ\text{C)}$$

2.3.2. Model D2: α -Si₃N₄ layer with liquid Si core

D2-A Concentration of N at the interface of the α -Si₃N₄ and liquid Si is zero.

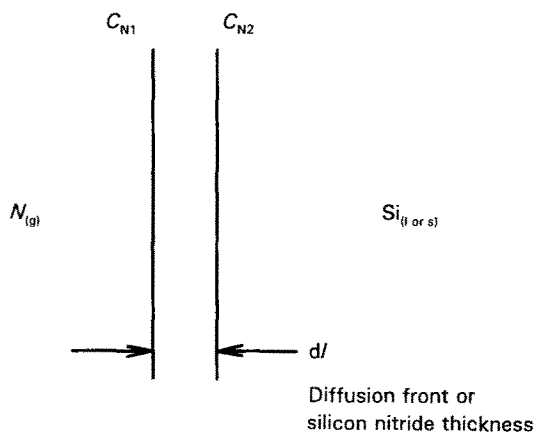


Figure 2 Diffusion model, Fick's first law. C_{N1} = concentration of nitrogen at surface; C_{N2} = concentration of nitrogen at interface.

D2-B Concentration of N at the interface of the α -Si₃N₄ and liquid Si is the saturation of N in liquid Si, 0.02 mol %.

assumption:

1. dl is the thickness of the α -Si₃N₄ layer.

$$D_{N, \alpha} = 7.02 \times 10^{-20} \text{ cm}^2 \text{ s}^{-1} \text{ at } 1683 \text{ K (1410}^\circ\text{C)}$$

2.3.3. Model D3: β 1-Si₃N₄ layer with liquid Si core

D3-A Concentration of N at the interface of the β 1-Si₃N₄ and liquid Si is zero.

D3-B Concentration of N at the interface of the β 1-Si₃N₄ and liquid Si is the saturation of N in liquid Si, 0.02 mol %.

assumptions:

1. dl is the thickness of the β 1-Si₃N₄ layer;
2. β 1 = β with some α and elemental Si;

$$D_{N, \beta 1} = 7.04 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \text{ at } 1683 \text{ K (1410}^\circ\text{C)}$$

2.3.4. Model D4: β 2-Si₃N₄ layer with liquid Si core

D4-A Concentration of N at the interface of the β 2-Si₃N₄ and liquid Si is zero.

D4-B Concentration of N at the interface of the β 2-Si₃N₄ and liquid Si is the saturation of N in liquid Si, 0.02 mol %.

assumptions:

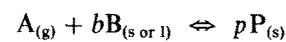
1. dl is the thickness of the β 2-Si₃N₄ layer;
2. β 2 = pure β -Si₃N₄.

$$D_{N, \beta 2} = 5.24 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1} \text{ at } 1683 \text{ K (1410}^\circ\text{C)}$$

2.3.5. Model D5: unreacted core model: film diffusion controls [12]

D5-A Solid silicon core.

D5-B Liquid silicon core.



$$\frac{t}{\tau} = X_B \quad (15)$$

$$\tau = \frac{\rho_B R_p}{3bk_g C_{Ag}} \quad (16)$$

assumptions:

1. isothermal condition;
2. steady state;
3. irreversible reaction;
4. no gaseous products;
5. spherical particles;
6. constant gaseous reactant concentration surrounding;
7. no N in silicon core.

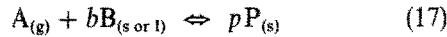
2.3.6. Model D6: unreacted core model: diffusion through ash layer controls [12]

D6-A Solid silicon core.

1. α -Si₃N₄ layer;
2. β 1-Si₃N₄ layer;
3. β 2-Si₃N₄ layer.

D6-B Liquid silicon core.

1. α -Si₃N₄ layer;
2. β 1-Si₃N₄ layer;
3. β 2-Si₃N₄ layer.



$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \quad (18)$$

$$\tau = \frac{\rho_B R_p^2}{6bD_e C_{Ag}} \quad (19)$$

assumptions:

1. isothermal condition;
2. steady state;
3. irreversible reaction;
4. no gaseous products;
5. spherical particles;
6. constant gaseous reactant concentration surrounding;
7. no N in silicon core.

3. Results

3.1. Time of flight

See Fig.3, the various atomizer heights are in metres.

3.2. Cooling time (from melt temperature to solidus temperature, T_m)

See Table I and Fig. 4, cooling time comparison of various cooling rates and various degrees superheat.

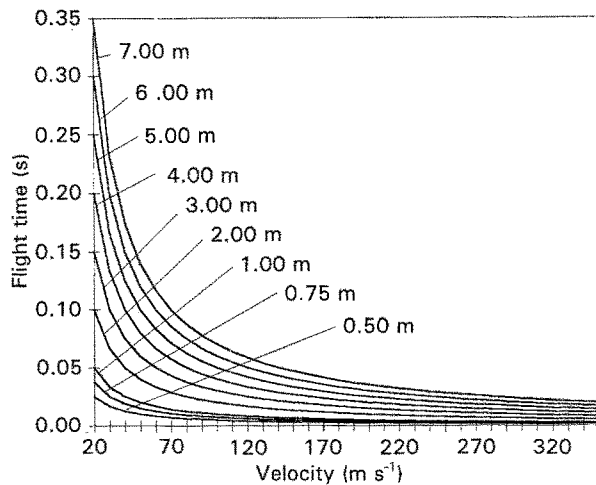


Figure 3 Flight time of various atomizer heights with various particle velocities, up to sonic velocity, assuming that particle velocity equals the velocity of the gas at the nozzle.

TABLE I Cooling time (s) to solidus temperature as a function of cooling rate and degrees above melting point.

$^{\circ}\text{C} + T_m$	Cooling rates ($^{\circ}\text{C s}^{-1}$)			
	10^3	10^4	10^5	10^6
10	1.0×10^{-2}	1.0×10^{-3}	1.0×10^{-4}	1.0×10^{-5}
20	2.0×10^{-2}	2.0×10^{-3}	2.0×10^{-4}	2.0×10^{-5}
30	3.0×10^{-2}	3.0×10^{-3}	3.0×10^{-4}	3.0×10^{-5}
40	4.0×10^{-2}	4.0×10^{-3}	4.0×10^{-4}	4.0×10^{-5}
50	5.0×10^{-2}	5.0×10^{-3}	5.0×10^{-4}	5.0×10^{-5}
60	6.0×10^{-2}	6.0×10^{-3}	6.0×10^{-4}	6.0×10^{-5}
70	7.0×10^{-2}	7.0×10^{-3}	7.0×10^{-4}	7.0×10^{-5}
80	8.0×10^{-2}	8.0×10^{-3}	8.0×10^{-4}	8.0×10^{-5}
90	9.0×10^{-2}	9.0×10^{-3}	9.0×10^{-4}	9.0×10^{-5}
100	1.0×10^{-1}	1.0×10^{-2}	1.0×10^{-3}	1.0×10^{-4}
110	1.1×10^{-1}	1.1×10^{-2}	1.1×10^{-3}	1.1×10^{-4}
120	1.2×10^{-1}	1.2×10^{-2}	1.2×10^{-3}	1.2×10^{-4}
130	1.3×10^{-1}	1.3×10^{-2}	1.3×10^{-3}	1.3×10^{-4}
140	1.4×10^{-1}	1.4×10^{-2}	1.4×10^{-3}	1.4×10^{-4}
150	1.5×10^{-1}	1.5×10^{-2}	1.5×10^{-3}	1.5×10^{-4}

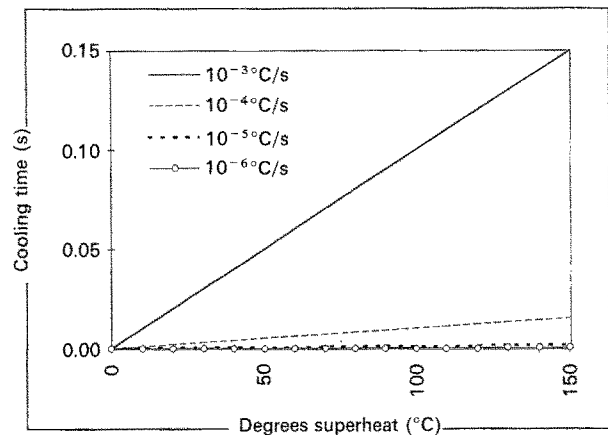


Figure 4 Cooling time (superheated liquid to solidus) comparison for various cooling rates and various degrees of superheat.

3.3. Kinetic models

See Table II and Figs 5 and 6 for the results of the kinetic models. Figs 5 and 6 are representative figures of the models.

3.4. Diffusion models

See Fig. 7 and Table III for the results of the diffusion models.

3.5. Nitrogen concentration

Fig. 8 is a graph of N and N₂ concentrations as a function of temperature. This was used to indicate the

TABLE II Results of kinetic models K1 and K2

Model	Model number	Solid/liquid core	Time for 100% conversion (s)
Literature 1 [8]	K1-A	Solid	9.23×10^{-2}
Literature 1 [8]	K1-B	Liquid	7.00×10^{-5}
Literature 2 [1]	K2-A	Solid	5.45×10^{-3}
Literature 2 [1]	K2-B	Liquid	4.10×10^{-4}

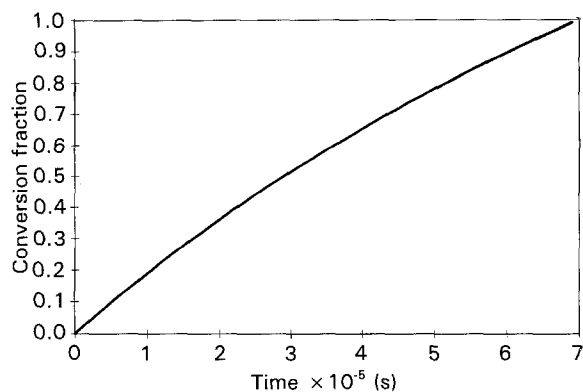


Figure 5 A representative figure of conversion vs time from kinetics model K1

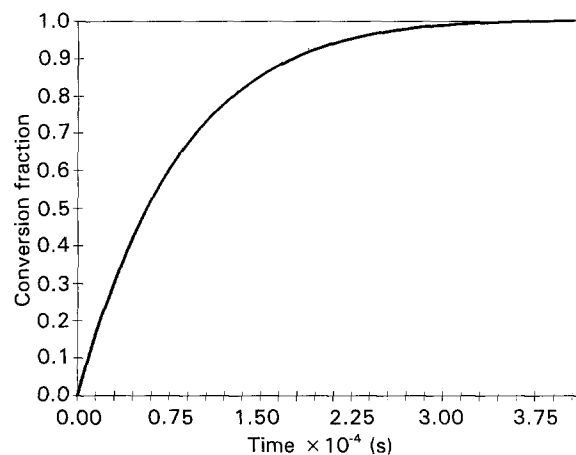


Figure 6 A representative figure of conversion vs time from kinetics model K2.

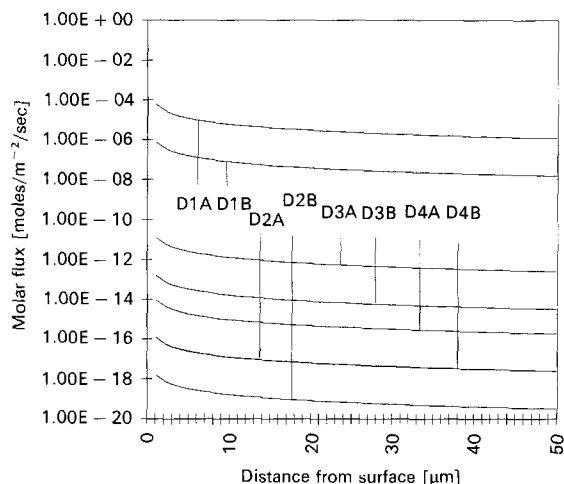


Figure 7 Molar fluxes for diffusion models D1 to D4 as a function of distance from the surface.

critical temperature of nitrogen concentration in diffusion models that assumed saturated silicon cores.

4. Discussion

The sequence by which the results were analysed is presented in Fig. 9. The analysis sequence could be

TABLE III Results of diffusion models D5 and D6: unreacted core model

Model	Model number	Solid/liquid core	Time of diffusion for unreacted-core 100% conversion (s)
Film diffusion	D5-A	Solid	1.91×10^{-7}
Film diffusion	D5-B	Liquid	2.08×10^{-7}
α -ash layer diffusion	D6-A1	Solid	1.79×10^{17}
α -ash layer diffusion	D6-B1	Liquid	1.95×10^{17}
β_1 -ash layer diffusion	D6-A2	Solid	1.79×10^{12}
β_1 -ash layer diffusion	D6-B2	Liquid	1.95×10^{12}
β_2 -ash layer diffusion	D6-A3	Solid	2.40×10^{15}
β_2 -ash layer diffusion	D6-B3	Liquid	2.62×10^{15}

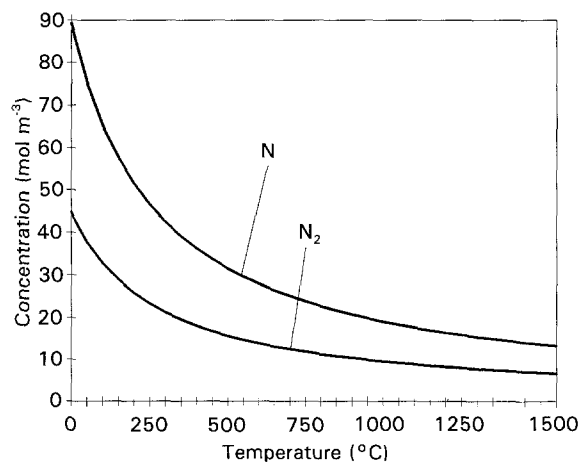


Figure 8 Nitrogen concentration as a function of temperature

reversed to find the flight time and the atomizer height required for the desired conversion. The time for a particle to cool to solid form and the reaction kinetics determined the amount of silicon nitride formed. The reaction kinetics depended on whether the particles were in the liquid or solid form. The rate constants for the liquid, $k_{\alpha,l} = 1.31 \times 10^4 \text{ s}^{-1}$ (1733 K) and $k_{\beta,l} = 2.21 \times 10^3 \text{ s}^{-1}$ (1733 K), were estimated to be much higher than the rate constants for the solid, $k_{\alpha,s} = 1.00 \times 10^{-3} \text{ s}^{-1}$ (1623 K) and $k_{\beta,s} = 1.68 \times 10^{-4} \text{ s}^{-1}$ (1623 K). Thus, the bulk amount of silicon nitride formed would be from the liquid Si reaction, which is why the liquid Si is circled in Fig. 9. The amount of silicon nitride affected the role of the diffusion of nitrogen through the silicon nitride layer. If the diffusion, compared to the reaction kinetics, was the limiting step in the process, the silicon nitride formed would affect the subsequent formation of silicon nitride. The above steps determine the final amount of silicon nitride formed from the process.

4.1. Atomization parameters

Fig. 9 illustrates the parameters of the proposed atomization process. The flight time and the cooling rate were parallel for the entire process. They depended on the conditions inside the atomizer. The conditions were the gas temperature, gas pressure, gas velocity, molten metal temperature and the atomizer height.

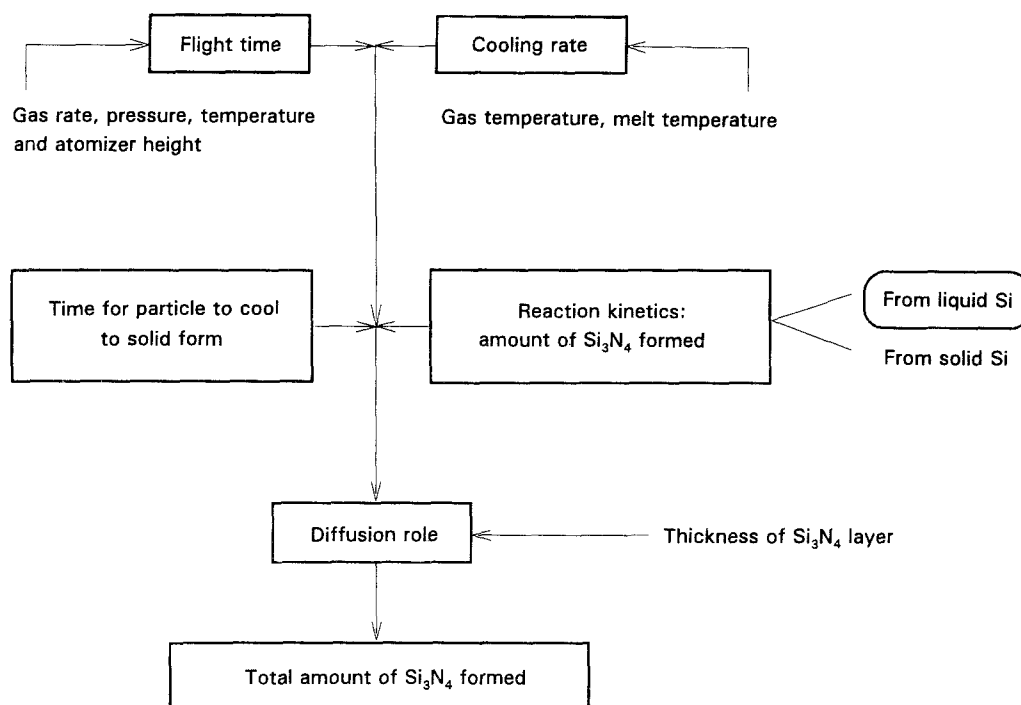


Figure 9 Analysis sequence for the proposed process of atomization to produce silicon nitride powder

A range of values for the flight time limit could be obtained by assuming various atomizing gas velocities and various atomizer heights (Fig. 3). The flight time was equal to the atomizer height divided by particle velocity. The particle velocity was assumed to be the same as the atomizing gas velocity. The range of atomizing gas velocities was $20\text{--}340\text{ m s}^{-1}$ [13] and the range for the atomizer heights was assumed to be $0.5\text{--}7\text{ m}$ [9, 13]. The flight times ranged from 0.0014 to 0.35 s (see Fig. 3).

In reality, the particles and the atomizing gas would not have constant velocity and the particle velocity would not be the same as the gas velocity. The calculated velocity profiles of atomization gas and droplets have been studied by Liang *et al.* [14]. According to them the gas velocity would drop as it moved away from the nozzle. The particles, on the other hand, would accelerate near the nozzle and reach a maximum velocity, which was less than that of the initial gas velocity, at some distance downstream from the nozzle. The velocity would then drop as they moved further away from the nozzle. Thus, the assumption that particle velocity equals the initial atomizing gas velocity is conservative in that it represents the shortest possible flight time.

By assuming a range of cooling rates and the degrees superheat above the melting point of silicon (1410°C), a range of times for the molten silicon to cool to solid could be obtained for the analysis (Table I and Fig. 4). The time for cooling was equal to the degrees superheat divided by the cooling rate. A range of the degrees superheat of the molten metal is given in [13]. The range given was $20\text{--}75^\circ\text{C}$ over the melting point of the atomizing metal. The cooling rate range was $10^3\text{--}10^6\text{ }^\circ\text{C s}^{-1}$ for normal atomization [13]. The range of cooling rates included water atomization that had higher cooling rates than gas atomization. In this analysis, a value of $10^3\text{ }^\circ\text{C s}^{-1}$ for the cooling rate was

assumed. Given these assumed parameter values, cooling time ranged from 0.02 to 0.075 s (see Table I and Fig. 4). The pressure of the gas inside the atomizer was assumed to be $1.013 \times 10^5\text{ Pa}$.

4.2. Kinetics models

The results of the kinetics models K1–K2 are in Table II. The values presented are for 100% conversion of silicon to silicon nitride. The implications of each result are discussed below.

A critical assumption in kinetics models K1 and K2 is the assumption that the Arrhenius coefficient, k_0 in Equation 5, is the same for both the solid and liquid-phase reaction. Because the reaction rate constants and the value of k_0 are not available for the reaction between molten Si and nitrogen, they must be estimated or determined empirically. The Arrhenius equation can be used to estimate the reaction rate constants for the liquid-phase reactions, if the activation energies for both the solid- and liquid-phase reactions, E_s and E_l , respectively, are available from the literature (which they are [10]) and if k_0 is either known or is assumed to be the same for both the solid and liquid-phase reaction. The assumption about the Arrhenius constant, k_0 , is neither supported nor contradicted by the literature. The validity of the assumption must be experimentally determined. If this assumption is not valid, however, the order of magnitude difference can be great and the results of kinetics models K1 and K2 should be re-evaluated.

In model K1, the conversion fraction was based on the normalized conversion of silicon to silicon nitride. The limiting feature of this model is that this model requires the knowledge of the total amount of silicon which will react with the nitrogen in order to find the actual amount of silicon reacted at time t . In this model, both the α - and β -phases were taken into

account in the conversion, and the reactions were parallel to each other. Model K1 gives a relationship between conversion and time that is almost linear (see Fig. 5).

Model K2 is similar to model K1, except that model K2 was not based on the normalized conversion of silicon to silicon nitride. In model K2, the normalized conversion factor was eliminated and replaced with the actual amount of silicon that had reacted. The relationship between conversion and time in model K2 was not linear and the curve asymptotically approached 100% conversion (see Fig. 6). This model is more realistic than model K1. As more product is formed, it is more difficult to find reactants to react and the time will be longer as the conversion approaches 100%.

4.3. Diffusion models

The diffusion models D1–D4 are all based on Fick's first law, so the graphical representations of the results of each are very similar, see Fig. 7. The only differences between them are the actual values of molar fluxes. The differences are caused by the different diffusion coefficients of different materials (Si vs Si_3N_4) and of different nitride phases (α , β_1 , β_2). The diffusion flux is much greater into the liquid silicon than through any of the nitride phases, with a difference of at least seven orders of magnitude. Among the three nitride phases, diffusion through the β_1 -phase is the fastest, whereas diffusion through the α -phase is slowest. These results indicate the importance of the nitride phase and the coherency of the nitride phase on the rate of nitrogen diffusion. Nitrogen diffusion is fastest if the nitride is not coherent, thus requiring the nitrogen to diffuse through the liquid silicon. Nitrogen diffusion is slowest if the nitride is coherent and of the α -phase. The most likely phase of the silicon nitride product was the β_2 -phase, because the reaction was essentially with the liquid silicon, as defined in the atomization process. From previous work, whenever a liquid is present during the reaction condition, the product is essentially all β -phase [4, 7, 15].

It is also important to point out that the concentration of the nitrogen gas in the immediate surroundings of the particles (i.e. the difference between the A version and the B version of models D1–D4) had some effect on the diffusion rates of the nitrogen atoms (see Fig. 7).

The concentration of nitrogen atoms around the particle was important for each diffusion model that assumed a saturated molten silicon core. The saturated molten silicon cores contained 0.02 mol % N [7], which was about 17.88 mol of N per m^3 of molten silicon. The concentration of N in the gas phase was a function of temperature. Fig. 8 indicates that the concentration of N in the gaseous phase at ca. 1100 °C (1373 K) was just about equal to that of the saturated molten silicon, assuming the latter to be independent of temperature. This indicated that when the temperature of the nitrogen gas was greater than 1100 °C, the N concentration in the gas was less than that of saturated molten Si. Because the melting

point of silicon is 1410 °C, the temperature of the proposed atomization process is higher than 1100 °C; therefore, the molten silicon during the atomization process would not be saturated with atomic nitrogen. The diffusion models with silicon cores saturated with N will be the ultimate boundary condition for the analysis. It is possible that the atomizing gas would not have enough time to absorb enough heat to reach the melt temperature, so the gas temperature in the atomizer would probably be around the initial temperature of gas. Further investigation of the rate of nitrogen atom diffusion into the molten silicon is needed.

Diffusion models D5 and D6 are based on the unreacted core model. Model D5 is the film diffusion model, which assumes an isothermal steady-state condition with no gaseous products and constant gaseous reactant concentration. The calculated result, given in Table III, shows that the time required for 100% conversion was 10^{-7} s. By comparing this with the values of 10^{-5} and 10^{-4} s for kinetic models K1-B and K2-B, respectively, the film diffusion's value was much smaller. This indicated that the film diffusion of the nitrogen gas was not a limiting step.

Model D6 is the diffusion through ash layer model. This model again emphasized the importance of the product phase(s) in the diffusion of nitrogen. For α -phase silicon nitride, the time for complete conversion was of the order of 10^{17} s, while for β -phase silicon nitride the times were of the order of $10^{12} - 10^{15}$ s. By comparing these values with the values of 10^{-5} and 10^{-4} s for kinetic models K1-B and K2-B, respectively, it is clear that on the basis of the unreacted core model, the diffusion of nitrogen through the nitride layer is much slower than the reaction kinetics, and is therefore rate limiting regardless of the nitride phase. It is not known whether the assumption of a coherent nitride (ash) layer is valid. If it is not, the unreacted core model is not valid, and the nitrogen will be diffusing through the liquid silicon instead of through the nitride layer. This diffusion through the liquid silicon is orders of magnitude faster than that through any of the nitride layers, as previously discussed. Further investigation is needed to determine the time for complete conversion if the nitride is formed within the silicon, instead of as a coherent ash layer.

5. Conclusions

The results of this study indicate that the production of silicon nitride powder through the atomization process is feasible only if the nitride layer is not coherent and if the time for complete conversion, assuming diffusion through liquid silicon, is less than the time for solidification of the atomized droplets.

The time required for the solidification of 100 μm silicon droplets, assuming a cooling rate of $10^3 \text{ }^\circ\text{C s}^{-1}$ and a median value of 50 °C superheat, was 0.05 s (see Table IV). This time was longer than the 4.1×10^{-4} s required for complete conversion to silicon nitride, given the most conservative yet realistic reaction kinetics model, model K2-B. The solidification time was

TABLE IV Select comparison of results (see results section for more details). The temperature for conversion is assumed to be the melting point of silicon, 1683 K

Degrees superheat (°C)	50
Solidification time at cooling rate of $10^3\text{ }^\circ\text{C s}^{-1}$ (s)	5.0×10^{-2}
Time for complete conversion, Model K2-B (s)	4.1×10^{-4}
Time for complete conversion, Model D5-B (s)	2.1×10^{-7}
Time for complete conversion, Model D6-B3 (s)	2.6×10^{15}

also longer than the 2.1×10^{-7} s required for complete conversion, given the most conservative unreacted core, film diffusion controls model, model D5-B. The solidification time, however, was orders of magnitude shorter than the 2.6×10^{15} s required for complete conversion, given the most conservative yet realistic unreacted core, nitride (ash) layer diffusion controls model, model D6-B3.

These results indicate that diffusion through the nitride (ash) layer is the rate limiting step, given all of the assumptions utilized in this analysis, and if the assumption of the coherent ash layer, as assumed for the unreacted core model, is valid for the process being analysed. If this key assumption is not valid, the diffusion will be controlled by the diffusion of nitrogen through liquid silicon, which is ten orders of magnitude greater than that through β 2-phase silicon nitride, the ash layer assumed for model D6-B3. Further investigation is needed to determine whether the coherent ash layer assumption in the unreacted core model is valid for the silicon-silicon nitride system, and, if not, to determine the time required for complete conversion, assuming diffusion of nitrogen through the liquid silicon is the limiting step.

Another key assumption, which requires further discussion, is the pressure of nitrogen at the reaction condition. From Kaiser and Thurmond [16], the reaction between static liquid silicon and static nitrogen gas occurs only at very low pressures. For the present analysis the pressure was assumed to be 1.013×10^5 Pa. If Kaiser and Thurmond's [16] work is valid for this particular atomization process, ammonia gas should be used instead of nitrogen gas, because the ammonia gas would react instantaneously with liquid silicon at various pressures to form silicon nitride. If

ammonia gas was used, some of the results presented here would no longer be valid, and new analysis based on the reaction kinetics of silicon with ammonia and the dissociation of ammonia molecules to form nitrogen atoms would be needed. The diffusion analysis, however, might still be applicable under this condition, because the diffusion models are for nitrogen atoms not nitrogen molecules or ammonia molecules. Once atomic nitrogen is formed from ammonia dissociation, the diffusion of atomic nitrogen is still the same. More studies need to be done on this process to determine if the various assumptions presented here are valid and to experimentally test the results.

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