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A Kinetic Model for Reaction Bonding Process of Silicon Powder Compact

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Abstract

In order to obtain detailed information about the kinetics and the reaction nature of a complex reaction process like reaction bonding of silicon nitride, mathematical modelling of the process is necessary. The previous quantitative models for this process have been based only on the mechanism that the nitrogen diffuses through the solid silicon nitride without taking into account the multiple reaction mechanisms. In the present study, a comprehensive kinetic model, which is based on analysis of the multiple mechanisms in a silicon powder compact reacting with nitrogen gas and forming silicon nitride, is constructed for a solid–gas reaction bonding process with specific application to the reaction-bonding of silicon nitride. The model will incorporate the rate equation for each mechanism into a constitutive equation from which more complete information of process kinetics can be predicted. The results predicted by the present model have been compared with previous experimental results and satisfactory agreement obtained. © 1997 Elsevier Science Limited.

Notation

A_N Molecular weight of nitrogen (kg mol^{-1})
A_S Molecular weight of silicon (kg mol^{-1})
A_{SN} Molecular weight of silicon nitride (kg mol^{-1})
c Constant defined in the radial density function for a random dense packing[15]
C Concentration of nitrogen or silicon (mol m^{-3})
C_{NC} Concentration of nitrogen at the interface between silicon core and Si_3N_4 shell (mol m^{-3})
C_{Ng} Concentration of N_2 (mol m^{-3})
C_{NS} Concentration of nitrogen at particle surface (mol m^{-3})
C^0_S Concentration of Si corresponding to the equilibrium pressure of Si at temperature T (mol m^{-3})
C_{SC} Concentration of Si being equilibrium to that in the Si_3N_4 at the interface (mol m^{-3})
C^*_{SC} Concentration of Si near the surface of the pores at the interface (mol m^{-3})
C_{SS} Concentration of silicon at particle surface (mol m^{-3})
C^*_{SS} Concentration of silicon in the atmosphere (mol m^{-3})
D Instant solidity ratio of the compact (dimensionless)
$\dot{D}$ Changing rate of the instantaneous solidity of the powder compact (s^{-1})
D_0 Initial solidity ratio of the compact (dimensionless)
D_b Diffusion coefficient along boundaries (m^2 s^{-1})
D_V Diffusion coefficient in the particle (m^2 s^{-1})
D_N Diffusion coefficient of nitrogen in solid silicon nitride layer (m^2 s^{-1})
$D_{N,K}$ Knudsen diffusion coefficient of nitrogen gas (m^2 s^{-1})
D_S Diffusion coefficient of silicon in solid silicon nitride layer (m^2 s^{-1})
$D_{S,K}$ Knudsen diffusion coefficient of silicon vapour (m^2 s^{-1})
E_C Activation energy of reaction (J mol^{-1})
f Volume fraction of converted silicon (dimensionless)
f_d Adjustable constant (dimensionless)
f_S Fraction of effective surface of a particle for diffusion (dimensionless)
ΔH Reaction heat of the nitridation reaction (J kg^{-1})
J_i Mass flux of transportation for step i (i = 1, 2....) (mol s^{-1} m^{-2})
k_c Rate constant of reaction at the Si/Si_3N_4 interface (m s^{-1})
k_{CO} Pre-exponential factor of k_c (m s^{-1})
k_g Rate constant of nitrogen transportation in the gas film (m s^{-1})
k_s Rate constant of reaction at the outer surface of the formed Si_3N_4 layer (m s^{-1})
L Length of the cylindrical compact (m)

M_N Accumulated consumption of nitrogen per particle at time t (mol)
$\dot{M}_N$ Consumption rate of nitrogen per particle (mol s^{-1})
$\dot{M}_{N,i}$ Consumption rate of nitrogen per particle via path i (i = 1, 2 or 3) (mol s^{-1})
M_S Accumulated consumption of silicon per particle (mol)
$\dot{M}_S$ Consumption rate of silicon per particle (mol s^{-1})
$\dot{M}_{S,i}$ Consumption rate of silicon per particle via path i (i = 1, 2 or 3) (mol s^{-1})
$_C\dot{M}_S$ Rate of Si consumption for the entire compact (mol s^{-1})
$_CM_S$ Accumulated consumption of silicon for the compact (mol)
P_S^o Equilibrium pressure of silicon at temperature T (Pa)
P_{SC}^* Vapour pressure of silicon near the surface of the pores at the interface (Pa)
r Radial coordinate for a particle (m)
R Radial coordinate for a compact (m)
r_c Radius of silicon core (m)
$\dot{r}_C$ Change rate of r_c (m s^{-1})
r_{ch} Mean radius of the channel (m)
r_o Initial radius of the particle (m)
r_p Pore radius (m)
r_s Instant radius of the particle (m)
R_s Radius of the compact (m)
S Surface area of a particle (m^2)
t Time (s)
T Temperature (K)
$\dot{V}_C$ Rate of volume change per particle due to reaction (m^3 s^{-1})
$\dot{V}_{ex}$ Rate of change of overlapped volume per particle (m^3 s^{-1})
$\dot{V}_r$ Rate of volume change per particle due to reaction (m^3 s^{-1})
$\dot{V}_s$ Rate of volume change per particle due to sintering (m^3 s^{-1})
z Average coordination number
z_O Initial average coordination number
α_C Specific heat of the compact (J kg^{-1} K^{-1})
γ Surface energy of Si_3N_4 (J m^{-2})
δ Thickness of interparticle boundaries (m)
ε Instant porosity of the compact (dimensionless)
ε_0 Initial porosity of the compact (dimensionless)
ε_{SN} Porosity of Si_3N_4 layer (dimensionless)
λ_N Diffusion coefficient of N_2 in the compact (m^2 s^{-1})
λ_T Heat diffusivity of the compact (m^2 s^{-1})
ρ_c Density of compact (kg m^{-3})
ρ_{SN} Density of Si_3N_4 (kg m^{-3})
ρ_s Density of silicon (kg m^{-3})
Ω Atomic volume of silicon (m^3)
τ Tortuosity factor of the channels (dimensionless)

1 Introduction

Reaction bonded silicon nitride (RBSN) is of great importance as a high-temperature structural material, due to its high-temperature strength, good thermal shock resistance, low specific density and high heat resistance. Since the chemical reaction and sintering take place simultaneously during the process and a great number of material parameters and processing variables such as temperature, pressure, gas composition, particle size, compact size, the heat generation and thermal diffusivity, etc. can affect the nitriding process, the overall mechanism is very complex. Moreover, certain extrinsic factors such as the purity of the starting powder also have an effect on the kinetics of nitridation. All these variables and factors make experimental studies of the process very costly and time-consuming. Failure to account for some factors which complicate the process often invalidates direct comparison of experimental results between different works. Efforts have been made to resolve the problem by modelling, but a deviation between experimental and theoretical results is usually encountered due to absence of a general and comprehensive model for the process.

As far as the modelling of the RBSN process is concerned, the particle–pellet model was suggested to describe the kinetics of the process[1–4] which considered the pellet as composed of discrete particles. These single particles, because of their low voidage, were assumed to follow the sharp interface model.[5] Hughes *et al.*[2,3] considered the diffusion of nitrogen through the formed product to be the dominant mechanism. Ku and Gregory[1] have considered the changes of grain size and the specific surface area due to the sintering effect, and developed a mathematical model under isothermal conditions and constant concentration of nitrogen through the powder compact. To the best of the authors' knowledge, all of the previous quantitative models of the RBSN process are based on a single mechanism that the nitrogen atoms diffuse through the Si_3N_4 layer and react with solid silicon on the interface between silicon and silicon nitride, although a number of researchers have noticed that some mechanisms other than nitrogen diffusion, for example reaction between silicon vapour and nitrogen gas,[6] may contribute to the reaction kinetics. It is a general consideration that multiple mechanisms, operating simultaneously or consecutively, should be involved in the reaction-bonding process. Under different conditions, different mechanisms will become determinants in controlling the process kinetics. It seems that no single rate law is likely to universally describe the nitridation of

silicon in all cases. In the present paper, a number of mechanisms which may be involved in the reaction-bonding process are considered and a rate equation for each individual mechanism is derived. These rate equations are then incorporated into a overall rate equation for a single particle. Combining the constitutive rate equation with theories of heat conduction and sintering, nitridation kinetics for a powder compact can be analytically described. Much important information about the RBSN process, such as the conversion fraction of silicon, densification rate of the compact, controlling mechanism, the effect on nitridation of the processing parameters and material properties etc., can be obtained from the present model. Moreover the model could be applied to any reaction bonding process of gas-powder compact with limited modification.

2 Modelling

2.1 General consideration

It is well established that the reaction starts from the surface of particles, forming a layer of silicon nitride surrounding a reactant core. The reaction is continued by inward growth of the Si_3N_4 shell by nitrogen diffusing inwards and silicon diffusing outwards through the shell to the reaction sites.[7] A comprehensive model should concern the nitridation of individual particles, sintering of the powder compact and the mutual effect of these two processes. In the present model, the rate equations for nitridation are derived first for a single silicon particle and then for the entire powder compact.

For a single particle, silicon and nitrogen can react with each other through different paths (Fig. 1). Each path is composed of several elementary steps which act sequentially or simultaneously during RBSN process:

Path I

This path consists of four elementary steps (steps 1–4 in Fig. 1). In step 1, during the mass transfer of nitrogen at the particle surface, a series of consecutive processes may take place:[8] (a) transport of nitrogen molecules by diffusion (or convection) through the gas film[9] to the particle surface. A part of the nitrogen molecules will enter the openings of channels in the formed product layer. Those channels are supposed to form by the irregular pores and flaws interconnecting with each other since the formed Si_3N_4 is usually porous, and the channels may offer a passage for diffusion of nitrogen molecules from the outer surface to the interface of silicon core and nitride shell. The rest of the nitrogen molecules will undergo the following steps:[8] (b) adsorption of nitrogen molecules at a particle surface; (c) decomposition of the adsorbed N_2 molecules into nitrogen atoms; and (d) solution of nitrogen atoms into the gas–solid phase boundary. Afterwards the nitrogen atoms will diffuse inwards through the Si_3N_4 layer surrounding a silicon core (step 2), while the part of nitrogen molecules which enter directly into the channels in the Si_3N_4 shell will diffuse (by Knudsen diffusion) along the channels to the interface of Si core/nitride (step 3).

Similar to the processes (a) to (d) in step 1, the transformation of N_2 to N will also take place when the nitrogen molecules transported through step 3 reach the interface of Si core/nitride, but at the nitridation temperature these processes are rapid and therefore supposed not to be rate determining and accordingly not taken into account in the mathematical treatments.

The N atoms transferred to the Si/Si_3N_4 interface will react with Si to form Si_3N_4 (step 4).

Path II

This path concerns the outward diffusion of silicon through the solid Si_3N_4 from the interface of

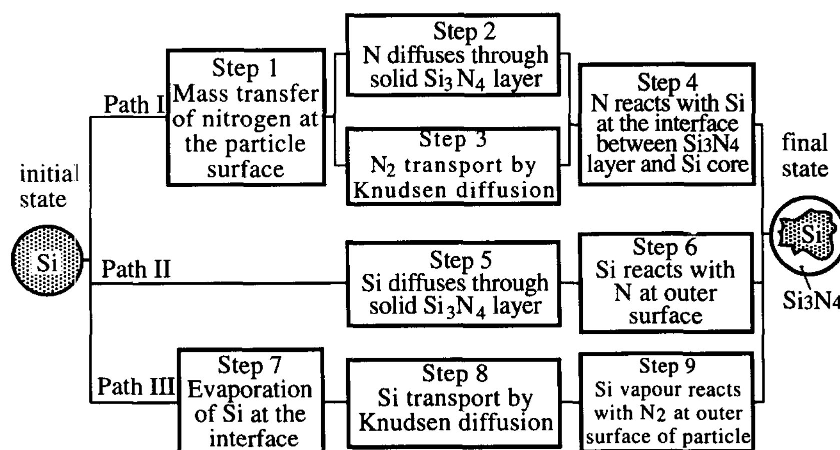

Fig. 1. Structure of the model for the reaction of a single silicon particle with nitrogen. Note that the other paths, which may exist but are trivial, are not shown in the figure.

Si core/nitride to the outer surface of the particle (step 5) and the reaction with nitrogen atoms at the outer surface (step 6).

Path III

Silicon can be evaporated in the pores at the Si/Si_3N_4 interface (step 7) and the Si vapour will diffuse by Knudsen diffusion to the outer surface of the particle through the channels in the Si_3N_4 layer (step 8) and reacted with N_2 (step 9).

2.2 Assumptions

In order to construct a mathematical model for the complex RBSN process, some assumptions have to be made for simplification. The general assumptions made in the present model are:

(1) The chemical reaction of silicon and nitrogen to Si_3N_4 is of first order and irreversible.
(2) A quasi-steady is assumed when the rate equations for each step are combined.
(3) The particles are single-sized spheres and sufficiently small so that temperature gradients inside a particle can be neglected.
(4) The reactants are considered to be pure.
(5) The powder compact is a long cylinder.

2.3 Modelling of a single silicon particle

Consider a silicon particle at a distance R from the centre of the compact (Fig. 2). For modelling, it has to be considered that the coordination number (the average number of contacts with surrounding particles) and the contact area per particle increase steadily during the RBSN process. The particle concerned is exposed to nitrogen at the non-contact surface area (the effective surface area) which is equal to unity at the beginning and decreases with the processing time.

2.3.1 Rate equation for nitrogen transportation and consumption (Path I)

Step 1. Nitrogen diffuses through the gas film. The flux, i.e. mass of nitrogen transferred per second through a unit area of gas film, J_1, is given by:

$$J_1 = k_g(C_{Ng} - C_{NS}) \tag{1}$$

where k_g is the mass transfer coefficient between the gas and the particle, C_{Ng} is the concentration of molecular nitrogen in the gas and C_{NS} the concentration of atomic nitrogen at the solid surface. For a single particle, the rate of mass transport of nitrogen, through the gas film and dissolved into the surface of the solid phase, $\dot{M}_{N,1}$, can be written as:

$$\begin{aligned}\dot{M}_{N,1} &= 4\pi r_S^2 f_S \cdot (1 - \varepsilon_{SN}) \cdot J_1 \\ &= 4\pi r_S^2 f_S \cdot (1 - \varepsilon_{SN}) k_g (C_{Ng} - C_{NS})\end{aligned} \tag{2}$$

where r_s is the instant radius of a particle and f_S is defined as a fraction of effective surface for nitrogen transportation, i.e. the ratio of non-contact area to total surface area of a single particle; ε_{SN} is the porosity in the Si_3N_4 layer.

Step 2. Nitrogen diffuses through the Si_3N_4 layer. According to Fick's diffusion law, the diffusion flux of nitrogen through the Si_3N_4 layer, J_2, can be expressed as (Appendix A1):

$$J_2 = D_N \frac{r_C \cdot r_S (C_{NS} - C_{NC})}{r^2 (r_S - r_C)} \tag{3}$$

where r_C is the radius of silicon core, C_{NC} the nitrogen concentration at the interface between the silicon core and the Si_3N_4 layer (Fig. 2), r the radial coordinate in a particle, and D_N the diffusion coefficient of nitrogen in solid Si_3N_4. Considering the effect of contact area for diffusion, the rate of N diffusion through the Si_3N_4 layer for a particle, $\dot{M}_{N,2}$, is equal to:

$$\begin{aligned}\dot{M}_{N,2} &= 4\pi r^2 f_S f_d \cdot (1 - \varepsilon_{SN}) J_2 \\ &= 4\pi \cdot r_C r_S f_S f_d \cdot (1 - \varepsilon_{SN}) D_N \frac{(C_{NS} - C_{NC})}{(r_S - r_C)}\end{aligned} \tag{4}$$

where f_d is a constant, approximately equal to one, introduced into the model due to the fact that the diffusion of nitrogen in the Si_3N_4 layer diverts radially since only a part of the particle surface area is exposed to nitrogen gas.

Step 3. N_2 gas diffuses through the some channels in the Si_3N_4 layer (Knudsen diffusion). Due to the fact discussed in Section 2.1 that the formed Si_3N_4 usually contains porosity, it is reasonable to assume that some irregular pores and flaws in the Si_3N_4 shell are interconnected, forming tortuous channels which offer a passage for gaseous nitrogen to diffuse in the Si_3N_4 shell. If the radius of the channels is of the same magnitude as, or smaller than the mean free path of nitrogen molecule,[10] Knudsen diffusion[11] may apply and the diffusion flux can be expressed as:

$$J_3 = D_{N,K} \cdot \frac{\partial C}{\partial r} \tag{5}$$

In eqn (5) the Knudsen diffusion coefficient $D_{N,K}$ is:[11]

$$D_{N,k} = \frac{2}{3} \cdot \frac{r_{ch}}{\tau} \sqrt{\frac{8RT}{\pi A_N}} \tag{6}$$

where R is gas constant, A_N the molecular weight of nitrogen, τ tortuosity factor of the channels, T temperature and r_{ch} mean radius of the channels which is related with average pore radius r_p by a factor 0·82 (Appendix A2). The nitrogen transport via Knudsen diffusion for a particle can be written by (Appendix A3):

$$\dot{M}_{N,3} = 4\pi\varepsilon_{SN}D_{N,K}\frac{r_C r_S(C_{Ng} - C_{NC})}{(r_S - r_C)} \quad (7)$$

Step 4. Nitrogen reacts with silicon at the interface between the Si_3N_4 shell and Si core. The nitrogen arriving at the Si/Si_3N_4 interface is assumed to distribute uniformly along the interface due to rapid interfacial diffusion before it reacts with the silicon at the interface. The reaction rate is therefore given by:

$$J_4 = k_C C_{NC} \quad (8)$$

and the corresponded nitrogen consumption via Step 4 is given by:

$$\dot{M}_{N,4} = 4\pi r_C^2 k_C C_{NC} \quad (9)$$

where k_C is the rate constant of reaction at the Si/Si_3N_4 interface which can be expressed by $k_C = k_{CO}\exp(-E_C/_{RT})$, where E_C is the activation energy of the reaction and k_{CO} the pre-exponential factor.

Four mechanisms are involved in Path I. Since Steps 2 and 3 act in a concurrent manner but Steps 1, 2 + 3, and 4 act in a consecutive manner (Fig. 1), they must be satisfied by:

$$\dot{M}_I = \dot{M}_{N,1} = \dot{M}_{N,2} + \dot{M}_{N,3} = \dot{M}_{N,4} \quad (10)$$

Combining eqn (10) with eqns (2), (4), (7), (9), a kinetic rate equation for Path I, i.e. the rate of nitrogen consumption through Path I, is obtained as:

$$\dot{M}_I = 4\pi \cdot r_S^2 \cdot C_{Ng}\left[\frac{1}{f_S k_g(1 - \varepsilon_{SN})} + \frac{r_S \cdot (r_S - r_c)}{r_c(f_S f_d(1 - \varepsilon_{SN})D_N + \varepsilon_{SN}D_{N,K})} + \frac{r_S^2}{r_C^2 \cdot k_C}\right]^{-1} \quad (11)$$

2.3.2 *Rate equation for silicon transportation (Paths II and III)*

As a counterpart of nitrogen diffusion inwards in RBSN process, silicon atoms can diffuse outwards from the Si/Si_3N_4 interface to the particle surface through the Si_3N_4 shell (Fig. 2). There exist two paths (Paths II and III in Fig. 1) for silicon diffusion. Path II consists of the diffusion of silicon through the shell (Step 5) and reaction with the atomic nitrogen on the outer surface of the particle (Step 6). Path III includes the evaporation of silicon in the pores locating at the Si/Si_3N_4 interface (Step 7), the outward transport of Si vapour by Knudsen diffusion through the channels in the Si_3N_4 shell (Step 8) and the reaction of Si vapour with nitrogen gas at the particle surface (Step 9).

(A) The rate equation for path II

Step 5. Silicon diffusion through the Si_3N_4 shell. Similar to Step 2, a rate equation for Step 5 can be derived (Appendix A4) as:

$$\dot{M}_{S,5} = 4\pi \cdot f_S \cdot (1 - \varepsilon_{SN}) \cdot D_s \cdot \frac{r_s r_C}{r_S - r_C} \cdot (C_{SC} - C_{SS}) \quad (12)$$

where $\dot{M}_{S,5}$ means mass diffusion of silicon by Step 5 per second for one particle, D_S is the diffusion coefficient of silicon in silicon nitride, C_{SC} silicon concentration being in equilibrium to that in the Si_3N_4 at the interface and C_{SS} concentration of silicon at particle surface.

Step 6. Silicon reaction with nitrogen at the outer surface of particle. The reaction rate by Step 6, $\dot{M}_{S,6}$ being similar to that by Step 4, can be expressed by:

$$\dot{M}_{S,6} = 4\pi r_S^2 f_S \cdot (1 - \varepsilon_{SN})k_C C_{SS} \quad (13)$$

Since Steps 5 and 6 in Path II act consecutively, it has $\dot{M}_{II} = \dot{M}_{S,5} = \dot{M}_{S,6}$ where $\dot{M}_{II}$ means the overall rate of silicon consumption in Path II for one particle which can be derived by combining eqns (12) and (13):

$$\dot{M}_{II} = \frac{4\pi \cdot r_S^2 \cdot (1 - \varepsilon_{SN})C_{SC}}{\frac{r_S \cdot (r_S - r_C)}{r_C f_S \cdot D_S} + \frac{1}{f_S \cdot k_C}} \quad (14)$$

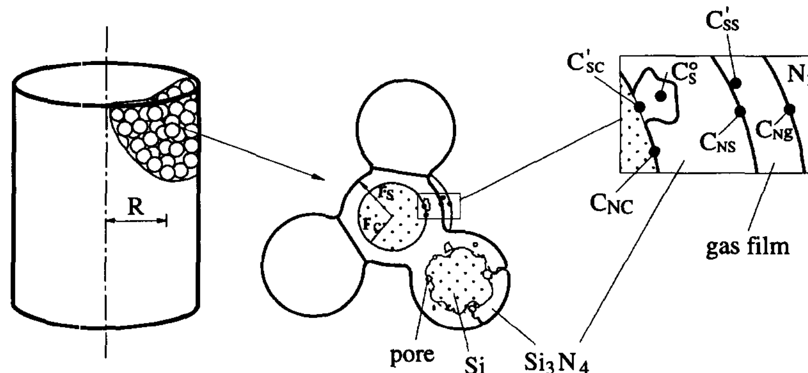

Fig. 2. Diagram of the structural model.

(B) The rate equation for path III

Step 7. Silicon evaporates from the surface of pores locating at the Si/Si$_3$N$_4$ interface. The flux of evaporation of Si by Step 7, J_7, can be calculated by:[12]

$$J_7 = \frac{P_S^o - P_{SC}^*}{\sqrt{2\pi A_S RT}} \quad (15)$$

The evaporation rate of silicon for one particle, $\dot{M}_{S,7}$, is equal to:

$$\dot{M}_{S,7} = 4\pi \cdot r_C^2 \cdot \varepsilon_{SN} J_7 = \frac{4\pi \cdot r_C^2 \cdot \varepsilon_{SN}}{\sqrt{2\pi A_S RT}} \cdot (P_S^o - P_{SC}^*) \quad (16)$$

where A_S is the molecular weight of silicon, P_S^o is the equilibrium pressure of silicon at temperature T, and P_{SC}^* vapour pressure of silicon near the surface of the pores at the interface (shown in Fig. 2C). Substituting gas equation $P = CRT$ for eqn (16) yields:

$$\dot{M}_{S,7} = r_C^2 \cdot \varepsilon_{SN} \sqrt{\frac{8\pi RT}{A_S}} \cdot (C_S^0 - C_{SC}^*) \quad (17)$$

where C_s^0 is the concentration of Si corresponding to the equilibrium pressure of Si at temperature T ($C_s^0 = P_s^0/RT$), and C_{SC}^* is the silicon concentration near the surface of the pores at the interface (Fig. 2C).

Step 8. Si diffuses by Knudsen mechanism through the channels in Si$_3$N$_4$ layer. Following similar procedures as in deriving eqns (5) and (7) for Step 3, the flux and the rate equations for Step 8. (Fig. 1) are derived and given as below:

$$J_8 = D_{S,K} \cdot \frac{\partial C}{\partial r} \quad (18)$$

$$\dot{M}_{S,8} = 4\pi \cdot \varepsilon_{SN} \cdot D_{S,K} \cdot \frac{r_S \cdot r_C \cdot (C_{SC}^* - C_{SS}^*)}{(r_S - r_C)} \quad (19)$$

where C_{SS}^* is the silicon concentration in the atmosphere at the outer surface of particle and other variables have the meaning denoted before (see Notation). $D_{S,K}$ in eqns (18) and (19), the Knudsen diffusion coefficient of silicon vapour, is given by:

$$D_{S,k} = \frac{2}{3} \cdot \frac{r_{ch}}{\tau} \sqrt{\frac{8RT}{\pi A_S}} \quad (20)$$

Step 9. Silicon reacts with nitrogen at the outer surface of particles. Similar to the derivation of eqns (8) and (9) for Step 4, the flux and rate equations for Step 9 can be shown as:

$$J_9 = k_S C_{SS}^* \quad (21)$$

$$\dot{M}_{S,9} = 4\pi \cdot r_S^2 f_S (1 - \varepsilon_{SN}) k_S C_{SS}^* \quad (22)$$

where k_s is the reaction constant of silicon vapour reacting with nitrogen gas at the outer surface of the particle. In the derivation of eqn (22), it is assumed that silicon vapour can react with nitrogen only at the outer surface of the particle.

The rate equations for steps 7, 8, and 9 in Path III must satisfy: $\dot{M}_{S,7} = \dot{M}_{S,8} = \dot{M}_{S,9}$. By combining this relation with eqns (17), (19) and (22), the overall rate of silicon consumption for a single particle through Path III can be expressed as:

$$\dot{M}_{III} = \dot{M}_{S,9} = \frac{4\pi r_S^2 C_S^o}{\dfrac{4\pi r_S^2}{r_C^2 \cdot \varepsilon_{SN}\sqrt{\dfrac{8\pi RT}{A_S}}} + \dfrac{r_S \cdot (r_S - r_C)}{r_C \cdot \varepsilon_{SN} D_{S,K}} + \dfrac{1}{f_S(1 - \varepsilon_{SN})k_S}} \quad (23)$$

2.3.3 Overall rate of RBSN process for a single silicon particle

The total consumption rate of silicon for one single particle, $\dot{M}_S$, is simply the sum of that by Paths I, II and III (Fig. 1), that is:

$$\dot{M}_S = \frac{3}{4}\dot{M}_I + \dot{M}_{II} + \dot{M}_{III} \quad (24)$$

where 3/4 is the stoichiometric ratio of reaction between silicon and nitrogen. The silicon consumption leads to a reduction of silicon cores. The rate of the radius change of the silicon core can be calculated by:

$$\dot{r}_C = -\frac{A_S}{4\pi r_C^2 \rho_S}\dot{M}_S \quad (25)$$

Integration of eqn (25) yields:

$$r_C^3 = r_0^3 - \frac{3A_S}{4\pi\rho_S}\int_0^t \dot{M}_S \, dt \quad (26)$$

where r_0 is the initial radius of the silicon particle, ρ_s density of silicon and t reaction time. In the derivation of eqn (26), it is assumed that the silicon core of a particle remains spherical during the process, in other words, the truncated core is replaced by a spherical equivalent volume.[13]

If the formed silicon nitride contains porosity, similar arguments as for eqns (25) and (26) lead to the rate of the outer radius change, r_s versus processing time as (Appendix A5):

$$\dot{r}_S = \frac{1}{4\pi r_S^2}\left[\frac{A_{SN}}{3\rho_{SN}(1 - \varepsilon_{SN})} - \frac{A_S}{\rho_S}\right]\dot{M}_S \quad (27)$$

and

$$r_S^3 = r_0^3 + \frac{3}{4\pi}\left[\frac{A_{SN}}{3\rho_{SN}(1 - \varepsilon_{SN})} - \frac{A_S}{\rho_S}\right]\int_0^t \dot{M}_S \, dt \quad (28)$$

where A_{SN} is the molecular weight of silicon nitride and ρ_{SN} is density of the formed Si_3N_4. The volume fraction of converted silicon, f, can be calculated by:

$$f = \frac{3A_S}{4\pi r_0^3 \rho_S}\int_0^t \dot{M}_S \, dt \quad (29)$$

Equations (11), (14), (23), (24) and (29) derived so far can only apply to a single particle.

3 Rate Equations for a Powder Compact

During the densification both the contact areas of a particle with its neighbours and the coordination number (the number of contacts per article) increase due to the shape and size of every particle in the powder compact changing. According to Arzt,[13] densification of a powder compact can be visualised as the shrinkage of the Voronoi polyhedron surfaces which are formed by perpendicular bisecting planes on all centre-to-centre connections between particles. The shape change of particles can be regarded as imposed by the boundaries of the polyhedra. Suppose that during densification both the particle centres and the polyhedra remain fixed, so that densification is simulated by the concentric growth of the spherical particles. After the spheres have grown into neighbouring polyhedra, some of them overlap. The excess volume outside the polyhedra, i.e. overlapped volume, has to be redistributed. The rate of overlap volume change per particle can be written as:[13,14]

$$\dot{V}_{ex} = \frac{r_0^3 \dot{D}}{3(DD_0^2)^{1/3}} G_1(D) \tag{30}$$

where $\dot{D}$ is the changing rate of instantaneous solidity of the powder compact and $G_1(D)$ is equal to:

$$G_1(D) = \left[\left(\frac{D}{D_0}\right)^{1/3} - 1\right]\left\{2z_0 + c\left[\left(\frac{D}{D_0}\right)^{1/3} - 1\right]\right\} \tag{31}$$

$$\left(\frac{D}{D_0}\right)^{1/3} = \frac{r_S}{r_0} \tag{32}$$

In eqns (30)–(32), z_0 (= 7·3) is the initial coordination number, c (= 15·5) a constant defined in the radial density function for a random dense packing, D and D_0 are respectively the instantaneous and the initial solidity of the powder compact defined as the ratio of the volume actually occupied by solid material to the volume of the powder compact. It obviously has that $D = 1 - \varepsilon$ and $D_O = 1 - \varepsilon_0$, where ε and ε_0 are respectively the instantaneous and the initial porosity of the compact. It should be pointed out that the porosity concerned here is the inter-particle porosity and the pores within the formed Si_3N_4 are not included. Therefore D is not equal to the overall relative density of the compact, although the difference between them is negligible at the beginning of the RBSN process.

The rate of the excess volume change of the compact, $\dot{V}_{ex}$, has to be compensated by the rate of volume changes caused by nitriding reaction, $\dot{V}_r$, and by that of sintering, $\dot{V}_S$, i.e.:

$$\dot{V}_{ex} = \dot{V}_S + \dot{V}_r \tag{33}$$

If $\dot{M}_S$ is known from eqn (24), the rate of volume change caused by reaction, $\dot{V}_r$, can be calculated by (Appendix A6):

$$\dot{V}_r = \left[\frac{A_{SN}}{3\rho_{SN}(1-\varepsilon_{SN})} - \frac{A_S}{\rho_S}\right]\left[2z_0\left(1 - \frac{r_0}{r_S}\right) + c\left(\frac{r_S}{r_0} + \frac{r_0}{r_S} - 2\right)\right]\dot{M}_S \tag{34}$$

Based on Ashby's theory,[14] the rate of volume transport by sintering, $\dot{V}_S$, in eqn (33), is given by (Appendix A7):

$$\dot{V}_S = \frac{48\pi\Omega\gamma D(1 - \sqrt{D - D_0})}{r_0(D - D_0)} \left[\frac{\delta D_b + r_0(D - D_0)D_V}{kT}\right] \tag{35}$$

where Ω, γ, δ, D_b and D_V are defined respectively as the atomic volume of silicon, surface energy of Si_3N_4, thickness of boundaries between particles, diffusion coefficient along boundaries and volumetric diffusion coefficient in the particle. k is Boltzmann's constant. Substituting eqns (34) and (35) for (33) and using eqn (30) yields:

$$\dot{D} = G_2(D)\frac{\Omega\gamma}{r_0^4}\left[\frac{\delta D_b + r_0(D - D_0)D_V}{kT}\right] + G_3(D)\frac{1}{r_0^3}\left[\frac{1}{3(1-\varepsilon_{SN})}\frac{A_{SN}}{\rho_{SN}} - \frac{A_S}{\rho_S}\right]\cdot\left[2z_0\left(1 - \frac{r_0}{r_S}\right) + c\left(\frac{r_S}{r_0} + \frac{r_0}{r_S} - 2\right)\right]\dot{M}_S \tag{36}$$

where

$$G_2(D) = \frac{144(D^4 D_0^2)^{1/3}[1 - \sqrt{D - D_0}]}{G_{1(D)}(D - D_0)} \tag{37}$$

and

$$G_3(D) = \frac{3(DD_0^2)^{1/3}}{\pi G_1(D)} \tag{38}$$

Considering the definition of f_S and using eqn (A6.3) in Appendix A6, the relation of the fraction of effective surface f_S to r_S and r_0 is shown as:

$$f_S = 1 - \frac{z_0}{2}\left(1 - \frac{r_0}{r_S}\right) - \frac{c}{4}\left(\frac{r_S}{r_0} + \frac{r_0}{r_S} - 2\right) \tag{39}$$

So far, the necessary equations for kinetic calculations of the RBSN process have been obtained. From eqns (24), (11), (14) and (23), it can be seen that the consumption of silicon and nitrogen are related to r_S, r_C, f_S and to the temperature through k_g, k_S, k_C, D_N, D_S, $D_{N,S}$, $D_{N,K}$, etc., and in addition to some material and processing variables such as r_0, r_S, D_0, A_S, A_{SN}, C_{Ng}, C_{SC}, etc., i.e.

$$\dot{M}_S = F_1(f_S, r_S, r_C, T, P_j) \quad (40)$$

where P_j represents a set of properties variables. In the same way, eqns (26), (28), (36) and (39) can be rewritten as:

$$r_C = F_2(\dot{M}_S, P_j) \quad (41)$$

$$r_S = F_3(\dot{M}_S, P_j) \quad (42)$$

$$\dot{D} = F_5(\dot{M}_S, T, P_j) \quad (43)$$

$$f_S = F_4(D, r_S, P_j) \quad (44)$$

The unknown functions (M_S, r_S, r_C, f_S and D) can, in principle, be obtained by solving eqns (40)–(44) under certain initial and boundary conditions by a numerical method. For a powder compact, which is, for simplification, assumed to have long cylindrical shape, three cases will be discussed below.

3.1 Uniform and constant nitrogen concentration over the pore space in an isothermal compact

In this case, r_S, and f_s as well as the accumulated consumption of silicon per particle M_S do not vary over the compact. The rate of Si consumption for the entire compact, ${}_C\dot{M}_S$, is simply given by integration of $\dot{M}_S$ over the compact volume (V) i.e.

$${}_C\dot{M}_S = \frac{3}{4\pi}\int_V \dot{M}_S \frac{D}{r_S^3}\,dV = \frac{3}{4\pi}\frac{\dot{M}_S DV}{r_S^3} = \frac{3}{4}\frac{R_S^2 LD}{r_S^3}\dot{M}_S \quad (45)$$

and

$${}_C M_S = \int_0^t {}_C\dot{M}_S\,dt = \frac{3}{4}\int_0^t \frac{R_S^2 LD}{r_S^3}\dot{M}_S\,dt \quad (46)$$

where ${}_C M_S$ is the accumulated consumption of silicon for the compact, R_S and L are the outer radius and length of the cylindrical compact, respectively.

3.2 Uniform and constant nitrogen concentration, but variable temperature over the compact

In this case, the temperature is constant at the surface of the compact but not uniform within the compact and varies with time. Consequently M_S, etc. are functions of time and distance from the centre of the compact. Taking into account reaction heat, the differential equation of heat conduction is as:[15]

$$\frac{\partial T}{\partial d} = \frac{\partial}{\partial R}\left(\lambda_T\frac{\partial T}{\partial R}\right) + \frac{\lambda_T}{R}\frac{\partial T}{\partial R} - \frac{DA_{SN}\Delta H}{12\pi r_S^3 \rho_C \alpha_C}\dot{M}_S \quad (47)$$

where R is the radial coordinate of the powder compact; λ_T and ρ_C are respectively the thermal diffusivity and density of the porous compact, α_C the specific heat of the compact and ΔH enthalpy change of the reaction. The last term in eqn (47) corresponds to the heat generated in the reaction. It can be seen from eqn (47) that in order to obtain the distribution of temperature, D and r_S which are specified by eqn (36), have to be known. ${}_C M_S$ is obtained by integration of $\dot{M}_S$:

$${}_C M_S = \frac{3}{2\pi}\int_0^t dt \int_0^L dL \int_0^R \dot{M}_S \frac{D}{r_S^3} R\,dR \quad (48)$$

3.3 Both temperature and nitrogen concentration vary over the compact

In this case, a differential equation for determining the concentration of nitrogen gas within the compact, C_{Ng} can be written as:

$$\frac{\partial C_{Ng}}{\partial t} = \frac{\partial}{\partial R}\left(\lambda_N\frac{\partial C_{Ng}}{\partial R}\right) + \frac{\lambda_N}{R}\frac{\partial C_{Ng}}{\partial R} - \frac{3D}{8\pi r_S^3}\dot{M}_S \quad (49)$$

where λ_N is the diffusion coefficient of nitrogen in the porous compact. The last term in eqn (49) corresponds to the nitrogen consumption caused by the reaction. The kinetic information is obtained by solving a set of eqns (24), (26), (28), (36), (39), (47) and (49) with certain initial and boundary conditions depending on the experimental conditions. In solving these equations, an iterative and numerical procedure has to be used because of their complexity.

4 Results and Discussion

The present model has been examined by comparing the theoretical calculation with the experimental data from Ref. 16, which exhibits satisfactory agreement shown in Figs 3 and 5. Due to lack of data about silicon diffusion in silicon nitride, which has been considered to be much slower than the diffusion of nitrogen atoms,[6] the contribution from mechanism Step 5 is neglected. The present model shows that during a nitridation of 25 h the rate of nitridation estimated by Knudsen diffusion (Step 3) of nitrogen gas, which is approximately 150 to 200 times higher than that estimated by the diffusion of nitrogen through solid silicon nitride seems to be consistent with the experimental results. This means that the Knudsen

diffusion of nitrogen makes a significant contribution and leads to a much faster rate of nitridation than that caused by the diffusion of nitrogen atoms in the solid Si_3N_4. A model based on a single mechanism of the diffusion of nitrogen in solid Si_3N_4 seems not to agree with the experimental results but gives a much lower rate of nitridation shown in Fig. 3.

By comparing the activation energy of nitrogen diffusion in silicon nitride (233–776 kJ/mol[6]) with the enthalpy of silicon evaporation (459–469 kJ/mol[17]), it has been argued in Refs 6 and 7 that silicon evaporation and effusion though Si_3N_4 might be a rate-dominant mechanism for the RBSN process. The rate of Knudsen diffusion of nitrogen has been compared with that of silicon vapour in the present model (see Fig. 4), which suggests that the Knudsen diffusion of nitrogen (Step 3 in Fig. 1) may take precedence over the outward transport of silicon vapour (Step 8). This is due to the fact that the vapour pressure of silicon at nitridation temperature which is about 10^{-7}–10^{-9} bar[10] is much lower than the nitrogen pressure (~1 bar) and the rate of nitrogen by Knudsen diffusion is hence about 10^7–10^9 times higher than the diffusion rate of silicon vapour.

Figure 5 shows the comparison between the calculated and the measured conversion fractions at three different temperatures. As can be seen, the variation of conversion fraction versus time predicted by the present model agrees well with the experiment at 1200°C. The deviation between the calculated and experimental results in the early stage of nitridation at 1300°C may be due to the following reasons: (a) the large exothermic heat generated by the reaction at elevated temperature; (b) the catalytic effect of hydrogen contained in the experimental nitriding atmosphere which may lead to a devitrification effect;[18,19] (c) the simplified assumption of single-size powders used in the model; (d) some other side-effects caused by impurities such as Fe, Al, etc. which may melt above 1207°C.[16,20] As the process proceeds, the effective particle surface for nitrogen diffusion gradually decreases and the curves in Fig. 5 become flatter.

The effect of particle size on the rate is shown in Fig. 6. Fine particles have a larger surface area for diffusion which favours the nitridation. If the silicon particles size is, on average, larger than 0·15 mm, it is difficult to achieve complete conversion within an economically acceptable time at 1200°C.

Figure 7 shows the variation of the relative density with time at three different temperatures, estimated by eqn (36). Although both chemical reaction and sintering contribute to the densification in the RBSN process (eqns (33) and (36)), the sintering effect is relatively obvious only at the

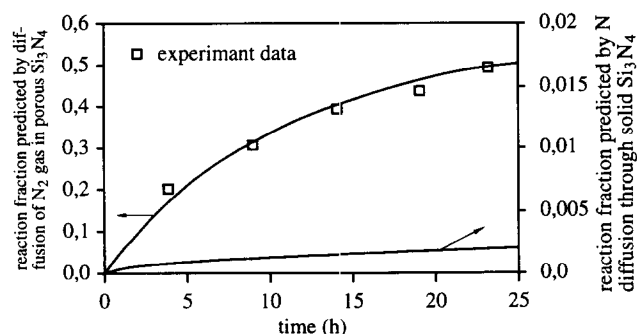

Fig. 3. Comparison of reaction rate through Knudsen diffusion of N_2 and through N diffusion in solid Si_3N_4 at 1200°C. Data used for calculation are shown in the table in Appendix B.

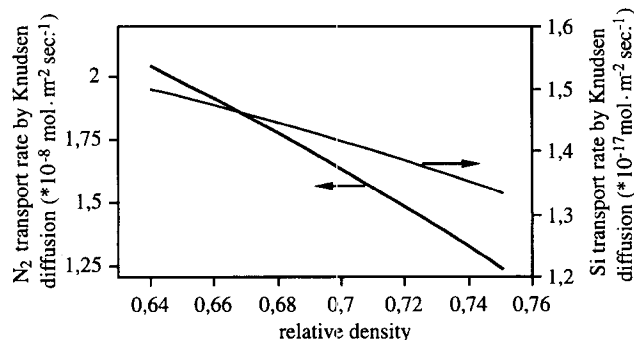

Fig. 4. Comparison of Knudsen diffusion of N_2 and that of Si vapour under the variation of relative density at 1200°C.

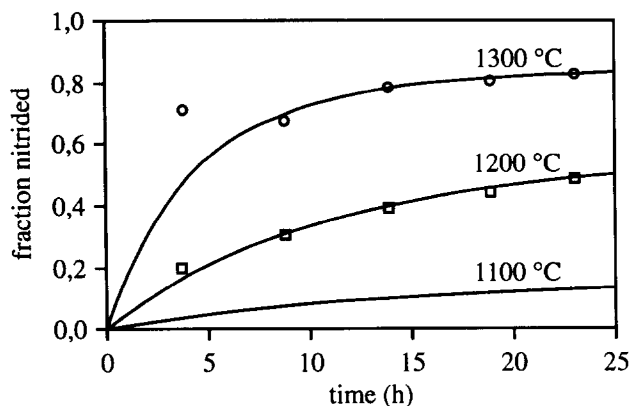

Fig. 5. Effect of temperature on the nitridation kinetics. The solid lines are results predicted by the present model and '○' and '□' indicate the experimental data respectively at 1300 and 1200°C from Ref. 16.

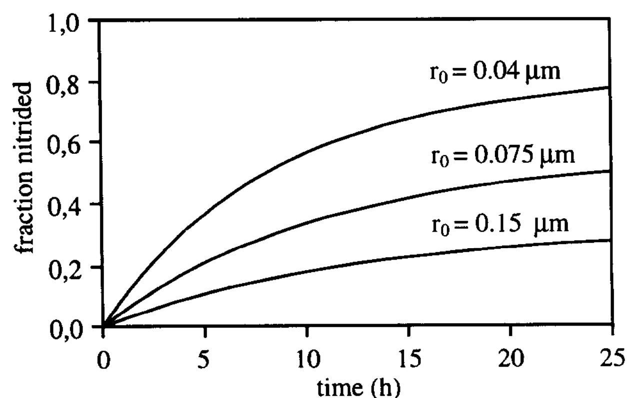

Fig. 6. Effect of particle size on the nitridation kinetics at 1200°C.

very beginning of the process. After a thin layer of nitride is formed on the particle surface, densification by sintering becomes more and more difficult while that by the reaction may dominate the overall densification rate. Both reaction and sintering mechanisms relate with diffusion which is largely dependent on the particle size, therefore the densification rate varies with the particle size as shown in Fig. 8.

The variation of effective surface area for reaction during the process was not considered until Ku and Gregory[1] who treated that by a computer simulation procedure. Based on Ashby's theory[14] the rate of volume change and the variation of the effective surface area due to reaction and sintering are included in this model in an analytic manner which gives a direct relation with the nitriding conversion.

Figure 9 indicates that both the relative density and effective surface area have nearly linear relationship with the conversion fraction, f. When around 80% reactant has been converted, the relative density increases by about 28% and the effective surface area is reduced by about 31% when the relative density reaches 0·82. This leads to an increasingly reduced rate of nitridation during the process. It can be seen from Figs 7–9 that there is still 18% porosity when 80% silicon has been converted. This means that the transport of reactants through the inter-particle pore may not be the hindered step at this reaction range. The effective surface area as a function of time, temperature and particle size is given in Figs 10 and 11.

There probably exist certain transportation routes for nitrogen and silicon, other than those shown in Fig 1. For example, sub-grain boundaries and dislocations in the Si_3N_4 shell may offer extra paths for nitrogen and silicon diffusion that contribute to the nitriding conversion, but it was found that the contributions from these extra paths are trivial, compared to the mechanisms listed in Fig. 1.

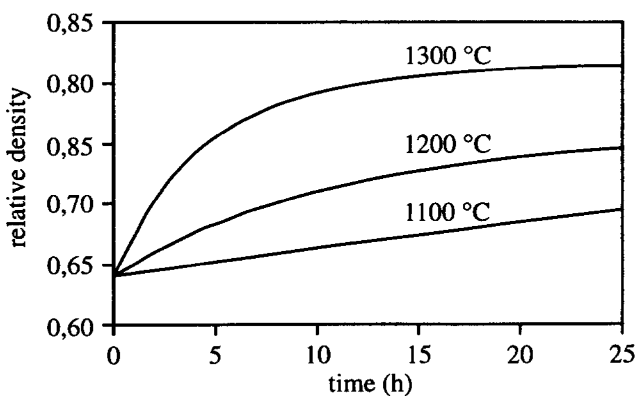

Fig. 7. Effect of temperature on the densification (r_0 = 0·0075 μm).

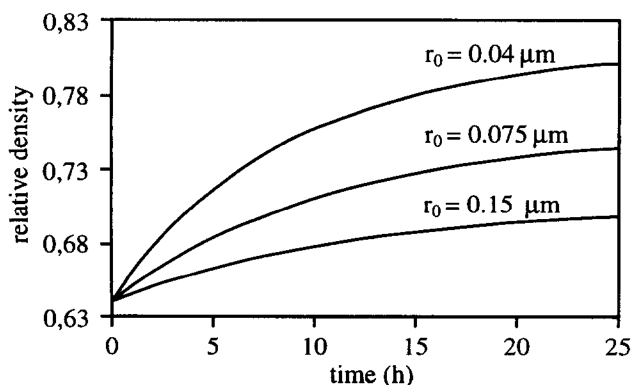

Fig. 8. Effect of particle size on densification at 1200°C.

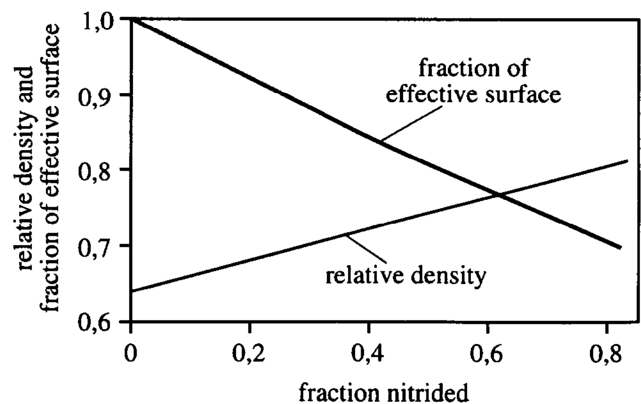

Fig. 9. Variation of relative density and effective surface as a function of conversion fraction at 1200°C.

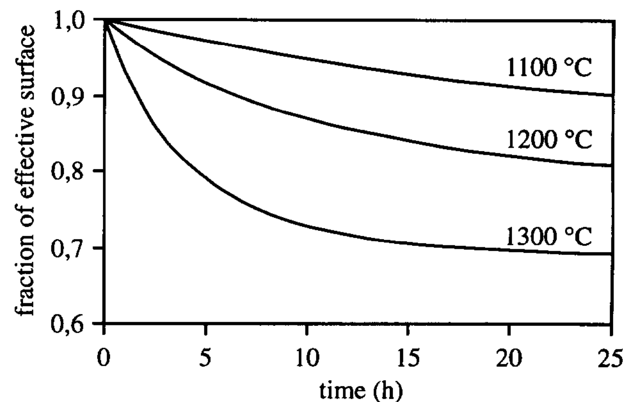

Fig. 10. Variation of effective surface area with time at different temperature (r_0 = 0·075 μm).

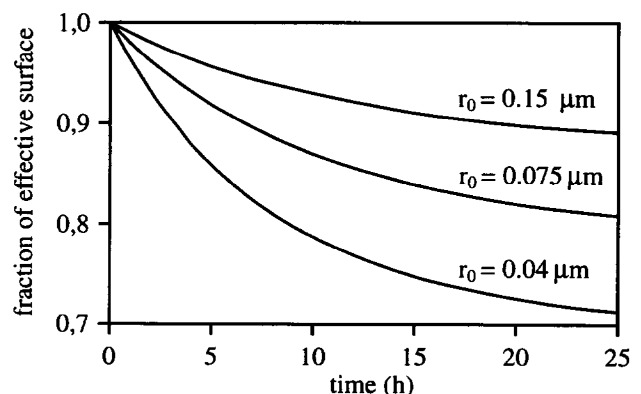

Fig. 11. Variation of effective surface area with time for different particle size (at 1200°C).

5 Summary

An analytical model for the kinetics of the RBSN process has been established. Preliminary study shows a satisfactory agreement between the theoretical and experimental data. The results suggest that the inward diffusion of the gaseous nitrogen through some channels in the Si_3N_4 shell (Knudsen diffusion) and reaction with silicon at the Si/Si_3N_4 interface is the dominant path for the RBSN process. The nitriding reaction via silicon evaporation and effusing outwards is relatively unimportant. Since the inter-particle pores have larger sizes than the pores formed in the Si_3N_4 shell and according to the densification behaviour estimated by this model, the transport of reactants through the inter-particle pores of the powder compact should not be the limiting step in the process.

It is impossible to describe such a complex process realistically by any simple analytical model. Instead a model based on multiple mechanisms and including more possible influences may provide meaningful predictions. The first step in developing such a model has been made by the method used in this work. Due to the nature of the present model, any new mechanism can be easily incorporated into it. Therefore it is instructive and has general significance for the kinetic study of any reaction bonded process.

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Appendix A

A1 Derivation of equation (3)

The diffusion equation in the case of the quasi-steady assumption is, in spherical coordinates, given by:

$$\frac{d}{dr}\left(r^2\frac{dC_N}{dr}\right) = 0 \tag{A1.1}$$

Solving eqn (A1.1) under the boundary conditions of $C_N = C_{NS}$ at $r = r_S$, and $C_N = C_{NC}$ at $r = r_C$ yields:

$$C_N = \frac{r_C C_{NC}(r_S - r) + r_S C_{NS}(r - r_C)}{r(r_S - r_C)} \tag{A1.2}$$

Using Fick's diffusion law, eqn (3) in the text is obtained.

A2 Relation between r_{ch} and r_p

The cross-section of the channel may not be uniform. Its radius is assumed to be an average size of the cross-section of the pores, i.e.:

$$\pi \cdot r_{ch}^2 = \frac{1}{r_p}\int_0^{\pi/2} \pi \cdot r_p^2 \cos^2\theta \cdot r_p \cos\theta \cdot d\theta \quad (A2.1)$$

By integration of eqn (A2.1), we have:

$$r_{ch} = r_p \cdot \sqrt{\frac{2}{3}} = 0{\cdot}82 \cdot r_p \quad (A2.2)$$

A3 Derivation of equation (7)

Concerning the diffusion of N_2, the diffusion flux for one particle is equal to:

$$\dot{M}_{N,3} = 4\pi \cdot r^2 \cdot \varepsilon_{SN} \cdot D_{N,K} \cdot \frac{\partial C_N}{\partial r} \quad (A3.1)$$

In a steady state, $\dot{M}_{N,3}$ should be independent of r, i.e.:

$$r^2 \cdot \frac{\partial C_N}{\partial r} = A \quad (A3.2)$$

where A is a constant. Integration of eqn (A3.2) from r_C to r_S gives:

$$\int_{r_C}^{r_S} dC_N = \int_{r_C}^{r_S} \frac{A}{r^2} dr$$

or

$$C_{Ng} - C_{NC} = -A \cdot \left(\frac{1}{r_S} - \frac{1}{r_C}\right) \quad (A3.3)$$

A can be solved from eqn (A3.3):

$$A = \frac{r_S \cdot r_C(C_{NG} - C_{NC})}{r_S - r_C} \quad (A3.4)$$

Combination of eqns (A3.2), (A3.4) with eqn (A3.1) yields eqn (7).

A4 Derivation of equation (12)

As derivation of eqn (3), the flux of silicon diffusion is,

$$J_5 = D_s \frac{r_S \cdot r_C}{r^2(r_S - r_C)} \cdot (C_{SS} - C_{SC}) \quad (A4.1)$$

where C_{SS} is the silicon concentration at the particle surface. The reaction rate per unit area at the surface of the particles is equal to,

$$J_6 = k_S C_{SS} \quad (A4.2)$$

Continuity requires:

$$4\pi r_S^2 f_S f_d(1 - \varepsilon_{SN}) J_5 = 4\pi r_S^2 f_S(1 - \varepsilon_{SN}) J_6 \quad (A4.3)$$

Combining eqns (A4.1), (A4.2) and (A4.3) yields eqn (12) in the text.

A5 Derivation of equation (27)

The consumption of silicon causes volumetrical decrease to the particle. In eqn (27), $\dot{M}_S A_S \rho_S^{-1}$ expresses the volume reduction of Si per second for a particle. Due to reaction, the volume increment per second for a particle is given by $\dot{M}_S A_{SN}[3\rho_{SN}(1 - \varepsilon_{SN})]^{-1}$. The net volume change per second for a particle is the difference between the two factors mentioned above, which from geometrical considerations should be equal to $4\pi r_S^2 \dot{r}$. Equation (27) is therefore confirmed.

A6 Derivation of equation (34)

Due to the reaction, the particles grow and intersect each other. The excess volume gained by the reaction must be redistributed over the free surface of the particles, leading to an incremental increase of the particle radius. This increment of r_S can be expressed as:[13]

$$\Delta r_S = \frac{4z_0(r_S - r_0)^2(2r_S - r_0) + \frac{c}{r_0}(r_S - r_0)^3(3r_S - r_0)}{12r_S[4r_S - 2z_0(r_S - r_0) - \frac{c}{r_0}(r_S - r_0)^2]} \quad (A6.1)$$

and the volumetric particle increment at the free surface due to Δr_S is:

$$\Delta V_r = \frac{4\pi}{3}\left[(r_S - \Delta r_S)^3 - r_S^3\right]\frac{S}{4\pi r_S^2} \quad (A6.2)$$

where S is the surface of a particle with radius r_S, reduced by the contact area between the particles and is given by:

$$S = 4\pi r_S^2 - 2\pi z_0 r_S(r_S - r_0) - c\pi\frac{r_S}{r_0}(r_S - r_0)^2 \quad (A6.3)$$

Solving eqns (A6.1)–(A6.3) and eqn (27) for $\dot{V}_r$, eqn (34) in the text is obtained.

A7 Derivation of equation (35)

Based on Ashby's theory of sintering,[14]

$$\dot{V}_S = \frac{4\pi\Omega Z\gamma(\delta D_b + \rho D_V)}{kT}\left(\frac{1}{\rho} - \frac{1}{\alpha}\right) \quad (A7.1)$$

where according to Helle's approximation,[14]

$$\left.\begin{aligned} Z &= 12D \\ \rho &= r_0(D - D_0) \\ k &= r_0 - \sqrt{D - D_0} \end{aligned}\right\} \quad (A7.2)$$

Substituting eqn (A7.2) into (A7.1) yields equation (35) in the text.

Appendix B

Data used for calculation

Symbol	*Value*	*Dimension*	*Ref*[a]
A_N	0·028	kg mol^{-1}	h
A_S	0·02806	kg mol^{-1}	h
A_{SN}	0·140	kg mol^{-1}	h
c	15·5	dimensionless	(15)
C_{Ng}	8(at 1473 K)	mol m^{-3}	N(h)
C^0_S	6×10^{-9}	mol m^{-3}	N(21)
C_{SC}	$8{\cdot}32 \times 10^4$	mol m^{-3}	N(h)
D_0	0·64	dimensionless	(15)
D_N	10^6 exp(−777000/RT)	m^2 s^{-1}	(6)
f_d	1	dimensionless	
k_c	$4{\cdot}4 \times 10^{19}$ exp(−661000/RT)	m s^{-1}	N(6)
k_g	0·109	m s^{-1}	N(22)
r_0	$7{\cdot}5 \times 10^{-8}$	m	N(16)
r_p	10^{-9}	m	N
z_O	7·5		(15)
ε_{SN}	0·1	dimensionless	N
ρ_s	2336	kg m^{-3}	h
ρ_{SN}	3187	kg m^{-3}	h

[a]h: handbook value. N: estimated by authors, basing on the data from literature (Ref. number)