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Nitridation Study of Reaction-Bonded Silicon Nitride *in situ* by High Temperature X-Ray Diffraction

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Abstract

The reaction-bonded silicon nitride (RBSN) nitriding process has been studied using a high temperature X-ray diffractometer (HT-XRD) under isothermal conditions in the temperature interval 1300–1400°C. With HT-XRD, the nitridation reaction and phases formed could be monitored almost instantaneously at temperature. The experimentally observed kinetics of the nitriding reaction were found to be in fair agreement with a theoretical model which predicts that the nitriding reaction occurs predominantly by Knudsen diffusion of nitrogen molecules through channels in a layer of growing Si_3N_4. However, no single rate law is likely to describe the whole nitridation process. Observation of the microstructure after nitridation indicates that the process occurs partly by reaction of Si vapour with nitrogen gas but that inward diffusion of nitrogen into particles also contributes significantly to the overall nitridation. The phase analysis showed that α-Si_3N_4 formation predominates over β-Si_3N_4 formation but the proportion of β-Si_3N_4 increases as nitridation continues. © 1997 Elsevier Science Limited.

Introduction

Reaction-bonded silicon nitride (RBSN), characterised by its excellent high-temperature mechanical and chemical properties, low thermal expansion and its moderate cost of production, is an important candidate for severe engineering applications and it has been an important member of the nitrogen ceramic family for decades. Much of the fundamental research devoted to RBSN has been related to the basic reaction process between silicon and nitrogen. Kinetic studies of the RBSN process consist of three aspects: (a) morphology of the nucleation and growth of the silicon nitride from silicon; (b) chemical reaction rates; (c) phase concentrations of the products. The subject of the nucleation and growth of silicon nitride has been addressed in several works;[1–4] a satisfactory description has still to be achieved. Many attempts have also been made to understand the nitridation kinetics both within silicon powder compacts and on bulk silicon.[4–8] However, reaction rates can vary by a factor of up to about one hundred even for seemingly similar conditions[4,8] due to the fact that a variety of factors influence the process, for example the heating profile and nitridation temperature, particle shape and size distribution, impurities in the starting powder, composition of the nitriding atmosphere, impurities from external sources such as the nitriding gases, crucible, furnace, etc.

Thermogravimetric analysis (TGA) has commonly been used to measure the reaction rates while X-ray diffraction analysis been used for phase composition measurement. The 'weight gain' measured by TGA includes in fact three parts: the real weight gain due to the conversion of silicon, the weight loss due to evaporation of silicon, and the weight gain or loss by the side reactions. Thus this method involves a degree of uncertainty since it is for example, very sensitive to the weight loss of silicon.[9] At 1350°C the vapour pressure of Si is 10^{-7} atm which results in an evaporation rate of silicon of 10^{-6} kg/m^2 s.[10] This implies a relatively high weight loss since the specimens used are usually only 200–500 mg. It has also been shown[11] that side reactions, for example the deposition of SiO_2 on to the thermal weight balance may cause up to 20–30% difference in the final conversion.

In most previous work the phase concentrations of α- and β-Si_3N_4 and other possible phases have usually been obtained by conventional XRD measurements at room temperature after cooling from the process temperature. Such an analysis necessarily includes changes occurring during firing

and cooling which may lead to large deviations particularly if the specimen is small.

The aim of the present work is to study *in situ* the nitridation kinetics of reaction-bonded silicon nitride by means of a high-temperature X-ray diffractometer (HT-XRD). With this technique the nitridation can be monitored practically continuously as it proceeds permitting a complete characterisation of the kinetics with relatively few isothermal heating cycles. The conversion rate and the phase concentration measured *in situ* by the integrated X-ray intensities are not so sensitive to the weight loss of silicon and the products formed by some side reactions and are therefore more reliable.

Experimental

The silicon powder used was produced by Kema-Nord Industrikemi AB, Ljungaverk, Sweden, with an impurity content as reported by the manufacturer in wt%: Fe = 0·07, Al = 0·07, Ca = 0·01, C = 0·06, O = 0·2–0·7 (depending on particle size). It was classified by wet sieving. The size distribution and morphology of the particles are shown in Fig. 1 and Fig. 2 respectively. The specimens for nitridation in the X-ray diffractometer were prepared by filling silicon powder in a boron nitride boat and pressing it by hand. The weight of specimen was around 200 mg.

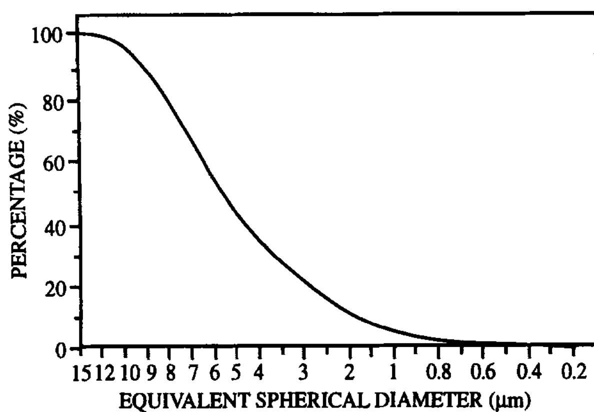

Fig. 1. Distribution of the silicon particle size.

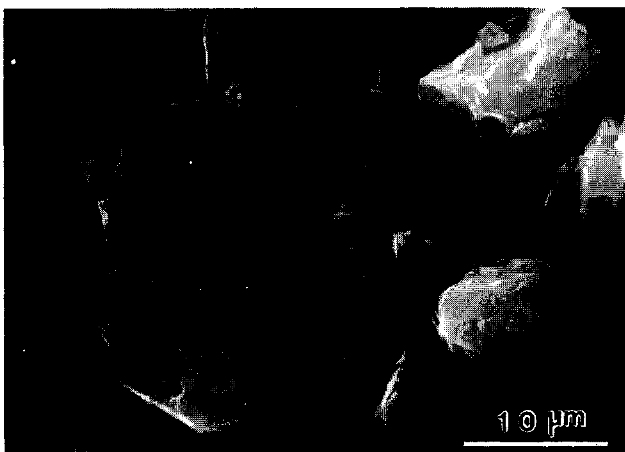

Fig. 2. SEM photograph of the silicon particles before nitridation.

The specimens were fired in the HT-XRD unit under flowing nitrogen that was gettered over copper. The heating element was made of graphite coated with silicon nitride to avoid carburisation of the samples. The temperature was ramped at a rate of 150°C/min to a constant nitriding temperature. The maximum deviation of the measured temperature was within ±5°C. Line intensities of Si, α- and β-Si_3N_4 were recorded using a high-temperature X-ray attachment based on a Philips PW-1710 automatic diffractometer. Cu K_α (50 kV, 30 mA) radiation with a graphite monochrometer was employed. The weight percent of Si and the intensity ratios for α- and β-Si_3N_4 were calculated by using the method described by Jack and Thompson.[12] The results of phase analyses by XRD were also checked on selected samples by quantitative metallography on polished sections. This was achieved by estimating the free Si content by point counting on optical micrographs and the porosity using an image analysis system attached to a scanning electron microscope (CAMSCAN). It can be noted that the X-ray penetration in silicon nitride for the experimental conditions used is estimated as approximately 60 μm i.e. several particle diameters.

Results

The progress of nitridation at different temperatures is shown in Fig. 3. The nitriding cycles at 1300 and 1325°C exhibited roughly linear dependence

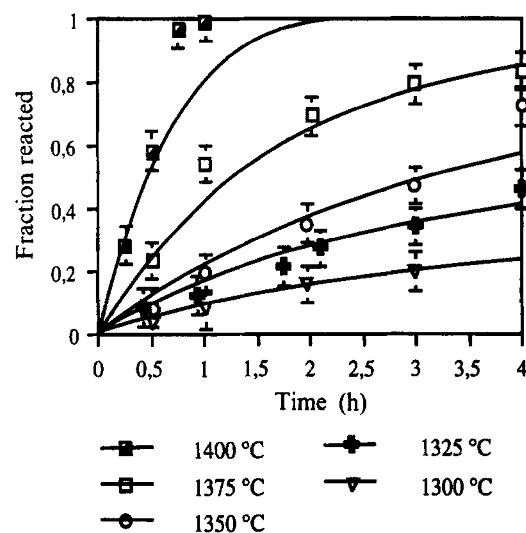

Fig. 3. Effect of temperature on nitridation kinetics measured in terms of fraction Si reacted. The solid lines are predicted by the theoretical model and the points show the experimental data.

throughout the isothermal treatment. This is consistent with the 'linear kinetics' stage proposed by Moulson[10] and explained by the existence of uncovered Si surface. In this stage the diffusion of reactants is not yet dominant. The nitridations between 1350 and 1400°C exhibited a less straightforward time dependence. However the decreasing rate at extended times reflects the fact that the unreacted silicon surface becomes obstructed by silicon nitride hindering the transport of silicon vapour and nitrogen to reaction sites so diffusion-controlled processes become more significant. At 1400°C the formation of SiC became apparent at half an hour when approximately 15–20% had formed. This was presumably due to reaction with carbon species originating from the heating element.

The ratios of α- and β-Si_3N_4 phases as measured by HT-XRD are shown in Fig. 4. This confirms the general tendency observed in earlier reports that the relative proportion of α-Si_3N_4 is higher during the early stages of nitridation, i.e. at lower temperatures and short nitridation times.

SEM micrographs of sample fracture surfaces observed after the isothermal runs are shown in Fig. 5. Approximate estimates of the corresponding phase proportions are included in the figure texts. Although all samples are characterised by the presence of a whisker mat filling the interparticle spaces, the observed microstructures indicate that a significant proportion of the reaction product remains in the form of granular particles with similar morphology to the original silicon. Up to 1375°C, the relative proportions of particles and whisker remain relatively constant and the particulate material seems to retain its original morphology even though at the higher temperatures significant conversion of Si to Si_3N_4 must have occurred in the particles. At 1400°C there is evidence of pore formation and break-up of particles.

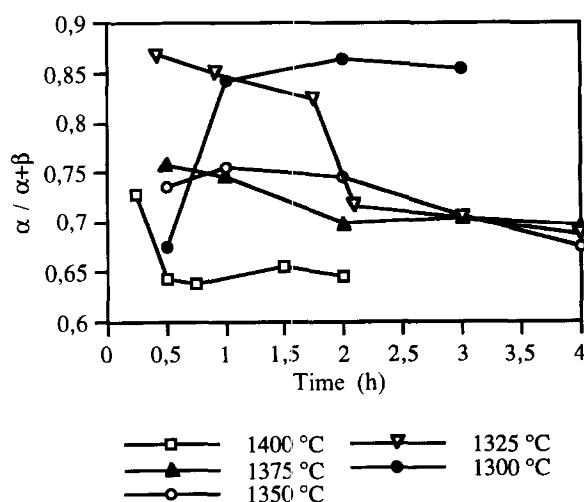

Fig. 4. The phase ratio measured at process temperatures by HT-XRD.

These observations are qualitatively consistent with the X-ray measurements of reaction kinetics and phase ratios if it is assumed that the whisker material is the α form of Si_3N_4 formed by reaction between Si vapour and molecular nitrogen as suggested by Jennings.[13] During the early stages of nitridation, Si vapour can be presumed to be readily available from uncovered Si surface. As nitridation proceeds, release of Si becomes increasingly restricted and β-Si_3N_4 formation becomes more significant. Since the particles retain the morphology of the original Si particles it must be assumed that the latter process must occur by transport of nitrogen through a nitride layer growing on the particles.

Discussion

A characteristic of the reaction-bonding process is that it occurs with little overall volume change of the powder compact in spite of the fact that the conversion of Si to Si_3N_4 involves a 22% volume increase. This implies that a proportion of Si must migrate out of the particles if unreasonable internal stresses are not to develop. This is consistent with the formation of interparticle nitride indicating the reaction of silicon vapour with molecular nitrogen. A further condition is that the outward migration must continue throughout the process even when the silicon surfaces are covered with nitride. An adequate outward migration cannot occur by solid state diffusion of Si through the nitride since this is prohibitively slow. A proposed mechanism that is partly supported by microstructural observation is that pores develop at the Si/Si_3N_4 interface thus creating fresh silicon surfaces; Si can then be released through breaks in the nitride layer.[13] The observations of this study are not fully consistent with this mechanism since it leads to a break-up of the original Si particle morphology whereas here the particle morphology remained undisturbed. An alternative explanation is that the nitride layer growing uniformly on the particles develops very fine channels or cracks permitting the Knudsen diffusion of Si vapour outwards while at the same time admitting nitrogen to the Si surface where surface adsorption and reaction to form β-Si_3N_4 can take place.[10,14] Since the vapour pressure of Si at typical nitridation temperatures is significantly lower than typical nitrogen pressures,[15] the inward diffusion of nitrogen is presumably much greater than the outward diffusion of Si vapour. This partly explains the increasing proportion of β formation as nitridation proceeds.

In the light of the above it is instructive to compare the experimental results with the theoretical

model development elsewhere.[14] and described briefly in the appendix, the predictions of which are included in Fig. 3. Assumptions of the model of significance to the present work are that the original silicon particles are spherical and of uniform size, that a nitride layer forms over the entire Si surface at the start of nitridation, that the nitride layer develops a porous structure with continuous channels the morphology and dimensions of which remain constant throughout the growth process and that a uniform temperature is maintained throughout the compact. For the purposes of calculation the channel diameter was assumed to be one tenth of the initial silicon particle size.

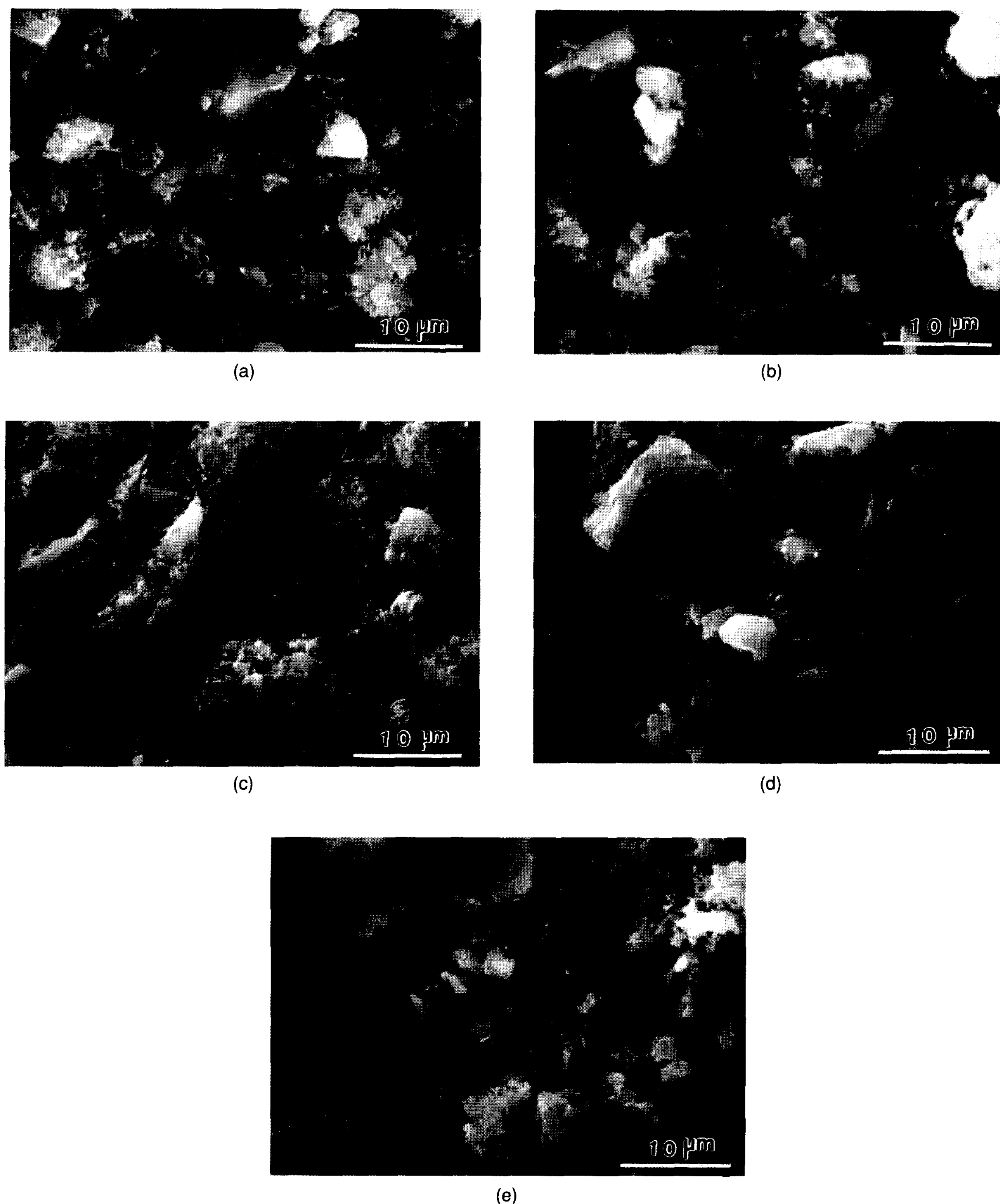

Fig. 5. SEM photograph of microstructure after nitridation at different temperatures. (a) after 3 h 1300°C (0·8 Si; 0·17 α-Si_3N_4; 0·03 β-Si_3N_4); (b) after 4 h at 1325°C (0·37 Si; 0·42 α-Si_3N_4; 0·21 β-Si_3N_4); (c) after 4 h at 1350°C (0·2 Si; 0·54 α-Si_3N_4; 0·26 β-Si_3N_4); (d) after 4 h at 1375°C (0·17 Si; 0·58 α-Si_3N_4; 0·25 β-Si_3N_4); (e) after 2 h at 1400°C (0·18 SiC; 0·53 α-Si_3N_4; 0·29 β-Si_3N_4).

Three possible reaction paths were considered, namely (i) diffusion of nitrogen inwards through the nitride layer, (ii) solid state diffusion of Si outwards through the layer, (iii) diffusion of silicon vapour outwards through the layer by Knudsen diffusion. For the relevant experimental conditions and with the above assumptions the model predictions are in good agreement with the magnitude of the observed reaction rates. It is to be noted, however, that the model predicts monotonically decreasing reaction rates whereas the experimental results for temperatures up to 1350°C suggest a more linear time dependence as has been proposed by Moulson[10] and assumed to be indicative of a non-covering nitride layer growth. However, considering the experimental scatter, the two types of growth kinetics are seen to be barely distinguishable and for extents of reaction beyond about 10%, a covering nitride layer seems to be a more reasonable assumption. A further apparent inconsistency is that the model predicts that the relative contributions to the overall reaction of paths (ii) and (iii) above are negligible, i.e. the process occurs predominantly by inward diffusion of molecular nitrogen by Knudsen diffusion. This is inconsistent with the need for simultaneous outward movement of silicon as discussed above. To meet this demand would require either a higher rate of transport of silicon, (e.g. via higher vapour pressure or higher diffusion constant) than that assumed in the model or an alternative transport mechanism. One alternative is that the high stresses generated in the nitride layer as it grows (tensile radial stress and compressive hoop stress) could cause it to buckle and be pushed out into the interparticle spaces, at the same time causing exposure of uncovered silicon surface. While plausible in the general case this explanation seems inconsistent with the experimental observation here that some grains retain morphology integrity throughout the nitridation process. Nevertheless, although the details of the mechanisms remain somewhat unclear it can be concluded that the inward diffusion of nitrogen through the reaction layer makes a significant contribution to the process.

Conclusions

High temperature X-ray diffraction was used successfully to monitor the nitridation of silicon powder compacts at temperature during isothermal treatments between 1300 and 1400°C. Both the rate of SiC conversion and the development of α- and β-Si_3N_4 were recorded.

The fair agreement of the prediction of the theoretical model with the magnitude of the reaction rates provides support for the conclusion that inward diffusion of nitrogen contributes significantly to the process.

The early stages of nitridation were dominated by α-Si_3N_4 formation but the proprtion of β-Si_3N_4 formation increased as nitridation continued. This observation and the fact that the original morphology of many silicon particles was maintained throughout nitridation led also to the conclusion that a process of inward Knudsen diffusion of nitrogen molecules through the growing reaction layer, makes a significant contribution to the nitridation process.

Acknowledgement

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Appendix

Concerning the multiple nitridation mechanisms in a nitriding process, the nitridation kinetics can be briefly summarised as:[14]

For a long cylindrical silicon powder compact under uniform and constant nitrogen concentration and isothermal condition, the amount of silicon consumption $_C M_S$ during time t can be expressed as:

$$_C M_S = \int_0^t {_C\dot{M}_S}\, dt = \frac{3}{4}\int_0^t \frac{R_S^2 L D}{r_S^3}\dot{M}_S dt \quad (1)$$

where the silicon consumption rate for the entire compact, $_C\dot{M}_S$ is given by:

$$_C\dot{M}_S = \frac{3}{4\pi}\int_V \dot{M}_S \frac{D}{r_S^3} dV = \frac{3}{4\pi}\frac{\dot{M}_S D V}{r_S^3} = \frac{3}{4}\frac{R_S^2 L D}{r_S^3}\dot{M}_S \quad (2)$$

where D is the instantaneous solidity of the powder compact defined as the ratio of the volume actually occupied by solid material to the volume of the powder compact, r_S is the instant radius of the particle, R_S and L are the outer radius and length of the compact, respectively. The consumption rate of silicon for one particle $\dot{M}_S$ is given by:

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

in which $\dot{M}_I$, $\dot{M}_{II}$ and $\dot{M}_{III}$ are the rates for three possible reaction paths given by:

(I) nitrogen transport inwards through nitride and reaction at the Si/Si_3N_4 interface.

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

(II) Solid state diffusion of silicon through nitride and reaction with nitrogen atoms at the outer surface of the particles.

$$\dot{M}_{II} = \frac{4\pi(1-\varepsilon_{SN})r_S^2 \cdot C_{SC}}{\frac{r_S(r_S - r_C)}{r_C \cdot f_S D_S} + \frac{1}{f_S \cdot k_C}} \quad (5)$$

(III) Silicon evaporation and reaction in the gas phase.

$$\dot{M}_{III} = 4\pi r_S^2 C_S^0 \cdot \left[\frac{4\pi r_S^2}{r_C^2 \cdot \varepsilon_{SN}\sqrt{\frac{8\pi RT}{A_S}}} + \frac{r_S(r_S - r_C)}{r_C \cdot \varepsilon_{SN} D_{S,K}} + \frac{1}{f_S(1-\varepsilon_{SN})k_S}\right]^{-1} \quad (6)$$

where f_S is the fraction of effective surface of a particle for diffusion, k_g is the mass transfer coefficient between the gas and solid phase at the particle surface, ε_{SN} porosity in the Si_3N_4 layer, C_{Ng} is the concentration of nitrogen in the nitriding atmosphere, r_C radius of silicon core, f_d adjustable constant, D_N diffusion coefficient of nitrogen in solid silicon nitride layer, $D_{N,K}$ Knudsen diffusion coefficient of nitrogen molecule, and k_C rate constant of reaction at the Si/Si_3N_4 interface, C_{SC} concentration of Si being equilibrium to that in the Si_3N_4 at the interface, D_S diffusion coefficient of silicon in solid silicon nitride layer, C_S^0 concentration of Si corresponding to the equilibrium pressure of Si at temperature T. R is the gas constant, A_S molecular weight of silicon, $D_{S,K}$ Knudsen diffusion coefficient of Si vapour, and k_S rate constant of reaction at the outer surface of the Si_3N_4. The values adopted for these constants are given in Ref. 14.