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Kinetics of α- and β-Si_3N_4 formation from oxide-free high-purity Si powder

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Available kinetic data for the nitridation of high-purity oxide-free Si powder are analysed. The analysis suggests that the α- and β-phases of Si_3N_4 are formed by separate and parallel reaction paths, and kinetic expressions for their formation are reported. The formation of the α-phase follows first-order kinetics, while the β-phase is formed by a phase-boundary-controlled rate law. These conclusions are consistent with other kinetic and micrographic analyses reported in the literature.

1. Introduction

Silicon nitride, Si_3N_4, is an advanced ceramic material, suitable for structural applications at high temperatures. A good combination of high-temperature strength, thermal shock resistance, and resistance to oxidation and erosion, makes silicon nitride an ideal material for high-temperature structural applications such as gas turbines, turbocharger rotors, and diesel engine components. In these applications, densified silicon nitride is required. Such material is prepared by densification of either silicon nitride powder or of reaction-bonded silicon nitride (RBSN) compacts. The silicon nitride powder or RBSN monolithic bodies can be prepared in a variety of ways, a common method being nitridation of Si in temperature range 1200–1400 °C. It is desirable to have a high α/β-Si_3N_4 phase ratio in the silicon nitride powder or in RBSN, because the $\alpha \rightarrow \beta$ phase transition during the post-sintering step (~ 1700–1800 °C) enhances the densification process, and leads to a microstructure which results in high mechanical strength and improved fracture toughness as a result of the interlocking effect of the β-Si_3N_4 grains. Excellent recent reviews of the thermodynamics, preparation, properties and applications of silicon nitride are available [1–3].

In spite of the importance of silicon nitride, the mechanism and kinetics of silicon nitridation are not well understood. Along with temperature, many other factors – such as purity and particle size of the starting silicon powder, presence and amount of metallic impurities, pretreatment conditions, nitriding gas composition – significantly influence the nitridation process in terms of microstructural development and rate of silicon nitride production. Of particular interest in this paper are the kinetics of α- and β-Si_3N_4 phase development under isothermal conditions where no silicide or silicate melts are present.

In this context, Rahaman and Moulson [4] have presented kinetic data for the relative rates of α- and β-Si_3N_4 formation from high-purity Si powder, which was first deoxidized by pretreatment in H_2 to remove the native silica layer (~ 3 nm thick) inherently present on Si powder, and then nitrided at 1623 K in a 95% N_2–5% H_2 gas mixture (see Fig. 2 of [4]). While they analysed their samples for α/β phase ratio development, along with the corresponding microstructure of fracture surfaces that resulted from the various pretreatment conditions and nitriding atmospheres, they did not attempt to elucidate the reaction kinetics. In this light, Rossetti and Denkewicz [5] have recently provided an analysis of the relative rates of α- and β-Si_3N_4 phase formation. However, there are some difficulties in their analysis. We first identify the source of these difficulties, and then present an alternative analysis of the reaction kinetics.

2. Kinetic analysis and results

Rossetti and Denkewicz [5] envision silicon nitridation to proceed by two parallel reaction pathways, one producing α-Si_3N_4 and the other leading to β-Si_3N_4, and represented the kinetics by

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

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

where ϕ_α and ϕ_β represent the normalized conversions of Si to α- and β-Si_3N_4, respectively, and k_α and k_β are the rate constants. Thus for example, ϕ_α is the conversion of Si to α-Si_3N_4 at time, t, divided by the final conversion of silicon to α-Si_3N_4. The initial conditions (ICs) for these equations are given by

$$\text{at } t = 0, \quad \phi_\alpha = 0, \quad \phi_\beta = 0 \quad (3)$$

Equation 1 implies that the formation of α-Si_3N_4 can be viewed as a first-order reaction, while Equation

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2 arises from a phase-boundary-controlled reaction which results in a constant velocity movement of the reaction interface in a particle of spherical geometry. Upon comparison with the experimental data of Rahaman and Moulson [4], Rossetti and Denkewicz [5] found the best fit values of the rate constants to be

$$k_\alpha^{\mathrm{i}} = 3k_\alpha = 1.0 \times 10^{-3}\,\mathrm{s}^{-1},$$
$$k_\beta = 1.68 \times 10^{-4}\,\mathrm{s}^{-1} \qquad (4)$$

Equations 1 and 2, along with the ICs of Equation 3, can be integrated analytically to give

$$-\ln(1 - \phi_\alpha) = 3k_\alpha t \qquad (5)$$
$$1 - (1 - \phi_\beta)^{1/3} = k_\beta t \qquad (6)$$

which describe the evolution of ϕ_α and ϕ_β with time, t. Eliminating t between Equations 5 and 6 gives

$$-\frac{1}{3k_\alpha}\ln(1 - \phi_\alpha) = \frac{1}{k_\beta}[1 - (1 - \phi_\beta)^{1/3}] \qquad (7)$$

which provides a relation between ϕ_α and ϕ_β. For the numerical values of k_α and k_β given by Equation 4, this relationship is shown in Fig. 1. Note that time t is a parameter along the curve; for any point on the curve, the corresponding value of t can be obtained equivalently from Equations 5 or 6. In Fig. 1, the ϕ_α versus ϕ_β relationship obtained from the experimental curves of Rahaman and Moulson [4] is also shown for comparison. As can be observed, the experimental values are represented well by Equation 7.

Upon further consideration of Equation 6, an interesting observation can be made. At $t = t_{\mathrm{cr}} = 1/k_\beta$, $\phi_\beta = 1$, i.e. no further conversion of Si to β-$\mathrm{Si_3N_4}$ occurs for $t \geqslant t_{\mathrm{cr}}$. This is a mathematical consequence of the specific model adopted for β-$\mathrm{Si_3N_4}$ formation, which as noted above, implies a movement of the reaction interface at constant velocity. For k_β given by Equation 4, t_{cr} is readily computed to be 1.65 h, which also compares favourably with the experimental data [4].

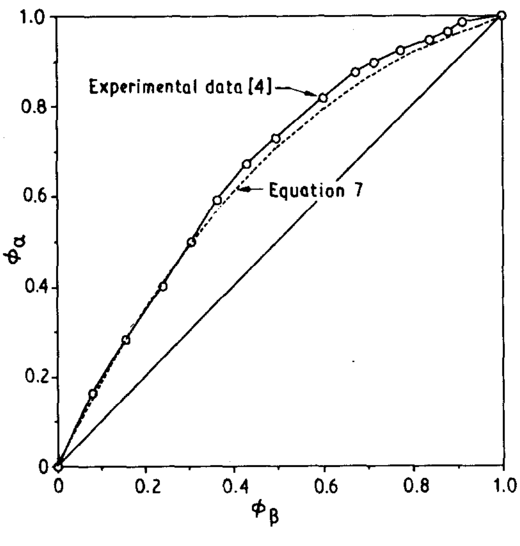

Figure 1 Plot of the normalized conversion of Si to α-$\mathrm{Si_3N_4}$ versus the normalized conversion to β-$\mathrm{Si_3N_4}$, as predicted by Equation 7. Experimental data taken from Fig. 2 of Rahaman and Moulson [4]. The 45° line represents the condition for which ϕ_α equal to ϕ_β for all time, t.

A quantity of considerable interest is the α/β-$\mathrm{Si_3N_4}$ phase ratio, and its evolution with time. Let us denote the final conversion of Si to α- and β-$\mathrm{Si_3N_4}$ by Φ_α and Φ_β, respectively. Then by definition, the conversion of Si to α-$\mathrm{Si_3N_4}$ at time t is $\phi_\alpha\Phi_\alpha$ and to β-$\mathrm{Si_3N_4}$ is $\phi_\beta\Phi_\beta$. The integrated α/β-$\mathrm{Si_3N_4}$ phase ratio at time t is thus given by

$$R = \frac{\phi_\alpha\Phi_\alpha}{\phi_\beta\Phi_\beta} \qquad (8)$$

and the overall conversion of silicon is

$$\phi = \phi_\alpha\Phi_\alpha + \phi_\beta\Phi_\beta \qquad (9)$$

It is in the evaluation of R, that the analysis of Rossetti and Denkewicz [5] has several difficulties. These authors develop an expression for $\mathrm{d}\phi_\alpha/\mathrm{d}\phi_\beta$, by dividing Equation 1 by Equation 2, but write it incorrectly as $\mathrm{d}R/\mathrm{d}\phi$ instead (Equation 10 [5]). Furthermore, while analysing this expression, they make the assumption that $\phi_\alpha \approx \phi_\beta \approx \phi$. This assumption can cause a substantial error which can be understood by examining Fig. 1. If $\phi_\alpha = \phi_\beta$, then the ϕ_α versus ϕ_β relationship would be given by the 45° line, and not by the actual curves shown. Finally, they used an incorrect value of k_α in their Equation 14 in order to obtain R at full conversion of Si (i.e. $\phi = 1$); this fortuitously gave $R(\phi = 1) = 4.46$, a value quite close to the experimental value of $R(\phi = 1) = 4.76$ (i.e. ratio of $\Phi_\alpha = 0.81/\Phi_\beta = 0.17$).

We can avoid these difficulties, and directly obtain an R versus ϕ relationship. This can be done by choosing a value of ϕ_α (or ϕ_β) between 0 and 1, obtaining the corresponding values of time t and ϕ_β (or ϕ_α) from Equations 5 and 6 (or 6 and 5), respectively, and then evaluating R and ϕ from Equations 8 and 9, respectively, with the knowledge that from the experimental data [4], $\Phi_\alpha = 0.81$ and $\Phi_\beta = 0.17$. Following this procedure gives the curve labelled 1 in Fig. 2, where curve 2 calculated from the

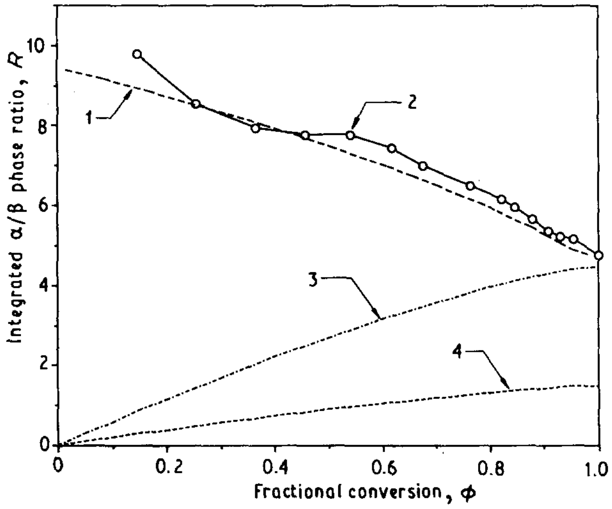

Figure 2 Plot of the integrated α/β phase ratio, R, as a function of the overall fractional conversion, ϕ. Curve 1 represents the functionality as predicted by Equations 8 and 9, using ϕ_α and ϕ_β calculated from Equations 5 and 6, respectively. Curve 2 shows the experimental data of Rahaman and Moulson [4]. Curves 3 and 4 represent the predictions based on Equation 14 of Rossetti and Denkewicz [5]: $k_\alpha = 1.0 \times 10^{-3}\,\mathrm{s}^{-1}$ (actual value used, shown by Curve 3) and $k_\alpha = 0.33 \times 10^{-3}\,\mathrm{s}^{-1}$ (correct value, shown by Curve 4).

experimental data is also shown. The two curves match favourably. In Fig. 2, predictions following Equation 14 of Rossetti and Denkewicz [5] are also shown, with the value of $k_\alpha = 1.0 \times 10^{-3}\,\mathrm{s}^{-1}$ used by them (curve 3), and the value ($k_\alpha = 0.33 \times 10^{-3}\,\mathrm{s}^{-1}$) which should have been used instead (curve 4). It is clear that neither of them is a satisfactory representation of the trend found experimentally.

As noted above, curves 1 and 2 of Fig. 2 match well. However, a practical problem is that curve 1 requires an a priori knowledge of Φ_α and Φ_β. At least one aim of determining reaction kinetics is to be able to predict the final conversions Φ_α and Φ_β. Thus we are led to the conclusion that representing silicon nitridation kinetics by Equations 1 and 2, which involve normalized Si conversions to α- and β-$\mathrm{Si_3N_4}$, is not appropriate and some alternative approach needs to be developed.

The power-law model provides such an alternative. In this model, we again describe silicon nitridation by two parallel reaction pathways, but represent the kinetics this time by

$$\frac{dx_\alpha}{dt} = \bar{k}_\alpha [1 - x_\alpha - x_\beta]^{n_\alpha} \qquad (10)$$

$$\frac{dx_\beta}{dt} = \bar{k}_\beta [1 - x_\alpha - x_\beta]^{n_\beta} \qquad (11)$$

where x_α and x_β represent the fractional conversions of Si to α- and β-$\mathrm{Si_3N_4}$, respectively; n_α, n_β are the reaction orders, and $\bar{k}_\alpha$, $\bar{k}_\beta$ are the reaction rate constants. The quantity $(1 - x_\alpha - x_\beta)$ represents the fraction of unreacted Si remaining at time t. The ICs for Equations 10 and 11 are

$$\text{at } t = 0, \quad x_\alpha = 0, \quad x_\beta = 0 \qquad (12)$$

Equations 10 and 11 cannot be integrated analytically, so the following procedure was adopted to obtain the kinetic parameters (i.e. $\bar{k}_\alpha$, $\bar{k}_\beta$, n_α and n_β). For various values of t, values of conversions x_α and x_β were read from Fig. 2 of Rahaman and Moulson [4]. In order to obtain the corresponding values of instantaneous rates dx_α/dt and dx_β/dt, the x_α–t and x_β–t curves were fit with separate fifth-degree polynomials in t (both fits had least squares correlation coefficients > 0.999), which yielded an accurate and convenient method for differentiating with respect to time, t. From Equation 10

$$\ln\left[\frac{dx_\alpha}{dt}\right] = n_\alpha \ln[1 - x_\alpha - x_\beta] + \ln \bar{k}_\alpha \qquad (13)$$

thus a plot of $\ln[dx_\alpha/dt]$ versus $\ln[1 - x_\alpha - x_\beta]$ gives a straight line with the slope equal to the reaction order, n_α. The same procedure was repeated for Equation 11, to give n_β. The values of n_α and n_β fit by least squares analysis were 1.20 and 0.56, respectively. Furthermore, because n_α was close to 1, its value was fixed as 1, and the corresponding least squares fit value of $\bar{k}_\alpha$ (correlation coefficient = 0.996) was obtained as shown in Fig. 3a to be $2.87\,\mathrm{h}^{-1}$. The value of n_β, on the other hand, was close to both 1/2 and 2/3. Thus both $n_\beta = 1/2$ and 2/3 were tried, and $n_\beta = 1/2$ was selected because it gave a better fit (correlation coefficient = 0.996); the corresponding value of $\bar{k}_\beta$ as shown in Fig. 3b was $0.331\,\mathrm{h}^{-1}$.

With these kinetic parameters at hand, the reaction kinetics given by Equations 10 and 11 are fully known. In order to provide a final comparison with the experiment, Equations 10 and 11, along with the ICs given by Equation 12, were integrated numerically using a fourth-order Runge–Kutta technique [6]. The calculated values of x_α, x_β and total conversion ($x_\alpha + x_\beta$) are shown in Fig. 4, and demonstrate a good match with the experimental data.

3. Discussion

The above analysis indicates that the kinetic data of Rahaman and Moulson [4] can be fitted consistently

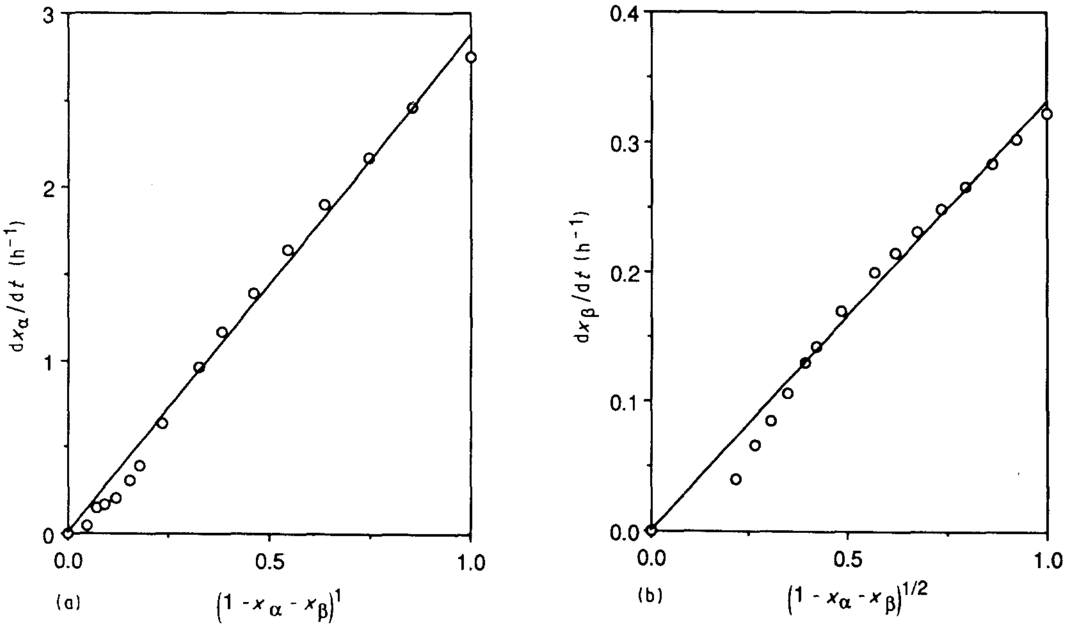

Figure 3 Least squares fit for determination of the power-law model reaction rate constants, (a) $\bar{k}_\alpha$ and (b) $\bar{k}_\beta$, based on Equations 10 and 11, respectively. The reaction orders were fixed at (a) $n_\alpha = 1$ and (b) $n_\beta = 0.5$, as determined by a preliminary least-squares analysis.

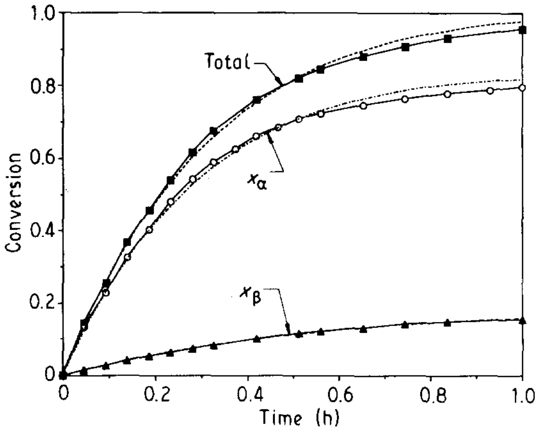

Figure 4 Conversion of Si to the α- and β-silicon nitride phases, as a function of time. Predicted values were obtained by a numerical solution of Equations 10 and 11. Experimental data taken from Fig. 2 of Rahaman and Moulson [4]. Predicted values; (– –) $x_\alpha + x_\beta$, (–·–) x_α, (– – –) x_β. Experimental values: (■) $x_\alpha + x_\beta$, (○) x_α, (▲) x_β. $n_\alpha = 1$, $n_\beta = 0.5$.

and adequately with a power-law model, where the reaction orders for α- and β-Si_3N_4 formation are 1 and 1/2, respectively. The analysis of models for solid state reactions has been discussed previously in the literature [7, 8]. A kinetic equation of first-order results when the rate-limiting step is a nucleation process, and when there is equal probability of nucleation at each active site [8]. Similarly, orders of 1/2 and 2/3 result from phase-boundary-controlled reactions for cylindrical and spherical-shaped particles, respectively. In the case of a gas–solid reaction, we can envision the reacting particle to be surrounded by the product layer, through which the reacting gas diffuses and reacts with the unreacted core. When diffusion through the product layer is fast as compared with the reaction, then the reaction occurs at a sharp interface between the product layer and the unreacted core, and the radius of the unreacted core shrinks at a constant rate. In the chemical engineering literature, the phase-boundary control is often referred to as a shrinking-core model [9, 10].

Based upon kinetic and SEM analyses, mechanisms for the formation of α- and β-Si_3N_4 have been discussed in the literature. The formation of the fine-grain matte-like structure for the α-phase is generally accepted to occur by chemisorption of N_2 on to the Si surface, followed by formation and growth of the nitride nuclei [2, 11]. A reaction order equal to 1 for α-Si_3N_4 suggests that the step involving nucleation of the nitride is rate controlling.

Similarly, in the absence of a liquid phase, β-Si_3N_4 is formed by the reaction of N_2 and Si, with N_2 diffusing through the solid product silicon nitride. The diffusion of N_2 through the large hexagonal tunnels in the β-crystals to the Si–Si_3N_4 interface is relatively fast, and reaction at the interface is expected to be the rate-limiting step [2].

In the light of the above discussion, the kinetic analysis of the present work appears to be consistent with the mechanistic details of the formation of α- and β-phases of silicon nitride reported previously in the literature. Because the kinetic data of Rahaman and Moulson [4] were limited to one temperature (1623 K), it was not possible to obtain activation energies for the rate constants. Experiments to obtain these, as well as to assess the influence of starting Si particle size, are currently in progress in our laboratory.

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