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A THERMOANALYTICAL STUDY OF THE ALPHA AND BETA FORMS OF SILICON NITRIDE

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ABSTRACT

The process of formation, some thermochemical properties and the behaviour of the α- and β-forms of silicon nitride in oxidizing and inert atmosphere were studied using TG–DTG–DTA techniques in the range 25–1600 °C, X-ray diffractometry and IR spectrophotometry.

INTRODUCTION

The silicon nitride phases have been established[1-4] to exist in two different forms designated as α- and β-silicon nitride. Both these forms are hexagonal[5]. Subsequent structure determinations[6] indicate that only the β-form is a true silicon nitride having the formula Si_3N_4. The α-form has been shown to be an oxynitride with unit cell contents $Si_{11.5}N_{15}O_{0.5}$ having a range of homogeneity (1.95–2.85 w/o O)[7]. The thermodynamic measurements in the system Si–N–O at low oxygen partial pressures ($p_{O_2} \approx 10^{-20}$ atm) as well as direct chemical analysis seem to confirm this conclusion[8].

In preparing these phases silicon or silicon–iron alloys are usually treated at temperatures above ca. 1200 °C or 600 °C, respectively, with nitrogen gas or ammonia. Since oxygen is present frequently in the nitriding atmospheres used the mixtures of α- and β-forms are usually obtained as primary products. The α-form may be converted to β on prolonged heating in nitrogen at temperatures above ca. 1450 °C[1-3]. No $\beta \rightarrow \alpha$ conversion has been observed. The $\alpha:\beta$ ratio in the nitride phases formed is indicated to be a function not only of the thermodynamic parameters but, to a high degree, of the kinetic factors also, such as inter alia the presence of excess silicon[1], the oxygen supply or the appearance of SiO(g)[6, 8]. The influence of the state of a very pure Si (l or s) and of the atmosphere in the nitridation kinetics is demonstrated[9].

The silicon nitride phases are very useful as multipurpose refractories. Also, they frequently appear as the second phase constituents in the iron matrix improving the mechanical properties of steels.

The present work has been undertaken in order to study the process of formation of silicon nitride phases from the commercial Si powder and N_2 ($p_{N_2} = 1$ atm) at

25–1600°C. Another aim is to examine some thermochemical properties of the phases formed and their behaviour in oxidizing and inert atmosphere. Thermal analysis techniques (TG–DTG–DTA) are employed. The ultimate aim is to use the results obtained in studying, with the aid of the same techniques, the second phases of the silicon nitrides in steels.

EXPERIMENTAL

The thermochemical measurements were made using a micro-thermobalance (Mettler) equipped with DTG and DTA units. The main features of the experiments were as already described[10, 11].

The characteristic parameters of the runs were as follows: silicon powder (purity: 97.5%, main impurity constituents: Fe, Co, Ni, Cu, grain size: 5–50 μ); the gases used: N_2(SR), Ar(SR), air, O_2, Ar + O_2 (p_{O_2} = 0.20 atm); gas flow: ca. 6–10 l h^{-1}.

The activity of oxygen in the N_2 and Ar gas used was tested at the gas flows given above. Iron powder was heated at constant temperatures between 800–1200°C. A constant weight gain per unit time was obtained which corresponded to 7–10 ppm oxygen in these gases. The specimens were examined using X-ray diffractometry and IR spectrometry.

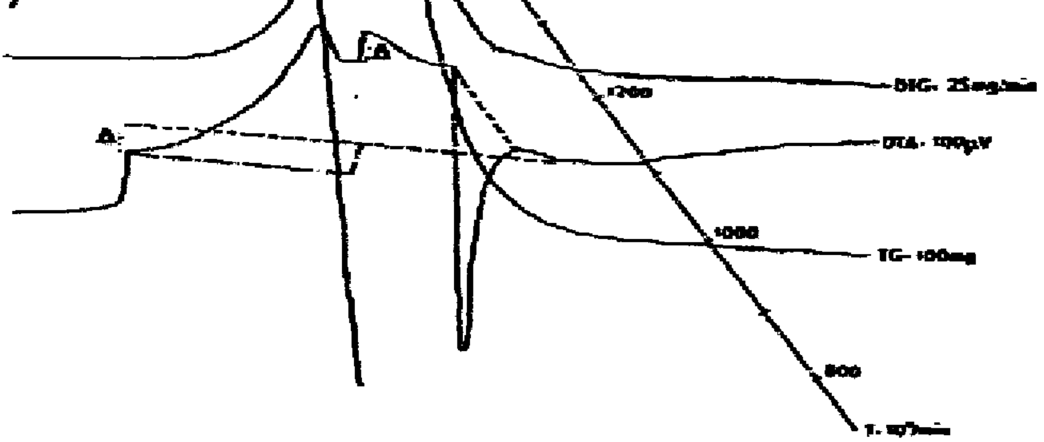

Fig. 1. Thermogram obtained in nitriding the Si powder in N_2(g) in the range 25–1600°C at 10° min^{-1}.

RESULTS AND DISCUSSION

Preparation and properties of the silicon nitride phases

A thermogram obtained on treating the Si powder (ca. 300 mg; alumina crucible) in N_2 gas between 25 and 1600°C at 10° min^{-1} is shown in Fig. 1. The departure of the TG-curve indicating the initiation of nitride formation may be observed at ca. 965°C. At 1220–1230°C the weight derivative (DTG) starts to increase more distinctly and the DTA curve displays an exothermal departure. This shows that the reaction between the silicon used and N_2(g) starts to occur rapidly at this point. At 1350°C an endothermal DTA peak appears which is due to the melting of the Si specimen. When making a run with the same sample amount in pure Ar(g) the DTA endothermal deflection is observed at 1310°C. This indicates that a melt phase appears already far below the melting point of pure Si (1410–1430°C)[12,13]. The solubility of the appearing metal impurities (ca. 2.5 w/o) in Si is found to be negligible[13]. A consideration of the phase diagrams Si–Me (Me = Fe, Co, Ni, Cu)[13] thus suggests that the impure Si used exists in the two-phase region of Si(s) and a melt phase within a large temperature interval below the melting point of pure Si. On approaching this melting point the relative amount of melt increases giving rise to the early endothermal DTA line deflection. In N_2(g) this deflection appears at a higher temperature (1350°C) since it is superimposed on the exothermal DTA peak due to nitride formation.

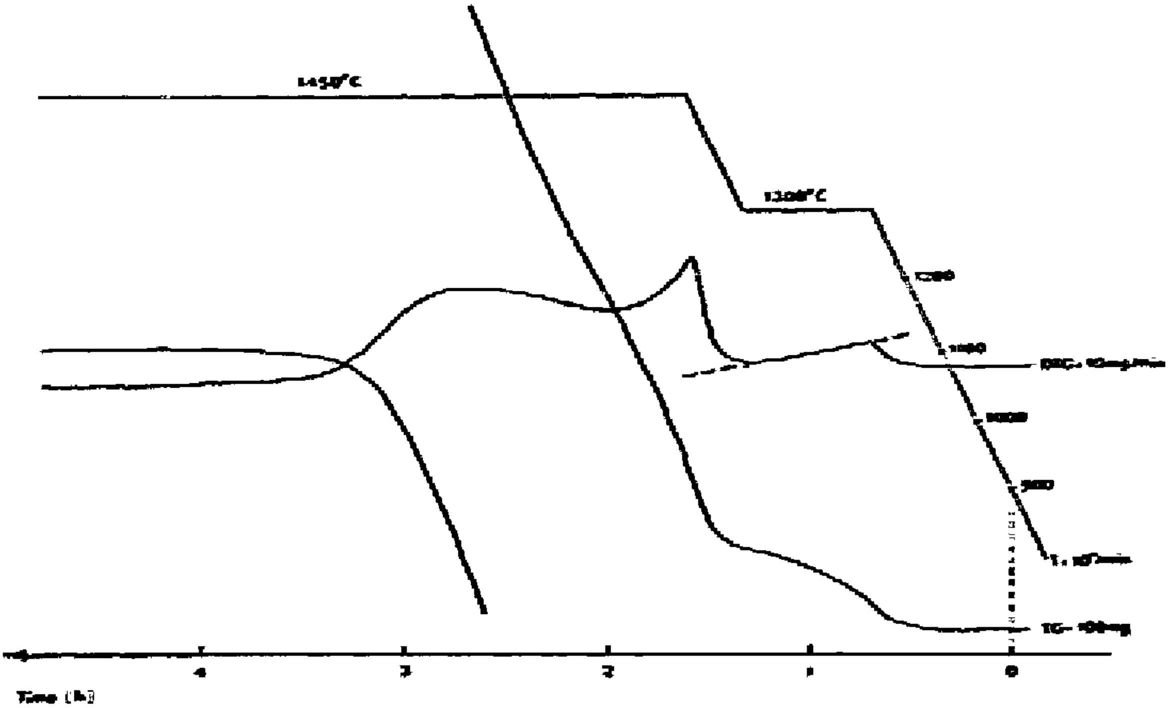

Fig. 2. TG–DTG curves obtained in nitriding the Si powder at 1300 and 1450°C.

During the melting process the reaction rate (DTG) is seen to be increased significantly. The rate starts increasing at ca. 1380 °C. At 1550 °C a further increase in the reaction rate is noted but the maximal rate is not attained until ca. 5 min after reaching the constant temperature (1600 °C). The DTA exothermal maximum is shifted considerably from that of DTG. The reason is probably the high thermal resistivity of the specimen and the walls of the Al_2O_3 crucible at this temperature.

The DTG curve is substantially stabilized after ca. 45 min at 1600 °C. The nitrogen uptake then amounts to 89% of that expected for the formation of β-Si_3N_4. The reaction rate is then very slow corresponding to ca. 1% conversion per hour. The impurity metals present do not form nitrides at p_{N_2} = 1 atm. They may enrich themselves in the Si melt phase, thus decreasing the rate of silicon nitride formation.

The nitriding process may be interrupted after the completion of melting as indicated by the endothermal peak. After cooling, the specimen appears as a homogeneous mixture of the grains of Si phase and nitride phase. This shows that, on melting, silicon does not form a continuous melt phase but appears rather as droplets homogeneously distributed within the nitride phase.

Figure 2 shows the TG–DTG curves obtained on nitriding the Si powder (ca. 250 mg) at constant temperatures of 1300 and 1450 °C, the heating rate being 10° min^{-1}. At 1300 °C (45 min: ca. 10% of the total weight gain) the weight derivative (DTG) appears to fall off linearly.

On increasing the temperature to 1450 °C the melting point of Si (1410–1430 °C) is passed. The reaction rate is shown to increase rapidly above ca. 1380 °C where the amount of melt phase presumably becomes significant. After ca. 20 min at the constant temperature the N_2 uptake is seen to be "self-accelerated" and a local DTG maximum appears. The heat produced by the nitride formation is carried away very sluggishly at these high temperatures, cf. the DTA–DTG curves in Fig. 1. The temperature within the sample may thus be raised far above 1450 °C and the reaction rate is then increased.

The enthalpy (ΔH_f) of nitride formation from the DTA peak area (Fig. 1) has been estimated considering only the reaction

$$3\,Si(s + l) + 2\,N_2(g) \rightarrow \beta\text{-}Si_3N_4(s)$$

The X-ray analysis has shown the β-form to predominate at 1600 °C. The enthalpies and free enthalpies of the α- and β-forms, moreover, appear to be very similar[8, 14, 15]. No significant error is thus introduced as compared to that involved in the DTA determination.

As indicated in Fig. 1 the base lines for the DTA responses are approximated by the dotted lines. The DTA base line corresponding to the response for the nitride formation is displaced by approximately 5 µV (Δ) on reaching the constant temperature. This shift occurs as a result of interrupting the linear heating rate at 1600 °C.

The reported molar enthalpies of melting for Si ($\Delta \bar{H}_m$(Si) = 11.1 kcal[12, 16] and 12.0 kcal[15]) have been used as the calibration values. The mean value is taken since neither of them seems to be preferable to the other one. The experimental enthalpy of nitride formation at 1220–1600 °C (the range of the exothermal DTA response) is found to be -185 ± 15 kcal mol^{-1} Si_3N_4.

For the reaction between Si(s) and N_2(g) several standard enthalpies are reported ranging from -163 to -179.3 kcal mol^{-1} [18–20]. The ΔH_f value calculated at 1294 °C for the range 300–1400 °C from the more recent data[8, 14] is -173.5 kcal mol^{-1}. The enthalpy does not seem to vary much with temperature[14, 17] and may thus be used directly in calculating the expected value for this reaction.

Using the thermogram in Fig. 1 it is found that only a negligible amount of Si(s) (~ 1.3%) may react with N_2(g) up to 1310 °C (the temperature of the DTA endothermal deflection in Ar(g)). It is assumed that, during the melting and later, nitride is formed between Si(l) and N_2(g). The reaction in the temperature range of the exothermal DTA response may thus be considered to occur essentially according to

$$3\,\mathrm{Si(l)} + 2\,\mathrm{N_2(g)} \rightarrow \beta\text{-}\mathrm{Si_3N_4(s)}$$

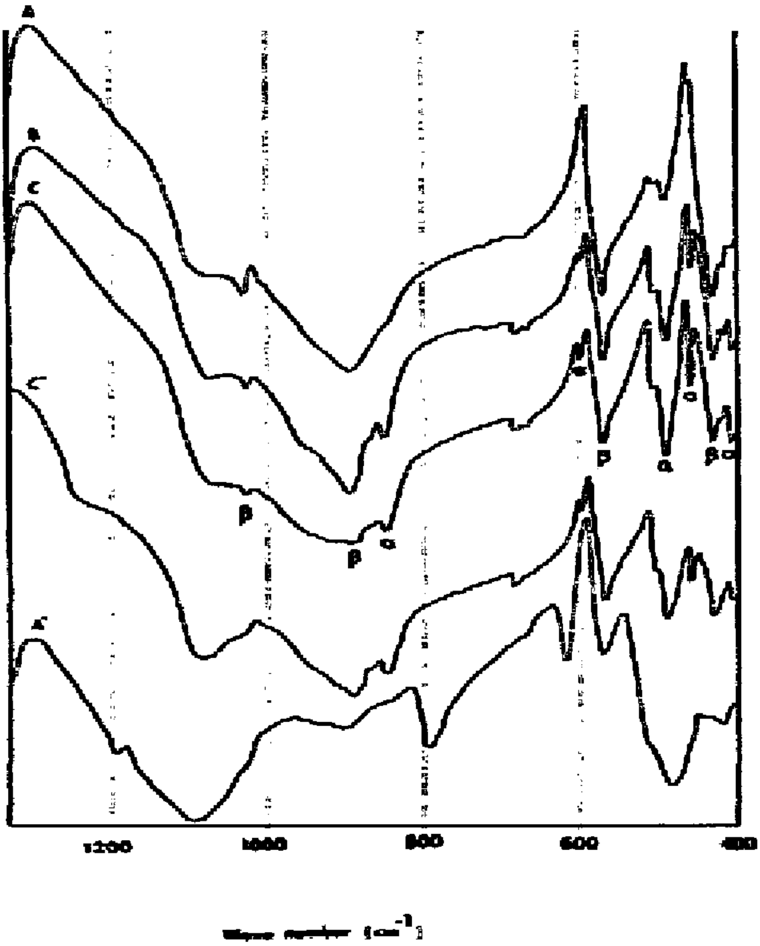

Fig. 3. IR spectra of the mixtures of the α- and β-forms of silicon nitride (α/β ratio increases from A to C) and of the mixtures A(A') and C(C') partially oxidized to SiO_2 (tridymite).

The calculated ΔH_f value is then -207 ± 3 kcal mole^{-1} Si_3N_4 using again the mean of the $\Delta \bar{H}_m(Si)$ values and the above enthalpy of -173.5 kcal. The experimental and the calculated enthalpy values agree reasonably well, especially considering the expected error in the base line approximation and the absence of the correction for the peak area variation with temperature.

In the runs made at 1300–1450 °C and 1600 °C (heat rate 10° min^{-1}; maximum time at constant temperature: 6 h) the mixtures of α- and β-forms have invariably been obtained. The TG-data is not accurate enough for calculation of the α : β ratios, because of the stoichiometric similarity of these forms. Instead, the intensities of the close X-ray reflexions (101) for α and (110) for β, are used to characterize their relative ratios. The typical values for α : β intensity ratios have been 0.80–1.30 and less than 0.25 at 1300–1450 °C and 1600 °C, respectively. Since, however, the oxygen impurity content in $N_2(g)$ has been controlled the highest possible content of α in a mixture is calculable. For the lowest α : β relative ratio (0.24) it is less than 5 w/o.

The treatment of Si by $N_2(g)$ containing some oxygen impurity involves consideration of the T–p_{O_2}–p_{N_2} equilibrium diagram in which the single phase regions correspond to three-dimensional volume sections. Thus, a single phase ought to be the most likely product for a given set of experimental conditions. The appearance of the α-form in β at 1600 °C and its documented conversion to β above 1450 °C[1,3] shows that the already suggested kinetic factors[1,6,7] and possibly also the low dissociation pressures of these phases must play a major role for a particular α : β ratio obtained in the mixtures. For β-Si_3N_4 the dissociation pressure can be calculated[3] at 1400 and 1600 °C to be of the order of 10^{-3} and 10^{-2} atm.

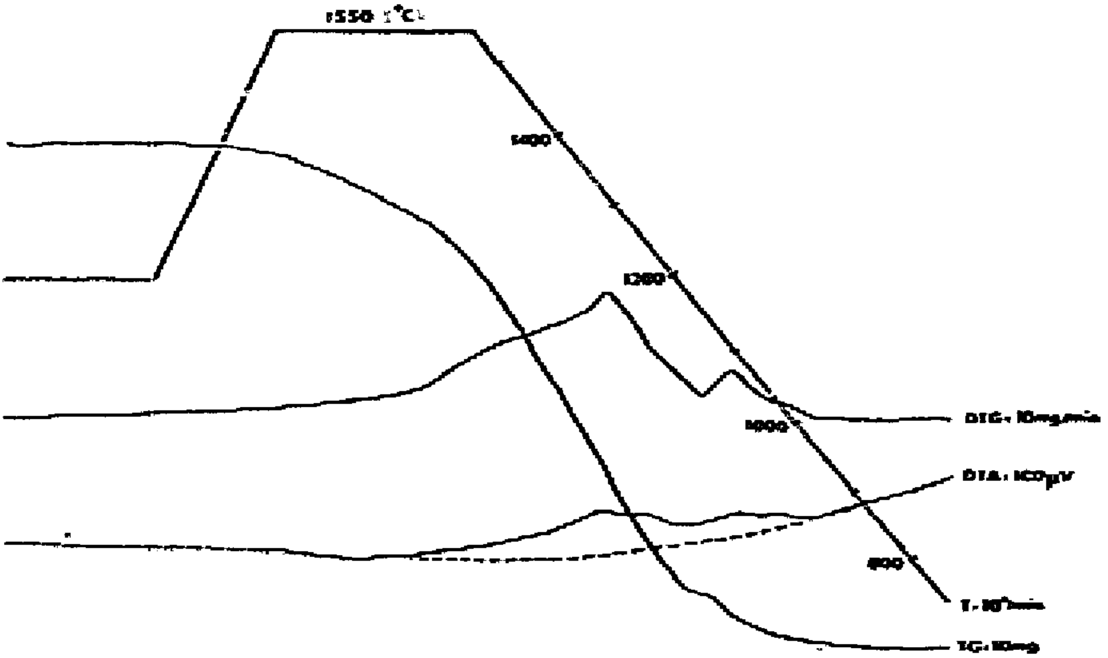

Fig. 4. Thermogram obtained in oxidizing the nitride phases in air in the range 25–1550 °C at 10° min^{-1}.

The α- and β-forms may be characterized by their IR spectra in the region 400–1300 cm^{-1}. For the samples A, B and C in Fig. 3 the α: β X-ray intensity ratios are 0.24, 0.81 and 1.28. The different frequencies are assigned to α or β on the basis of varying absorption intensities. For α the most intense independent absorption peak seems to be that at 490 cm^{-1} (20.4 μ). The major absorption frequency band for β appears at 893 cm^{-1} (11.2 μ), close to that previously reported[7].

Thermal analysis in oxidizing atmosphere

Figure 4 shows the thermogram obtained on oxidizing the nitride phases (ca. 75 mg; typical grain size: 10 μ; α: β relative ratio 0.24) in air (10° min^{-1}; TG–DTG–DTA sensitivity: 10 mg–10 mg min^{-1}–100 μV) in the range 25–1550°C. The oxidation of the nitride phases may be seen to be initiated at ca. 920°C. The departure of the DTA and DTG curves from their base lines at 960°C indicates the start of a more rapidly occurring reaction. At ca. 1100°C these curves display local minima. The maximal reaction rate is then attained at 1320°C. As further indicated by the TG–DTG curves the oxidation rate decreases virtually to zero when decreasing the temperature to 1200°C, after ca. ½ h at 1550°C. The oxidation processes, when employing O_2(g), Ar/O_2(g) or air and samples with various α: β ratios have essentially the same features.

The X-ray examinations reveal the presence of SiO_2 (tridymite) and the unreacted α- and β-forms. The product obtained after interrupting the oxidation at 1100°C (the DTG–DTA local minimum) contains, according to the X-ray and TG-analysis, a slight amount of SiO_2 (tridymite). The diffraction pattern of the α- and β-forms shows almost the same intensities as those of the starting product. The initial small DTG–DTA peaks seem thus to correspond to the formation of the protective surface oxide layer which temporarily decreases the oxidation rate.

The intensity ratios of the principal X-ray reflexes for the various α: β mixtures before and after oxidation at constant temperatures (1100–1550°C) remain essentially unchanged. The oxidation resistance of α- and β-forms therefore does not seem to be very different. The (002)-reflexion of tridymite has frequently an intensity which is up to 10 times as large as that expected. This suggests that the oxide grows on the nitride matrix in such a way that the (001) plane is preferentially developed.

The IR spectra of two oxidized samples are shown in Fig. 3. The samples C′ and A′ correspond, by their weight gain, to 7% and 48% conversion of the nitride phases C and A, respectively, to SiO_2. The typical Si–O stretching frequency (approximately 1090 cm^{-1}) is seen to appear in both samples. In the sample A′ the major β frequency band (893 cm^{-1}) is barely observable but that at 570 cm^{-1} is still clearly present. The α-form may be difficult to identify in well oxidized specimens such as A′. The strong absorption band of SiO_2 at approximately 480 cm^{-1} may overlap with that of α at 490 cm^{-1}.

The enthalpy of oxidation has roughly been estimated from the DTA peak area assuming only the reaction

$$\beta\text{-}Si_3N_4(s) + 3\,O_2(g) \rightarrow 3\,SiO_2(\text{tridymite}) + 2\,N_2(g)$$

The DTA base line is drawn as shown in Fig. 4. This approximation has been found to involve an error in area determination of ca. ± 10%. Therefore, no additional corrections for variation of the enthalpies[21] or heat transfer coefficient[22] have been made.

Using the molar transition enthalpy of K_2SO_4 (2.142 kcal)[15] the enthalpy of the oxidation occurring at 960–1550°C is found to be −450 ± 40 kcal mol^{-1} Si_3N_4. The mean value is in quite reasonable agreement with the value of −440.9 kcal mol^{-1} at 25°C[12], using the enthalpy of −173.5 kcal for Si_3N_4.

Thermal analysis in argon

A sample with the α: β relative intensity ratio 0.25 (less than 5 w/o α) has been heated in Ar(g) at 10° min^{-1} and then kept at the constant temperatures of 1200 and 1400°C for approximately 1 h. After this treatment, the intensities of the X-ray reflexions due to α and β are decreased by ca. 2% compared to those of the starting product. The TG-curve at 1200°C has shown only an irregular weight loss corresponding to a mean decomposition rate of less than 0.05% Si_3N_4 per hour if only the β-form is considered. At 1400°C the decomposition rate is linear with time corresponding to about 0.25% conversion of Si_3N_4 per hour. Because of the presence of O_2 impurity in Ar the free Si released during the reaction

$$Si_3N_4(s) \rightarrow 3\,Si(s) + 2\,N_2(g)$$

is very likely to form SiO(g). The rate of conversion may thus be somewhat lower than 0.25%. The rate (r) of this decomposition may be described in terms of the evaporation model[23, 24]. The rate may be given in the form

$$r = A \cdot \frac{P}{\sqrt{T}} \exp - \frac{\Delta H_A}{RT}$$

P(atm) is the decomposition pressure, ΔH_A (cal) the apparent activation enthalpy and R, T as usual. The constant A is characteristic of the particle size, the density and the composition of the reacting solid. For the typical particle size, 10 μ, in the present decomposition the magnitude of A is 10^9 when r is given as a fraction converted per hour. At 1400°C (1673 K) and $P \sim 10^{-3}$ atm the ΔH_A value is 53 ± 6 kcal mol^{-1}. The mean deviation corresponds to a variation in r by a power of ten.

The mean Si–N bonding energy in β-Si_3N_4 may be estimated roughly from the literature values[12] for the reaction

$$3\,Si(g) + 4\,N(g) \rightarrow \beta\text{-}Si_3N_4(s)$$

and the enthalpy of formation for β-Si_3N_4 (−173.5 kcal) to be about 80 kcal mol^{-1} for Si–N bonds. The bonding energy of the N atoms on the surface of the nitride particles may be expected to be between this mean value and the bonding energy of the $^{28}Si\,^{14}N$ molecule (105 ± 9 kcal)[12]. If the rate-determining step involves breaking of two Si–N bonds at the surface then the ΔH_A value corresponds to about onequarter of the sum of these bonding energies in agreement with the Eyring's empirical rule[25].

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