KINETIC STUDIES OF THE REACTIONS BETWEEN SILICON NITRIDE AND CARBON

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Abstract

The reactions between silicon nitride and carbon take place in two stages, the surface silica of silicon nitride powders reacts with carbon first followed by the decomposition of silicon nitride and the residual silicon reacting with carbon. The kinetics of the two stage reactions has been studied by isothermal thermogravimetric analysis. Physico-geometric models for both of the reaction stages have been proposed, and the kinetic parameters have been calculated. The implications of the kinetic models and parameters are discussed.

Introduction

Nonoxide covalent ceramics have been the subject of extensive studies for the past two decades because of their superior high-temperature properties and potential applications in areas such as heat engines and wear resistant parts. We have reported [1] that by partial carbothermal reduction of silicon nitride, silicon nitride and silicon carbide, the two major members of the covalent ceramics family, can be present in one system. Under appropriate conditions silicon carbide whiskers can be formed in situ in silicon nitride powders. Such a so-called 'chemical mixing process' has been utilized to make composites of a silicon nitride matrix reinforced with silicon carbide whiskers [2, 3].

In an effort to optimize the *in situ* silicon carbide whisker synthesis process and hence improve the composite properties, we have conducted a series of fundamental studies of the interactions between silicon nitride and carbon. It has been revealed through thermochemical studies [4] that the reactions between silicon nitride and carbon proceed in two stages. The first stage beginning at

around 1130°C is related to the reaction between carbon and the surface silica of the silicon nitride powders,

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g) \qquad (1)$$
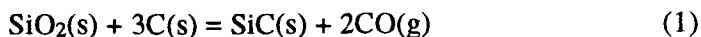
The second stage starting at about 1280°C corresponds to the decomposition of silicon nitride and the residual silicon reacting with carbon, as expressed in the overall reaction,

$$Si_3N_4(s) + 3C = 3SiC(s) + 2N_2(g) \qquad (2)$$

The purpose of the present study is to investigate the kinetics of these reactions and find out the physico-geometric mechanisms via which the reactions proceed. Since both stages of the process involve mass loss from which the fraction of reaction can be estimated, thermogravimetric analysis (TG) has been successfully used as the primary technique in the study.

For a solid state reaction with an evolving gas phase product, the fraction reacted, α, can be related to the fraction of mass loss as follows:

$$\alpha = \frac{M_o - M_t}{M_o - M_\infty} \qquad (3)$$

where M_o, M_∞ and M_t are the sample initial and final masses and mass at time t. The rate of the solid state reaction, $d\alpha/dt$, can be described as:

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (4)$$

in which k is the rate constant and $f(\alpha)$ a function of the sample composition that is characteristic of the reaction system. For most reactions, the rate constant is found to be temperature dependent according to the Arrhenius function,

$$k = A \exp(-E_a/RT) \qquad (5)$$

where A is the pre-exponential factor, E_a the activation energy, R the gas constant, and T the absolute temperature. Thus, during an isothermal test k remains constant. Rearranging Eq. (2) and integrating, we get,

$$\int \frac{d\alpha}{f(\alpha)} = k\int dt = kt \qquad (6)$$

The left-side of Eq. (4) is often called $g(\alpha)$ for convenience, that is,

$$g(\alpha) = kt \tag{7}$$

If a suitable $g(\alpha)$ that can best describe the reaction process is used, a plot of $g(\alpha)$ *vs.* t will give a straight line with its slope equal to the reaction constant k.

The form of function $g(\alpha)$ is related to the physico-geometric mechanism of the reaction. Various $g(\alpha)$ functions have been derived based on whether a reaction is controlled by: (i) diffusion, (ii) phase boundary movement, or (iii) random nucleation and growth of nuclei [5–7]. Therefore, through data analysis, the selected $g(\alpha)$ function will specify the physico-geometric model for the reaction. The kinetic models examined in the present study are listed in Table 1.

Table 1 Kinetic models examined in this study

Reaction model	$g(a)$	Symbol
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha + (1 - \alpha) \ln (1 - \alpha)$	D_2
Three-dimensional diffusion		
Jander equation	$[1 - (1 - \alpha)^{1/3}]^2$	D_3
Ginstling-Brounshtein equation	$[1 - (2/3)\,\alpha] - (1 - \alpha)^{2/3}$	D_4
Two-dimensional phase boundary reaction	$1 - (1 - \alpha)^{1/2}$	B_2
Three-dimensional phase boundary reaction	$1 - (1 - \alpha)^{1/3}$	B_3
Random nucleation		
First order equation	$-\ln (1 - \alpha)$	N_1
Avrami equation	$[-\ln (1 - \alpha)]^{1/2}$	N_2
Erofeev equation	$[-\ln (1 - \alpha)]^{1/3}$	N_3

By conducting isothermal test at different temperatures, we can obtain the data to make an Arrhenius plot of $\ln(k)$ *vs.* $1/T$ from which the kinetic parameters E_a and A can be estimated.

Experimental

Raw materials and sample preparation

The silicon nitride used in the present study was SN-E 10 Si_3N_4 powder produced by Ube Industries, Ltd. of Japan. The surface area of the powder is 11.5 m^2/g and the particle size is about 0.2 μm. The powder consists of more than 95% α-Si_3N_4. The carbon-source material was Monarch 900 carbon black produced by Cabot Corporation of the USA, its surface area is 230 m^2/g and particle size 15 nm.

The silicon nitride and carbon black powders were mixed (molar ratio Si_3N_4:C = 1:6) in propanol by ball milling for 24 hours using silicon nitride milling media. The slurry was then heated in an open container under a flame hood to fast evaporate the dispersant and prevent segregation. The mixture was further dried at 120°C for 8 hours and then sieved through a 100 mesh screes before subject to thermal analysis.

Thermal analysis

Samples of the Si_3N_4–C mixture were evenly charged in a covered graphite crucible (10 mm diameter and 7 mm height). Sample weights were kept at about 20 mg for all the tests to minimize the effects of sample size variation [8–10].

TG was conducted on a Setaram TAG 24 thermoanalyzer (Setaram France) under flowing helium (research grade, minimum purity 99.9995%) at a rate of approximately 40 ml·min^{-1}. Isothermal measurements were performed in the temperature ranges of 1130–1155°C for the first stage reaction and 1280–1350°C for the second stage reaction. To minimize the errors due to zero-time inaccuracy, the samples were brought up to the isothermal temperatures at the maximum allowable heating rate (99.99 deg·min^{-1}). A blank run under identical conditions using calcined graphite powders was conducted following each of the TG runs to compensate for the buoyancy effect. The baseline established in the blank run was subtracted from the sample TG curve. The thermoanalytical data were collected and stored on a microcomputer.

TG data analysis was performed on a Macintosh computer using Kaleida-Graph software. Correlation coefficients were used as a criterion to quantitatively compare the fit of data to various kinetic models.

Results and discussion

Overall view of the reaction between silicon nitride and carbon

Figure 1 is a TG graph showing the thermogravimetric and derivative thermogravimetric (DTG) traces of a silicon nitride and carbon black mixture. The sample was heated at 10 deg·min^{-1} in flowing He. A two stage mass loss process is clearly observed. The first stage, beginning at about 1130°C, had a mass loss of about 1.4%. During the second stage the sample lost about 26.3% of its mass. Those mas change values are in excellent agreement with the calculated values of 1.46% and 26.42%, respectively based on reactions (1) and (2) [4].
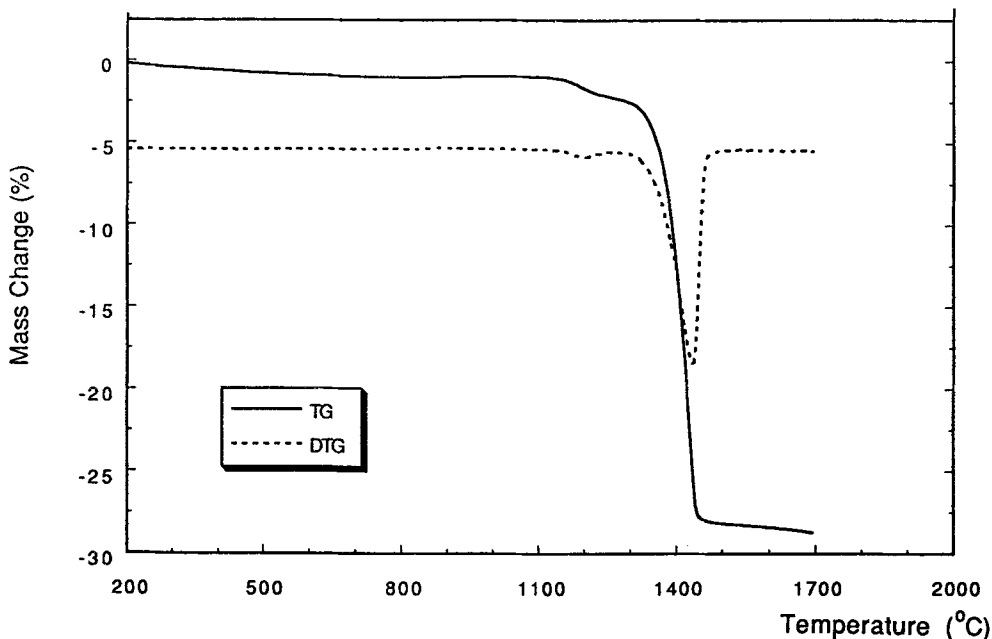

Fig. 1 TG and DTG curves of a mixture of silicon nitride and carbon black heated at 10 deg·min^{-1} in flowing helium

First stage reaction

The plot of fraction reacted α vs. time t for the first stage reaction is shown in Fig. 2. The isothermal α-t data were analyzed according to the kinetic models listed in Table 1 by using correlation coefficient as a quantitative criterion. The comparison among those models is given in Table 2. It is noted that the best fit

of the data is obtained at all isothermal temperatures with the Jander equation for three dimensional diffusion-controlled reactions.
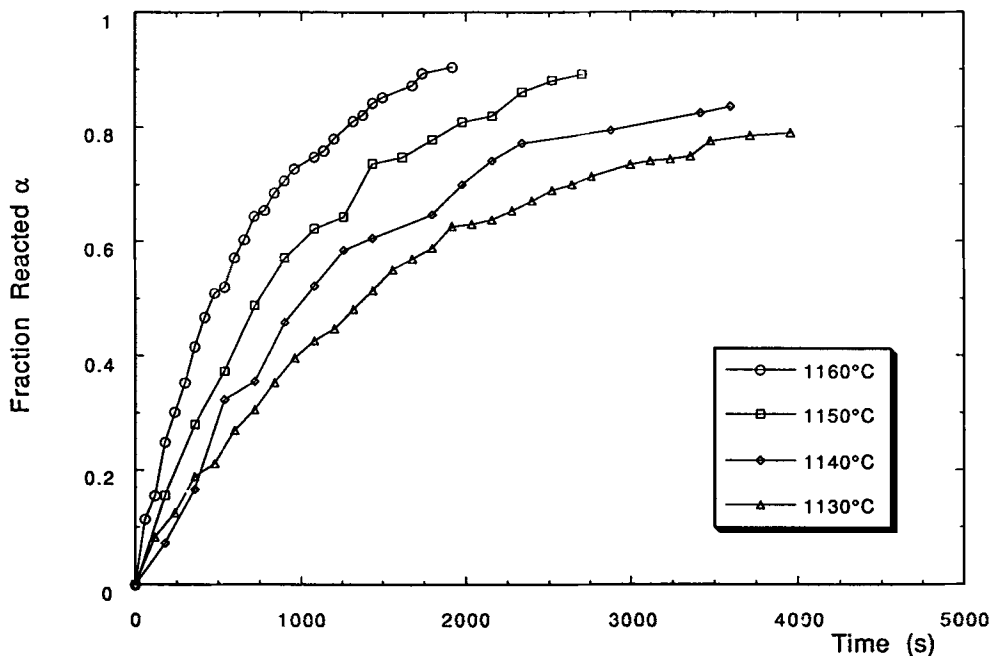

Fig. 2 Isothermal α *vs.* *t* curves for the first stage reaction between silicon nitride and carbon

Table 2 Comparison of correlation coefficients of various kinetic models for the first stage reaction

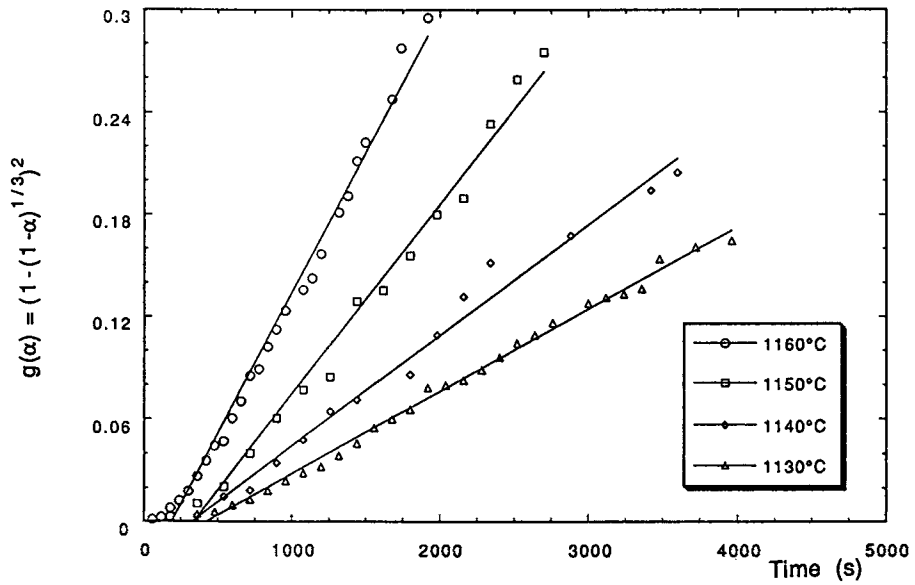| Model symbol	Correlation coefficient at			
	1130°C	1140°C	1150°C	1160°C
D_1	0.9780	0.9668	0.9869	0.9849
D_2	0.9855	0.9835	0.9946	0.9933
D_3	0.9908	0.9944	0.9966	0.9980
D_4	0.9878	0.9885	0.9963	0.9956
B_2	0.9553	0.9533	0.9730	0.9689
B_3	0.9616	0.9635	0.9800	0.9752
N_1	0.9727	0.9799	0.9907	0.9856
N_2	0.9274	0.9452	0.9585	0.9566
N_3	0.9007	0.9280	0.9394	0.9422

Fig. 3 The first stage reaction between silicon nitride and carbon according to the Jander three dimensional diffusion model at different temperatures
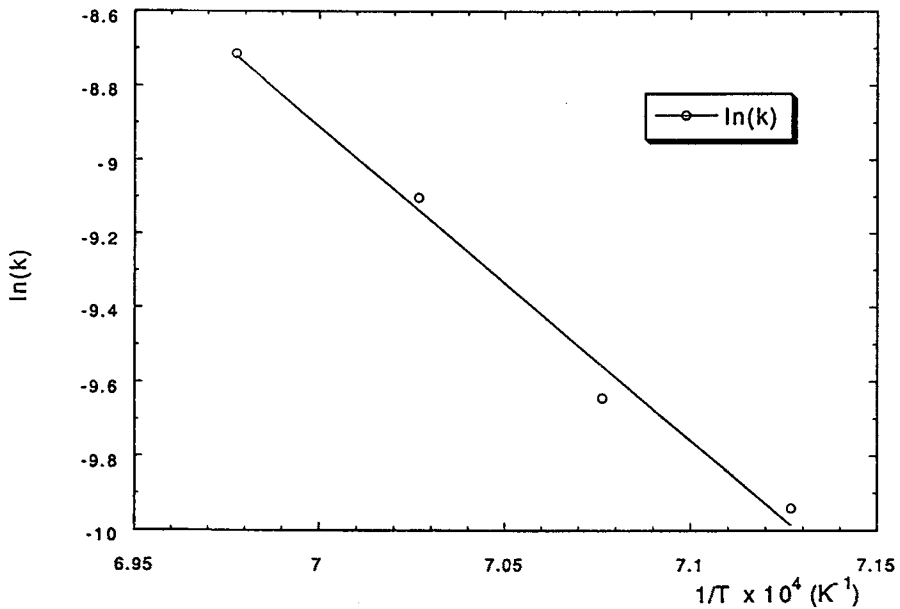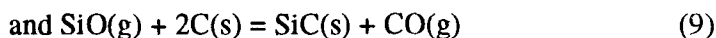

Fig. 4 The Arrhenius plot for the first stage reaction between silicon nitride and carbon

It has been reported that reaction (1) can be broken down to two steps [4, 11, 12]:

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \tag{8}$$

$$\text{and } SiO(g) + 2C(s) = SiC(s) + CO(g) \tag{9}$$

Therefore it is suggested that during this stage, the SiC is formed on the carbon black particles and the reaction is controlled by the diffusion of the reactants, SiO and C, through the SiC product layer on the carbon black particles.

To determine the kinetic parameters of the first stage reaction, a plot of the Jander equation in the temperature range of 1130 to 1160°C is shown in Fig. 3. The rate constants were estimated from the slopes of the lines. An Arrhenius plot of $\ln(k)$ *vs.* $1/T$ is shown in Fig. 4. The activation energy of the reaction, estimated from the slope in Fig. 4, is 599 kJ/mol. The enthalpy change for reaction (1) at 1400 K calculated using the thermodynamic data in the JANAF tables [13] is $\Delta H = 599.990$ kJ/mol. The pre-exponential factor A calculated from the intercept is 5.7×10^{17} s^{-1}.

Second stage reaction

The thermochemical studies show that the majority of the SiC is formed during this reaction stage [4]. The high signal to noise ratio results in a neat plot (Fig. 5) of fraction reacted (α) *vs.* time (t) for various isothermal temperatures as compared with Fig. 2. Using correlation coefficients as a judging criterion, it is found that at all temperatures the second stage reaction is best fitted by the Avrami random nucleation and growth model, Table 3.

Because the particle size of silicon nitride is more than ten times that of the carbon black, the surface of each silicon nitride particle is covered with many discrete carbon black particles. It is proposed that during this stage, silicon carbide is formed on silicon nitride particles. The silicon carbide nucleated randomly on the silicon nitride particle surfaces at the contact of silicon nitride and carbon black particles and grow until they impinge on each other.

This proposed physico-geometric model, however, can not be used to explain the formation of SiC whiskers by carbothermal reduction of silicon nitride [1]. As a matter of fact, no whisker formation was observed by the scanning electron microscopy (SEM) examination of the products in this study. It is noted that during the synthesis study [1], a much larger sample size was used and the reaction temperatures were higher than the isothermal temperatures in this kinetic study. These would all affect the local environment of the reaction

system, mainly the degree of supersaturation of the whisker growth species. Hence, a different reaction physico-geometric mechanism would be invoked for the synthesis process. Nonetheless, this kinetic study may tell us something about the initial stage of SiC whisker growth, i.e., the whiskers may be nucleated on the silicon nitride particle surfaces.
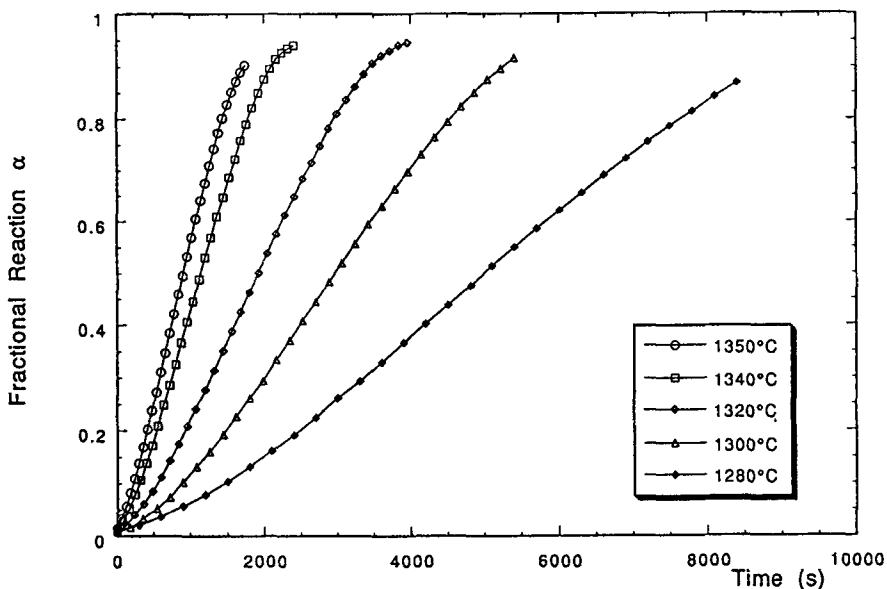

Fig. 5 Isothermal α vs. t curves for the second stage reaction between silicon nitride and carbon

Table 3 Comparison of correlation coefficients of various kinetic models for the second stage reaction

| Model symbol	Correlation coefficient at				
	1280°C	1300°C	1320°C	1340°C	1350°C
D_1	0.9568	0.9629	0.9750	0.9771	0.9728
D_2	0.9327	0.9376	0.9542	0.9581	0.9519
D_3	0.8941	0.8923	0.9109	0.9183	0.9142
D_4	0.9206	0.9237	0.9414	0.9463	0.9403
B_2	0.9881	0.9887	0.9923	0.9935	0.9934
B_3	0.9816	0.9809	0.9853	0.9874	0.9875
N_1	0.9626	0.9568	0.9604	0.9653	0.9687
N_2	0.9989	0.9983	0.9986	0.9990	0.9993
N_3	0.9974	0.9971	0.9971	0.9969	0.9966
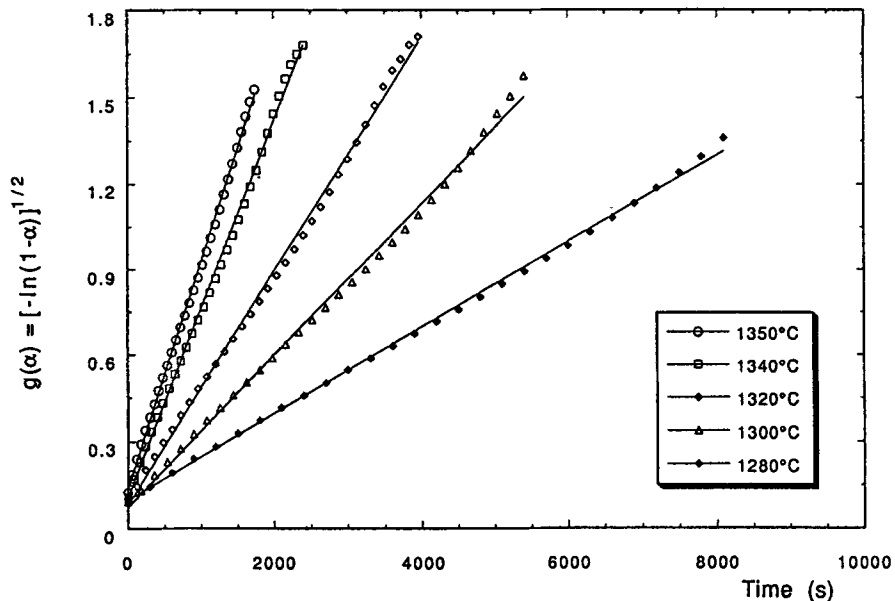
Fig. 6 The second stage reaction between silicon nitride and carbon according to the Avrami random nucleation and growth model at different temperatures
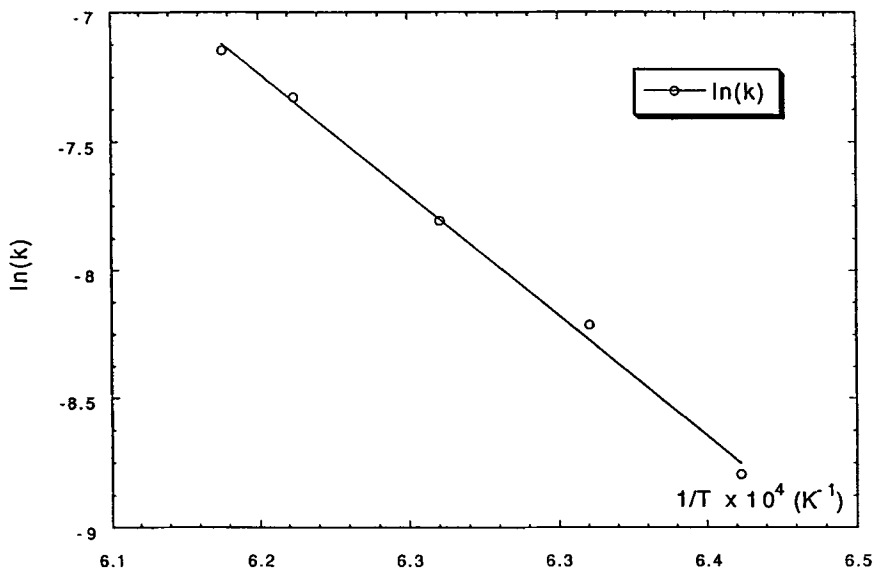

Fig. 7 The Arrhenius plot for the second stage reaction between silicon nitride and carbon

Using the Avrami equation, a plot of $[-\ln(1-\alpha)]^{1/2}$ *vs.* t for the various isothermal temperatures is generated, Fig. 6. The slopes are equal to the rate constants, k, for different temperatures. The Arrhenius plot of $\ln(k)$ *vs.* $1/T$ is shown in Fig. 7, with its slope yielding an activation energy of 489 kJ/mol, compared to the enthalpy change of reaction (2) at 1700 K of 512.015 kJ/mol calculated using reference 13. The intercept of the Arrhenius plot gives a pre-exponential factor of 4.5×10^{12} s^{-1}.

It is noted that although the second stage reaction takes place at a higher temperature, its activation energy is lower than that of the first stage. However, since the two reaction stages proceed via different physico-geometric mechanism and the pre-exponential factors are different, no direct comparison of the activation energies of the two stages can be made [14, 15].

Conclusions

Through isothermal kinetic studies, it is concluded that the first stage reaction between carbon and the surface silica nitride powders is best described by the Jander equation for three-dimensional diffusion and the activation energy is 599 kJ/mol. The second stage reaction, involving the decomposition of silicon nitride and the residual silicon reacting with carbon, is best fitted by the Avrami random nucleation and growth model with an activation energy of 489 kJ/mol. The activation energies estimated in this study are close to the values of the enthalpy changes of reaction (1) and (2) calculated using published data. It is noted that, because the process of synthesizing silicon carbide whiskers by carbothermal reduction of silicon nitride was carried out under different conditions, the proposed models may not be used to explain the formation of whiskers. Also, since the two reaction stages proceed via different physico-geometric mechanisms and the pre-exponential factors are not the same, no direct comparison between the activation energies of the two reaction stages should be made.

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Zusammenfassung — Die Reaktionen zwischen Siliziumnitrid und Kohlenstoff verlaufen in zwei Teilschritten. Zuerst reagiert das an der Oberfläche des Siliziumnitrides vorhandene Siliziumoxid mit Kohlenstoff, dem folgt eine Zersetzung von Siliziumnitrid und das zurückbleibende Silizium reagiert mit Kohlenstoff. Die Kinetik der beiden Teilreaktionen wurde mittels isothermer thermogravimetrischer Analyse untersucht. Es wurden physiko-geometrische Modelle für beide Reaktionsschritte vorgeschlagen und die kinetischen Parameter berechnet. Bedeutung von kinetischem Modell und Parametern werden diskutiert.