JOURNAL OF MATERIALS SCIENCE 26 (1991) 388–392

Kinetic studies on β-SiC formation from homogeneous precursors

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The kinetics of the carbothermic reduction of SiO_2 by carbon to produce β-SiC from a homogeneous organic precursor has been investigated over the temperature range 1500 to 1800 °C in nitrogen by the use of a high-temperature thermobalance. The kinetic behaviour differed significantly from that of the heterogeneous reaction of SiO_2 and carbon particles. The weight-loss curves could be fitted well by the Avrami–Erofe'ev equation with an exponent of 1.5. The result was interpreted as showing instantaneous nucleation in a homogeneous matrix followed by the diffusion-controlled growth of β-SiC. The obtained activation energy of 391 kJ mol^{-1} was consistent with the assumption that the reaction is controlled by the diffusion of carbon through the amorphous matrix to the growing surface of β-SiC.

1. Introduction

The industrial method of preparing easily sinterable SiC ceramics has attracted much attention because of its potential applicability to structural materials with excellent heat and oxidation resistances. In order to obtain well-densified SiC, it is essential to use fine β-SiC powders with a narrow particle size distribution as the starting material. Many synthetic methods to produce fine β-SiC powders have been reported, but the only industrially feasible method may be the carbothermic reduction of silica.

Recently, Tanaka and Kurachi [1] have proposed an excellent method to prepare very fine β-SiC particles from a homogeneous organic precursor derived from ethylsilicate and phenolic resin. Easily sinterable submicrometre powders were obtained by this method. The advantage of this method is the high purity of the powders, so that no treatments were required to remove unreacted SiO_2 and carbon. Moreover, the reaction temperature could be reduced by about 300 °C from that used in the conventional method of heterogeneous reduction of SiO_2 by carbon.

This method is very interesting from the kinetic point of view. Although a number of studies have been undertaken to shed light on the reaction mechanism of the carbothermic reduction of SiO_2 [2–6], the kinetic behaviour of the reaction is not well understood. Several conflicting results have been reported with regard to the rate-determining step of the reaction. The variation in reported kinetics may be partly attributed to the difference in the starting materials used in each investigation. In contrast, well-characterized homogeneous materials have been obtained by the use of organic precursors. As far as we know, no kinetic investigation has been carried out using a homogeneous precursor.

The purpose of this study is to investigate the kinetics and mechanism of the carbothermic reduction of SiO_2 at 1500 to 1800 °C, with special interest in the rate-determining step of the reaction and the nucleation and growth mechanism of β-SiC, using a homogeneous organic precursor. It was expected that the results obtained from the kinetic analysis of the reaction of the homogeneous precursor would serve in the elucidation of the more complex mechanism of heterogeneous reduction of SiO_2 powder by carbon.

2. Experimental procedure

The preparation of the organic precursor has been described in a previous paper [1]. In brief, ethylsilicate and phenolic resin were mixed at room temperature in the presence of toluene–sulphonic acid. As the reaction proceeded the heterogeneous liquid mixture became transparent, and finally yielded a homogeneous condensate. On the other hand, the mixture remained heterogeneous if the reaction temperature was high, e.g. 80 °C. This is probably due to the preferential condensation of phenolic resin. The condensate was pyrolysed at 1000 °C under N_2 to give a black glassy solid. The powder X-ray diffraction pattern of the precursor did not show any crystalline diffraction. Thus the precursor may be regarded as a completely amorphous material.

The kinetic analysis of the formation reaction of SiC was carried out by the use of a specially designed high-temperature thermobalance equipped with a YAG laser and an infrared furnace. This apparatus made it possible to measure weight loss at a constant temperature as well as at a constant heating rate. For the purpose of measuring the weight loss at constant temperature, the temperature was first raised to about 300 °C below the desired temperature by an infrared furnace, and then raised very quickly (3 to 5 sec) to the temperature of measurement using the YAG laser. This procedure minimizes the errors due to reaction during preheating. The measurements were carried out in a graphite cell. The microstructure of the precursor was observed under a Hitachi S-900 high-resolution scanning electron microscope using a platinum-sputtered sample.

TABLE I Fraction of volatilized silicon monoxide (SiO)

Chemical composition of precursor, C/Si	Temperature (°C)	Volatilized SiO, x
2.97	1750	0.20
2.65	1750	0.26
2.34	1600	0.22
2.34	1700	0.23
2.34	1750	0.22
2.34	1800	0.21
2.03	1750	0.35

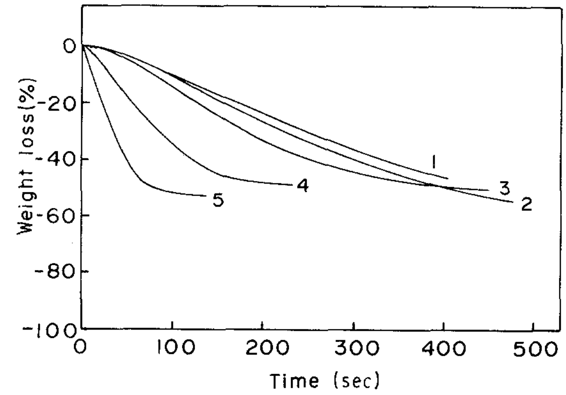

Figure 1 Plot of weight loss against time at constant temperature. Chemical composition of the precursor: C/Si = 2.65. (1) 1522 °C, (2) 1540 °C, (3) 1548 °C, (4) 1608 °C, (5) 1689 °C.

3. Results and discussion

3.1. Analysis of the reaction by thermobalance

The overall reaction of the β-SiC formation from SiO_2 and carbon is represented by

$$SiO_2 + 3C = SiC + 2CO \qquad (1)$$

The detailed mechanism of the reaction is not known, but it is well recognized that silicon monoxide is an important reaction intermediate. According to Klinger *et al.* [7], Equation 1 could be divided into two elementary reaction steps

$$SiO_2 + C = SiO + CO \qquad (2)$$

$$SiO + 2C = SiC + CO \qquad (3)$$

It should be noted that the weight loss of the sample arises not only from the volatilization of CO but also of SiO. Assuming that a fraction x of SiO is not converted to SiC and volatilized from the reaction system [1], Equation 1 is rewritten as

$$SiO_2 + (3 - 2x)C = (1 - x)SiC + xSiO + (2 - x)CO \qquad (4)$$

If x is a constant throughout the reaction, the ratio of volatilized SiO to CO is also a constant. Then the total weight loss W is directly proportional to the yield of SiC, α:

$$\alpha = W/(W_0 - W) \qquad (5)$$

where W_0 and W are the initial and final weight of the sample, respectively. The above assumption is easily checked from the weight loss and SiC content in the product. Table I shows the effect of the composition of the precursor (C/Si) and the temperature on the value of x. It may be seen that the fraction of volatilized SiO is almost constant, unless the C/Si ratio is low. Thus we can safely estimate the degree of formation of β-SiC directly from the weight loss.

3.2. Weight loss at constant temperature

Fig. 1 shows the relationship between the weight loss and the reaction time. The important feature of the weight loss curves is that a distinct induction period is observed, especially in low-temperature experiments. This behaviour is quite distinct from the heterogeneous reaction of SiO_2 and carbon particles in which the maximum reaction rate is observed at initial time. In the case of the heterogeneous reaction, the reaction would proceed at the surface of SiO_2 and/or carbon particles. The growth of an SiC layer at the surface of the particles decreases the area of reaction surface. This leads to a decrease of reaction rate according to the contracting volume theory of solid-state reaction [8]:

$$1 - (1 - \alpha)^{1/3} = k_R t \qquad (6)$$

(Phase boundary control)

$$[1 - (1 - \alpha)^{1/3}]^2 = k_D t \qquad (7)$$

(Diffusion control)

where k_R and k_D are the rate constants when the overall rate is controlled by phase boundary and diffusion processes, respectively. Fig. 2 shows the applicability of Equations 6 and 7 to the reaction of the present organic precursor. Evidently the kinetic equations based on contracting volume are not obeyed. This result strongly suggests that the precursor is homogeneous, and that the nucleation and growth processes of SiC play an essential role in determining the reaction rate. In fact, no large-scale inhomogeneity was found by SEM observations as will be shown later.

When a reaction is accompanied by the nucleation and growth of the reaction product in the solid state, the following Avrami–Erofe'ev (AE) equation is frequently obeyed [8]:

$$[\ln(1 - \alpha)]^{1/n} = kt \qquad (8)$$

When the rate is controlled by a phase-boundary process, the exponent n is represented by $n = \beta + \lambda$,

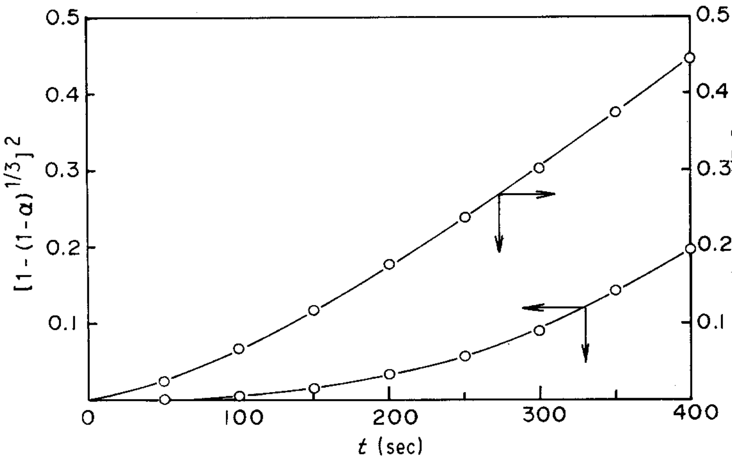

Figure 2 Applicability of contracting volume theory to β-SiC formation.

where β is the number of steps involved in nucleus formation and λ is the number of dimensions in which the nuclei grow. On the other hand, $n = \beta + (\lambda/2)$ when the rate is diffusion-controlled. In general $\beta = 0$ or 1 and $\lambda = 3$ for spheric growth.

Fig. 3 shows the plot of $\ln[-\ln(1-\alpha)]$ against logarithmic time. It may be seen that the plot is well represented by a straight line, the slope of which gives the AE exponent n. The slope at each temperature is summarized in Table II. The AE exponent was found to be 1.5 within the experimental error. The straight lines in Fig. 3 were drawn by linear regression analysis, keeping the slope at 1.5.

Taking into account the three-dimensional growth of SiC nuclei, i.e. $\lambda = 3$, the only possible explanation is that $\beta = 0$ under diffusion control. This means that SiC crystals grow from the originally existing nuclei in the reaction system, and that SiC formation is controlled by the diffusion of SiO or carbon to the growing surface.

It is not clear at present what kind of chemical species is involved in the diffusion-controlled reaction. The diffusion of SiO and/or carbon in the amorphous SiO_2–C composite phase could both control the formation of SiC. As mentioned before, the reaction intermediate SiO is a gaseous product and it would diffuse much faster than carbon in the solid. Thus it may be reasonable to consider that the growth of SiC crystals is controlled by the diffusion of carbon in the amorphous matrix.

TABLE II Avrami–Erofe'ev exponent

Temperature (°C)	Exponent, n
1522	1.48
1540	1.51
1548	1.55
1608	1.48
1689	1.40
Average	1.484 ± 0.055

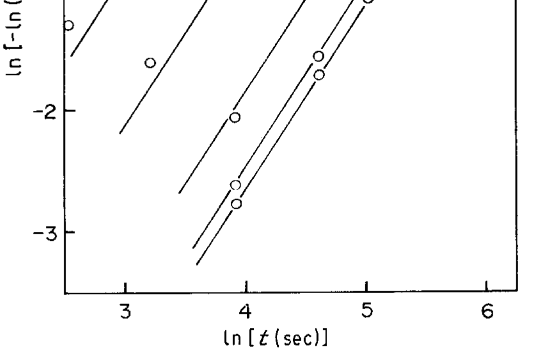

Figure 3 Plot of $\ln[-\ln(1\text{-}\alpha)]$ against logarithmic time.

The logarithm of the Avrami–Erofe'ev rate constant k is plotted against the reciprocal temperature in Fig. 4. The activation energy calculated from the slope of the plot is 391 kJ mol^{-1}. This value is too large to consider that the process is controlled by the diffusion of gaseous SiO. As far as we know, the activation energy value of the diffusion of carbon in an amorphous SiO_2 matrix is not available, while that in the phase boundary of SiC has been reported to be 305 kJ mol^{-1} [9]. Thus the calculated activation energy value seems to be consistent with the assumption that the carbothermic reduction of SiO_2 by carbon in an amorphous SiO_2–C matrix is controlled by the diffusion of carbon to the growing surface of the β-SiC crystal.

3.3. Weight loss at constant heating rate

As revealed in the previous section, the kinetic behaviour of β-SiC is well represented by the AE equation with the exponent $n = 1.5$:

$$[-\ln(1-\alpha)]^{1.5} = kt \qquad (9)$$

By differentiating Equation 9,

$$\frac{2b}{3[-\ln(1-\alpha)]^{1/3}(1-\alpha)}\frac{d\alpha}{dT} = A\exp(-\Delta E/RT) \qquad (10)$$

where b is the heating rate, dT/dt, and ΔE is the activation energy. Then the activation energy can be

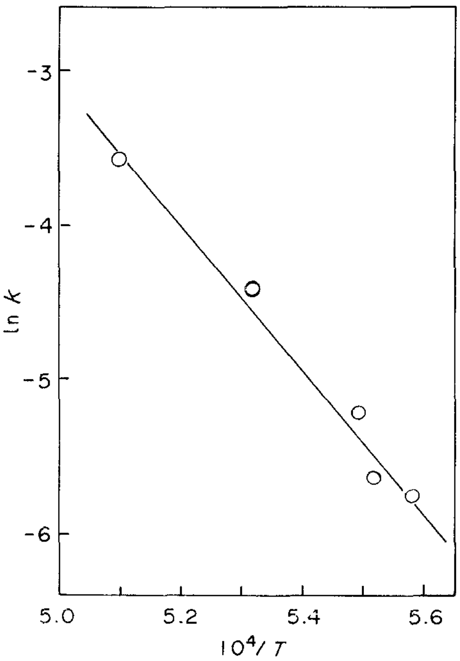

Figure 4 Plot of the logarithm of the Avrami–Erofe'ev rate constant against reciprocal temperature. C/Si = 2.65; ΔE (from slope) = 391 kJ mol^{-1}.

alternatively calculated by plotting $\ln k'$ against $1/T$, where

$$k' = \frac{2b(\mathrm{d}\alpha/\mathrm{d}T)}{3[-\ln(1-\alpha)]^{1/3}(1-\alpha)}$$

Fig. 5 shows typical weight-loss curves at several constant heating rates. Needless to say, the weight-loss curve is shifted to the higher-temperature side

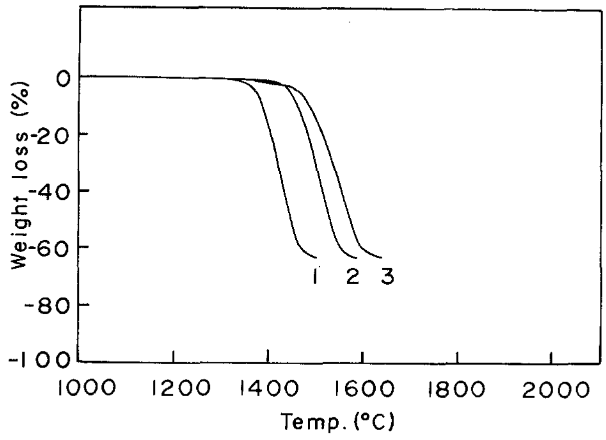

Figure 5 Weight-loss curves at constant heating rate. C/Si = 2.65. (1) 2 °C min^{-1}, (2) 5 °C min^{-1}, (3) 10 °C min^{-1}.

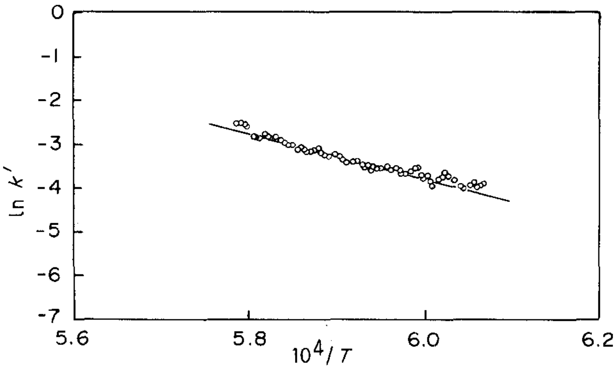

Figure 6 Arrhenius-type plot of rate constant k' at constant heating rate of 2 °C min^{-1}.

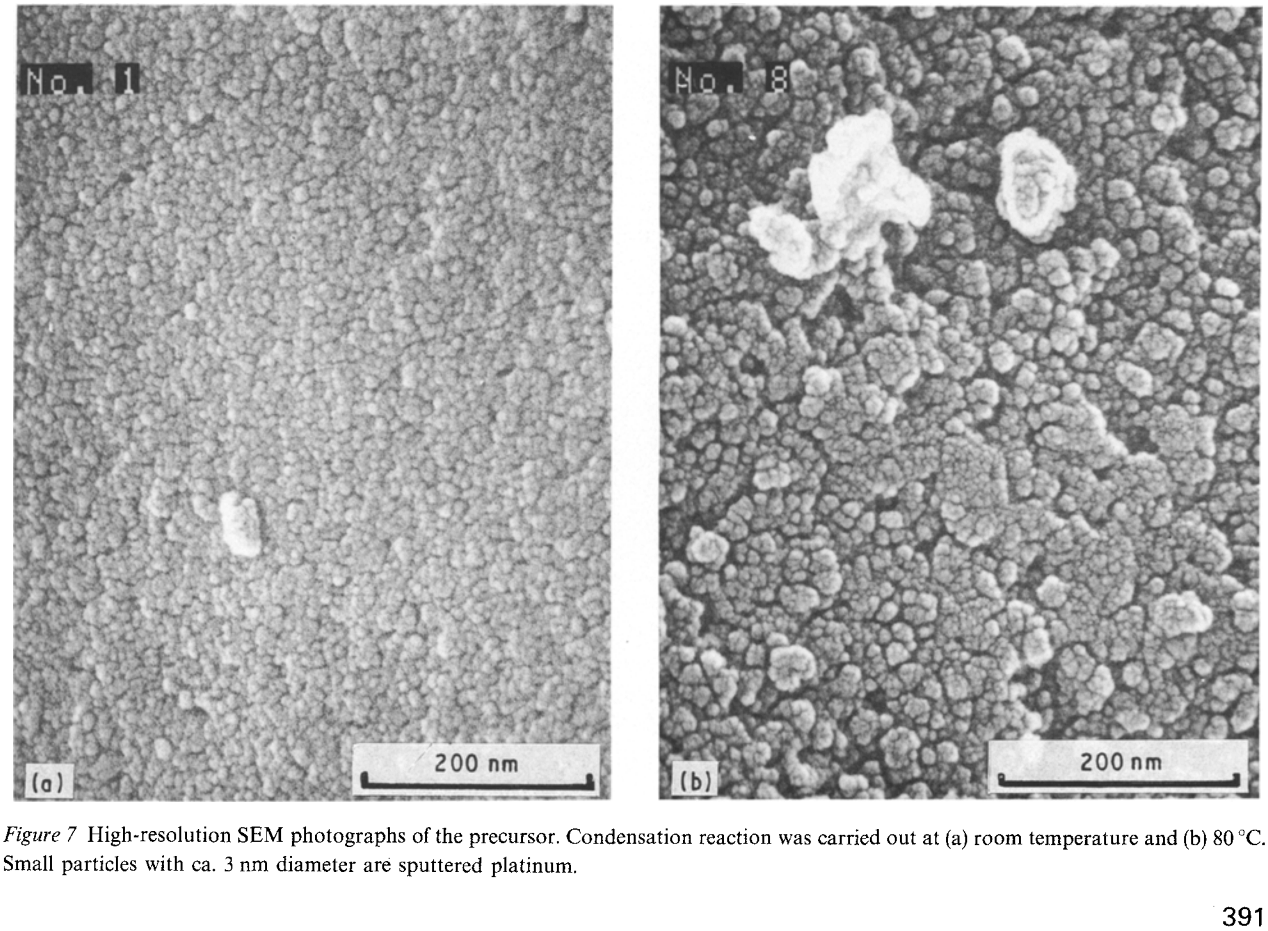

Figure 7 High-resolution SEM photographs of the precursor. Condensation reaction was carried out at (a) room temperature and (b) 80 °C. Small particles with ca. 3 nm diameter are sputtered platinum.

with decreasing heating rate. The plot corresponding to Equation 10 is shown in Fig. 6. It may be seen that the plot is well approximated by a straight line, the slope of which gives an activation energy of 449 kJ mol^{-1} when the heating rate is 2 °C min^{-1}. Although several simplifying assumptions have been introduced, this value is in fair agreement with that obtained from the constant-temperature experiments. Hence our model of the nucleation and growth of SiC seems to be valid over a relatively wide temperature range.

3.5. SEM observation of the precursor

The above kinetic analysis showed that the homogeneity of the precursor plays an essential role in determining the rate and mechanism of carbothermic reduction of SiO_2. The presence of an induction period seems to be a characteristic feature of the homogeneous reaction. In fact, if we use a heterogeneous precursor derived from the condensate of ethylsilicate and phenolic resin at 80 °C, the induction period disappeared.

Fig. 7 shows scanning electron micrographs of the precursors derived from the reaction product of ethylsilicate and phenolic resin at room temperature (Fig. 7a) and at 80 °C (Fig. 7b). As shown in Fig. 7a, no specific structure was found in the homogeneous precursor except for the sputtered particles of platinum. On the other hand, particles of ca. 20 nm were observed for the heterogeneous precursor as shown in Fig. 7b. These particles are probably formed by the preferential condensation of phenolic resin, before the condensation of ethylsilicate takes place. In this case, SiC formation occurs on the surface of the particle, and the rate-determining step should be the diffusion of carbon in SiC [6]. This results in the disappearance of the induction period at constant temperature, as shown by experiments.

4. Concluding remarks

It has been shown that the kinetic behaviour of SiC formation from homogeneous organic precursors is characterized by the presence of an induction period. This can be explained by the nucleation and growth mechanism of β-SiC in the homogeneous matrix of SiO_2 and carbon. The initial acceleratory region may originate from the increasing surface area of the nuclei. The weight-loss curves obtained from thermobalance experiments could be simulated by the Avrami–Erofe'ev equation with instantaneous nucleation and the growth under diffusion control. The activation energy of the reaction was consistent with the above model. The SEM photograph of the precursor did not show any large-scale inhomogeneity. The reaction mechanism of the precursor obtained under heterogeneous conditions was significantly altered. Small particles were present in the precursor, and the induction period was no longer observed.

References

1. H. TANAKA and Y. KURACHI, *Ceramics Int.* **14** (1988) 109.
2. M. S. KHRUSHCHEV, *Izv. Akad. Nauk SSSR, Met.* (1984) 23.
3. K. SCHWERDTFEGER, *Trans. Met. Soc. AIME* **236** (1966) 1152.
4. A. G. VODOPY'ANOV, S. V. BARANOV and G. N. KOZHEBNIKOV, *Izv. Akad. Nauk SSSR, Met.* (1983) 28.
5. T. SHIMOO, F. MIZUTAKI, S. ANDO and H. KIMURA, *J. Jpn Inst. Metals* **52** (1988) 279.
6. *Idem, ibid.* **52** (1988) 945.
7. N. KLINGER, E. L. STRAUSS and K. L. KOMAREK, *J. Amer. Ceram. Soc.* **49** (1966) 369.
8. W. E. BROWN, D. DOLLIMORE and A. K. GALWAY, in "Comprehensive Chemical Kinetics", edited by C. H. Bamford and C. F. H. Tipper, Vol. 22 (Elsevier/North Holland, New York, 1980) Ch. 3.
9. T. L. FRANCIS and R. L. COLBE, *J. Amer. Ceram. Soc.* **51** (1968) 115.

Received 1 August 1989
and accepted 19 February 1990