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Oxidation of SiC powders in SiC/alumina/zirconia compacts

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Abstract

Oxidation of SiC powder in compacts of SiC/alumina/zirconia was studied between 1000 and 1200°C in air for up to 10 h. The thermogravimetric analysis showed that the weight gain due to passive SiC powder oxidation became significant at temperatures $\geqslant$937°C. After oxidation, the particle usually consisted of a SiC core surrounded by a layer of amorphous silica. However, the amorphous layer would crystallize into cristobalite if the powders were oxidized at 1200°C for a longer time ($\geqslant$8 h). The oxidation rate decreased if cristobalite formed. The square of weight gain fraction after oxidation was linearly proportional to the oxidation time when the weight gain fraction was less than 0.34. The activation energy of the oxidation of SiC powders was estimated to be 213.1 kJ/mol. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Activation energy; A. Powders; D. SiC

1. Introduction

Silicon carbide (SiC) is a candidate material for high temperature structural applications because of good mechanical properties and excellent corrosion and oxidation resistance. Although SiC powder could be processed into dense SiC pieces and be applied in various areas, it is also used as a reinforcing agent to fabricate ceramic composites. Since SiC or SiC-containing composites are intended for high temperature applications, their oxidation behavior is an important issue.

The oxidation behaviors of SiC can be divided into two categories: passive and active. Passive oxidation forms a coherent, dense SiO_2 layer on the surface, which drastically reduces oxidation rate. On the contrary, active oxidation forms gaseous SiO, which dissipates away and the oxidation becomes severe [1–3]. The temperature, which the oxidation changes from passive to active, decreases with the decrease of oxygen partial pressure. (The transition temperatures are about 1350 and 1550°C for partial oxygen pressure of 2.5 and 123 Pa, respectively [1].) For most applications, the oxidation of SiC should be controlled in the region of passive oxidation.

In the study of SiC passive oxidation at elevated temperatures, it is generally believed that the oxidation of SiC is similar to the oxidation of silicon. The oxidation process is accomplished by the diffusion of oxygen molecules (or oxygen ions) through the oxide layer [2–5]. Consequently, the oxidation layer thickness varies with the oxidation time in a parabolic way (i.e. the thickness is linearly proportional to the square root of oxidation time.) Nevertheless, measuring the thickness of oxidation layer is not an easy task. It is tedious, though possible, when the SiC are single crystals, thin films or monoliths. It becomes almost impossible if SiC are powders (or dispersed particles) with a wide range of size distributions. Hence, in many studies of SiC oxidation, weight gain per unit surface area of the samples was used as the parameter [3,6–9]. Some of these studies also revealed that the weight gain of the sample was also in a parabolic relationship with oxidation time [3,6–8].

The oxidation of SiC is not only important in the industrial applications of SiC composites, it is also an essential step in the fabrication of some SiC-containing composites. For example, Holz and Claussen [10] and Wu and Claussen [11] obtained compacts of alumina, silica and SiC by oxidation of Al and SiC powder compacts. Then, reaction sintering combined alumina and silica layers to form mullite. This process resulted in dense mullite/SiC composites with high strength and low sintering shrinkage. In another report, Sakka et al.

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[12] started from alumina and SiC powder mixtures to fabricate SiC/mullite/alumina nanocomposites using similar procedures. Nevertheless, none of them attempted to systematically vary the oxidation extents to change the composition of SiC/mullite in the samples.

For better composites, it is often necessary to optimize the amount of each phase in the composites. Hence, it is desirable to control the amount of mullite in the reaction sintering of SiC/mullite composites. Since mullite is the reaction product of alumina and silica, its amount is closely related to the amount of silica. And the amount of silica is determined by the oxidation extent of SiC. Therefore, it is essential to know the oxidation kinetics of SiC in the powder compacts so that the control of mullite amount is possible.

In this research, we studied the oxidation kinetics of SiC powder in SiC/alumina/zirconia powder compacts. These oxidation data would be the basis for the oxidation treatment (to yield appropriate amount of silica) in subsequent reaction sintering of SiC/mullite/zirconia, which will be reported elsewhere. Because the oxidation of SiC would be influenced by the impurities in the environment [5], oxidation studies conducted in SiC/alumina/zirconia powder compacts are essential for the good control of oxidation extent of SiC (i.e., control of silica and SiC amounts) in the compacts.

2. Experiments

Powders of silicon carbide, alumina and 3 mol% yttria-doped zirconia were used in this study. The characteristics of these starting powders are listed in Table 1. Before mixing and compacting the powder mixtures, the oxidation temperature of SiC powder was determined by the thermogravimetric analysis (TGA)(SSC 5000, Seiko Instruments Inc., Tokyo, Japan) in flowing air. The oxidation layers of the SiC powders were studied with X-ray diffractometry (XRD)(D-5000, Siemens, Karlsruhe, Germany) and transmission electron microscopy (TEM) (H-800 STEM, Hitachi, Tokyo, Japan) after they were oxidized at 1100°C.

Table 1
The characteristics of starting powders[a]

Starting powders	SiC[b]	Al_2O_3 (alpha)[c]	3Y-ZrO_2[d]
Purity (wt%)	97[e]	99.99	99.9
Ave. particle size (μm)	0.45	~0.41	~0.17
BET Surface area (m^2/g)	18	15	30

[a] All data except particle sizes were supplied by the manufacturers.

[b] A-1, Showa Denko Co., Ltd., Tokyo, Japan.

[c] Baikalox CR15, Baikowski International Corp., Charlotte, NC, USA.

[d] OZC-3YA, Osaka Cement Co., Ltd., Osaka, Japan.

[e] Major impurities in SiC powders: 1.4 wt% free carbon; 0.7 wt% SiO_2; 0.01 wt% Al; 0.04 wt% Fe.

For the kinetic studies, compacts of SiC, alumina and zirconia powders were used. Powder mixtures of SiC, alumina and 3 mol% yttria-doped zirconia (3Y-ZrO_2) (weight ratio was 4:4:2 unless stated otherwise) were ball-milled with 1 wt% of PVA (polyvinyl alcohol) for 20 h in ethanol in polyethylene bottles. The milling balls were 3Y-TZP (3 mol% yttria tetragonal zirconia polycrystals) of 3 mm in diameter. After the milling, the slurry was dried under infrared light, softly ground and sieved to pass 80 mesh to obtain free flowing granules. Powder compacts were obtained by uniaxial dry pressing at 300 MPa, followed by a burnout treatment at 700°C for 6 h. (From the thermogravimetric analysis (TGA) results, SiC powder would not significantly oxidize at this burnout temperature). The powder compacts were about 0.5 g and were 10 mm in diameter and about 3 mm in thickness.

Oxidation of the powder compacts was performed in a tube furnace in static air between 1000 and 1200°C for up to 10 h. The samples were heated at a rate of 10°C/min. and cooled in the furnace. During the cooling, the furnace was purged with flowing argon gas to reduce oxidation during the cooling process. Weights of samples before and after oxidation treatments were measured with an electronic balance (±0.1 mg, Precisa 125A, Precisa Instruments AG, Dietikon, Swiss). Before each weight measurement, the samples were oven-dried at 100°C for 12 h, followed by 150°C for 2 h, then cooled in a dessicator.

The weight gain fractions (F_w) of the samples were calculated as $F_w = W_2 - W_1/(W_1{}^*X)$; where

W_2: weight of the sample after oxidation treatment,
W_1: weight of the sample before oxidation treatment,
X: fraction of SiC in the powder compacts.

The weight gain of the samples after oxidation was assumed to derive completely from the passive oxidation of SiC: $SiC_{(s)} + 2O_{2(g)} \text{-----}> SiO_{2(s)} + CO_{2(g)}$. Therefore, the weight gain of the samples reflected the oxidation extent of SiC powders in the samples.

3. Oxidation analysis

For isothermal oxidation of powders, Carter's equation is followed: [13,14]

$$z - (z-1)(1-R)^{2/3} - [1 + (z-1)R]^{2/3} = [(z-1)/z][2kt/r^2] \tag{1}$$

where R is the degree of reaction (i.e. the volume fraction of the initial powders which reacts after time t), k is the rate constant, r is the particle radius of the initial powder and z is the ratio of molar volume of the product to the molar volume of the reactant. When oxidation degree $R \leqslant 0.4$, Eq. (1) can be simplified as [14]:

$$R^2 = 18kt/(z^2r^2) \quad (2)$$

In such case, the oxidation of powders could be described by the relation: $R^2 \propto t$.

In order to analyze the oxidation kinetics of SiC powder with gravimetric method, reaction degree R (i.e. volume fraction of SiC that oxidizes) is converted into weight gain fraction (F_w) of the SiC as followed:

$$F_w = [((1 - R)\rho_{SiC} + zR\rho_{SiO2}) - \rho_{SiC}]/\rho_{SiC}$$

$$= 0.497R \quad (3)$$

where ρ_{SiC} is the density of SiC ($\rho_{SiC} = 3.21 g/cm^3$), ρ_{SiO2} is the density of SiO_2 ($\rho_{SiO2} = 2.2$ g/cm^3), z is the ratio of molar volume of SiO_2 to the molar volume of the SiC ($z = 27.3$ cm^3/12.5 cm^3). Combining Eqs. (2) and (3) and substituting the values of z and the average SiC particle size, we get

$$(F_w)^2 = 18.4 \times 10^8 kt \quad (4)$$

(t in hour and k in cm^2/h)

Eq. (4) is accurate for $F_w \leqslant 0.2$ (i.e. $(F_w)^2 \leqslant 0.04$). Hence, the rate constant k at each temperature could be obtained from the slope of the fitting line in a plot of $(F_w)^2$ versus t.

4. Results

Fig. 1 is the TGA curve of the SiC powder. It revealed that the weight of SiC powder decreased initially with temperature below 937°C, then increased with temperatures above 937°C. The weight loss at temperatures below 937°C was believed due to the loss of absorbed water and carbon impurity [12]. The weight gain at temperatures above 937°C was attributed to the passive oxidation of SiC. From the TGA curve, it was determined that the temperature for significant oxidation of the SiC powder was 937°C.

Figs. 2 and 3 are XRD patterns and TEM micrographs of SiC powders after oxidation treatment at 1100°C in static air. A layer of silica surrounding the SiC core could be seen in the micrograph. The XRD patterns showed a hump around 2 theta equal to 22°, indicating that the silica was amorphous.

Fig. 4 is the plot of weight gain fraction square vs oxidation time. Generally, the weight gain fraction square, $(F_w)^2$, varied linearly with the oxidation time (t) when samples were oxidized at temperatures between 1000 and 1200°C for up to 10 h. It was noted that these fitting lines did not go through the origin. The intercept of each line (i.e. at $t = 0$) corresponded to the square of the weight gain of each sample during the heating ramp.

As mentioned before that Eq. (4) is accurate for $(F_w)^2 \leqslant 0.04$. Nevertheless, Fig. 4 showed that the linear relationship between $(F_w)^2$ and t was followed for $(F_w)^2$

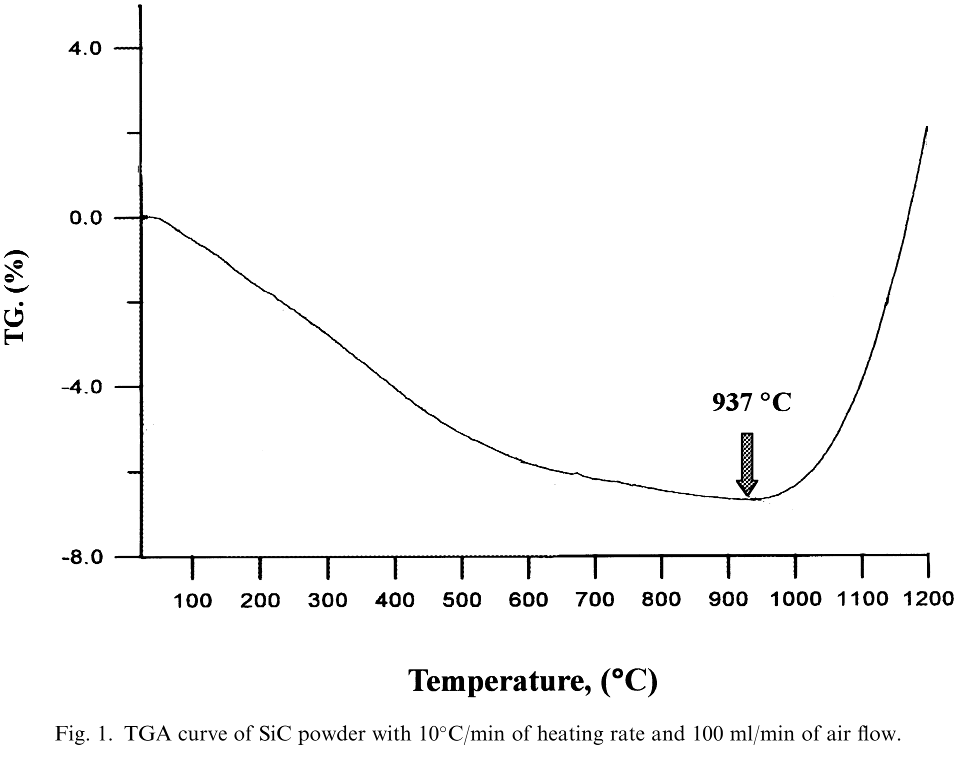

Fig. 1. TGA curve of SiC powder with 10°C/min of heating rate and 100 ml/min of air flow.

up to ≈0.12 (i.e. $F_w \leqslant 0.34$). When $(F_w)^2$ became greater than ~0.12 (in the samples oxidized at 1200°C for 8 and 10 h), the data deviated from the linear relationship and exhibited lower weight gains. This deviation in weight gain was not merely due to the fact that Eq. (4) was no longer accurate for large weight gain fraction.

To examine the deviation of weight gain of the samples treated at 1200°C, we plotted the relationship between $(F_w)^2$ and t according to the Carter's equation (the dotted line in Fig. 4). It was apparent that the weight gain fractions of the samples oxidized at 1200°C for more than 8 h were significantly lower than the values predicted by the Carter's equation. Hence the weight gains of these samples actually decreased. The decrease in the weight gain fraction of the samples oxidized at 1200°C for more than 8 h was associated with the structural change in the oxidation layer. Fig. 5 revealed that the amorphous silica layer had crystallized into cristobalite in the sample oxidized at 1200°C for 10 h. The formation of cristobalite in the oxidation layer was shown to reduce the oxidation rate of SiC. [3,6,15].

The rate constants (k) were calculated from the slopes of each line in Fig. 4 and were listed in Table 2. The Arrhenius plot of rate constant k and the oxidation temperature were shown in Fig. 6. From the slopes of the straight line in Fig. 6, the activation energy of the oxidation was calculated to be 213.1 kJ/mol (slope = -activation energy/gas constant).

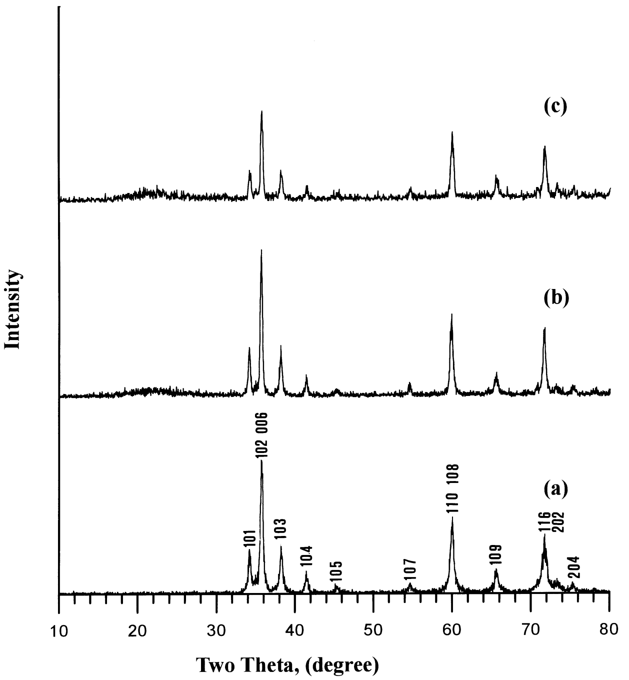

Fig. 2. XRD patterns of SiC powder oxidized in air, (a) as-received, (b) 1100°C/3 h, (c) 1100°C/5 h.

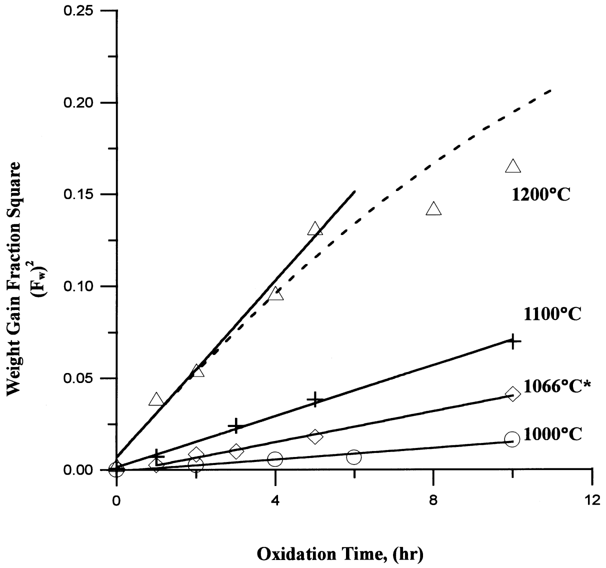

Fig. 4. Square of weight gain fraction versus oxidation time for powder compacts after oxidation treatments at various temperatures. The relation predicted by Carter's equation was plotted as the dotted line curve. (*Data from powder compacts of Al_2O_3: SiC = 1:1 by weight).

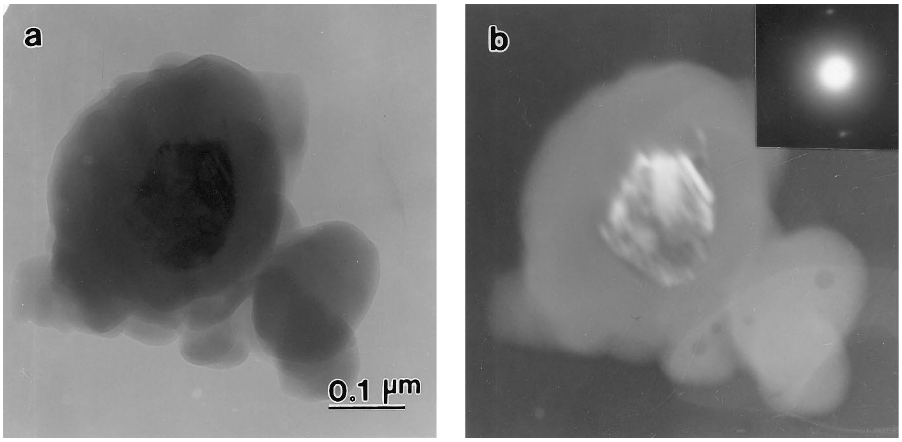

Fig. 3. TEM micrographs of a SiC particle after 1100°C/3 h oxidation, (a) bright field, (b) dark field and selected area diffraction pattern (insert).

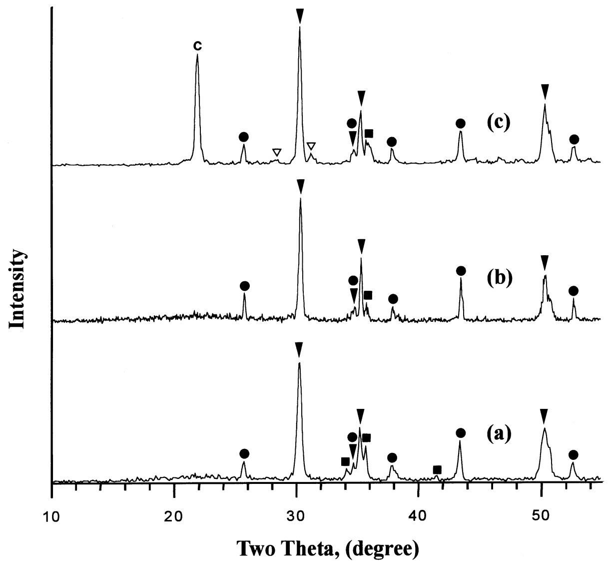

Fig. 5. XRD patterns of green compacts oxidized in air, (a) 1100°C/10 h, (b) 1200°C/5 h, (c) 1200°C/10 h [note the significant cristobalite peak in (c)] ■:SiC; ●:alumina; c: cristobalite; ▼: tetragonal zirconia; ▽: monoclinic zirconia.

Table 2
The rate constant at each temperature

Temperature (°C)	Rate constant k (cm^2/h)
1000	0.85×10^{-12}
1066	2.28×10^{-12}
1100	3.78×10^{-12}
1200	13.0×10^{-12}

5. Discussion

The oxidation temperature of SiC powder was determined to be 937°C from the TGA analysis. It was the temperature at which the weight of sample started to increase due to the oxidation of SiC powders. However, the oxidation of SiC was reported to occur at lower temperatures than 937°C. The diffusion-controlled oxidation was shown to occur at 650°C in nano-sized SiC powders [16]. In micrometer-sized SiC powders, the weight gain due to oxidation was reported to become apparent at 820°C [11]. The inconsistency in the oxidation temperatures of SiC powder could arise from the variations in powder purity and particle size.

The activation energy of SiC oxidation was quite inconsistent in the literature. It varied with the sample conditions (bulk, film or powder; single crystal or polycrystals) and testing environments and ranged from ~ 100 to 500 kJ/mol [2,5,6,17–19]. Nevertheless, the proposed mechanisms of oxidation of SiC were quite consistent. The oxidation mechanisms were believed to be the permeation of molecular oxygen at lower temperatures ($\leqslant$1350°C) and the diffusion of oxygen ions at higher temperatures ($\geqslant$1350°C) [3,20,21]. The activation energies are 113 kJ/mol for oxygen molecule permeating through silica glass network and 298 kJ/mol for oxygen ions diffusing in silica glass [22,23]. The activation energy of oxidation of SiC powder in our study (213.1 kJ/mol) lay in the lower region of the reported activation energy spectrum. This value was neither close to that for molecular oxygen permeation nor close to that for oxygen ion diffusion.

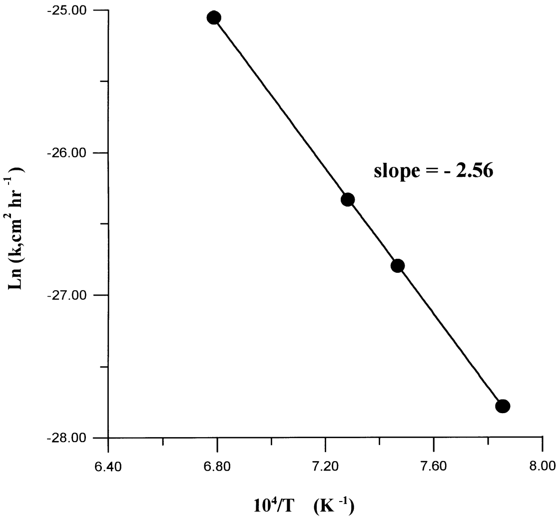

Fig. 6. Arrhenius plot of oxidation rate constants k versus oxidation temperatures. The activation energy of the oxidation could be estimated from the slope of the fitting line.

6. Conclusions

1. From the thermogravimetric analysis, the significant weight gain of SiC powders due to oxidation started around 937°C.
2. When a SiC particle oxidized between 1000 and 1200°C for up to 10 h, a layer of amorphous silica (SiO_2) usually formed. But the amorphous silica would crystallize into cristobalite if the particles were oxidized at higher temperatures for a longer time (e.g. 1200°C for 10 h).
3. The square of weight gain fraction of the SiC powder in compacts of alumina, SiC and 3 mol% yttria-zirconia was linearly proportional to the oxidation time when the weight gain fraction was less than 0.34. The oxidation rate decreased if cristobalite formed.
4. The activation energy of the oxidation of SiC powder was 213.1 kJ/mol.

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