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Short communication

Effect of particle size on oxidation of silicon carbide powders

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Abstract

Oxidation kinetics of micro-sized and nano-sized SiC powders was investigated by using thermogravimetry (TG) analysis. The oxidation kinetics of SiC powders was strongly influenced by particle size; the weight gain and rate constant increased with decreasing particle size of SiC powders. The inceptive oxidation temperatures of micro-sized and nano-sized SiC powders were 843 and 783 °C, respectively. The weight gain of micro-sized and nano-sized SiC powders was in a parabolic relationship with oxidation time over 1100–1200 °C. The values of the parabolic rate constant at 1100, 1150 and 1200 °C were 5.02×10^{-6}, 6.58×10^{-6} and 9.65×10^{-6} $mg^2\ mm^{-4}\ min^{-1}$, respectively, for micro-sized SiC powders, and 8.11×10^{-6}, 10.34×10^{-6} and 13.20×10^{-6} $mg^2\ mm^{-4}\ min^{-1}$, respectively, for nano-sized SiC powders. The oxidation activation energy of micro-sized and nano-sized SiC powders was about 110.74 and 82.64 kJ mol^{-1}, respectively. The oxidation mechanism of SiC powders was controlled by the permeation of molecular oxygen.

Keywords: Oxidation kinetics; SiC powders; Particle size; Activation energy

1. Introduction

Silicon carbide (SiC) is widely used as a high temperature structural material and refractories due to reasonable strength properties, high thermal conductivity, and excellent corrosion and oxidation resistance. The oxidation of SiC is important in the industrial applications of SiC composites.

The SiC passive oxidation is controlled by the diffusion of oxygen molecules (or oxygen ions) through the oxide thin film [1–5]. At temperatures above 600 °C in air, SiC will react with air to form a silica-rich surface layer. Numerous studies have shown that the oxidation of SiC above 1000 °C follows a parabolic rate law, which indicates that the oxidation process is controlled by diffusion [3–9]. Zheng et al. [10] using $^{16}O_2$ and $^{18}O_2$ found that the oxidation process was dominated by the transport of molecular oxygen at lower temperatures (<1300 °C) with a substantial contribution from diffusion of ionic oxygen at higher temperatures. The oxidation behavior of SiC is also influenced by factors such as moisture in the environment, particle size and metal impurities in the powders [11–13].

The oxidation kinetics of SiC-containing ceramic was reported in some papers [6–8,14,15]; however, reports on oxidation kinetics of the micro-sized and nano-sized SiC powders are few [15–17]. This paper reports the results of our investigations on the oxidation kinetics of the micro-sized and nano-sized SiC powders at different temperature by using thermogravimetry (TG) analysis.

2. Experimental procedure

Micro-sized SiC (designed as M-SiC) and nano-sized SiC (designed as N-SiC) powder used in the present study were all Chinese commercial products, the characteristic of samples are listed in Table 1.

Oxidation kinetics was measured by two conventional methods in thermogravimetry (TG-DTA, NETZSCH STA449C, Germany): (1) in non-isothermal oxidation, the sample (20 mg in Al_2O_3 crucible) was heated from 20 to 1300 °C at a rate of 10 °C min^{-1} in a flow of synthetic air (H_2O < 10 ppm, flow rate 50 ml min^{-1}), and (2) in isothermal oxidation, first the specimens were heated in flowing N_2 up to the designated test temperature, such as 1100, 1150 and 1200 °C, and then oxidized in flowing synthetic air for 2 h. Non-isothermal oxidation was used to choose the suitable isothermal oxidation temperature range.

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Table 1
The characteristic of micro-sized and nano-sized powders

Specimens	SiC (wt.%)	Average particle size (μm)	Specific surface area[a] ($m^2\ g^{-1}$)	Impurity chemical composition (wt.%)				
				Al_2O_3	SiO_2	Fe_2O_3	C	Si
Micro-sized SiC	97.2	1.20	4.69	0.45	0.50	0.60	0.20	0.84
Nano-sized SiC	97.8	0.20	6.71	0.41	0.33	0.10	0.10	1.02

[a] BET method, Quantachrome NovaWin2, liquid nitrogen absorbate.

The identification of minerals before oxidation of SiC powders was done by Philips X'Pert PRO diffractometer (using Cu Kα radiation, Ni as filter and Silicon as internal standard, 40 kV, 40 mA, time per step 3.80 s) from 5° to 90° (2θ) with a step width of 0.02°. The microstructure of SiC powders before oxidation was characterized by using scanning electronic microscopy (SEM) (JSM-5610LV, JEOL, Tokyo, Japan).

3. Results and discussion

XRD patterns and SEM micrographs of M-SiC and N-SiC powders are shown in Figs. 1 and 2. The XRD patterns indicate that the crystalline phase of the SiC powder is 6H-SiC, and that the SiC phase is nearly pure. Fig. 2 shows that particle size was about 0.5–2 μm and 0.2 μm for M-SiC and N-SiC powders, respectively.

Non-isothermal oxidation results (TG curves in flowing synthetic air) of M-SiC and N-SiC powders are shown in Fig. 3. These results indicate that the total weight gain of M-SiC is about 8.5%, and the initial oxidation temperature is about 843 °C, which is nearly equal to 820 °C for micrometer-sized SiC [18]. However, the weight gain of N-SiC is about 18%, the initial oxidation temperature is 783 °C, which is higher than 650 °C in nano-sized SiC powders by diffusion-controlled oxidation [16]. TG curves of M-SiC and N-SiC powders also indicate that the oxidation of N-SiC is faster than M-SiC powders; the weight gain of N-SiC powders after oxidation was about three times as much as that of M-SiC powders. It may be attributed to the high specific surface area, low packing density, smaller particle sizes and lower apparent activation energy of nano-sized powders. Specific surface area (by BET method, liquid nitrogen absorbate) and particle size of N-SiC and M-SiC are listed in Table 1, which shows that the values were about 6.71 and 4.69 $m^2\ g^{-1}$, and 1.2 and 0.2 μm, respectively. Smaller particle sizes create larger interfacial areas and increase the numbers of atoms at the particle interfaces, which favors oxidation. The weight gain of all samples was dramatically increased when temperature ranged from 1100 to 1250 °C in non-isothermal oxidation test. So, the isothermal oxidation temperatures were chosen at 1100, 1150 and 1200 °C.

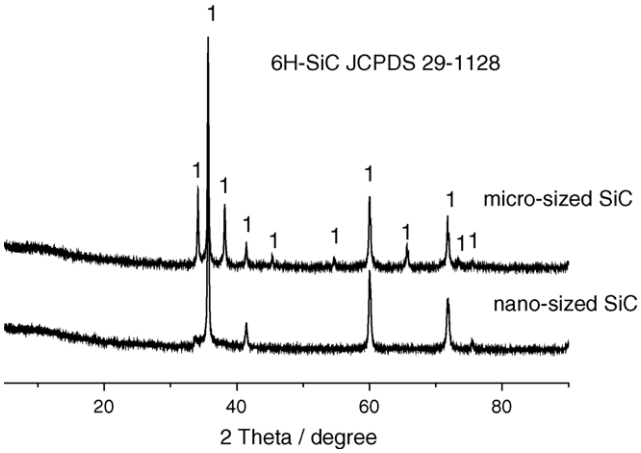
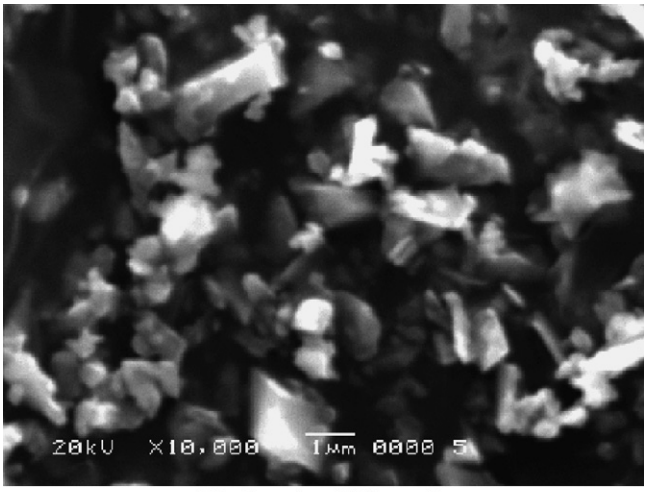
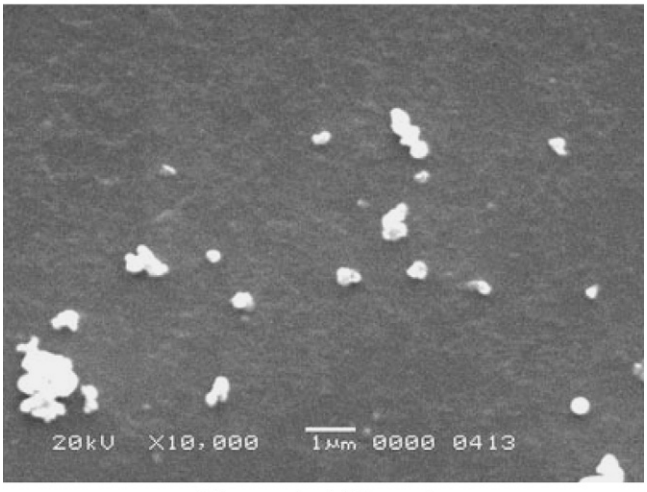


Fig. 1. XRD patterns of micro-sized SiC and nano-sized SiC powders.



(a) micro-sized SiC powder



(b) nano-sized SiC powder

Fig. 2. SEM micrograph of micro-sized SiC and nano-sized SiC powders.

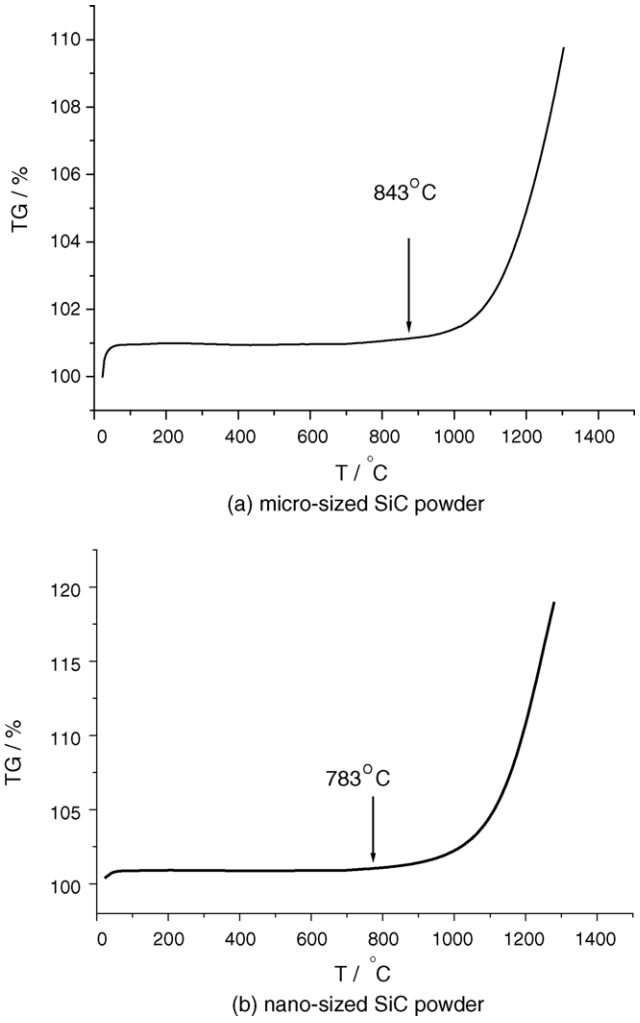


Fig. 3. TG curves of micro-sized and nano-sized SiC powders.

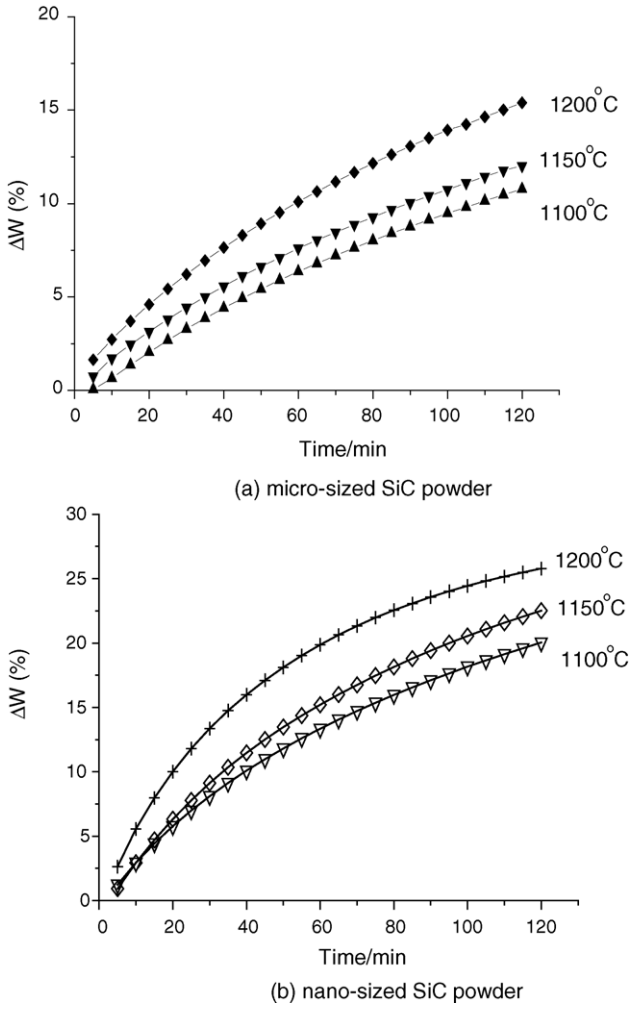


Fig. 4. Weight gain vs. oxidation time of micro-sized and nano-sized powders.

Curves for weight gain plotted as a function of time for isothermal oxidation of M-SiC and N-SiC powders are shown in Fig. 4. The weight gain behavior of all specimens over 1100–1200 °C was approximated by the classical parabolic equation:

$$W^2 = Kt + b \approx Kt$$

where $W = \Delta W/A$ is the weight gain per unit area (g cm^{-2}) at time t, $K = K_0\exp(-E_a/RT)$ (g^2 cm^{-4} min^{-1}) is the parabolic rate constant and b is a constant which accounts for the effect of a possible nonparabolic initial stage, i.e. for the uncertainty of the exact definition of the beginning ($t = 0$) of the parabolic process. Fig. 4 also shows that the magnitude of the weight gain increased with increasing oxidation temperature, and the weight gain of N-SiC powders was much more than that of M-SiC.

The squared weight gain to surface area $(\Delta W/A)^2$ versus time graphs of M-SiC and N-SiC powders are shown in Fig. 5. The value of parabolic rate constant of SiC powders, k ((weight gain per unit surface area)$^2 = k \times$ time), was 5.02×10^{-6}, 6.58×10^{-6} and 9.65×10^{-6} mg^2 mm^{-4} min^{-1} for M-SiC powder oxidized at 1100, 1150 and 1200 °C, respectively. As for N-SiC powder, k value was 8.11×10^{-6}, 10.34×10^{-6} and 13.20×10^{-6} mg^2 mm^{-4} min^{-1}, respectively. The Arrhenius plots of rate constant (k) and oxidation temperature are shown in Fig. 6. From the slopes of the least-squares lines in this figure, the oxidation activation energies for parabolic oxidation of M-SiC and N-SiC powders in dry air could be determined (slope = −activation energy/gas constant). The oxidation activation energy was 110.74 and 82.64 kJ mol^{-1} for

Table 2
The rate constant and oxidation activation energy of micro-sized and nano-sized powders

Samples	Temperature (°C)	Rate constant $k_s \times 10^{-6}$ (mg^2 mm^{-4} min^{-1})	Activation energy (kJ mol^{-1})
Micro-sized SiC	1100	5.02	110.74
	1150	6.58	
	1200	9.65	
Nano-sized SiC	1100	8.11	82.64
	1150	10.34	
	1200	13.20	

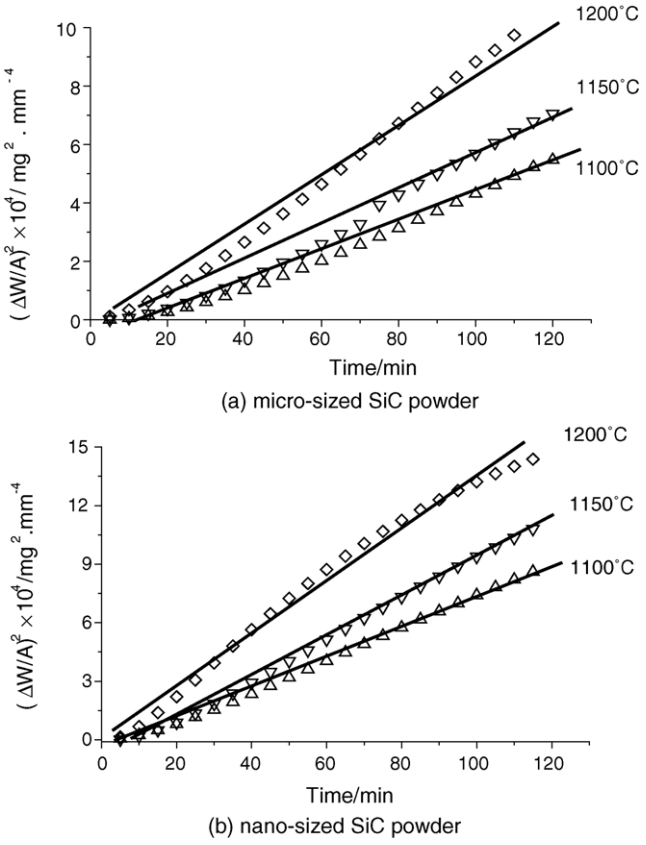


Fig. 5. Relationship between square of weight gain per unit area and oxidation time of SiC powders at 1100, 1150 and 1200 °C (fitted line) (1100 °C: $R^2 = 0.998$; 1150 °C: $R^2 = 0.998$; 1200 °C: $R^2 = 0.983$; R: fitted linear coefficient).

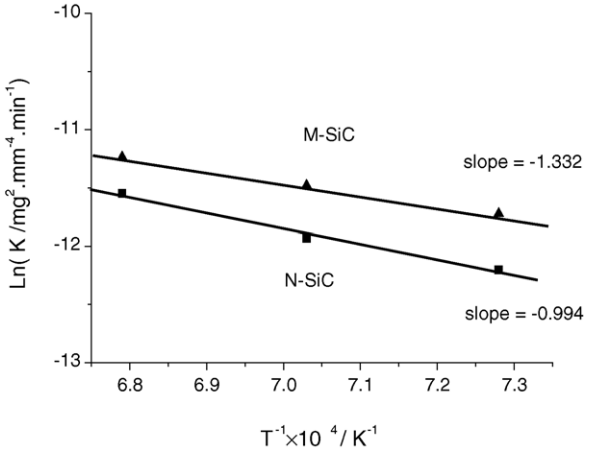


Fig. 6. Arrhenius plot of the oxidation of micro-sized and nano-sized powders.

M-SiC and N-SiC powders, respectively. The values of parabolic rate constant and oxidation activation energies are listed in Table 2. The oxidation activation energy of M-SiC powders was fairly close to 113 kJ mol^{-1} reported by Norton [19], which indicated that the oxidation mechanism of SiC powders was controlled by the permeation of molecular oxygen.

4. Conclusions

Oxidation kinetics of SiC powders was studied by using TG analysis. The initial oxidation temperatures of micro-sized and nano-sized SiC powders were 843 and 783 °C, respectively. The weight gain of SiC powders was in a parabolic relationship with oxidation time over 1100–1200 °C. The oxidation kinetics of SiC powders was strongly influenced by particle size, and the weight gain and rate constant increased with decreasing the SiC particle size. The values of parabolic rate constant at 1100, 1150 and 1200 °C were 5.02×10^{-6}, 6.58×10^{-6} and 9.65×10^{-6} mg^2 mm^{-4} min^{-1}, respectively, for micro-sized SiC powders, and 8.11×10^{-6}, 10.34×10^{-6} and 13.20×10^{-6} mg^2 mm^{-4} min^{-1}, respectively, for nano-sized SiC powders. The oxidation activation energy of micro-sized and nano-sized SiC powders was about 110.74 and 82.64 kJ mol^{-1}, respectively. The oxidation mechanism of SiC powders was controlled by the permeation of molecular oxygen.

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