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Oxidation behavior of polymer derived SiCO powders

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Abstract

Polymer derived SiCO ceramic powders were fabricated by pyrolysis of polycarbosilane precursor. The oxidation behaviors of these powders were studied by thermogravimetric analysis at the temperature range of 900–1400 °C. The oxidation parabolic constants at different temperatures were calculated. From these parabolic constants, the apparent activation energies for oxidation could also be obtained. These results indicated that SiCO powders have a close oxidation rate to that of pure silicon carbide. The crystallinity of SiCO ceramics and silica scales has little effect on the oxidation rates. The results also elucidated that the oxidation mechanism for amorphous and crystalline silica is the same.

Keywords: A: Precursors: organic; C: Corrosion; D: SiC; Oxidation mechanism

1. Introduction

Silicon-based ceramics such as SiC and Si_3N_4 are considered as structural materials for high temperature application because of their excellent thermo-mechanical properties [1]. In addition to the conventional processing for these materials, silicon-based non-oxide ceramics can be alternatively synthesized by thermal decomposition of polymer precursors, referred to as polymer derived ceramics (PDCs). One of the advantages of PDCs is their high purity so that they exhibit excellent high temperature properties, such as resistance to creep [2,3]. With ultrahigh temperature thermal stability [4], PDCs show promise for applications at elevated temperatures.

The structural materials for high temperature applications in oxygen-containing environments must embody excellent resistance to oxidation. Hence, the oxidation behavior is one of the subjects for PDCs' studies [5–9]. It has been found that the polymer derived SiCN and SiBCN ceramics exhibited oxidation rates similar to pure silicon carbide [5,6]. Recent research has indicated that SiAlCN ceramics have much better oxidation and corrosion resistance than other ceramics up to 1400 °C [7–11]. These results demonstrated that PDCs have the potential applications in combustion environments.

As to the oxidation of silicon-based ceramics, it is known that protective SiO_2 layer will be formed during oxidation at high temperatures and high oxygen partial pressures [12]. Oxygen diffuses through the SiO_2 scales via two mechanisms: molecular oxygen diffuses through the scales, and the so-called network oxygen ion diffuses through the SiO_2 [13]. These two mechanisms happen simultaneously and show different temperature dependency. Therefore, oxidation at different temperatures could be governed by either mechanism. ^{18}O isotope diffusion experiments [14,15] indicated that the oxidation rate at low temperatures is dominated by molecular oxygen diffusion. However, at high temperatures (>1300 °C), SIMS studies [15,16] found extensive interchange between the interstitial and network oxygen species. Network oxygen ion diffusion becomes appreciable. Oxidation studies of silicon-based ceramics [8,17] indicated significant cristobalite content in the oxides at temperatures higher than 1300 °C, and observations suggested that the oxygen diffusion through the cristobalite is slower than through amorphous silica [18,19]. One would expect that the lower diffusion rate is due to the mechanism changing for oxygen through silica scales. Thus, it was considered that the crystallization of silica scale is the reason for network diffusion.

In this study, the oxidation kinetics of polymer derived SiCO powders was studied. The oxidation rate constants for

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amorphous and crystalline SiCO powders were obtained. In order to identify the crystalline silica effect on the oxidation rate, the parabolic constants for amorphous silica scales and crystalline scales were plotted together. The results showed that there is not a significant difference in the activation energy, which suggested that the oxidation mechanism is the same for the amorphous and crystalline silica.

2. Experimental procedure

SiCO powders were prepared by pyrolysis of polycarbosilane precursor, which was purchased from Xiamen University. The cross-linking and pyrolysis of this precursor was described in a previous study [20]. The pyrolysized ceramics were ball-milled into fine powders, and then were heat-treated at 1150 °C and 1500 °C in argon for 4 h, separately. X-ray fluorescence spectrometry (XRF, S4 Pioneer, Bruker, Germany) was used to determine the compositions of these two kinds of powders. The specific area was measured by BET (Quantachrome, USA).

Thermogravimetric analysis (TGA) (Netzsch STA-409C, Germany) was used to measure the oxidation rates. 40–60 mg samples were weighed for the oxidation process. During the temperature ramping process, ultra-high purity argon gas was used to protect the powders from oxidation. When the temperature reached the set value, several minutes were required to stabilize the temperature. Then, the dry air flow in the chamber was started with a rate of 50 ml/min. The oxidation time varied from 20 min to 120 min dependent on the oxidation temperatures. The weight gain was recorded by the computer as a function of oxidation time.

The crystallinity of oxide scales were characterized by XRD. XRD was carried out by using a Rigaku D/max-2400 diffractometer (Tokyo, Japan) with a copper Kα radiation. Data were digitally recorded in a continuous scan in the range of angle (2θ) from 15° to 75° with a scanning rate of 0.08°/s.

3. Results

3.1. The properties of SiCO powders

After treatment at 1150 °C and 1500 °C, polymer derived SiCO powders were amorphous and crystalline (Fig. 1), respectively. The composition and specific surface area of these powders are shown in Table 1.

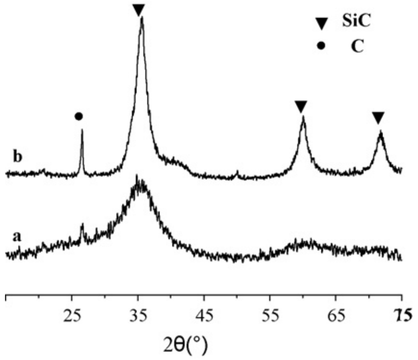

Fig. 1. The XRD pattern of SiCO powders treated at 1150 °C and 1500 °C.

3.2. The oxidation of amorphous SiCO powders

The square of specific weight change as a function of oxidation time is shown in Fig. 2a. It is known that PDCs powders are porous [21]. In order to avoid the oxidation area changing due to the pore sealing [22], a shorter oxidation time is required for a higher temperature. The oxidation time ranges from 80 min at 900 °C to 20 min at 1050 °C.

Passive oxidation kinetics is typically described in terms of a parabolic rate constant k_p [23], as defined below:

$$w^2 = k_p t + w_0^2 \tag{1}$$

where w is the specific weight change during oxidation, t the time, and w_0^2 an adjust parameter. If an oxide scale exists before the oxidation, w_0^2 is greater than 0. Linear regression of the oxidation data was preformed by using Eq. (1) for the oxidation data of amorphous SiCO powders. The estimated parabolic rate constants from the data are listed in Table 1. These parabolic rate constants are also plotted in Fig. 2b as a function of temperature. The apparent activation energy for oxidation can be calculated from these rate constants at different tem-

Table 1
The properties of SiCO powders

	Composition	Specific surface area (m^2/g)	k_p			Activation energy (kJ/mol)
			Temperature (°C)	g^2/m^4 s ($\times 10^{-6}$)	m^2/s ($\times 10^{-18}$)	
Amorphous SiCO powder	$SiC_{1.12}O_{0.12}$	3.5	900	0.167	0.376	121
			950	0.265	0.600	
			1000	0.480	1.08	
			1050	0.656	1.48	
Crystalline SiCO powder	$SiC_{1.11}O_{0.15}$	3.32	900	0.155	0.366	140
			1000	0.596	1.40	
			1100	1.56	3.67	
			1200	4.00	9.44	
		Oxidized at 1300 °C	1300	6.18	14.6	
		for 1 h 0.21	1400	14.4	33.9	

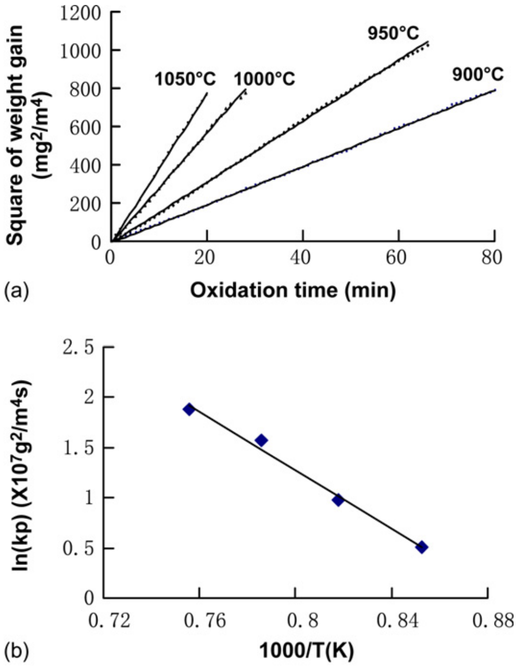

Fig. 2. Oxidation behavior of amorphous SiCO powders.

peratures using the Arrhenius law:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where k is the parabolic rate constant, A is a constant, E_a is the apparent activation energy, R is the gas constant, and T is the oxidation temperature.

XRD (Fig. 3a) results indicated that the oxide scales of amorphous SiCO powders are amorphous at the temperature range of 900–1050 °C.

3.3. The oxidation of crystalline SiCO powders

The SiCO powders were treated at 1500 °C for 4 h in order to crystallize them. Meanwhile, the structure of SiCO was stabilized.

The oxidation of crystalline powders at temperatures from 900 °C to 1100 °C was performed as described in the previous section. At temperatures higher than 1200 °C, the times for sealing pores are so short that the oxidation parabolic constants cannot be obtained from the data of as-received powders. However, the pore-sealed powders can be also used to study the oxidation kinetics. The only thing required is to re-measure the specific surface area of the pore-sealed powders. Attention should be also paid to the oxide thickness of powders. It should be thin compared to the diameter of the powder particles, which makes sure that the oxidation area is constant during oxidation. Hence, at high temperatures, the oxidation time should be short, from 90 min for 1200 °C to 20 min for 1400 °C.

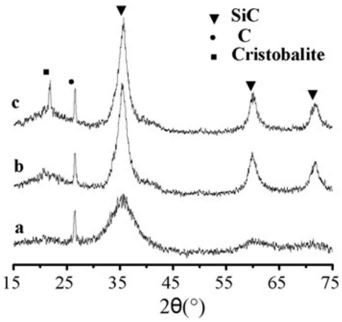

Fig. 3. XRD patterns of oxidized SiCO powders: (a) amorphous SiCO powders oxidized at 1050 °C; (b) crystalline SiCO powders oxidized at 1200 °C; (c) crystalline SiCO powders oxidized at 1300 °C.

The square specific weight changes as a function of oxidation time are shown in Fig. 4a (≤1100 °C) and Fig. 4b (≥1200 °C). The parabolic constants can be obtained by linear regression of these data using Eq. (1). The values are listed in Table 1. XRD indicated that the oxides are amorphous at temperatures lower than 1200 °C (Fig. 3b), and that the oxides become cristobalite at temperatures higher than 1300 °C (Fig. 3c). Plot all k_p values for the crystalline silica and amorphous silica together (Fig. 4c), it was found that they lie in a line with an activation energy of 140 kJ/mol.

4. Discussion

At the temperatures of 900–1100 °C, the amorphous and crystalline SiCO powders have close oxidation rates and activation energies (Table 1). These results indicated that the crystallinity of SiCO has little effect on the oxidation behavior. By comparison the oxidation activation energy for SiCO with that for pure silicon or pure SiC, it is believed that the controlling step for SiCO oxidation at the temperatures of 900–1100 °C is molecular oxygen diffusion through the amorphous oxide scales [7].

Although the structures of oxide scales change from amorphous SiO_2 (≤1200 °C) to crystalline SiO_2 (≥1300 °C) (Fig. 3), the activation energy for oxidation is unchanged (Fig. 4c). It indicated that the oxidation mechanism should be the same regardless of the crystallinity of oxide scales. Similar phenomena were also observed in polymer derived SiCN ceramics [8] and high purity SiC ceramics [17]. Ramberg and Worrell [17] attributed this to the high purity of silica. Previous studies [24] for microstructure of silica indicated that the molecular oxygen diffusion through 6-membered or higher rings is the controlling process for oxidation. The activation energy for this process is close to 120–160 kJ/mol [24]. The activation energy calculated from Fig. 4c is 140 kJ/mol, which shows the oxygen molecular diffusion through crystalline silica scales is the controlling process.

Some experiments [18,19] indicated an activation energy change at high temperatures, at which the oxide scales are crystalline. Ramberg and Worrell [17] pointed out that the impurities would lead to this kind of mechanism change. It is known that the network diffusion at high temperatures is due to the oxygen ion exchanging through network. The obvious intrinsic defects of oxygen for pure silica can only happen at temperatures close to its melting point. Impurities however, even in ppm level, can greatly increase the oxygen defects. The

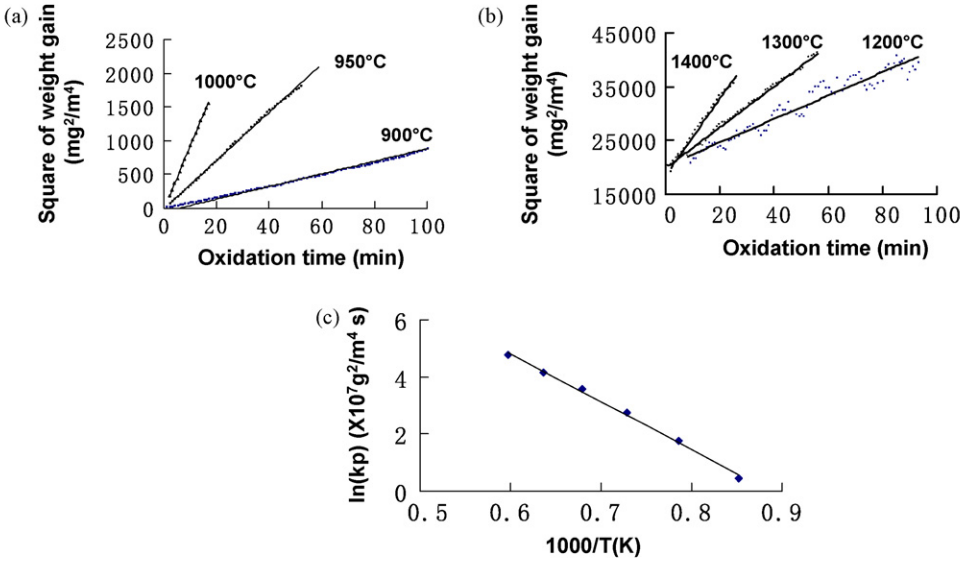

Fig. 4. The oxidation behavior of crystalline SiCO powders.

network diffusion then can be observed at low temperatures and the activation energy will transit at the temperature as low as 1300 °C. Hence, the oxidation mechanism change is due to the oxygen defects in silica over a certain level, regardless of crystallinity of silica.

5. Conclusion

In this study, SiCO powders were prepared by pyrolysis of polycarbosilane precursors. The oxidation behavior of SiCO powders was studied by TGA. The results indicated that the crystallinity of SiCO has little effect on the oxidation behavior. The oxidation mechanism is the same for the amorphous and crystalline silica scales in this study. The mechanism changing from molecular oxygen diffusion to network ion diffusion is due to the oxygen defects in the silica.

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