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Preparation of carbon–silicon carbide composite powder *via* a mechanochemical route

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Abstract

A carbon–silicon carbide (C_p–SiC) composite powder was prepared with nano-carbon (C_p) and silicon (Si) powders as starting materials *via* a mechanochemical treatment in Ar atmosphere in a stirred ball mill. The composite powder was characterized by X-ray diffraction (XRD), thermogravimetry/differential scanning calorimetry (TG/DSC), scanning electron microscopy (SEM) and transmission electron microscopy/high resolution transmission microscopy (TEM/HRTEM). Effects of parameters (such as grinding time, ratio of ball to powder, grinding mode and atmosphere) on the synthesis of β-SiC particles, and the simultaneous preparation of C_p–SiC composite powder with the synthesized particles of β-SiC and the remaining C_p by mechanochemical treatment were investigated. The results show that β-SiC particles can be synthesized and the C_p–SiC composite powder in the presence of excessive nano-sized carbon can be simultaneously obtained *via* the mechanochemical route.

Keywords: D. Carbon; D. SiC; Composite powder; Mechanochemistry

1. Introduction

Carbon–silicon carbide (C_p–SiC) ceramic matrix composite is a major representative in glass industry [1]. This ceramic composite material can be used for trestle table in a glass furnace instead of graphite material. In the application, the C_p–SiC composite possesses some superior properties like high strength and anti-oxidation/corrosion resistances besides well-machining properties, compared to graphite material. The existing preparation method of C_p–SiC ceramic composite is a pressureless sintering of mechanically mixed carbon black and silicon carbide powders. However, the performance of the ceramic composite can be reduced due to the poor uniformity of the powders mixed by conventional mixing methods.

Also, the existing methods for the preparation of C/SiC composites are mainly chemical vapor deposition and infiltration (CVD and CVI) [2,3], liquid and solid infiltration [4,5] and polymer infiltration and pyrolysis (PIP) technique [6]. However, their development and application are restricted due to the higher production cost and complex processes [7]. Mechanochemical method has attracted considerable interest in the preparation of ceramic composite materials in recent years [8–15]. This is due to a wide range of materials exhibiting the intriguing properties and structures that can be prepared using this method. Recent work reported that silicon carbide (SiC) can be synthesized with silicon (Si) and carbon (C) powders *via* a mechanochemical method (or mechanical milling) [16–24]. Therefore, it is possible to prepare a C_p–SiC composite powder when SiC can be synthesized with Si and an excessive amount of C powder by means of mechanochemical treatment.

The objective of this paper was to prepare a carbon–silicon carbide composite powder *via* a solid reaction between silicon and an excessive amount of nano-sized

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carbon powder by a mechanochemical route in a high energy stirred ball mill. Effects of parameters (i.e., milling time, ball to powder ratio, grinding mode and atmosphere) on the synthesis reaction of β-SiC, and the simultaneous preparation of C_p–SiC powder in the presence of excessive nano-sized carbon powder by the mechanochemical treatment were investigated.

2. Experimental

2.1. Materials

Nano-sized carbon black powder (purity ≥99%, Jiangdu Tianyuan Carbon Co. Ltd., China) and silicon powder (purity 99.9%, Fujian Fengli Mechanical Technology Co. Ltd., China) were used as the starting materials. The specific surface area of carbon black powder is 75–89 m^2/g. The median sizes (d_{50}) of silicon powders used were 1.59 μm, 76.45 μm and 194.90 μm.

2.2. Procedure

28.0 g of silicon powder was mixed with an excessive amount of carbon black powder of 22.0 g in a molar ratio of Si:C = 1.0:1.8 (or a mass ratio of 1.3:1.0), and ground in a mode QM-1 planetary stirred ball mill (Nanjing Scientific Apparatus Research Institute, China) under various conditions, such as milling time, ratio of ball to powder, grinding mode and atmosphere, to synthesize SiC and simultaneously prepare a C_p–SiC composite powder. Table 1 shows the operating parameters. The stainless steel balls in the size range from 5 mm to 20 mm were used as grinding media. The starting material with argon (Ar) or ethyl alcohol in a hardened-steel barrel was ground in the mill. The synthesis of β-SiC in the mill could occur according to

$$C + Si \xrightarrow{\text{milling}} SiC \quad (1)$$

In the chemical formula (1), a β-SiC powder of 39.9 g could be synthesized with the silicon powder of 28.0 g and the carbon powder of 11.9 g. The remaining carbon powder of 10.1 g (or 0.8 mole) and the synthesized β-SiC could be used to prepare a C_p–SiC composite powder in the mill. The composite powder was rinsed with distilled water 5 times, and dried in a dryer at 80 °C (see Fig. 2(b)). The final weight of the C_p–SiC composite powder after rinsing and drying was 47.2 g. The free carbon that could not be composited was 2.8 g. The mass percentage of carbon in the C_p–SiC composite powder was 15.4 %. All the samples were prepared in the mill under various conditions as given in Table 1 for the subsequent characterization.

2.3. Characterization

The crystalline phase of ground samples was identified by X-ray powder diffraction (XRD) (Shimadzu Co., Japan). The formation of the samples was observed by scanning electron microscopy (SEM) (mode SSX-550, Shimadzu Co., Japan) and transmission electron microscopy (TEM/HRTEM) (mode JEM-3010, JE0L Tokyo, Japan). The simultaneous thermal analysis of the samples was determined by thermogravimetry/differential scanning calorimetry (TG/DSC) (mode STA-409PC, NETZSCH Co. Ltd., Germany).

3. Results and discussion

3.1. Synthesis of silicon carbide

Fig. 1(a) shows the XRD patterns of Si–C mixtures ground for various treatment durations. It is seen that the peaks identifying silicon exhibit a trend to be broader and weaker due to the accumulation of cold-work-induced strain and reduction of grain size, indicating the amorphousness of silicon particles. The carbon atoms could be readily diffused into the amorphous silicon particles rather than the crystalline silicon under mechanical stress. In the continuous intensive mechanochemical treatment, the recrystallization of the amorphous silicon with carbon black particles could occur to form silicon carbide [25]. The XRD pattern of sample ground for 12 h in Fig. 1 shows a peak of β-SiC phase. For the samples ground for 12, 18 and 24 h, the prolonged milling time could enhance the intensity of peak of β-SiC phase. However, the intensity of peak of β-SiC could be decreased due to the increased amorphousness of β-SiC particles after intensive milling for over 48 h. Silicon could not be detected for the samples treated over 24 h, indicating that silicon was totally consumed in the reaction between silicon and carbon black induced by the mechanical stress. The grain size of synthesized β-SiC treated for 24 h was around 200 nm. Only β-SiC and α-Fe phases exist in the sample treated for 24 h, which can be detected. Note that Fe_3C is transferred

Table 1
Operating parameters.

No.	Grinding mode and atmosphere	Rotation speed (rpm)	Milling time (h)	Ball-to-powder ratio
1	Dry milling in Ar	170	12	25:1
2	Dry milling in Ar	170	18	25:1
3	Dry milling in Ar or wet milling in ethyl alcohol	170	24	4:1/12:1/20:1/25:1/40:1
4	Dry milling in Ar	170	48	25:1
5	Dry milling in Ar	170	72	25:1

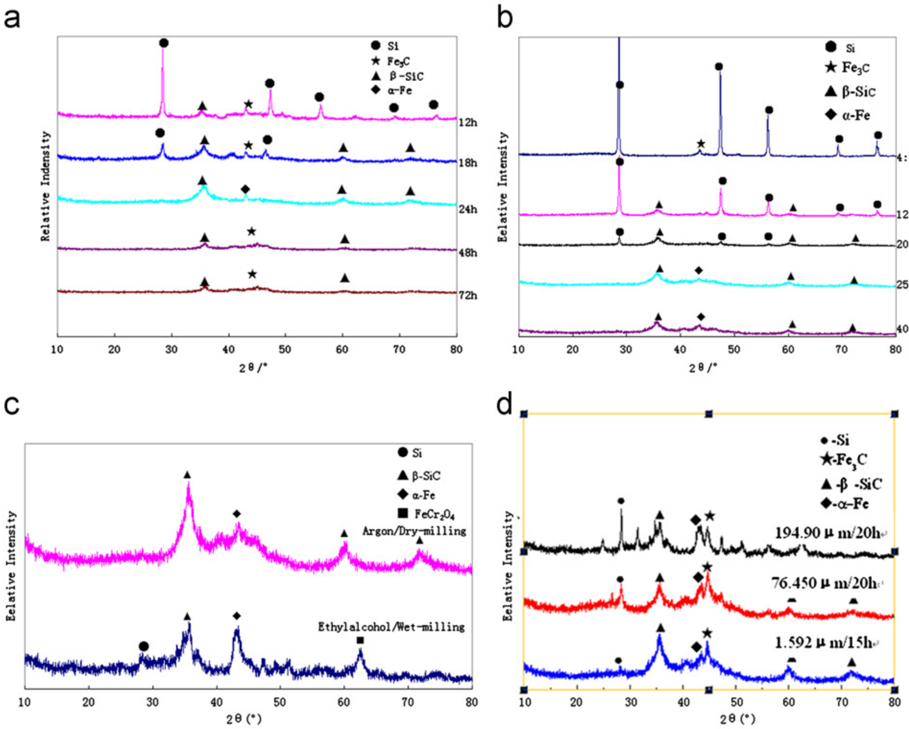

Fig. 1. XRD patterns of Si–C mixed powders treated at different milling durations (a), ball to powder ratios (b), grinding modes and atmospheres (c) and particle sizes of silicon (d).

to α-Fe and carbon black due to structure deformation induced by an intensive milling treatment [19]. Fe_3C could be detected due to the reaction of excessive carbon black and iron contamination from grinding steel balls during prolonged grinding for over 24 h.

Fig. 1(b) shows the XRD patterns of Si–C mixtures ground for 24 h at various ball to powder ratios. Clearly, the ball to powder ratio has an effect on the reaction between silicon and carbon particles under the condition of mechanochemical treatment. There is no peak of β-SiC in the pattern of the sample at a ball to powder ratio of 4:1. However, the peaks of β-SiC appear in patterns for the samples treated at a ball to powder ratio range from 12:1 to 40:1, and the intensity of peak of β-SiC increases with the increase of the ball to powder ratio. The peaks of silicon cannot be detected for the samples treated at a ball to powder ratio of 25:1 and 40:1, indicating that a greater ball to powder ratio could favor the completion of the reaction between silicon and carbon particles. The specific grinding energy of the mill, W_T, could be expressed by [26]

$$W_T = \frac{m_1}{m_2} b n \tau D \tag{2}$$

where n is the rotation speed, b is the acceleration, τ is the milling time, D is the inner diameter of the barrel, m_1/m_2 is the weight ratio of ball to powder. Clearly, a higher ball to powder weight ratio gives a greater specific grinding energy when other parameters are kept constant. However, over-large ball to powder ratio could cause a great quantity of impure phases, and also decreased yield of the powder. Therefore, an optimized ball to powder ratio could be 25:1.

Fig. 1(c) shows the XRD patterns of Si–C mixtures treated in various grinding modes and atmospheres. Compared to the sample wet treated in ethyl alcohol, the peaks of silicon disappeared for the sample dry treated in argon atmosphere for 24 h. It is thus suggested that the dry treatment of the sample in argon atmosphere could be more effective to complete the synthesis reaction. The Si–C mixture dry ground in argon atmosphere for 24 h showed some intensive peaks of β-SiC. Since some unrelated chemical reactions in the synthesis process could not occur in the presence of argon atmosphere, the grinding energy could be mainly used to enhance the synthesis reaction between Si and C. However, the excess energy of wet grinding in ethyl alcohol could be needed during the synthesis process. Unlike dry particles ground in the mill, the Si and C particles could be immersed in ethyl alcohol when the wet particles with ethyl alcohol were treated in the mill, and the ethyl alcohol layer could be formed on particle surfaces *via* the adsorption of ethyl alcohol molecules. The occurrence of ethyl alcohol molecules adsorption points to a non-electrostatic contribution to the interaction energy. In addition, the energy potential barrier between the wet particles also exists due to the presence of ethyl alcohol layer on the particle surfaces. Thus, excess energy should be consumed to eliminate the potential barrier between the wet particles in ethyl alcohol for the effective contact and interaction of Si and C particles during the synthesis process in the mill.

Fig. 1(d) shows the XRD patterns of the samples with various particle sizes of silicon as starting materials treated for 20 h. A finer particle size possesses a greater surface

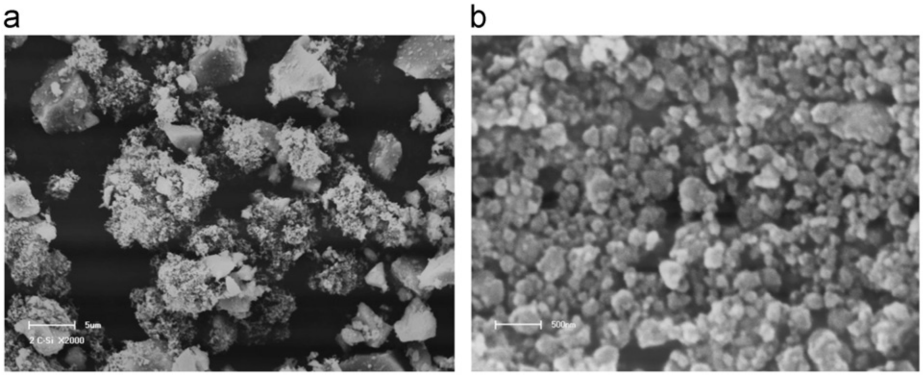

Fig. 2. SEM images of Si–C mixture powders (a) before and (b) after mechanochemical treatment.

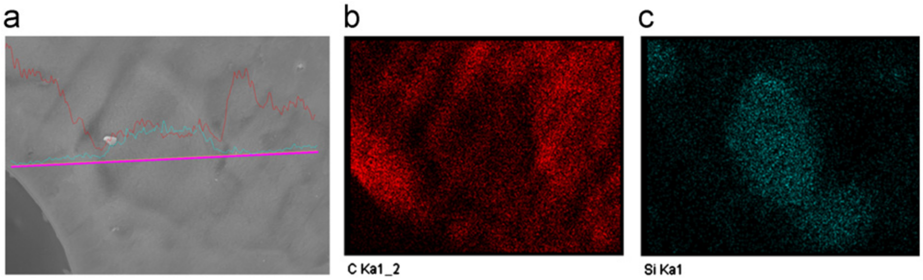

Fig. 3. SEM images of composite particles: (a) surface topography and line scanning, (b) distribution of carbon, and (c) distribution of silicon (For interpretation of the references to color in this figure, the reader is referred to the web version of this article).

area and surface energy, leading to a greater probability of the inter-particle contacts and reactivity for the effective synthesis under mild mechanochemical treatment conditions. As shown in Fig. 4, the mixture sample with a finer particle size silicon of 1.592 μm is more effective to complete the synthesis reaction of silicon and carbon particles. The peak of silicon became less intensive and the peaks of β-SiC appeared more intensive when the particle size of silicon in the mixture decreased. Also, contaminations like α-Fe and Fe_3C reduced with the decrease of particle size of silicon in the mixture. Clearly, the finer particle sizes in the mixture could favor the synthesis of β-SiC due to the higher inter-particle contact probability and reactivity. It could be assumed that the use of finer particles in the mixture for the synthesis reaction could shorten the duration of synthesis, resulting in the reduction of energy consumed in mechanochemical treatment in the mill. This also reflects that the synthesis could be performed under mild mechanochemical conditions when finer particles of materials are used [13].

3.2. *Preparation of carbon–silicon carbide composite powder*

It was assumed that a C_p–SiC composite particulate material could be prepared with an excessive amount of carbon powder and β-SiC particles synthesized *via* mechanochemical treatment in the mill. Fig. 2 shows the SEM photographs of Si and C mixture samples prepared before and after mechanochemical treatment method. The particle sizes and morphologies of the samples before and after mechanochemical treatment appear totally different. Fig. 2(a) indicates the mechanically mixed sample of carbon and silicon particles. The carbon particles mixed with silicon particles before mechanochemical treatment appeared as a simple mixture without any composition.

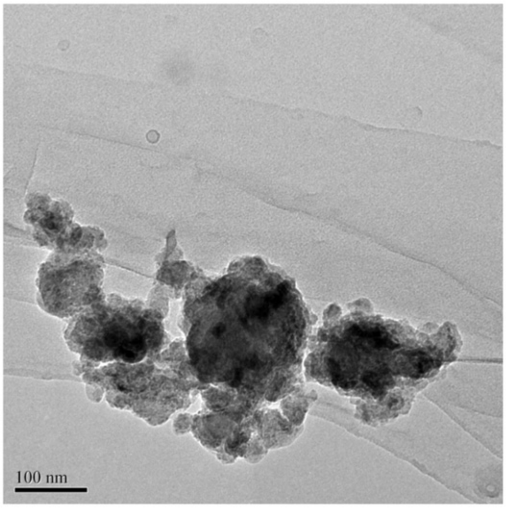

Fig. 4. TEM image of C_p–SiC composite particle.

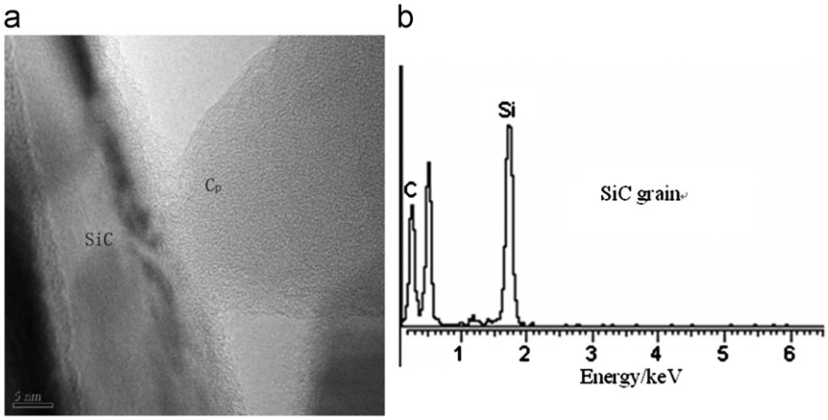

Fig. 5. HRTEM image of C_p–SiC composite particle prepared by a powder composite process.

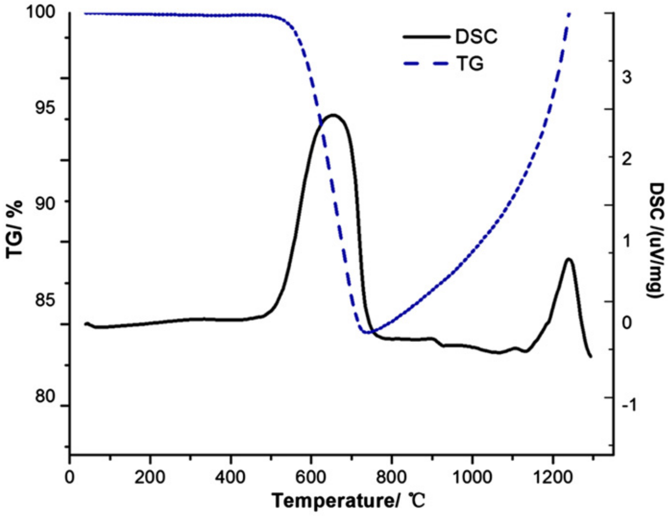

Fig. 6. TG/DSC curves of C_p–SiC composite powders.

However, the sample treated after mechanochemical method appeared as a composite particulate material, as shown in Fig. 2(b). The solid reaction between carbon and silicon particles could be stimulated by mechanical stress *via* the grinding beads in the mill. The silicon carbide particles, which were synthesized during the mechanochemical treatment, could be simultaneously compounded with the carbon particles during the solid reaction [27]. Hence, a C_p–SiC composite powder was prepared by the mechanochemical reaction between silicon carbide particles and excessive carbon powder induced by the milling process. The excessive carbon particles could be dispersed within the synthesized particles of SiC. Fig. 3 shows the line-scanning and area-scanning images of the composite particles. SiC particle is surrounded by carbon black at a mole ratio of Si element to C element of 1:1 (the red indicates C element and the blue is Si element). In addition, it can be confirmed that SiC particles synthesized were actually compounded by carbon particles (see Fig. 4).

Furthermore, Fig. 5 shows a high-resolution TEM (HRTEM) image of a C_p–SiC composite particle. Clearly, a carbon nano-particle could be directly bonded onto a SiC particle. In the nano-scale, the interface between the C_p and SiC particles appeared flat. Such a direct-bonded interface should be more intensive than the interface of physically adsorbed particles. The bonding between C_p and SiC particles occurred due to the mechanochemical reaction during mechanical milling at ambient temperature, which could be similar to the initial stage of sintering. This phenomenon should result from the solid reaction among Si and C particles and/or SiC particles.

Fig. 6 shows the results of thermal analysis of C_p–SiC composite powder. A mass loss detected between 500 and 700 °C occurred due to the oxidation of excessive carbon particles in the composite powder. When the temperature was >700 °C, the mass of sample started to increase due to the oxidation of SiC in the composite powder.

4. Summary

β-SiC particles were synthesized with silicon and nano-sized carbon powders *via* a mechanochemical route in a high energy stirred bead mill. The optimal synthesis reaction could occur when the powders were treated in Ar atmosphere at a ball to powder ratio of 25:1 for 24 h. The C_p–SiC composite powder was simultaneously obtained with the synthesized β-SiC particles and excessive amount of nano-sized carbon powder in dry mechanochemical treatment. The C_p–SiC composite powder prepared via the mechanochemical powder composite process can be used as a promising trestle table material in the glass industry. The corresponding work is going to be carried out.

Acknowledgments

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