Journal of Advanced Ceramics
2013, 2(2): 128–134
DOI: 10.1007/s40145-013-0050-4 ISSN 2226-4108

Research Article

Preparation of SiC powders by carbothermal reduction with bamboo charcoal as renewable carbon source

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Received: January 23, 2013; Revised: February 24, 2013; Accepted: February 27, 2013
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Abstract: Bamboo charcoal was expected to be a renewable carbon source for carbide materials in carbothermal reduction because of its superior characteristics. SiC powders with characteristic shapes were fabricated by carbothermal reduction with industrial silica sol and bamboo charcoal particles as silicon and carbon sources respectively, and the effects of reacting temperature and time on shape evolutions and properties of the as-prepared SiC powders were investigated. The silica sol/bamboo charcoal system was firstly transformed into SiO_2/C system by the transition of silica sol and graphitization of bamboo charcoal, and the carbothermal reduction between SiO_2 and C occurred at/above 1600 ℃. The characteristic shapes of SiC particles were transformed from string-beads-like to dumbbell-like and rod-like with the increase of reacting temperature. The prepared SiC powders are expected to become new raw material for silicon carbide ceramic composites.

Keywords: carbides; chemical synthesis; X-ray diffraction (XRD); microstructure

1 Introduction

Carbides (Me_xC_y, Me = Si, B, Ti, Zr, W, etc.) are a whole family of advanced materials and have been widely applied in modern industrial fields because of their unique properties, such as high mechanical properties, good resistance to corrosion, and high thermal stabilities [1–3]. Carbothermal reduction is the preferred method for industrial synthesis of carbide powder materials [3–7]. Wherein, the choice of carbon source is one of the key conditions of the carbothermal reduction and also is the decisive factor for carbide synthesis. The present carbon resources mainly include petroleum products (e.g., carbon black, petroleum coke, asphalt), coal products (e.g., coke), graphite mining, and other mineral resources [4–7]. These mineral carbons are exhaustible-type carbon sources, and there exist complex procedures, high energy consumption and serious environmental pollution in the production processes. Furthermore, the existing industrial processes of carbide materials generally have the fundamental problems, such as high synthesis temperature (up to 2400 ℃), energy consumption, impurities, uniform compositions, and acid-base washing [1–3]. Therefore, it is necessary to develop a new industrial carbon source and improve the industrial synthesis of carbide materials.

Bamboo charcoal is a new natural carbon material, which comes from bamboo carbonized in a high-temperature (about 700 ℃) and less-oxygen environment [8]. Compared with mineral carbons, the production process of bamboo charcoal is simple, and its development is competitive because of rich resource and fast growing of bamboo. More importantly,

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bamboo charcoal possesses superior features unmatched by other carbon sources: ① high specific surface area (up to 700 m^2/g); ② high carbon content (more than 95%) and containing Si, Mg, Ca, P, Al, and other trace elements; ③ unique graphitization and layered microcrystalline structure; ④ good electrical properties (3.85 Ω·cm at 1000 ℃) [9]. Therefore, it is hopeful that bamboo charcoal is used as a new and renewable carbon source for the synthesis of carbide materials.

In this work, we demonstrate the synthesis of SiC powder material (as an example of carbide materials) by carbothermal reduction using bamboo charcoal as carbon source. The effects of reacting temperature and time on the synthesis of SiC powders and the shape evolutions of the SiC powders are carefully investigated.

2 Materials and methods

Industrial silica sol with 36 wt% solid content (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and 0.5–2 μm bamboo charcoal particles (Suichuang Biyan Bamboo Charcoal Co. Ltd., Suichuang, China) were used as silicon and carbon sources, respectively. The graphitization of bamboo charcoal was firstly carried out at 1600 ℃, 1700 ℃ and 1800 ℃, each for 2 h in a vacuum furnace with Ar atmosphere. The detail of the preparation of SiC powders is as follows. The industrial silica sol and bamboo charcoal particles were mixed with the mass ratio of 15 : 85 (molar ratio 1 : 1). The mixture was mechanically stirred for 12 h after ultrasound for 30 min, and then dried at 100 ℃ to form the silica sol/bamboo charcoal system. The carbothermal reduction of the complex system was carried out at 1400–1800 ℃ for 1–8 h in a vacuum furnace with Ar atmosphere.

The prepared SiC particles were identified by X-ray diffraction (XRD) method on a Rigaku D/max-RA X-ray Diffractometer using nickel-filtered Cu Kα radiation in the range of $2\theta = 10°–80°$ with a scanning speed of 2 (°)/min. The morphology and microstructure of the particles were investigated using scanning electronic microscopy (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEM1230).

3 Results and discussion

3.1 Graphitization of bamboo charcoal

As we known, the graphitization of bamboo charcoal occurs at high temperature [9]. Figure 1 shows the XRD patterns of bamboo charcoal after heat treatment at different temperatures. It is noted that bamboo charcoal is amorphous, but there is a little crystalline graphite-2H in it, indicating the existence of graphitization during the carbonation of bamboo. The major phase of bamboo charcoal is graphite-2H (JCPDS 41-1487), with the existence of some 3C-SiC (JCPDS 29-1129). The graphite-2H is attributed to the graphitization of bamboo charcoal, and 3C-SiC is the result of the reaction between graphite and residual silicon element in ash. After heat treatment, bamboo charcoal shows absolutely layered microcrystalline structure of graphite (as shown in Fig. 2). In the previous research [9–11], we have confirmed that the ash content is very low in bamboo charcoal, while there exist K, Si, Cl, Mg, S, P, Al, Na, and other trace elements in the ash. Wherein, Si element can directly join the carbothermal reaction of carbon and silicon, and K, Mg, Na and other elements can play a catalytic role in the reaction, which is beneficial to the decrease of reacting temperature.

3.2 Characteristics of the prepared SiC powders

Figure 3 shows the XRD patterns of the prepared SiC powders at different reacting temperatures and time.

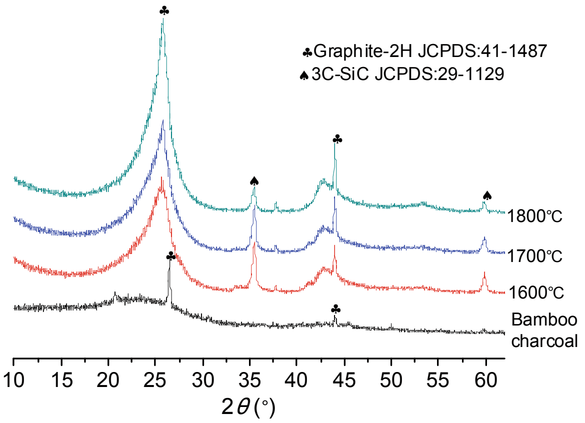

Fig. 1 XRD patterns of bamboo charcoal after heat treatment at different temperatures.

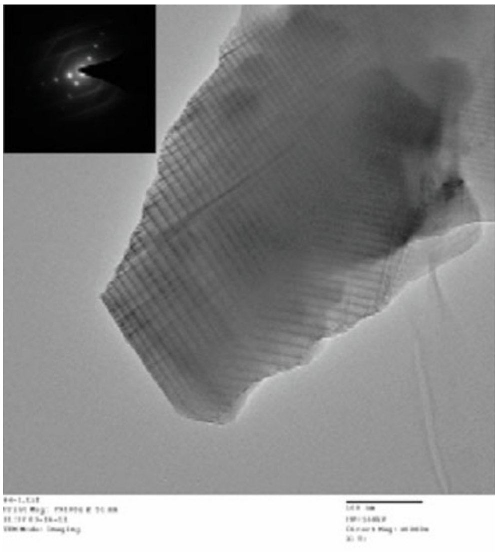

Fig. 2 TEM photo of bamboo charcoal heat-treated at 1800 ℃.

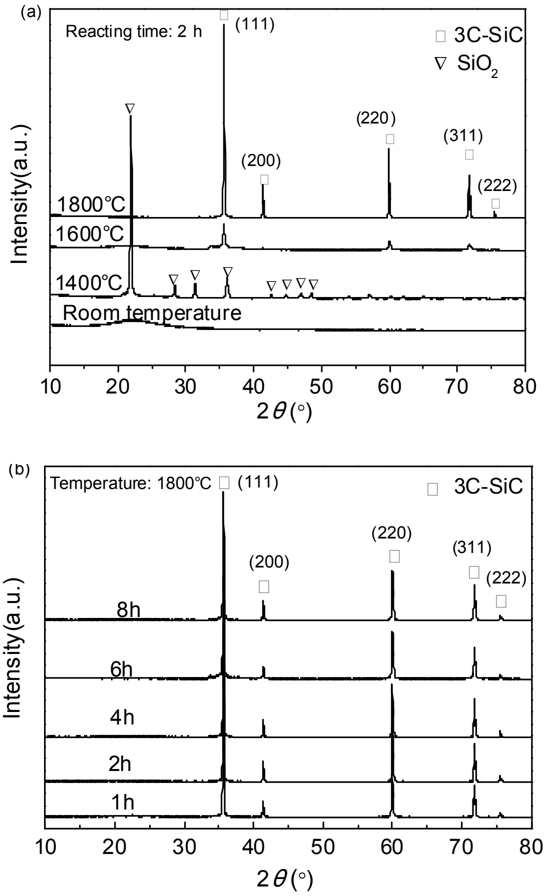

Fig. 3 XRD patterns of the prepared SiC powders at different reacting temperatures and time.

The silica sol/bamboo charcoal complex system is amorphous at room temperature. It indicates that the system is constructed by amorphous bamboo charcoal particles and attaching SiO_2 xerogel. At 1400 ℃, there is more SiO_2 phase in the system, while no SiC phase exists, which indicates that carbothermal reduction does not occur at/below 1400 ℃. Because of the graphitization of bamboo charcoal (Fig. 1), the complex system is firstly transformed into SiO_2/C system. At 1600 ℃, the diffraction intensity of SiO_2 phase decreases, and 3C-SiC (i.e., β-SiC) appears, inferring the occurrence of carbothermal reaction. At 1800 ℃, 3C-SiC becomes a unique phase with high diffraction intensity, indicating complete crystal growth. With the increase of reacting time (Fig. 3(b)), there is only 3C-SiC phase in all the samples for different reacting time, and the intensity of the same five diffraction peaks heightens with the increase of reacting time.

Compared with the purchased SiC nanopowders, the as-prepared SiC particles have the same five characteristic diffraction peaks ($2\theta = 35.56°$, 41.06°, 60.06°, 71.84° and 75.64°) in the XRD patterns, confirming the pure 3C-SiC phase. From Fig. 3, it is also found that the relative ratios of (111)/(311) and (220)/(311) reflections of the prepared SiC powders are larger than the standard values in JCPDS card No. 29-1129, especially for the (111)/(311) ratio, confirming the preferential orientation growth in the [111] direction. Burda *et al.* have previously reported that each SiC molecule is a single crystal grain, which grows in a preferential crystallographic direction, i.e., [111] direction, because the (111) plane has the lowest surface energy among the SiC surface planes [12–16].

Figure 4 shows the infrared (IR) spectra of the as-prepared SiC particles at different reacting temperatures and time. From Fig. 4(a), the strong peaks near 1094.34 cm^{-1} and 482.14 cm^{-1} are assigned as Si–O–Si stretching and anti-stretching vibrations at 1400 ℃, indicating the existence of SiO_2. The peak near 781.77 cm^{-1} found in the IR spectra is attributed to Si–C stretching vibration, implying the generation of SiC at this temperature [11]. The peak near 1631.63 cm^{-1} is the result of C–C stretching vibration, and the peak near 3422.89 cm^{-1} is attributed to O–H vibration of bridging oxygen in the H_2O molecule. At 1600 ℃, there are still Si–O–Si stretching and anti-stretching vibrations, but Si–C stretching vibration at 781.77 cm^{-1} becomes strong, indicating the production of more SiC. At 1800 ℃, it is found that the Si–O–Si stretching and anti-stretching vibration peaks have disappeared, indicating that there is no

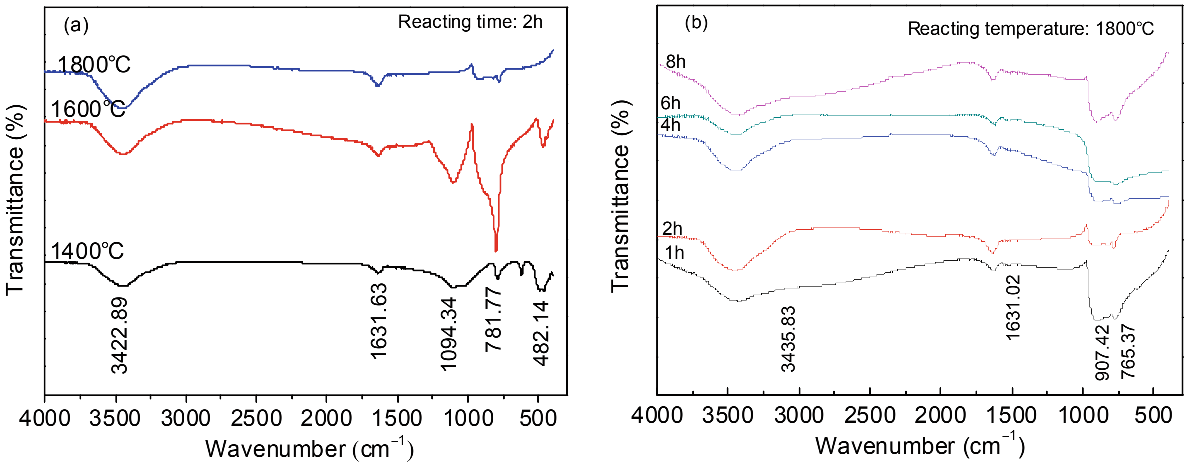

Fig. 4 IR spectra of the prepared SiC powders at different reacting temperatures and time.

existence of SiO_2 in the prepared SiC. With the increase of reacting time (Fig. 4(b)), the stretching vibration peaks of Si–C gradually sharp. This similarly proves that the growth of SiC becomes more complete, which coordinates with the XRD results.

3.3 Microstructure of the as-prepared SiC powders

Figure 5 shows the SEM images of the prepared SiC powders at different reacting temperatures for 2 h. It is observed that there are mainly micron-sized bamboo charcoal particles at room temperature, and SiO_2 nanoparticles attach on the surface of bamboo charcoal. Both particles contact each other to form the aggregates with different sizes. At 1400 ℃, the aggregates become regular with large size and loose structure, and there exist some SiO_2 whiskers in the aggregates (see the upper right inset of Fig. 5(b)). It

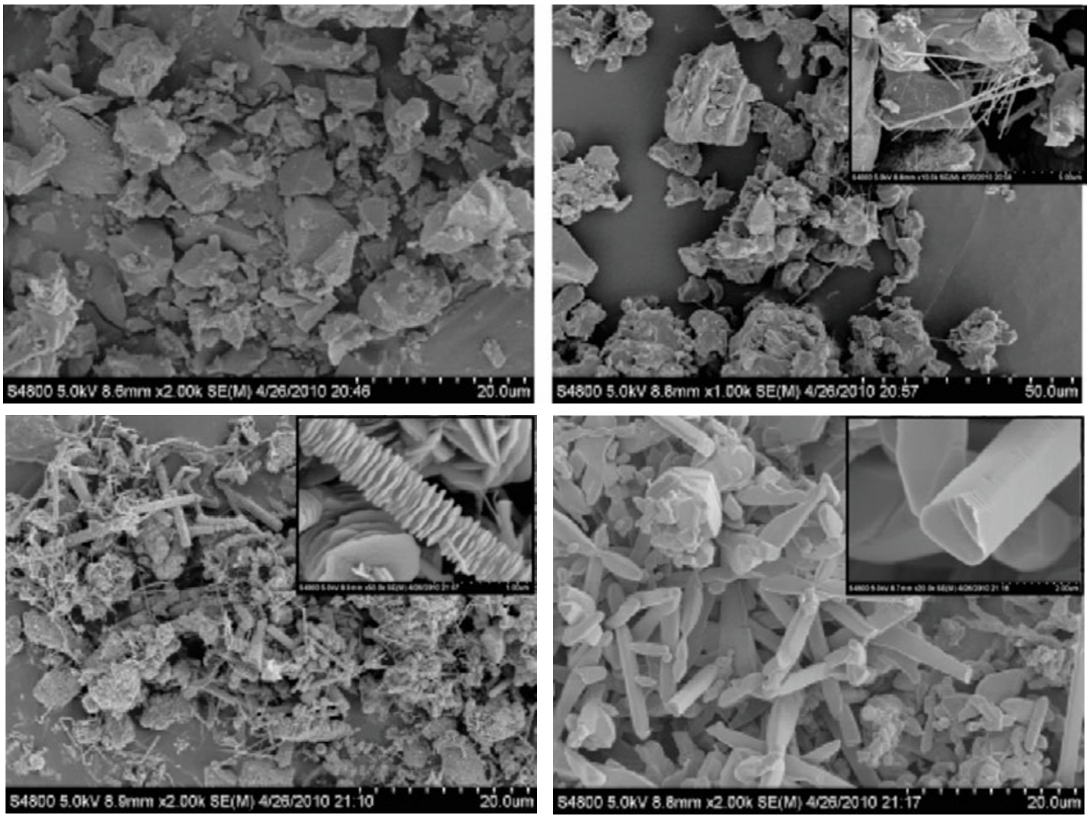

Fig. 5 SEM images of the prepared SiC at (a) room temperature, (b) 1400 ℃, (c) 1600 ℃, and (d) 1800 ℃.

also confirms that silicon sol is firstly transformed into SiO_2 nanoparticles or whiskers. At 1600 ℃, a lot of slice SiC crystals occur and some crystals stack to form string-beads-like or cluster-like crystals. It confirms that SiO_2 nanoparticles firstly react with bamboo charcoal particles to form slice SiC crystals, and stack to form string-beads-like or cluster-like crystals by slice superposition. At 1800 ℃, most of SiC crystals are rod-like, and the surface is smooth and regular, indicating relatively complete crystal growth. The length size of crystal becomes larger and is about 5–20 μm, confirming obvious orientation growth on the [111] direction, which coordinates with the XRD results.

Figure 6 shows the SEM images of the prepared SiC powders at 1800 ℃ for different reacting time. When the reaction time is 1 h, there exist a lot of small SiC crystals. With the increase of reacting time, the small SiC crystals stack to form rod-like SiC crystals and the surface becomes smoother. It intuitively indicates that longer reacting time can heighten the conversion rate of silica and bamboo charcoal to SiC and improve the growth of complete rod-like crystals.

Figure 7 shows characteristic TEM images and selected area electron diffraction (SAED) patterns of three typical SiC crystals. The SAED patterns and the clear surface of this 1D structure indicate a high degree of crystallinity. The observation of typical SiC crystals is attributed to the apparent orientation growth in the [111] direction, irregular stacking area, and stacking faults, which is similar to the β-SiC whisker [15,16].

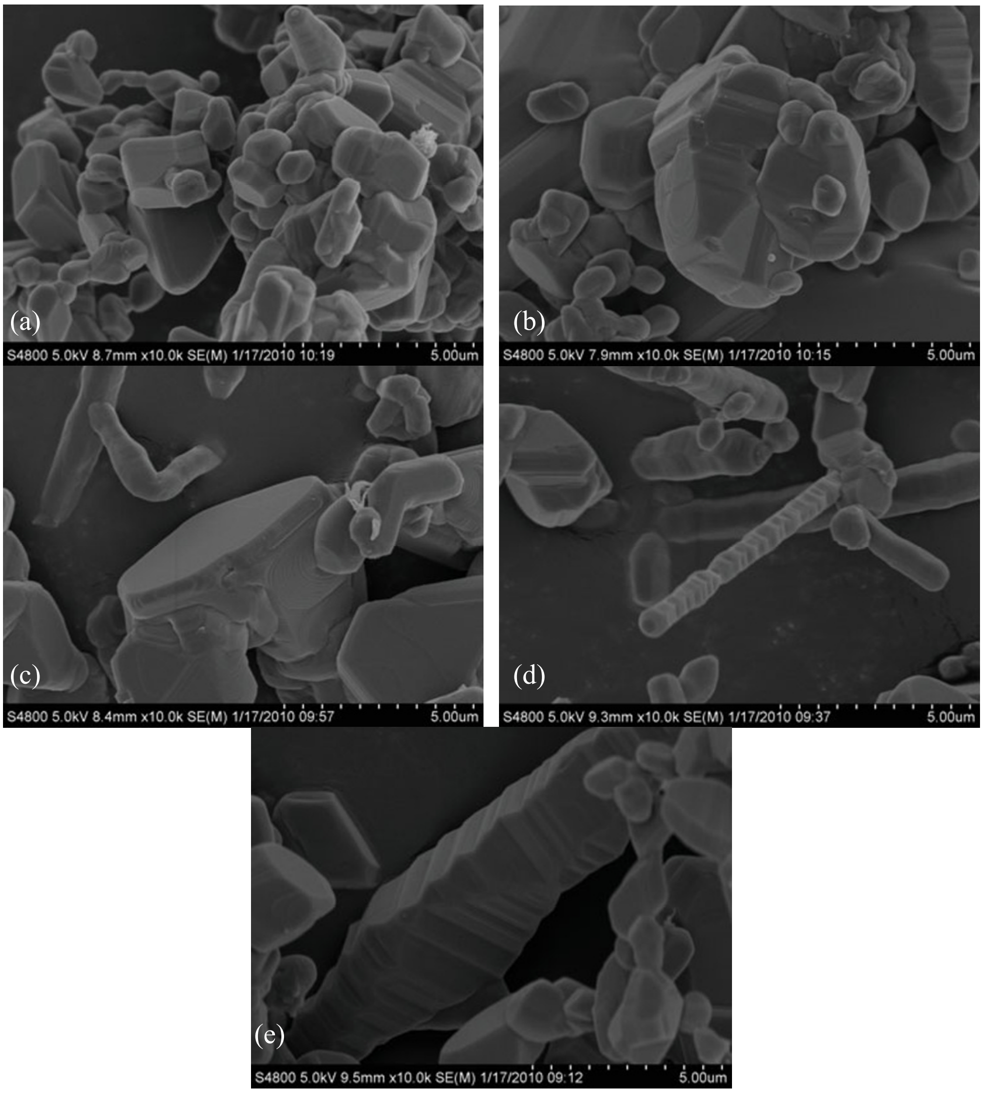

Fig. 6 SEM images of the prepared SiC at 1800 ℃ for (a) 1 h, (b) 2 h, (c) 4 h, (d) 6 h, and (e) 8 h.

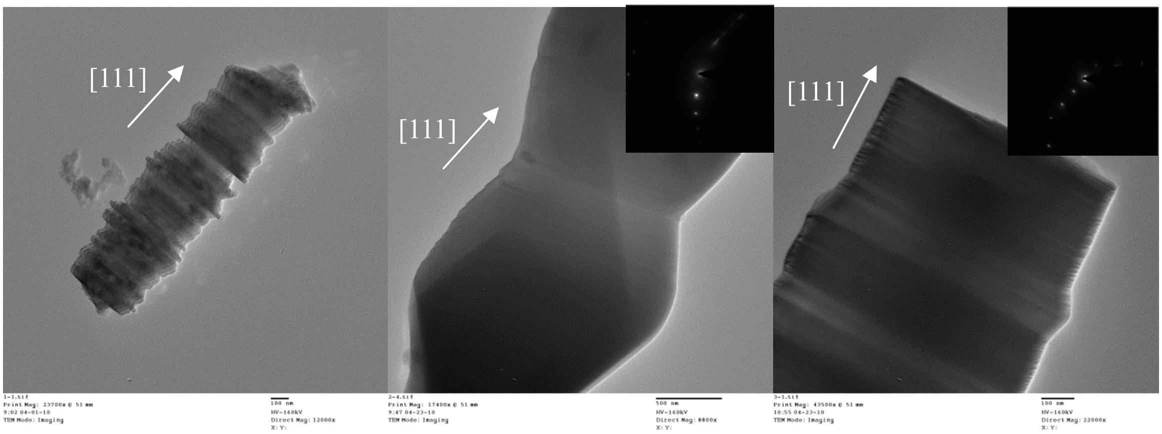

Fig. 7 TEM images and SEAD patterns of typical SiC crystals.

3.4 Appearance of the as-prepared SiC powders

The appearance of the prepared SiC powders at 1800 ℃ or 2 h shows gray-green color (shown in Fig. 8), which is similar to the industrial high-quality SiC powders prepared using petroleum coke and silica as main raw materials and salt as catalyst [17]. The present industrial SiC powders are prepared by Acheson method, and the shape of SiC powders is relatively simple (most is blocky or granular after grinding). In this work, different characteristic shapes such as rod-like and granular can be obtained in the SiC powders simultaneously. It proves that the as-prepared SiC powders possess superior characteristics such as high purity, hardness and strength. It will provide high-quality raw materials for the preparation of SiC-based ceramic composites.

Fig. 8 Photo of the as-prepared SiC powders by carbothermal reduction at 1800 ℃ for 2 h.

4 Conclusions

The SiC powders with characteristic shapes were fabricated by carbothermal reduction with industrial silica sol and bamboo charcoal as silicon and carbon sources, respectively. Silica sol/bamboo charcoal system was firstly transformed into SiO_2/C system by the transition of silica sol and graphitization of bamboo charcoal. The carbothermal reduction between SiO_2 and C occurred at/above 1600 ℃, and generated the slice SiC crystals. The slice SiC crystals stacked and grew with the increase of temperature, and the characteristic shapes were transformed from string-beads-like into dumbbell-like and rod-like. The gray-green SiC powders with characteristic shapes are expected to be a new raw material for the silicon carbide ceramic composites.

Acknowledgements

This work is supported by the High Science & Technique Brainstorm Project of Zhejiang Province of China (No. 2012C01032-1), Zhejiang Key Innovation Team Projects (No. 2009R50010), and Innovation Fund for Technology Based Firms (No. 12C26113303061).

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