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Catalytic effect of cobalt on microwave synthesis of β-SiC powder

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ABSTRACT

β-SiC was synthesized by a microwave reaction method in Ar, using silicon powder and phenolic resin as raw materials, and cobalt nitrate as a catalyst precursor. The effects of temperature, time, and catalyst content on the formation of SiC were investigated. When 1.0–2.0 wt% Co was used as a catalyst, phase pure β-SiC was formed after 30 min at 1150 °C. This synthesis temperature was 100 °C lower than that required by the conventional heating route catalyzed by with the identical amounts of catalyst. When a catalyst was absent, the synthesis temperature of β-SiC was as high as 1250 °C even in the case of using microwave heating. β-SiC particulates were formed, along with some whisker-shaped β-SiC of 30–100 nm in diameter and up to 20 μm in length. Density Functional Theory (DFT) calculations suggest that under the test conditions the formation of Co/Si alloy was energetically favorable, and played an important role in the Si—Si bond breaking and the subsequent SiC formation.

1. Introduction

Silicon carbide (SiC), as an important ceramic material, possesses many excellent properties, including high melting point (2827 °C), high hardness, high abrasion resistance, good chemical resistance, good radiation resistance, high thermal conductivity, low thermal expansion coefficient, and excellent thermal shock resistance. It is thus extensively used in many areas, for example, as wear-resistant materials, catalyst supports, filters for molten metals or hot gases, high-temperature structural materials, and reinforcement in composites [1–8].

SiC is industrially produced via the well-known Acheson Process, which relies on carbothermal reduction of silica sand with petrol coke at a temperature above 2400 °C and for a long period. In addition to the requirements of high temperature and long reaction time, SiC products resultant from this process always consist of large sized grains which are heavily agglomerated together. Therefore, a subsequent energy-intensive grinding process has to be used. For these reasons, it is difficult to use the Acheson process to prepare high quality ultrafine, in particular, nanosized SiC powders, for some demanding applications.

Considering this, several improved routes were investigated and used to prepare ultrafine SiC materials. Most of these researches used liquid phenolic resin as a carbon source. For example, Zhang et al. [9] prepared single crystalline SiC nanowires via carbothermal reduction of silica fume with phenolic resin in a molten salt medium at 1450 °C. Shi et al. [10] successfully prepared 0.2 μm β-SiC powder at 1500 °C for 2 h using commercial silicon powder and phenolic resin as raw materials. Zhao et al. [11] also synthesized SiC nanowires up to several millimeters long at 1500 °C for 2 h using silicon powder and phenolic resin as raw materials. In addition to ordinary and bamboo-like SiC nanowires, some spindle SiC nanochains were formed. By using the same raw materials, Wang et al. [12] also synthesized SiC nanowires of 30–100 nm in diameter and several micrometers in length. They found that SiC nanowires started to form at around 1100 °C. All these results demonstrated that liquid phenolic resin is much better than other solid carbon sources conventionally used, in reducing the synthesis temperature and morphology/size control.

To further reduce the synthesis temperature of SiC and control its morphologies, a catalytic reaction method has been developed recently. Zhang et al. [13] prepared ultra-long SiC/SiO_2 core–shell nanowires on a graphite felt coated with $Ni(NO_3)_2$ via a conventional molten-salt-mediated carbothermal reduction route at 1400 °C, using silica fume and phenolic resin as starting materials. As-synthesized nanowires were 150–500 nm in diameter and up to several hundred microns in length. By using a similar method, they [14] also successfully prepared ultra-long single crystalline β-SiC whiskers of 100–300 nm in diameter and up to millimeters in length at 1350 °C, using silicon and phenolic resin as starting materials. All these results demonstrated that use of a catalyst is not only effective in the reduction of synthesis temperature of SiC but also beneficial to its morphology control.

As for heating method, apart from the conventional heating, microwave heating is extensively used for preparation of various materials [15–19]. For example, Satapathy et al. [20] synthesized SiC powder via direct reaction of silicon with amorphous carbon at 1300 °C for <5 min using microwave heating. Moshtaghioun et al. [21] synthesized high purity SiC nanopowders from silica by microwave carbothermal reduction at 1200 °C for 5 min. Our group also synthesized several

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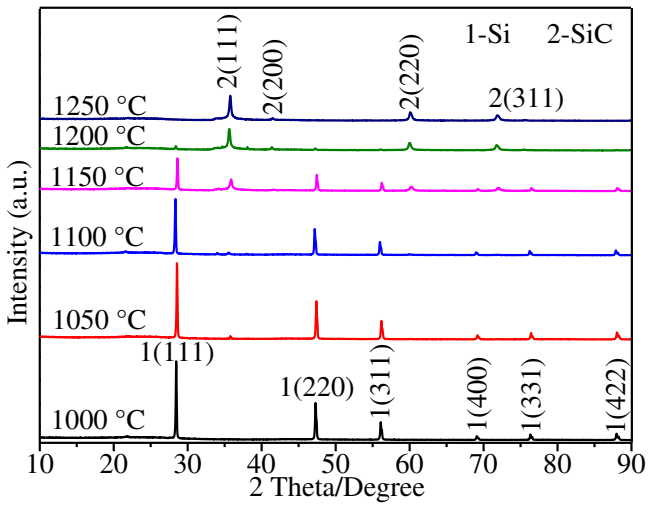

Fig. 1. XRD of samples without catalyst resulted from 30 min microwave heating at various temperatures (Si: ICDD No.01-077-2109; SiC: ICDD No.01-073-1708).

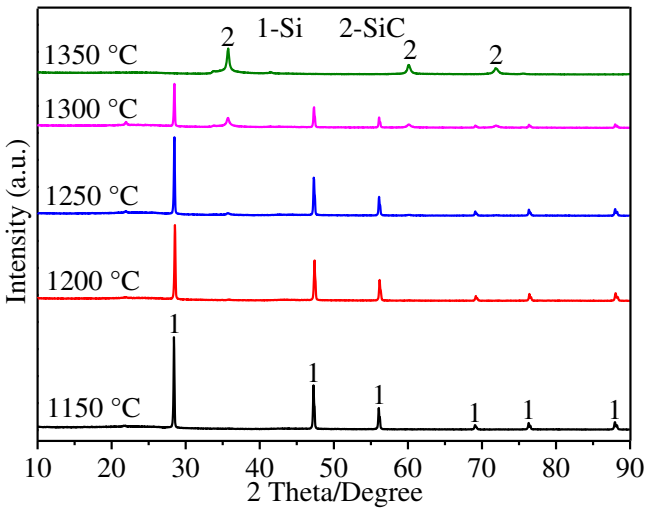

Fig. 3. XRD results of samples without catalyst after 3 h firing at various temperatures using the conventional heating method (Si: ICDD No.01-077-2109; SiC: ICDD No.01-073-1708).

types of ultrafine non-oxide powders using microwave heating. For example, phase pure nanosized TiC was prepared at 1200 °C [22], phase pure ultrafine ZrB_2-SiC composite powders were prepared by a combined sol–gel and microwave boro/carbothermal reduction method at 1300 °C (at least 200 °C lower than that required by the conventional method) [23]. All these results indicated that microwave heating is more effective than the conventional heating, in the reduction of synthesis temperature and time.

In this paper, for the first time, a combined catalytic reaction and microwave heating method was developed to synthesize SiC powders by using silicon powder and liquid phenolic resin as main materials, and cobalt nitrate as a catalyst precursor. The effects of reaction temperature/time, and catalyst amount on the formation of SiC powders were investigated, and the corresponding reaction mechanisms discussed based on the experimental results and density functional theory (DFT) calculations.

2. Experimental

2.1. Raw materials

Silicon powder (99%) with an average particle size of 1.8 μm and liquid phenolic resin (Wuhan Lifa Chemical Co., Ltd., 2221) were used as raw materials. $Co(NO_3)_2 \cdot 6H_2O$ (≥99%, Guoyao Chem. Co. Ltd., Shanghai China) was used as a catalyst precursor, and C_2H_5OH (Bodi Chem. Co. Ltd., Tianjin, China) used as a solvent.

2.2. Sample preparation and characterization

In a typical synthesis process, silicon powder was initially impregnated with $Co(NO_3)_2 \cdot 6H_2O$-ethanol solution (Co/Si weight ratio = 0, 0.5, 1.0, 1.5 and 2.0%), and subjected to 30 min sonication, followed by heating at 80 °C to evaporate the ethanol. The resultant dry powders were calcined at 600 °C for 2 h in argon (Ar) to obtain Co containing Si powders. On the other hand, 100 g liquid phenolic resin was dissolved in ethanol, and heated at 80 °C under vigorous stirring for 10 min to obtain a homogeneous phenolic resin solution. The as-prepared Co containing Si powders were carefully added into the phenolic resin solution to obtain a sol. The sol was heated for 12 h at 80 °C in a water bath under vigorous stirring to evaporate the ethanol and oven cured at 120 °C for 24 h. Finally, the cured samples were grinded into powders before being fired in flowing Ar (99.999 wt% pure) at 1000–1300 °C for 10–30 min in a microwave heating furnace (Model: HAMiLab-V3000, 3 kW, 2.45 GHz, by Changsha Longtech CO., Ltd., Hunan province,

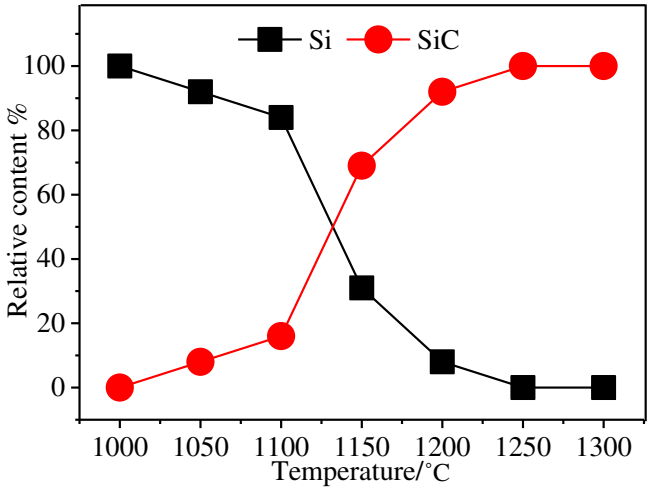

Fig. 2. Relative contents of Si and SiC in the samples whose XRD patterns are shown in Fig. 1.

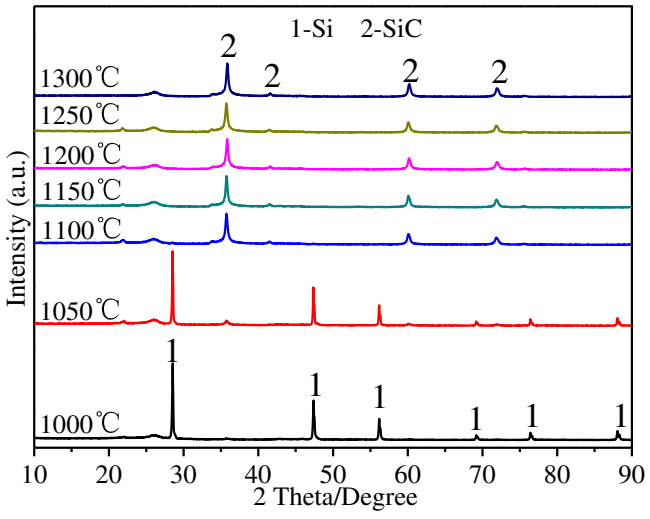

Fig. 4. XRD patterns of samples containing 2.0 wt% Co after 30 min microwave firing at various temperatures (Si: ICDD No.01-077-2109; SiC: ICDD No.01-073-1708).