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Materials

Preparation of β-SiC by combustion synthesis in a large-scale reactor

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Abstract: The feasibility of 5 kg β-SiC synthesized in one batch was demonstrated through igniting the mixture of Si, C-black and polytetrafluoroethylene (PTFE) under different nitrogen pressures. The effect of experimental parameters, including the contents of PTFE, nitrogen pressure, preheating, and raw materials distribution forms were investigated. The results show that the products are β-SiC with equiaxed grains. The average grain size is less than 200 nm. The powders loaded loosely promote reaction heat dispersing, resulting in small grains. High purity β-SiC powders are obtained when the PTFE content is as low as 5wt%, which simplifies the process and decreases the cost effectively. The ceramic sintered from the obtained β-SiC powders presents the hardness of 22.20 GPa, the bending strength as high as 715.15 MPa and the fracture toughness of 8.179 MPa·m$^{1/2}$, which are higher than those of ceramics fabricated with α-SiC produced by combustion synthesis.

Key words: silicon carbide; combustion synthesis; β-SiC; reaction parameter; large-scale reactor; self-propagating high-temperature synthesis

1. Introduction

Silicon carbide is one of the most advanced ceramic materials for its remarkable chemical and thermomechanical properties [1]. Of the two common kinds of crystal structures of SiC, β-SiC has attracted many researchers' attention for its excellent properties such as high hardness, good toughness, high thermal conductivity and low thermal expansion in comparison with α-SiC [2-3]. The methods for production of SiC include the Acheson process, the chemical vapor deposition (CVD) and the molecular beam epitaxy (MBE) method *etc.* [4-6].

Self-propagating high-temperature synthesis (SHS) has been developed as a promising alternative to the conventional methods of producing advanced materials, including ceramic powders, metal inter-metallic compounds, and composite materials [7-9]. The principle of SHS is to utilize external heat instantaneously to induce high-temperature chemical reactions. After the reaction, combustion wave is formed, and it will spread forward and make the reaction continuous. Therefore, the most prominent advantages of combustion synthesis technology are rapid response, high product purity, energy conservation, simple equipment, and cost effectiveness. Zhang *et al.* [10] synthesized pure β-SiC powders by SHS with packed raw materials and the polytetrafluoroethylene (PTFE) content as much as 25wt%. Residual MgO included in the products was removed through pickling. Yamada *et al.* [11-13] synthesized β-SiC powders *via* SHS under certain nitrogen pressure or argon press. All these works were performed with the product amount less than 500 g in a small scale reactor.

In this work we explored the possibility to produce β-SiC by an SHS approach in industrial scale. A reactor with the capacity of 60 L was used to synthesize 5 kg pure β-SiC in one batch. The effects of reaction conditions on the composition and phases as well as morphology of the products were investigated. The mechanical properties of β-SiC were measured compared with those of the commercial α-SiC in this work.

2. Experiment

Silicon powder (99%, average particle size of 3 μm), carbon black (99%, average particle size of 24 nm), and PTFE (99%) were used as raw materials. The starting materials according to stoichiometric ratio were thoroughly ball milled in ethanol medium for 10 h and dried at 100°C in air for about 24 h. The

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as-milled powders were packed directly into a graphite crucible, or were first pressed into pellets and put into a graphite crucible. The crucible was pushed into a SHS reactor of 60 L volume under a nitrogen atmosphere. The raw materials were ignited with a tungsten spiral by passing through electrical current at one point of the powder bed. The tungsten spiral was covered with titanium powder as an ignition promoter. Once the mixed powder was ignited, the formed high-temperature reaction wave propagated spontaneously passing through all the bed. After the propagating wave, products were obtained.

The phases of the products were identified by X-ray diffraction (XRD, the Japanese Rigaku D/MAX-RB rotating anode X-ray diffraction), powder morphologies were observed by scanning electron microscopy (SEM; LEO-435VP, British) and the specific surface areas of the products were calculated by BET (QS-18, America QUANTACHROME Company). The powders as produced were sintered and the mechanical properties were compared with those derived from commercial α-SiC.

3. Results and discussion

3.1. Effect of nitrogen pressure on combustion reaction

To study the influence of nitrogen pressure on the properties of final products, the experiment was performed with different nitrogen pressures of 0.5, 3, 5 and 8 MPa by keeping the mole ratio of C to Si of 1:1 and the PTFE content of 5wt%. When the nitrogen pressure was below 0.5 MPa, combustion synthesis could not be ignited. With increasing nitrogen pressure, combustion synthesis was ignited easily and the reaction time decreased significantly owing to high system temperature, but the particle size of products increased. Nitrogen acts as a medium in the reaction, which reacted with Si firstly and decomposed at last following by a great deal of energy. All nitrogen pressures changed from 0.5 to 8 MPa, β-SiC powders were obtained, as shown in Fig. 1. For the purpose of economical efficiency, 0.5 MPa nitrogen pressure is used.

3.2. Effect of PTFE $(-C_2F_4-)_n$ content on combustion reaction

The calculated adiabatic temperature of the Si/C system is 1600-1700 K, which is too low to enable the SHS reaction [10]. So it is necessary to provide an additional energy source to trigger the combustion synthesis of SiC [11, 14]. Here PTFE was used to provide an additional energy source. After adding PTFE to 5wt% based on the total powder weight, the C-Si mixtures were ignited and the reaction was self-sustained. According to Yang *et al.* [13], PTFE can react with silicon powders as described in the following equations:

$$\mathrm{Si\,(s)} + (-\mathrm{C_2F_4}-)_n\ \mathrm{(s)} \rightarrow \mathrm{SiF_4\ (g)} + \mathrm{C\,(s)} \qquad (1)$$

$$\mathrm{Si} + \mathrm{C} \rightarrow \mathrm{SiC} \qquad (2)$$

At first, Eq. (1) is an exothermic reaction, which starts in the early stage. Eq. (2) is achieved by the high heat source from Eq. (1). So PTFE is used as promoter.

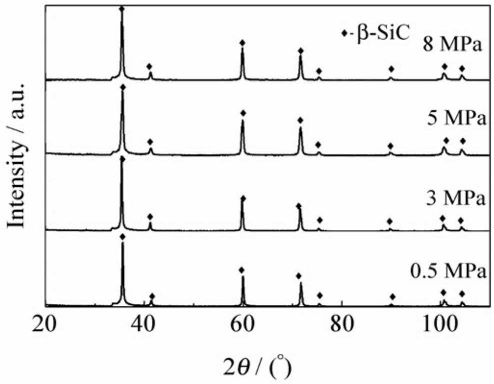

Fig. 1. XRD patterns of products under different nitrogen pressures with 5wt% PTFE.

Nersisyan *et al.* reported the combustion synthesis of SiC powders by using about 18wt% PTFE promoter in argon atmosphere [15]. In our work, based on lots of experiments, self-propagating reactions occurred successfully when the PTFE content was 5wt% or over, but could not be ignited below 5wt% PTFE. The PTFE content changed from 5wt% to 20wt% by keeping the C/Si mole ratio of 1:1 constant and nitrogen pressure of 0.5 MPa to investigate the effect of promoter content on product properties. As the PTFE content was raised, the product color varied from light green to black green. After being calcined at 500°C for 2 h, the powders produced with 5wt% PTFE had no decrease in weight; but the other three powders presented a slight decrease in weight. Residual carbon from the decomposition of excessive PTFE should be responsible for this phenomenon. Therefore, ultra β-phase silicon carbide can be obtained by SHS with as low as 5wt% PTFE. Fig. 2 shows the XRD analysis of products. As can be seen, all the products were β-SiC.

Fig. 3 depicts the SEM photographs of β-SiC as obtained with different PTFE contents. All the products consist of pure equiaxed grains. With increasing PTFE content, the average particle diameter became larger. The corresponding grain sizes were 120, 300, 400 and 500 nm. These are attributed to the fact that the system temperature increases with increasing PTFE content.