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Reaction coupling preparation of high sintering activity boron carbide nano-powders

Jilin Wang[a,b], Fei Long[a,*], Weimin Wang[c,*], Shuyi Mo[a], Zhengguang Zou[a], Zhengyi Fu[c]

[a]School of Materials Science and Engineering, Key Laboratory of Nonferrous Materials and New Processing Technology of Ministry of Education, Guilin University of Technology, Guilin 541004, China

[b]Guangxi Key Laboratory in Universities of Clean Metallurgy and Comprehensive Utilization for Non-ferrous Metals Resources, Guilin University of Technology, Guilin 541004, China

[c]The State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

Received 4 November 2015; received in revised form 1 January 2016; accepted 10 January 2016

Abstract

Large scale B_4C nano-powders were synthesized via a novel ball milling assisted reaction coupling self-propagating high temperature synthesis method using Mg, B_2O_3 and CH_2H_3Cl as the starting materials. The XRD, FTIR, Raman, EDX, FSEM, TEM, HRTEM and SAED were used to characterize the B_4C samples. The optimum endothermic rate was 35%, when the samples presented fine and uniform regular morphology with an average particle diameter of about 100 nm. In addition, the reaction coupling principle, possible chemical reaction mechanism and the effects of the endothermic reaction rate were also discussed. Moreover, the commercial B_4C (C-B_4C) and homemade B_4C (H-B_4C) ceramics were prepared by spark-plasma sintering method at 1700 °C under 30 Mpa. Compared with the C-B_4C ceramic, the values of relative density, vickers hardness and fracture toughness of the H-B_4C ceramic were increased by 2.1%, 9.2% and 20.1%, respectively, demonstrating high sintering activity of the homemade B_4C nano-powders.

Keywords: A. Powders: chemical preparation; Sintering; C. Mechanical properties; D. Carbides

1. Introduction

Boron carbide (B_4C) is one of the interesting and promising non-oxide light-element solid materials. It has an unique rhombohedral structure consists of covalently bonded distorted $B_{11}C$ icosahedra and C-B-C three-atom linear chain [1,2]. The high stability covalence bonds between B and C atoms as well as the special crystal structure make B_4C revealing a series of excellent properties, such as low density, high melting point, high hardness, low thermal expansion coefficient, high neutron absorption cross-section, excellent thermoelectric properties, strong high-temperature chemical stability, and so on. These attractive physiochemical properties give boron carbide great potential modern multifunctional applications in the fields of wear resistant materials, high performance engineering ceramics, controlling and neutron shielding materials, body and vehicle armor, strengthening medium, cutting tools, etc. [3–6].

However, the high degree covalent bonds between B and C atoms and low self-diffusion coefficient of the B_4C will lead to poor sinterability and densification difficulty, limiting the further applications of this material [5,7,8]. Generally, there are three ways employed to solve the sintering densification problem of the B_4C ceramics: (1) using sintering aid additives to lower the densification temperatures of B_4C ceramics [9,10]; (2) developing and using more advanced sintering techniques to prepare B_4C ceramics (such as spark-plasma) [11,12]; (3) using higher chemical activity B_4C powders with a smaller particle size [13–16]. In these solutions, the first approach will

*Corresponding authors. Tel.: +86 773 5896700; fax: +86 773 5896436.
E-mail addresses: jilinwang@glut.edu.cn (J. Wang), long.drf@gmail.com (F. Long).

http://dx.doi.org/10.1016/j.ceramint.2016.01.083
0272-8842/

bring the other composition additive and reduce the purity of the final B_4C products. The second approach usually needs more expensive equipment or harsh sintering condition. The third approach may be the best way to solve the sintering densification problem of the B_4C ceramics.

It is well known that high quality powders are the indispensable prerequisite to prepare the high temperature structure ceramics and the corresponding composites with distinguished properties. Compared with the traditional micron-sized particles, high purity nano-sized powders have a smaller particle size, higher chemical activity and better sintering ability, making it easier to fabricate the related ceramic materials [13,17–20]. If nano-sized B_4C powder is used, even traditional sintering techniques (without the help of additive) might also prepare high performance B_4C ceramics or related composites which could only be achieved through more expensive equipment at the harsh sintering conditions previously.

As to the preparation of nano-sized B_4C powders, several methods such as high energy ball milling, self-propagating high temperature synthesis (SHS) process, solvothermal reaction, laser vapor phase reaction, ion beam synthesis, and sol–gel method have been attempted [3,15,21–27]. In these methods, SHS technology has an enormous development potential for low cost, high efficiency and large scale industrial production of nano-sized B_4C powders. On the one hand, due to its simple equipment, convenient operation process, as well as high efficiency in energy and time, SHS technology has been successfully used to produce many advanced high-temperature ceramic materials, intermetallic compounds, etc. [23,28–31]. On the other hand, because of the high cooling rate and defect concentration, the prepared powders usually contain many non-equilibrium state metastable structures, leading to higher chemical reaction activity or better sinter ability [32,33]. However, given that the excessive exothermic energy in a much shorter time, it is difficult to control the traditional SHS process. Finally, this problem will lead to high-temperature sintering agglomeration, exceptional grain growth, and/or many hardly removed impurities in the product. Therefore, how to effectively control the excessive high exothermic energy in the whole reaction system is a key problem for obtaining high quality B_4C nano-powders. In our opinion, it is worth introducing the endothermic reaction into the exothermic reaction, then effectively controlling the heat, temperature and the grain growth conditions of the whole reaction system, finally fabricating high quality goal products.

In this work, large scale fine and uniform nano-sized B_4C powders were synthesized via a novel ball milling assisted reaction coupling self-propagating high temperature synthesis method. The reaction coupling principle, possible chemical reaction mechanism, and the effects of the endothermic reaction rate for the structure/morphology/composition of the as-synthesized products were discussed. In addition, the high sintering activity of the as-synthesized B_4C nano-powders was also demonstrated through investigating the structure and property of the different B_4C ceramics prepared by spark-plasma sintering commercial and as-synthesized B_4C powders.

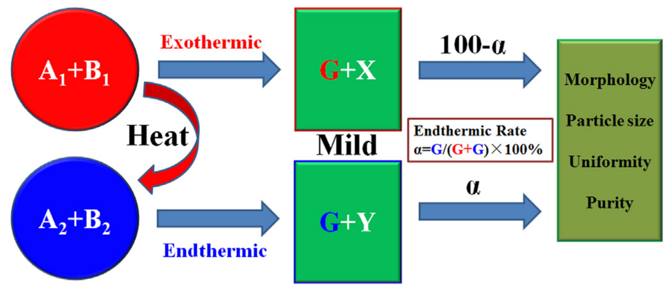

Fig. 1. Schematic diagram of the reaction coupling SHS method. (A_1, B_1, A_2, B_2) – reactants; G – goal product; (X, Y) – byproducts.

2. Experimental

2.1. Raw materials

The starting materials, magnesium (Mg), boron oxide (B_2O_3) and polyvinyl chloride (CH_2H_3Cl) powders were of analytical pure grade with the particle size in the range of 50–100 μm. The commercially available micron-sized B_4C powders were purchased from Mudanjiang Boron Carbide Co., PR China (purity $>98\%$, particle size of about 3.5 μm).

2.2. Reaction coupling principles and the theoretical calculations

Fig. 1 presents the schematic diagram of the reaction coupling SHS method. (A_1, B_1, A_2, B_2) stands for reactants, G stands for goal product and (X, Y) stands for byproducts. The reaction ($A_1+B_1 \rightarrow G+X$) will release enormous amount heat energy (red, extremely exothermic, such as Eq. (1)). On the contrary, the reaction ($A_2+B_2 \rightarrow G+Y$) will absorb considerable heat energy (blue, highly endothermic, such as Eq. (2)). In addition, the goal product (G) must be obtained through each reaction. Accordingly, the heat energy and corresponding temperature of the whole SHS reaction system could be effectively controlled through changing the endothermic reaction rate (the percentage of goal product prepared through endothermic reaction, here the goal product is B_4C). Finally, it is likely that the particle size, structure, purity and morphology of the goal product could also be controlled via changing the endothermic reaction rate [32].

In this study, two kind chemical reaction equations are likely to occur in the whole SHS reaction system $Mg/B_2O_3/CH_2H_3Cl$:

$$6Mg+2B_2O_3+C_2H_3Cl=B_4C+6MgO+1/2H_2+1/2HCl \quad (1)$$

$$2B_2O_3+2C_2H_3Cl=B_4C+3HCl+5CO+H_2O+2H_2 \quad (2)$$

It is obvious that Eq. (1) is different from Eq. (2). The former belongs to magnesiothermic reduction reaction, but the latter is carbothermal reduction. The standard molal enthalpies of Eqs. (1) and (2) were calculated as -1208.75 kJ/mol (B_4C) and 1330.92 kJ/mol (B_4C), respectively. Therefore, Eq. (1)