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Short communication

Fabrication of B_4C from $Na_2B_4O_7 + Mg + C$ by SHS method

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Abstract

This paper deals with the formation of boron carbide (B_4C) powders from $Na_2B_4O_7 + Mg + C$ system by self-propagating high-temperature synthesis (SHS) method. B_4C without impurities could be obtained after the acid enrichment and distilled water washing. The reaction mechanism of SHS of B_4C was proposed: the synthesis of B_4C is a process involving the decomposition of $Na_2B_4O_7$ into the intermediate phase B_2O_3, which reacts with Mg and carbon to form B_4C.

Keywords: Boron carbide; Self-propagating high-temperature synthesis; Borax

1. Introduction

B_4C possesses a combination of properties, such as high melting point (2447 °C), outstanding hardness (28–35 GPa Knoop hardness), low density (2.52×10^3 kg/m^3), high Young's modulus (450–470 GPa), high chemical stability, good wear resistance and so forth, which gives rise to numerous applications, including uses as an abrasive wear-resistant material, ceramic armor and an ideal neutron moderator and shielding material in nuclear industry [1,2].

Much work on B_4C was carried out on powder preparation by many methods, such as elemental direct reaction of carbon with boron [3], metallothermic and carbothermic processes with boric acid (H_3BO_3) and boron oxide (B_2O_3) as starting materials in a batch electric arc or resistance furnace [4,5], laser irradiation chemical vapor deposit [6], co-reduction route with BBr_3 and CCl_4 as the reactants and metallic Na as the co-reductant [7], and sol–gel [8]. Although B_4C powder could be synthesized through these routes, there are many drawbacks for these methods, for example, the method of elemental direct reaction does not allow low cost as well as powder properties; carbon-thermal reduction method, the main industry route, requires high temperature and the process is time consuming and high cost [4,5]; laser process requires expensive equipment and production rate is low [6]; the raw material for sol–gel method is very expensive and process is cumbersome [8].

To overcome the aforementioned shortcomings of traditional routes, self-propagating high-temperature synthesis (SHS) was employed in this study. This technique consists of initiating locally a very exothermic reaction within a mixture of reactive powders and to use the heat released by this reaction to obtain, in a few seconds, a complete consumption of the reactants in the whole sample. So it presents an attractive, promising and energy saving practical alternative to conventional methods of materials' preparation. By using SHS technique, B_4C had been fabricated with B_2O_3 as a source of boron [9]. However, it is difficult to fabricate fine B_2O_3 particle and easy for B_2O_3 to absorb water to form H_3BO_3. In the present study, borax ($Na_2B_4O_7$) was chosen as raw material for it is fine and chemically stable. Here, for the first time, the preparation of B_4C from $Na_2B_4O_7 + Mg + C$ by SHS is reported and the reaction mechanism on the system by SHS is proposed.

2. Experimental procedures

A number of powder mixtures of $Na_2B_4O_7$, magnesium (Mg) and carbon (C) with different ratios were mixed thoroughly in a ceramic mortar and the milling performed at a horizontal rotation velocity of 50 rpm for 24 h, followed by drying at 60 °C in a vacuum drying oven. They were then

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weighed out and cold stamped into stainless steel mold to form cylindrical specimens under different pressures. After packing, the samples were introduced into the SHS apparatus and the experiments were conducted under argon pressure. At the start of the experiment, the combustion chamber was sealed, evacuated and purged with argon. The chamber was then filled with argon to a high pressure to inhibit the possible evaporation of Mg during the combustion. After the reactions, the specimens were removed from the SHS apparatus and then washed with enrichment acid and distilled water to eliminate MgO and Na_2O from the reaction products. At last, they were dried in a vacuum drying furnace at 110 °C and then characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. Results and discussion

The B_4C powders were prepared from $Na_2B_4O_7$ + Mg + C system by SHS method with an extra amount of Mg (the mole ratio of $Mg/Na_2B_4O_7$ from 6.1 to 7.2). The XRD patterns of the SHS-products obtained from the reactant mixtures with $Mg/Na_2B_4O_7$ = 6.2, 6.5 and 7.2 are shown in Fig. 1. As seen from XRD results, the combustion products are mainly composed of MgO, B_4C, $Mg_3(BO_3)_2$ and $NaBO_2{\cdot}H_2O$ at $6.5Mg/Na_2B_4O_7$ or less and the concentration of $Mg_3(BO_3)_2$ and $NaBO_2{\cdot}H_2O$ decreases with the increase of Mg amount. From our experimental results, the phase composition of combustion products does not change significantly for the reactants' mixtures of $Mg/Na_2B_4O_7$ from 6.5 to 7.0. However, $NaBO_2{\cdot}H_2O$ cannot be detected in the XRD pattern at $7.2Mg/Na_2B_4O_7$. The reasonable explanation of that is the loss of magnesium during SHS process because of the higher evaporation pressure of Mg (303 Pa at 1361 K [10]), which caused the incomplete reduction reaction and thus the diffraction peaks of $Mg_3(BO_3)_2$ and $NaBO_2{\cdot}H_2O$ were detected in the XRD analysis of combustion products. In order to increase the complete degree of reduction reaction, it is necessary to add an extra amount of Mg to reactants' mixture to provide an adequate reductive condition for the reaction. Moreover, the possible reason of formation of $Mg_3(BO_3)_2$ is the reaction between B_2O_3 and MgO [11]. The former is from the decomposition of $Na_2B_4O_7$ and the latter is from the product of

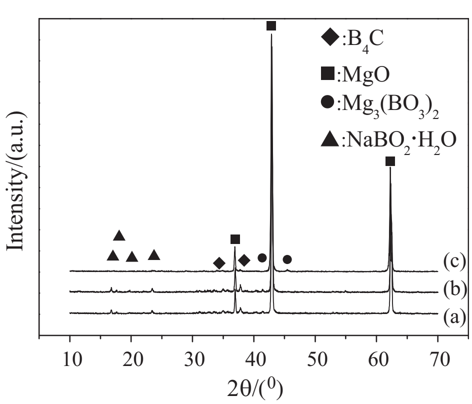

Fig. 1. XRD patterns of combustion products synthesized at different molar ratios of $Mg/Na_2B_4O_7$: (a) 6.2, (b) 6.5 and (c) 7.2.

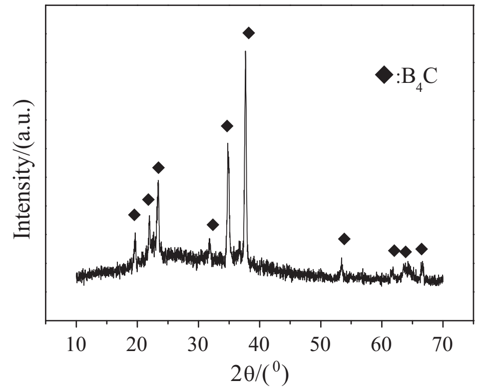

Fig. 2. XRD pattern of the combustion product after the acid enrichment and distilled water washing.

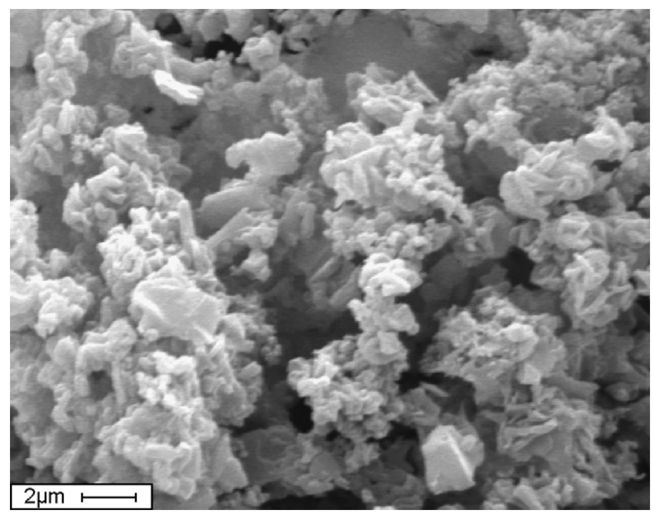

Fig. 3. SEM micrograph of the combustion product after the acid enrichment and distilled water washing.

the reaction of Mg and B_2O_3. The presence of another combustion product $NaBO_2{\cdot}H_2O$ is possibly associated with the interaction of B_2O_3, Na_2O from the decomposition of $Na_2B_4O_7$ and the possibly absorptive H_2O during the process of mixing of reactant chemicals or after-treating of combustion products. From these compositions of combustion products, the approximate reaction mechanism for combustion synthesis of B_4C can be proposed. At high temperature during combustion, $Na_2B_4O_7$ decomposes into B_2O_3 and the latter reacts with Mg to form B and MgO. B_4C can be obtained from the reaction between B and C.

The XRD pattern and the corresponding SEM morphology of after-treatment combustion product are shown in Figs. 2 and 3, respectively. As seen, any secondary phases were not detected in X-ray analysis (Fig. 2) and the mean particle size of B_4C crystal is about 0.6 μm (Fig. 3).

4. Conclusion

Experimental studies were carried out to synthesize B_4C by SHS method with $Na_2B_4O_7$, Mg and carbon as raw chemicals. B_4C with the size of about 0.6 μm could be obtained after the acid enrichment and distilled water washing. The reaction mechanism of SHS is considered, in which special role is assigned to the decomposition of $Na_2B_4O_7$ into the intermediate phase B_2O_3, which reacts with Mg and carbon to form B_4C.

Acknowledgements

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References

[1] F. Thevenot, A review on boron carbide, Key Eng. Ceram. Soc. 6 (1990) 202–205.

[2] D.K. Bose, K.U. Nair, C.K. Gupta, Production of high purity boron carbide, High Temp. Mater. Process. 7 (2–3) (1986) 133–140.

[3] S.T. Benton, D.R. Masters, Method for preparing boron carbide articles, US Patent 3,914,371 (21 October 1975).

[4] G. Goller, C. Toy, A. Tekin, C.K. Gupta, The production of boron carbide by carbothermic reduction, High Temp. Mater. Process. 15 (1–2) (1996) 117–122.

[5] E.G. Gray, Process for the production of boron carbide, US Patent 2,834,651 (13 May 1958).

[6] T. Oyama, K. Takcuchi, Gas-phase synthesis of crystalline B_4C encapsulated in graphitic particles by pulsed-laser irradiation, Carbon 37 (3) (1999) 433–436.

[7] L. Shi, Y. Gu, L. Chen, Y. Qian, Z. Yang, J. Ma, A low temperature synthesis of crystalline B_4C ultrafine powders, Solid State Commun. 128 (2003) 5–7.

[8] A. Sinha, T. Mahata, B.P. Sharma, Carbothermal route for preparation of boron carbide powder from boric acid-citric acid gel precursor, J. Nucl. Mater. 301 (2002) 165–169.

[9] L.L. Wang, Z.A. Munir, J. Birch, Formation of $MgO–B_4C$ composite via a thermite-based combustion reaction, J. Am. Ceram. Soc. 78 (1995) 756–764.

[10] M.W. Chase Jr., J.L. Curnutt, R.A. Mcdonald, A.N. Syverud, JANAF Thermochemical Tables, 1978 Supplement, J. Phys. Chem. Ref. Data 7 (3) (1978) 793–940.

[11] T. Mutluer, M. Timucin, Phase equilibria in the system $MgO–B_2O_3$, J. Am. Ceram. Soc. 58 (5–6) (1975) 196–197.