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Synthesis 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 .

1. Introduction

Dense B_4C ceramic is a promising material in numerous applications, including uses as an abrasive wear-resistant material, ceramic armor, an ideal neutron moderator and shielding material in nuclear industry primary due to its high melting point, outstanding hardness, low density, high Young's modulus, high chemical stability, good wear resistance and so forth [1-2].

B_4C powder could be prepared through many methods, such as elemental direct reaction of carbon with boron [3], metallothermic and carbothermic processes of boron-oxygen compounds such as boron oxide (B_2O_3), boric acid (H_3BO_3), etc. in a batch electric arc or resistance furnace [4,5], laser irradiation chemical vapor deposit (LICVD) [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 exists one or more following drawbacks for these methods, such as low efficiency and production rate, high cost in the terms of raw materials, equipments and process, and so on.

To solve the aforementioned shortcomings of traditional routes, self-propagating high-temperature synthesis (SHS) was employed in this study. Comparing to the above methods, self-propagating high-temperature synthesis (SHS, or Combustion synthesis, CS) is an attractive, promising and energy saving practical alternative to conventional methods of materials' preparation. This method uses the fact that the mixtures of fine powders can be ignited to produce a combustion-like reaction. By application of SHS technique, B_4C had been produced with B_2O_3 as a source of boron [9]. However, it is difficult to obtain fine B_2O_3 powder and easy for B_2O_3 to absorb water to form H_3BO_3 . In the present work, borax ($Na_2B_4O_7$) instead of B_2O_3 was chosen as raw material for it is fine and chemically stable. Here, for the first time, the fabrication of B_4C powder from $Na_2B_4O_7+Mg+C$ by SHS process is reported and the reaction mechanism on the system by SHS is proposed at last.

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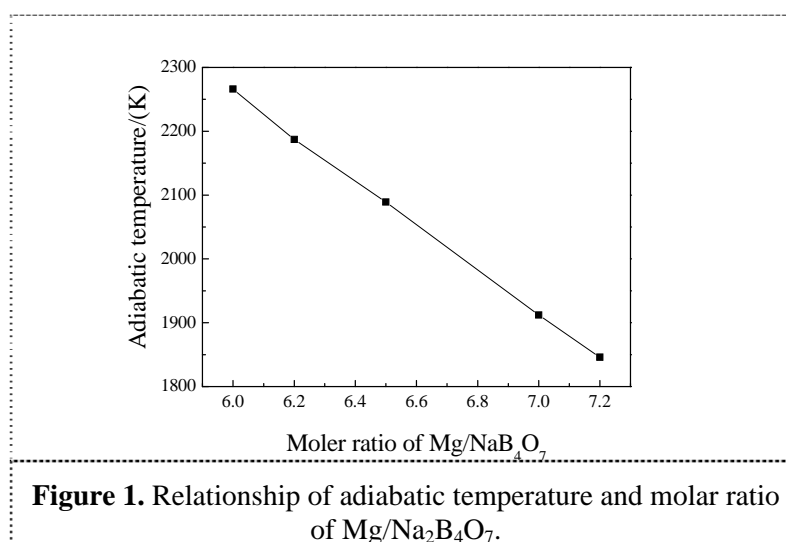
2. Experimental procedure

The reactant powder mixtures of $\text{Na}_2\text{B}_4\text{O}_7$, magnesium (Mg) and carbon (C) with different ratios were mixed thoroughly in a ceramic mortar at a horizontal rotation velocity of 50rpm for 24h, followed by drying at 60°C in a vacuum drying oven. The powder mixtures were then weighed out and cold stamped into a stainless steel mold to form cylindrical specimens under different pressures. After packing, the samples were introduced into the SHS apparatus and experiments were conducted under argon pressure. At the start of experiments, 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

For the reaction $\text{Na}_2\text{B}_4\text{O}_7 + 6\text{Mg} + \text{C} = \text{B}_4\text{C} + 6\text{MgO} + \text{Na}_2\text{O}$, the adiabatic temperature (T_{ad}) of B_4C is 2266K, which is considerably higher than the empirically established minimum of 1800K for SHS reactions. B_4C could be produced through the combustion of $\text{Na}_2\text{B}_4\text{O}_7$, Mg and Carbon. Details of calculations of adiabatic temperature have been discussed in some references [10].

As a rule, fabrications of materials by magnesium-thermal reduction have been reported to be associated with the loss of magnesium during combustion because of the higher evaporation pressure of Mg (303Pa at 1361K [11]), so it is necessary that an extra amount of Mg be added to reactant mixtures to provide an adequate reductive condition. The effect of the molar ratio of $\text{Mg}/\text{Na}_2\text{B}_4\text{O}_7$ on the adiabatic temperature (T_{ad}) of the reaction system is shown in Figure 1. When the molar ratio of $\text{Mg}/\text{Na}_2\text{B}_4\text{O}_7$ increases from 6.0 to 7.2, the adiabatic temperature decreases from 2266K to 1846K. With the increase of $\text{Mg}/\text{Na}_2\text{B}_4\text{O}_7$, the adiabatic temperature will change lower.



In order to direct the synthesis process of B_4C , it is important to study the reaction mechanism of B_4C from $\text{Na}_2\text{B}_4\text{O}_7 + \text{Mg} + \text{C}$ system by SHS. In the present research, combustion-front quenching technique is applied to study the reaction mechanism. The phase composition of the quenched specimen were identified through a layer-to-layer X-ray diffraction analyses at three relatively distinct zones with different colors (reactants' mixtures are black while the combustion products are Khaki), whose X-ray diffraction analysis results on these zones are shown in Figure 2. From XRD results, Mg, $\text{Na}_2\text{B}_4\text{O}_7$ are present in the lower part (Fig. 2(a)). B_2O_3 suddenly appears in middle part (Fig. 2(b)). The upper part (Fig. 2(c)) consists of MgO, $\text{Mg}_3(\text{BO}_3)_2$, $\text{NaBO}_2 \cdot \text{H}_2\text{O}$ and minor amounts of target

product B_4C . Thus, from the above results, synthesis of B_4C is composed of two consecutive stages: oxide reduction and boron carburization. The chemical interaction in this system starts by decomposition of $Na_2B_4O_7$ to form intermediary product B_2O_3 , which then reacts with magnesium to form the second intermediary phase B. The appearance of B_2O_3 in the final products was recorded by XRD analysis (Fig. 2(a)). Because elemental B is possibly in an amorphous state, it cannot be determined by X-ray. $Mg_3(BO_3)_2$ is probably from the reaction between B_2O_3 liquid point and MgO [12]. 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.

In the present work, the following experimental investigation was carried out on the $Na_2B_4O_7 + Mg + C$ system. The reaction starts from the ignition of the pellet and then $Na_2B_4O_7$ reacts with Mg and C in combustion wave mode to form loose, porous combustion products with the color of Khaki. The effect of molar ratio of $Mg/Na_2B_4O_7$ on the phase composition of the final products was studied. B_4C powder was prepared from $Na_2B_4O_7 + Mg + C$ system by SHS method with an extra amount of Mg. The XRD patterns of the SHS-products obtained from the reactant mixtures with $Mg/Na_2B_4O_7 = 6.2$ and 7.2 are shown in Figure 2(b). The combustion products are mainly composed of MgO , B_4C , $Mg_3(BO_3)_2$ and $NaBO_2 \cdot H_2O$ at $6.2Mg/Na_2B_4O_7$ or less and the concentration of $Mg_3(BO_3)_2$ and $NaBO_2 \cdot H_2O$ decreases with the increase of Mg amount. Comparing the phase composition of combustion products from the reactants' mixture of $6.2Mg/Na_2B_4O_7$ and $7.2Mg/Na_2B_4O_7$, $NaBO_2 \cdot H_2O$ can not be detected in the XRD patterns from $7.2Mg/Na_2B_4O_7$. The reasonable explanation of that is the loss of magnesium during SHS process because of the higher evaporation pressure of Mg (303Pa at 1361K [10]), which caused the incomplete reduction reaction and thus the diffraction peaks of $NaBO_2 \cdot H_2O$ was detected in the XRD analysis of combustion products.

After combustion, samples were kept up in the reactor up to complete cooling. Usual operations of washing by acid enrichment and water for elimination of MgO and Na_2O from the reaction products and drying in vacuum drying furnace at the temperature $110^\circ C$ of final products were made. The XRD pattern and the corresponding SEM morphology of after-treatment combustion product are shown in Fig. 3. As seen, the formation of any secondary phases was not recorded by X-ray analysis (Fig. 3(a)) and the mean particle size of rhombohedral B_4C crystal is about $0.6\mu m$ from SEM result (Fig. 3(b)).

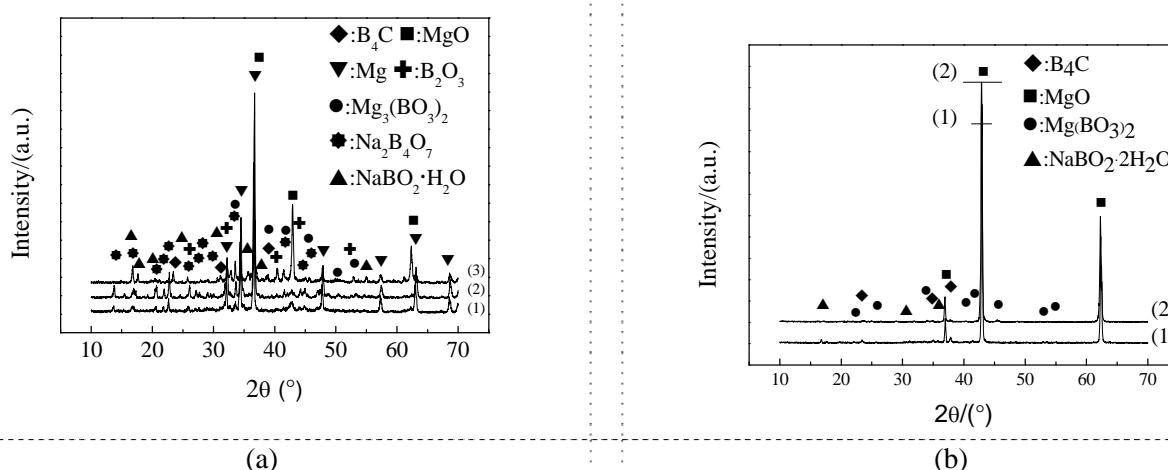


Figure 2. (a) XRD patterns of the quenched sample (1) lower part (2) middle part (3) upper part

(b) XRD patterns of combustion products synthesized at different mole ratios of $Mg/Na_2B_4O_7$ (1) 6.1 (2) 7.2.

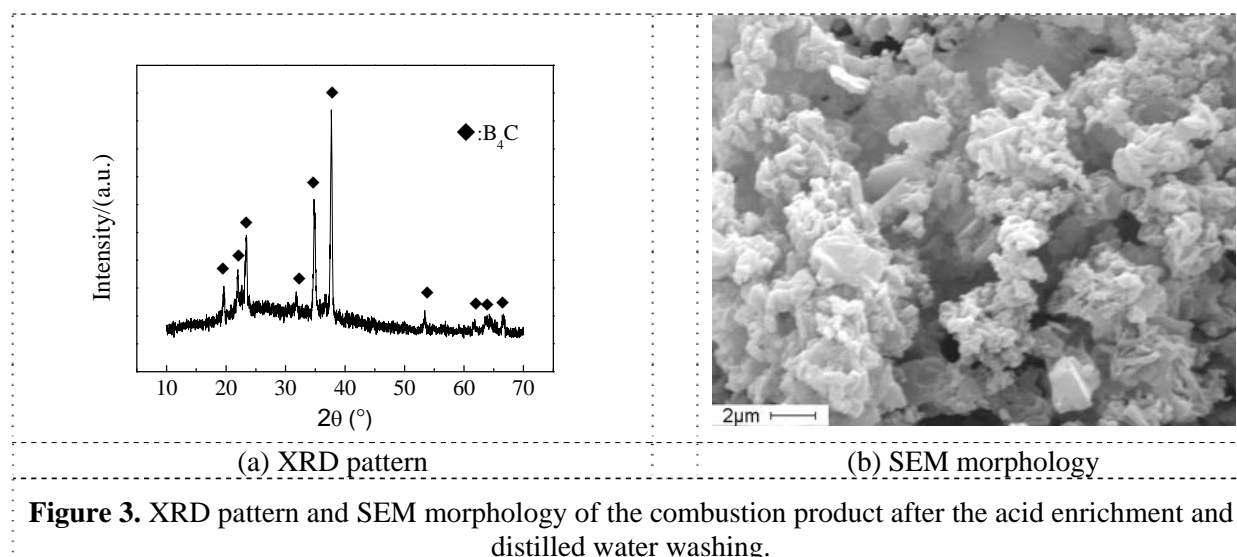


Figure 3. XRD pattern and SEM morphology of the combustion product after the acid enrichment and distilled water washing.

4. Conclusions

Experimental studies were carried out to synthesize B₄C by Self-propagating High-temperature Synthesis method with borax (Na₂B₄O₇), Mg and Carbon as raw chemicals. The reaction mechanism of SHS is proposed, in which special role is assigned to the decomposition of Na₂B₄O₇ into the intermediate phase B₂O₃, which reacts with Mg and Carbon to form Boron Carbide. The optimum conditions (molar ratio of Mg/Na₂B₄O₇) for single phase B₄C were established. The structure of B₄C powders synthesized by the given technique is rhombohedral and has a size of about 0.6 μm.

Acknowledgements

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References

- [1] Thevenot F *Key Eng. 1990 Ceram. Soc.* **6** 202
- [2] Bose D K, Nair K U and Gupta C K 1986 *High Temp. Mater. Process.* **7** 133
- [3] Benton S T and Masters D R 1975 U.S. Patent 3,914,371
- [4] Goller G, Toy C, Tekin A. and Gupta C K 1996 *High Temp. Mater. Process.* **15** 117
- [5] Gray E G 1958 U.S. Patent 2,834,651
- [6] Oyama T, Takcuchi K 1999 *Carbon* **37** 433
- [7] Liang Shi, Gu Y L, Chen L Y, Qian Y T, Yang Z H, Ma J H 2003 *Solid State Commun.* **128** 5
- [8] Sinha A, Mahata T, Sharma B P 2002 *J. Nucl. Mater.* **301** 165
- [9] Wang L L, Munir Z A, Birch J 1995 *J. Am. Ceram. Soc.* **78** 756
- [10] Munir Z A 1988 *Am. Ceram. Soc. Bull.* **67** 342
- [11] Chase Jr M W, Curnutt J L, Mcdonald R A and Syverud A N 1978 *J. Phys. Chem. Ref Data* **7** 793
- [12] Mutluer T and Timucin M 1975 *J. Am. Ceram. Soc.* **58** 196