Combustion of $Na_2B_4O_7$ + Mg + C to synthesis B_4C powders

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ABSTRACT

Boron carbide powder was fabricated by combustion synthesis (CS) method directly from mixed powders of borax ($Na_2B_4O_7$), magnesium (Mg) and carbon. The adiabatic temperature of the combustion reaction of $Na_2B_4O_7$ + 6 Mg + C was calculated. The control of the reactions was achieved by selecting reactant composition, relative density of powder compact and gas pressure in CS reactor. The effects of these different influential factors on the composition and morphologies of combustion products were investigated. The results show that, it is advantageous for more $Mg/Na_2B_4O_7$ than stoichiometric ratio in $Na_2B_4O_7$ + Mg + C system and high atmosphere pressure in the CS reactor to increase the conversion degree of reactants to end product. The final product with the minimal impurities' content could be fabricated at appropriate relative density of powder compact. At last, boron carbide without impurities could be obtained after the acid enrichment and distilled water washing.

1. Introduction

Boron carbide (B_4C), which exhibits a number of excellent properties such as high melting point, extreme hardness, low density, high Young's modulus, high chemical stability and good wear resistance, is a particularly well-adapted material for many applications, such as an abrasive material in polishing and grinding media, lightweight armor ceramic composites, blasting nozzles, ceramic bearing and wire drawing dies. In the aerospace industry, B_4C powder is a promising candidate for a rocket propellant due to its capacity to generate an intense amount of heat when combined with oxygen [1–3]. B_4C is an ideal control and shielding material in nuclear industry due to large neutron absorption cross-section of boron atoms [1].

A number of processes are available for the synthesis of B_4C powders and each process varies in the characteristics of the powder produced and processing cost. B_4C powder can be synthesized from elemental boron and carbon directly [4], but the high cost of these elements has made this method economically unattractive. Carbothermal reduction 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 is main industrial method for the production of B_4C [5,6]. However, the method requires high temperature and the process is time consuming and expensive. Moreover, the product obtained is in the chunk form and coarse grained, so it needs subsequently crushing and intensively milling to produce powder, in which process milled powder is inherently associated with

contamination resulting from the grinding media and hence requires an acid leaching for purification. In recent years, much effort has been directed towards the fabrication of B_4C powder and various methods have been explored for its manufacturing, such as laser irradiation chemical vapor deposit (LICVD) [7], co-reduction route with BBr_3 and CCl_4 as the reactants and metallic Na as the co-reductant [8], and sol–gel [9]. However, some limitations for these routes retard their large-scale production, for example, laser process requires expensive equipment and its productivity is low, and as for sol–gel method, the raw materials are very expensive and process is cumbersome.

Comparing with the above methods, combustion synthesis (CS) that was employed in this study, in which highly exothermic reactions between the constituents become self-sustaining and proceed via a combustion propagation wave through an entire sample, provide an attractive low cost alternative to conventional methods of producing advanced materials. The energy-efficient nature of the process stems from the fact that the energy required is provided by the reaction enthalpy. An external energy source is only used for local ignition of reactant powders or a compact on one end. Once initiated by a hot wire the external heat source is shut up immediately and the process requires no further addition of energy. The process is simple and lacks a need for complicated expensive experimental configurations. The reaction is complete within seconds rather than hours, which makes CS an economical process. By using CS method, B_4C have been fabricated from the combustion reaction of B_2O_3 + Mg + C system [10]. However, B_2O_3 particle of industrial production is always coarse and it absorbs water easily to form boric acid, which holds back the further improvement of B_4C powders with fine particle. In the present

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work, borax ($Na_2B_4O_7$) was chosen as raw material for it is fine and chemically stable. Despite the obvious attractiveness, no previous results on the combustion synthesis of B_4C from borax have been reported. The aim of this study is to demonstrate an experimental opportunity of combustion synthesis of B_4C from borax and discuss the role of experimental conditions (molar ratio of Mg to $Na_2B_4O_7$, relative density of powder compact and gas pressure in the CS reactor) on the product quality as a whole.

2. Experimental procedures

In order to synthesize B_4C, borax ($Na_2B_4O_7$), magnesium (Mg), and carbon (C) were used as starting chemicals. An appropriate amount of these powders according to a certain ratio were mixed thoroughly in a ceramic mortar and the milling performed at a horizontal rotation velocity of 50 rpm for 24 h. Milling conditions were the same for all the powders. After milling the slurries were dried at 60 °C in a vacuum drying oven. To form a compacted sample, the appropriate quantity of mixed powder was weighed out and poured into cylindrical stainless steel mould with 30 mm thickness, 10 mm diameter, and 50 mm height and then cold pressed into a circle-shape powder compact. After packing, the powder compact was put into a carbon crucible and then the crucible was introduced into the CS reactor. The experiments were conducted under argon pressure. At the start of the experiments, the combustion chamber was sealed, evacuated and purged with argon. The chamber was then filled with argon to a high pressure to suppress the possible evaporation of Mg during the combustion. The mixed powder was ignited by a tungsten coil which was applied by an electric voltage of about 30 V. After cooling, the combustion products were removed from the CS reactor and then washed with enrichment acid and distilled water. In the process, the combustion products were dissolved in 1% HCl acid solution for 1 h to eliminate MgO and Na_2O. Sequentially the enrichment products were washed by distilled water for several times to eliminate extra HCl acid until the pH value is about 7. In the end, the products were heated at the temperature of 110 °C in the vacuum drying oven for 30 min to get rid of H_2O. The phase composition of combustion products with or without the enrichment process with acid and water was identified by powder X-ray diffraction (XRD), employing a scanning rate of $0.05° s^{-1}$ with a 2θ range from 10° to 70°, using a Rigaku Dmax γA X-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.15406 nm). The morphologies of combustion products were observed by using scanning electron microscopy (SEM) and electron microprobe.

3. Results and discussion

3.1. Thermodynamic analysis of the combustion synthesis of $Na_2B_4O_7$ + Mg + C system

As explained previously, for the reaction to be self-sustaining, CS process must be associated with high-temperature reactions and meet with some requirement. An important thermodynamic parameter in this regard is the adiabatic temperature of combustion, T_{ad}, or maximum attainable temperature, to which the product is raised under adiabatic conditions as a consequence of heat evolution from the reaction. Preliminary thermodynamic analysis of $Na_2B_4O_7$ + Mg + C system was performed to determine adiabatic temperature. The T_{ad} of the combustion reaction in stoichiometric mixtures consisting of $Na_2B_4O_7$ + 6 Mg + C is 2128 K, which is bigger than 1800 K, an empirical criterion typically adopted for determining the feasibility of CS reaction [11], and demonstrates B_4C could be synthesized from $Na_2B_4O_7$ + Mg + C system by CS technique.

3.2. Combustion synthesis of B_4C in $Na_2B_4O_7$ + Mg + C system

3.2.1. Experimental phenomena of combustion synthesis in $Na_2B_4O_7$ + Mg + C system

Upon ignition, a combustion wave propagated through the powder compacts of raw chemicals and the initial reactants, $Na_2B_4O_7$, Mg and C transform instantaneously into B_4C with a high exothermic heat of reaction. The combusted products are uniformly porous, loose and have a color of khaki. The XRD pattern of typical combustion product is shown in Fig. 1. From viewing the XRD result, it can be seen B_4C, MgO, $Mg_3(BO_3)_2$ and $NaBO_2 \cdot H_2O$ are the main constituents of the combustion products. In these compounds, $Mg_3(BO_3)_2$ maybe comes from the reaction between MgO and B_2O_3 [12]. $NaBO_2 \cdot H_2O$ is possibly related with the reaction of B_2O_3, Na_2O and H_2O, in which Na_2O is from the decomposition of $Na_2B_4O_7$, and H_2O is the possible absorbent of the reaction mixture from environment during the process of mixing of raw chemicals or after-treating of combustion products. From these results, B_4C was found to be successfully fabricated by CS method. As may be seen from the SEM micrograph of the typical combustion product (Fig. 2), the different constitutes in the combustion product vary in their shapes, in which the morphology of B_4C is rhombohedral, MgO cobble-shaped and $Mg_3(BO_3)_2$ continuous flocculence, respectively.

3.2.2. Effect of $Mg/Na_2B_4O_7$ molar ratio on the combustion synthesis of B_4C

Numerous factors could affect the combustion wave progress through the reactants. However, the initial reactant ratio is the most influential factor to determine the conversion degree of reactants to end product. In the combustion process of
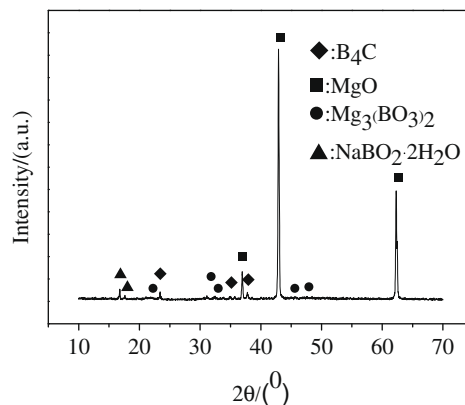

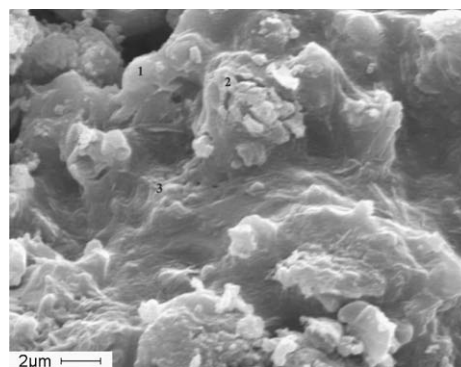**Fig. 1.** XRD pattern of the typical combustion product.

Fig. 2. SEM micrograph of the typical combustion product. 1: MgO, cobble-shaped; 2: B_4C, rhombohedral; 3: $Mg_3(BO_3)_2$, continuous flocculence.

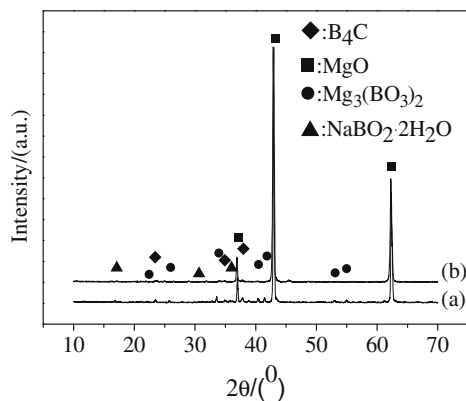**Fig. 3.** XRD patterns of combustion products synthesized from reactant mixtures with different $Mg/Na_2B_4O_7$ molar ratios. (a) 6.1 and (b) 7.2.
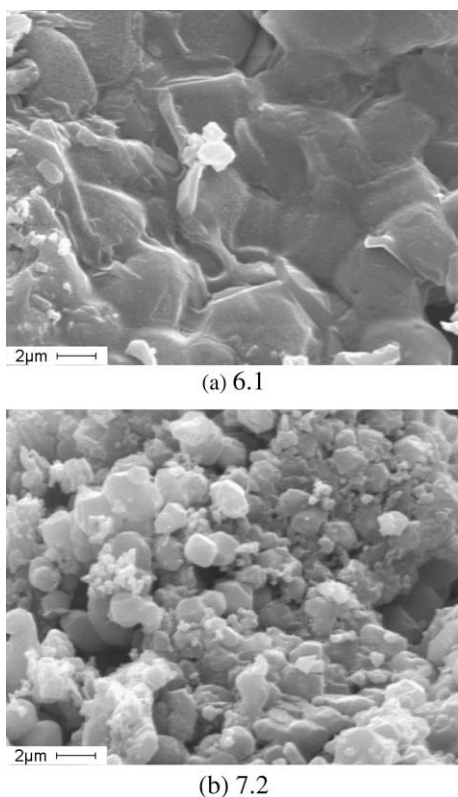

Fig. 4. SEM micrographs of combustion products synthesized from reactant mixtures with different $Mg/Na_2B_4O_7$ molar ratios.

$Na_2B_4O_7 + Mg + C$ system, Mg plays a key role in the formation of B_4C for it acts as a reducing agent of $Na_2B_4O_7$. However, because metal Mg has a lower melting point (the melting point of Mg is 924 K) and lower boiling point (the evaporation pressure of Mg is 303 Pa at 1361 K [13]), elemental Mg boils and partly evaporates during high temperature produced by combustion reaction, which lead to the loss of elemental Mg in reactant mixture. Therefore, Mg in excess of the stoichiometric quantity is needed in the aforesaid reactant mixture to compensate for the possible loss of Mg during combustion. In this study, the impact of different $Mg/Na_2B_4O_7$ molar ratios on the phase composition of final products was investigated. The XRD patterns of the CS-products obtained from reactant mixtures with different $Mg/Na_2B_4O_7$ molar ratios are

shown in Fig. 3. The corresponding SEM morphologies of combustion products are presented in Fig. 4.

According to XRD analysis, the phase composition of end product from $6.1 Mg + Na_2B_4O_7 + C$ includes MgO, B_4C, $Mg_3(BO_3)_2$ and $NaBO_2 \cdot H_2O$. However, no $NaBO_2 \cdot H_2O$ was detected in the CS-product synthesized from $7.2 Mg + Na_2B_4O_7 + C$. The result indicated that the content of $Mg_3(BO_3)_2$ and $NaBO_2 \cdot H_2O$ decreases with increasing Mg amount. The reasonable explanation is that evaporation of Mg at high combustion temperature leads to the loss of some Mg and the actual composition of combusting chemicals deviation from the starting reactant ratio arising therefrom. As a result, the combustion reaction is not complete and a certain quantity of impure products such as $Mg_3(BO_3)_2$ and $NaBO_2 \cdot H_2O$ remains in the final products. In order to improve the conversion extent of $Na_2B_4O_7$, excessive amount of Mg in the initiate mixture must be added to compensate for the loss of some Mg. SEM studies gave a clear indication of well-developed B_4C crystal obtained from $7.2 Mg + Na_2B_4O_7 + C$ (Fig. 4b) in comparison with that from $6.1 Mg + Na_2B_4O_7 + C$ (Fig. 4a). The change of molar ratio of Mg to $Na_2B_4O_7$ from 6.1 to 7.2 means an increasing content of Mg involved in the CS reaction, leading to higher combustion temperature and faster kinetics of the crystal growth.

3.2.3. Effect of relative density of powder compact on the combustion synthesis of B_4C

Apart from the aforementioned reactant composition, relative density of powder compact is another significant influential factor on combustion synthesis of solid–solid systems. As we know, relative density equals to compacting density divided by theoretic density, where compacting density equals to the mass of reactants divided by their volume and theoretic density can be considered as the sum of the corresponding theoretic density of each reactant multiplied with its volume fraction for all reactant components. In this work, the influence of different relative densities of powder compacts on the combustion synthesis of B_4C was studied. XRD patterns and the corresponding SEM morphologies of combustion products fabricated at different relative densities (23%, 29% and 48%) of powder compacts are shown in Figs. 5 and 6, respectively. XRD pattern indicated the quantity of impure products such as $Mg_3(BO_3)_2$ and $NaBO_2 \cdot H_2O$ first decrease and then increase with increasing relative density and it is minimal at the relative density of 29%.

This behavior is most likely attributed to the duel effects of relative densities of powder compacts. On the one hand, the thermal conductivity of powder compact is associated with relative density. The heat flux transfer ahead of combustion wave increases with higher relative density, which lowers the temperature of
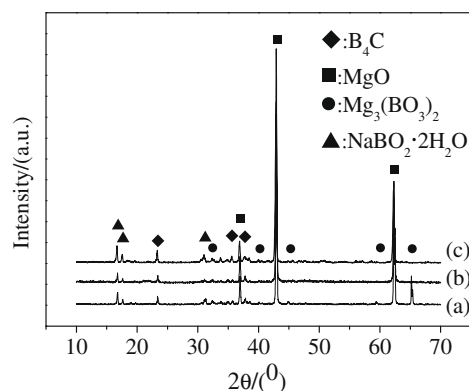

Fig. 5. XRD patterns of combustion products synthesized at different relative densities of powder compacts. (a) 23%, (b) 29%, and (c) 48%.
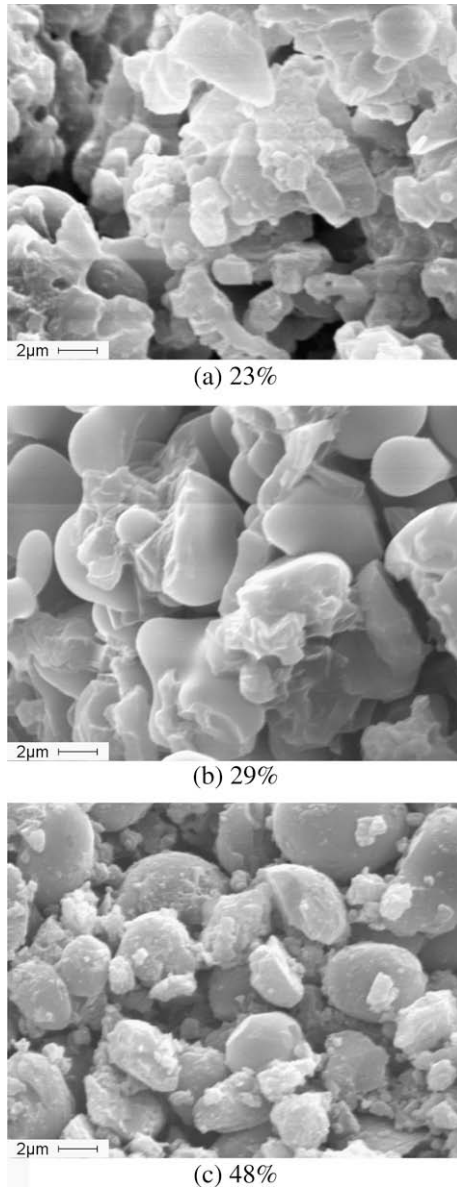
(a) 23%

(b) 29%

(c) 48%

Fig. 6. SEM micrographs of combustion products synthesized at different relative densities of powder compacts.

combustion zone and leads to the incompleteness of combustion reaction. On the other hand, the decreasing relative density causes a lower contact area among reactants, which also results in lower combustion temperature and imperfection of reaction. Only appropriate relative density can balance the impacts of heat transfer and reactants' contact area on the temperature of combustion zone and the complete extent of combustion reaction such incurred. In the present work, the relative density of 29% of powder compact was the most prefer condition.

3.2.4. Effect of gas pressure in the CS reactor on the combustion synthesis of B_4C

Along with major influential factors such as molar ratio of Mg to $Na_2B_4O_7$ and relative density of powder compact discussed previously, gas pressure in the CS reactor is another factor which must also be considered because higher gas pressure can be used to suppress the possible evaporation of Mg at high temperature produced by combustion reaction. In this work, the impact of different gas pressures on the combustion synthesis of B_4C was studied by comparing the composition and morphologies of combustion

products fabricated at different gas pressures. The XRD patterns and the corresponding SEM morphologies of the CS-products obtained at the pressure of 10 and 50 atm are shown in Figs. 1, 2, 5b, and 6b, respectively. By comparing Fig. 1 with Fig. 5b, the content of $Mg_3(BO_3)_2$, $NaBO_2 \cdot H_2O$ and other impurities in combustion product synthesized at gas pressure of 10 atm are more than that at 50 atm, which is related with the suppression of evaporation of Mg by higher gas pressure and relatively more complete extent of reduction reaction it caused. The comparison of SEM morphologies (Figs. 2 and 6b) also confirms the above-mentioned explanation. In the combustion product obtained at higher gas pressure (50 atm) (Fig. 6b), the growth of B_4C crystal is more complete and the color of combustion product is light-black. The mark of some sintering phenomena owing to higher combustion temperature is clearly observed in the combustion product so that it is not easy to break it. Conversely, combustion product fabricated at 10 atm is loose and its color is Khaki.

3.3. Combustion products after the wash with enrichment acid and distilled water

The aforesaid combustion products were purified by using acid enrichment to eliminate MgO and Na_2O, followed by washing with distilled water to get rid of surplus acid. The XRD pattern of the purified product is shown in Fig. 7. Diffraction peaks of B_4C are neatly expressed and the purified product did not contain any impurities. The corresponding SEM morphology of the purified product is presented in Fig. 8. As seen, these particles are mainly crystalline in shape and the mean size is about 0.6 μm.
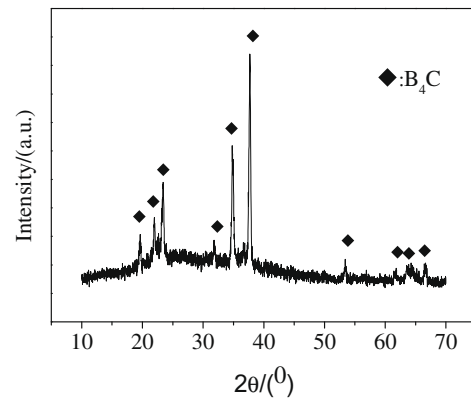

Fig. 7. XRD pattern of the purified product after the acid enrichment and distilled water washing.
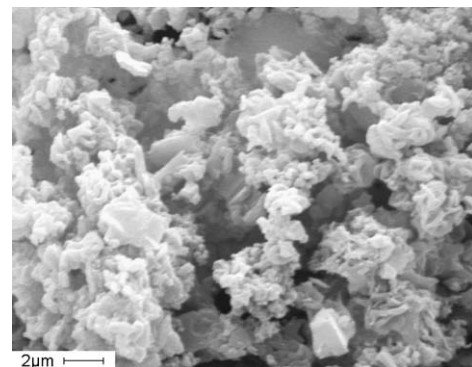

Fig. 8. SEM micrograph of the purified product after the acid enrichment and distilled water washing.

The averaged yields of B_4C per reaction before and after washing are 95% and 14%, respectively.

4. Conclusion

In this study, combustion synthesis, a cost-effective and rapid synthetic process, was successfully developed for the production of B_4C powder by using borax, magnesium, and carbon as starting chemicals. The fabricated powder has diameters of about 0.6 μm which has a rhombohedral structure. In combustion synthesis processes, different starting conditions (molar ratio of Mg to $Na_2B_4O_7$, relative density of powder compact and gas pressure in the CS reactor) play important roles in controlling the phase components of synthesized products. With the increase of excessive Mg in reactant mixture, the impurity content in fabricated product remarkably decreases. Similar results were observed when the gas pressure in the CS reactor increases from 10 to 50 atm. XRD analysis indicates that the optimum relative density of powder compact is 29%. When relative density is higher or lower than this value, a significant increase of the impurities content takes place. This behavior was attributed to the duel effect of relative density, i.e., contact area among reactants and the heat transfer in the reactant system.

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