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Preparation of niobium borides NbB and NbB₂ by self-propagating combustion synthesis

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Abstract

Preparation of niobium borides NbB and NbB₂ was conducted by self-propagating high-temperature synthesis (SHS) from elemental powder compacts in this study. Effects of the sample green density, preheating temperature and starting stoichiometry on combustion characteristics, as well as on the composition of final products were studied. Experimental evidence indicates the self-sustained reaction zone propagating along a spiral trajectory for the reactant compacts without prior heating or preheated at 100 °C. The increase of initial sample temperature to 200 and 300 °C by prior heating brings about a planar flame-front propagating in a steady mode. As the preheating temperature or sample green density increased, the combustion temperature was found to increase and the propagation rate of combustion wave was correspondingly enhanced. According to the temperature dependence of combustion wave velocity, the activation energies associated with the Nb + B and Nb + 2B reactions were determined to be 151.8 and 132.4 kJ/mol, respectively. As indicated by the XRD analysis, the final composition of burned products was essentially governed by the starting stoichiometry of reactant compacts. Synthesized products composed of a single boride phase NbB and a small amount of unreacted Nb were obtained from the reactant compacts of Nb:B = 1:1. In addition, the SHS reaction of powder compacts with an initial composition Nb:B = 1:2 yielded niobium diboride NbB₂ as the dominant phase, along with another boride phase Nb₃B₄ in a minor quantity.

Keywords: NbB; NbB2; SHS; Preheating temperature; Activation energy

1. Introduction

With the advantages of time and energy savings, simplicity and high-purity products, combustion synthesis especially in the mode of self-propagating high-temperature synthesis (SHS) has been employed as an alternative route to the conventional methods of producing advanced materials, including borides, carbides, hydrides, nitrides, silicides, carbonitrides, intermetallics, etc. [1–5]. Therefore, the preparation of a variety of transition metal borides such as TiB₂, ZrB₂, HfB₂, NbB₂ and TaB₂ by the SHS technique was demonstrated in a number of investigations [6–12]. Most of the previous studies [7–10] focused largely on the formation of TiB₂ and ZrB₂. Regarding the niobium borides, combustion synthesis of NbB and NbB₂ was conducted by Zenin et al. [11,12] with an emphasis on the analysis of thermal wave structure of the reaction process. Due to many excellent prop-

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Lately, the discovery of superconductivity at 39 K in MgB₂ [15] has motivated new investigations on similar metal diborides MB_2 (M = Be, Al, Nb, Mo, Ta, Ti, Hf, V and Cr) [16–19]. Among those diborides, Takeya et al. [16] found a superconducting phase with a transition up to 8 K in Nb_xB₂ (x = 0.67 - 1.11) produced by combustion synthesis. Yamamoto et al. [17] sintered Nb_{1-x}B₂ (x=0-0.48) from elemental powders at 5 GPa and showed the transition temperature (T_c) with a maximum value of 9.2 K at x = 0.24. Additionally, Zlotnikov et al. [20] demonstrated the preparation of bulk MgB₂ superconductor from elemental Mg-B blends by combustion synthesis in the thermal explosion mode and reported a transition temperature at 39K for all the specimens regardless of their porosity and the amount of second phases. By using the combustion synthesis in the SHS mode, Przybylski et al. [21,22] successfully fabricated bulk MgB₂ samples (with $T_c = 37.24$ K) consisting of

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very small and uniformly distributed MgO particles acting as the strong pinning centers.

The objective of this study was to experimentally investigate the synthesis of niobium borides NbB and NbB₂ by self-sustaining combustion using compacted reactants from elemental powders. Effects of the starting stoichiometry, sample green density and preheating temperature on combustion characteristics, as well as on the final composition of burned products were studied. The propagation rate of combustion wave and the temperature of reaction front were measured as a function of experimental variables. In addition, a mechanistic investigation to deduce the activation energies associated with the synthesis of NbB and NbB₂ was performed by correlating the temperature dependence of combustion wave velocity.

2. Experimental methods of approach

Test samples used in this study were prepared by niobium (Strem Chemicals, -325 mesh, 99.8% purity) and amorphous boron (Noah Technologies Corp., 1 µm, 92% purity) powders, which were dry mixed in a ball mill for 10 h with molar compositions according to the stoichiometric ratios of Nb:B = 1:1 and 1:2 for the synthesis of NbB and NbB₂, respectively. The niobium particles have irregular shape and an average size of about 45 µm, as shown in Fig. 1. Mixed powders in a stainless-steel mold were uniaxially pressed at pressures of about 35–65 MPa into cylindrical samples (having a diameter of 7 mm and a height of 12 mm) with density ranging from 45 to 60% of the theoretical maximum density (TMD) of powder mixtures, in order to study the influence of sample green density on the formation of niobium borides. The effect of initial sample temperature was studied by heating up the compacted reactant prior to ignition and the preheating temperature (T_p) adopted in this study was up to 300 °C.

The SHS experiments were conducted in a stainless-steel windowed combustion chamber under an atmosphere of high purity argon (99.99%). The sample holder was equipped with a 600 W cartridge heater used to raise the initial temperature of test samples prior to ignition. Details of the experimental setup and measurement approach were reported elsewhere [23–25]. However, it was found that for the reactant compacts of Nb:B = 1:2 the combustion wave could not be well established and finally came to extinction, when the reaction was initiated by a heated tungsten coil with a voltage of 60 V and a current of 5 A. Therefore, a compacted pellet (2 mm in height and 7 mm in diameter) made up of the mixture of titanium (Ti) and carbon black (C) powders (with a molar ratio Ti:C = 1:1) was placed on the top of the Nb + 2B samples to serve as an ignition enhancer in order to ensure the initiation of SHS reactions. On the other hand, for the pow-



Fig. 1. SEM micrograph of niobium (Nb) particles.

der compacts of Nb:B = 1:1 the self-sustaining combustion was easily achieved upon ignition by a heated tungsten coil. The final composition of burned products was identified by an X-ray diffractometer (Shimadzu XRD-6000) with Cu K α radiation operating at 40 kV. The diffractograms were recorded with a scanning rate of 4.0° min⁻¹ and a sampling pitch of 0.02°.

3. Results and discussion

3.1. Observation of combustion characteristics

Experimental observations of this study indicate that the combustion behavior of Nb-B powder compacts is significantly affected by the initial sample temperature (i.e., the preheating temperature). Typical SHS processes of reactant compacts under a preheating temperature of 200 °C are illustrated in Fig. 2(a and b), within which the flame propagation sequences of test samples with initial compositions of Nb:B = 1:1 and 1:2 are presented, respectively. As shown in Fig. 2(a and b), upon ignition a planar combustion front forms and traverses the entire sample in a self-sustaining manner. Based upon the flame-front trajectory constructed from the recorded film images, the combustion wave was found to propagate in a steady mode. In addition to similar combustion behavior, both types of the samples experienced a volume expansion during the combustion. Moreover, it was found that the burned product of the Nb+2B reactant expanded more considerably than did the Nb+B compact after reaction. In general, the volume increase of combustion synthesized products could be attributed to the intrinsic volume change associated with the conversion of reactants to the final product, and to the vaporization of volatile impurities due to high temperatures [26,27]. In this study, it is believed that the vaporization of low boiling point impurities in amorphous boron generated gases which expanded under high temperatures and were then expelled from the pores of the compacted sample, leading to the augmentation of sample porosity and the size expansion of the burned product. As shown in Fig. 2(b), the expulsion of gaseous substances with the propagation of the combustion front produces visible yellow smokes surrounding the test sample. The above postulation also provides a reasonable explanation for the fact that a greater degree of volume increase was observed for the Nb+2B reactant, which contained a higher content of boron in comparison to the sample compact of Nb:B = 1:1.

A typical series of recorded combustion images in association with the test condition under a preheating temperature of 100 °C is shown in Fig. 3, which illustrates the reaction of a powder compact with Nb:B = 1:1. It is evident in Fig. 3 that shortly after the initiation of a distinct combustion front, the planar front is transformed into a localized combustion zone moving along a spiral trajectory on the sample surface. The spinning combustion wave traveling from right to left is clearly observable between t = 1.2 and 6.2 s in Fig. 3. Furthermore, because of the spinning motion of the reaction zone, Fig. 3 indicates numerous cracks formed on the burned sample with the advance of the combustion wave and the significant fracture eventually results in substantial elongation of the end product. It is taken for granted that the heat generated from the igniter along with the thermal energy liberated from the Nb/B reaction within the combustion zone support



Fig. 2. Recorded SHS processes illustrating steady planar combustion fronts associated with 55% TMD samples preheated at 200 $^{\circ}$ C and initially composed of (a) Nb:B = 1:1 and (b) Nb:B = 1:2.

the steady propagation of a planar front before the appearance of the spinning combustion wave. With the fading of the heat input from the igniter, combustion becomes self-sustained. According to Ivleva and Merzhanov [28], once the heat flux generated from the self-sustained combustion is no longer sufficient to maintain the steady propagation of a planar front, the flame-front forms one or several localized reaction zones.

Based upon the experimental observations of this study, it was found that the propagation mode of the self-sustained reaction was varied by the initial sample temperature. That is, under the condition at $T_p = 100$ °C or without any prior heating, the self-sustained combustion for both types of the reactant compacts (including Nb:B = 1:1 and 1:2) was restricted on a

localized region propagating in a spinning mode, as shown in Fig. 3. With an increase in the initial sample temperature by preheating at 200 and 300 $^{\circ}$ C, a planar combustion front steadily spreading the entire compact was attained, as shown in Fig. 2.

3.2. Measurement of combustion temperature

Fig. 4 depicts two typical temperature profiles: one features a spinning combustion wave and the other a steady planar flame-front. As shown in Fig. 4, the reaction temperature profile measured from a powder compact (made up of Nb:B = 1:1) with $T_p = 300$ °C exhibits an abrupt rise signifying the rapid



Fig. 3. Recorded SHS process illustrating a spinning combustion wave associated with a 60% TMD sample with an initial stoichiometry of Nb:B = 1:1 and preheated at 100 $^{\circ}$ C.



Fig. 4. Effect of preheating temperature on combustion temperature of reactant compacts with a starting composition of Nb:B = 1:1.

arrival of a planar combustion front. After reaching the peak value that corresponds to the temperature of combustion front, the temperature profile reveals a gradual decline due to the heat loss to the surroundings. The other temperature curve plotted in Fig. 4 is associated with an Nb + B sample preheated at 100 °C and illustrates two consecutive peaks, which were most likely caused by the progression of a spinning combustion wave that passed through the thermocouple twice. Fig. 4 also indicates the increase of the reaction front temperature roughly from 1460 to 1610 °C with the increase of the sample preheating temperature from 100 to 300 °C.

Additionally, the combustion temperature was found to increase with increasing sample density, as shown in Fig. 5 which presents three temperature profiles detected from the Nb+2B samples with different compacted densities of 45, 50 and 55% TMD. Fig. 5 indicates a slight increase in the peak temperature from 1520 °C for the 45% TMD compact to about 1600 °C for the 55% TMD sample. As also revealed in Fig. 5, due to the preheating temperature of 200 °C, all three temperature curves are single-peak profiles indicative of the propagation of planar flame-fronts.



Fig. 5. Effect of sample green density on combustion temperature of reactant compacts with a starting composition of Nb:B = 1:2.



Fig. 6. Effects of initial sample density and preheating temperature on flamefront velocity of reactant compacts with a starting composition of Nb:B = 1:1.

3.3. Measurement of flame-front propagation velocity

Effects of the sample green density and preheating temperature on the average velocity of the flame-front (V_f) in the longitudinal direction are presented in Figs. 6 and 7 for the powder compacts with starting stoichiometries of Nb:B = 1:1 and 1:2, respectively. It was found that the propagation rate of the combustion front was increased by increasing the initial sample temperature, on account of the increase of combustion temperature with preheating temperature. Furthermore, the variation of preheating temperature substantially alters the propagation mode of the reaction front, as mentioned in Figs. 2 and 3. Obviously, the planar flame-front propagates more quickly in the longitudinal direction than does a spinning combustion wave.

Figs. 6 and 7 show that the flame-front velocity increases with sample green density, as well. The influence of the sample density on the propagation rate of solid–solid reactions can be attributed to two competing phenomena [4]. As the green density increases, the intimate contact between the reactant particles is augmented, which enhances the reaction and consequently



Fig. 7. Effects of initial sample density and preheating temperature on flame-front velocity of reactant compacts with a starting composition of Nb:B = 1:2.



Fig. 8. Relation between flame-front velocity and combustion temperature for determination of activation energies of NbB and NbB₂ by SHS reactions.

increases the propagation rate of the combustion front. On the other hand, the thermal conductivity of the reactant compact also increases with sample density, which causes more thermal loss by conduction from the reaction zone and hence leads to a decrease in the reaction rate [4]. According to the results presented in Figs. 6 and 7, it is suggested that the former phenomenon predominates in this study.

The activation energy of a self-sustained reaction is generally determined by means of realizing the dependence of reaction front velocity on combustion temperature. Such a relationship is expressed in the following simplified form [23,24]

$$\left(\frac{V_{\rm f}}{T_{\rm c}}\right)^2 = f(n) \left(\frac{R}{E_{\rm a}}\right) K \exp\left(-\frac{E_{\rm a}}{RT_{\rm c}}\right) \tag{1}$$

where $V_{\rm f}$ is the flame-front velocity, $T_{\rm c}$ the combustion front temperature, E_a the activation energy of the reaction, R the universal gas constant, f(n) a function of the kinetic order of the reaction and K a constant which includes the heat capacity of the product, thermal conductivity and the heat of reaction. As a result, the slope of a plot correlating $\ln(V_f/T_c)^2$ with $1/T_c$ can provide the activation energy of the process. Based upon the slopes of best-fit lines for two sets of the data reported in Fig. 8, the activation energies deduced for combustion synthesis of NbB and NbB₂ were 151.8 and 132.4 kJ/mol, respectively. It should be noted that in the determination of activation energy, only the results obtained under the preheating temperatures of $T_p = 200$ and $300 \,^{\circ}\text{C}$ were adopted. This is because in the cases of $T_p = 100 \,^{\circ}\text{C}$ and without preheating, the self-sustained combustion is featured by a localized reaction zone traveling in a spinning mode, implying an unsteady three-dimensional motion that is inappropriate to be described by Eq. (1) [29].

3.4. Composition analysis of combustion products

The XRD spectrum of the combustion product synthesized from a reactant compact of Nb:B = 1:1 is shown in Fig. 9, with an indicative of the formation of niobium boride NbB. Fig. 9 also reveals a little of elemental Nb left unreacted in the final product.



Fig. 9. XRD spectrum of combustion product obtained from a 55% TMD compact with Nb:B = 1:1 and preheating at $T_p = 200$ °C.

Moreover, it was found that the composition of final products obtained from the compacts of Nb:B = 1:1 is independent of the variations in sample density and preheating temperature.

For the reactant with a composition Nb:B = 1:2, the XRD analysis presented in Fig. 10 identifies the formation of niobium diboride NbB₂ as the dominant phase, along with the presence of minor amounts of Nb₃B₄ and unreacted Nb. Similar to the case of Nb:B = 1:1, the preheating temperature and initial sample density did not affect the final composition of burned products converted from the reactants made up of Nb:B = 1:2. Above results imply that the composition of the end product is essentially governed by the starting stoichiometry of the reactant.

Even though the preheating temperature had no influence on the composition of burned products, experiments with high preheating temperatures of 200 and 300 °C yielded porous but relatively firm products, in contrast to those with a number of cracks caused by the spinning combustion wave under the conditions at $T_p = 100$ °C or without prior heating. It has been known that [30] a porous product obtained by an SHS reaction can be significantly densified by applying a suitable consolidation pressure either during or immediately after the reaction is completed,



Fig. 10. XRD spectrum of combustion product obtained from a 55% TMD compact with Nb:B = 1:2 and preheating at $T_p = 200$ °C.

while the synthesized products are still in a plastic state at high temperatures. In most cases, however, experiments must be conducted using a graphite die with the pressure applied through a ram [30].

4. Conclusions

This study presents an experimental investigation on the preparation of niobium borides NbB and NbB₂ using the SHS approach from elemental powder compacts. Experimental observations indicate that the propagation mode of the selfsustained combustion wave is strongly dependent upon the initial sample temperature. At a preheating temperature of 100 °C and in the case of without preheating, the self-sustained reaction was confined to a small area, which spirally proceeded on the Nb-B compact. For the reactant compacts heated at 200 and 300 °C prior to ignition, however, upon initiation a planar combustion front formed and propagated steadily along the sample. Moreover, the burned samples exhibited an obvious expansion in dimensions after combustion, due primarily to the expulsion of gases generated from the evaporation of low boiling point impurities in amorphous boron during the progression of the combustion wave.

The spinning combustion wave not only caused a number of fractures on the burned sample, but was responsible for the double-peak profile observed in the temperature measurement. On the contrary, a single-peak temperature profile signifying the steady propagation of a planar flame-front was detected from the compact ignited at $T_p = 200$ and 300 °C. Moreover, the temperature of the reaction front was found to increase with initial sample temperature and sample green density. The increase of flame-front propagation velocity with preheating temperature and sample density was observed in a manner consistent with the combustion temperature. Based upon the temperature dependence of combustion wave velocity, the activation energies of 151.8 and 132.4 kJ/mol were deduced for the combustion synthesis of NbB and NbB₂, respectively.

The XRD analysis identifies the formation of niobium boride NbB from the SHS reaction of compacted reactants initially made up of Nb:B = 1:1. Besides a secondary boride phase Nb₃B₄ in a small quantity, the combustion of powder compacts with Nb:B = 1:2 yielded predominantly niobium diboride NbB₂. Even though the preheating temperature and sample density significantly affected the dynamics of the combustion wave, these two parameters had nearly no effect on the final composition of burned products. In contrast, the starting stoichiometry of the reactant compact plays a decisive role in the boride phase formed in the end products.

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