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Synthesis of niobium carbonitride by self-propagating combustion of Nb–C system in nitrogen

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Abstract

An experimental investigation on the preparation of niobium carbonitrides by self-propagating high-temperature synthesis (SHS) was conducted using compacted samples of niobium and carbon powders ignited in gaseous nitrogen. Effects of the carbon content, nitrogen pressure, and NbN addition on the combustion behavior and the degree of conversion were studied. Due to the nature of reaction in the combustion front, steady propagation of the combustion wave is observed in the sample of Nb + 0.3C, whereas the flame front associated with the samples of Nb + 0.5C and Nb + 0.7C travels in an oscillatory manner. Moreover, the flame-front propagation velocity was found to decrease with an increase in the carbon content of the sample. For the samples of Nb + 0.3C and Nb + 0.5C, after the passage of the combustion front the reaction continues lengthily in an afterburning stage, resulting in the nitridation percentage as high as about 80% that is nearly unaffected by the variation of nitrogen pressure. However, due to the lack of afterburning combustion the degree of nitridation in the sample of Nb + 0.7C was decreased to between 53 and 67%. The XRD analysis of final products indicates that in addition to the dominant phase of Nb(C,N), there exist small amounts of Nb and carbon left unreacted.

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1. Introduction

Carbides, nitrides, and carbonitrides of early transition metals (such as Ti, Zr, Nb, and Ta) have received considerable attention in recent years, due to their unique chemical and physical properties, including high melting point, superior hardness, good thermal and chemical stability, and metallic electrical conductivity [1,2]. In particular, for niobium carbide (NbC) and nitride (NbN), extensive studies on the electronic properties as well as on the phonon spectra have been performed, mainly because these two compounds have high superconducting transition temperatures [3].

Over the past decades many carbides and nitrides of transition metals (especially in groups of IVB and VB) have been produced by means of the combustion synthesis [4–8], which utilizes the highly exothermic nature of reactions between these metals and carbon or nitrogen to sustain the combustion in a self-propagating manner. Combustion synthesis or self-propagating high-temperature synthesis (SHS) with the advantages of time and energy savings has been recognized as a promising alternative to the conventional methods of producing advanced materials, including carbides, borides, nitrides, silicides, carbonitrides, and intermetallics, etc. [4–8]. A survey of literature points out that the preparation of NbC [9,10] and NbN [11–15] by SHS has been broadly investigated. However, relatively few studies have been devoted to the production of transition metal carbonitrides using the SHS approach and relevant studies were focused only on the synthesis of titanium carbonitride, Ti(C,N) [16,17]. With the addition of TiN as a diluent to the green compacts of a powder mixture composed of titanium and carbon black, Eslamloo-Grami and Munir [16] produced the carbonitride of $TiC_{0.5}N_{0.5}$ directly by SHS under nitrogen. The solid-phase additive, TiN, plays an important role in the combustion synthesis of Ti(C,N) to

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suppress the melting of test samples and thus to facilitate the filtration of nitrogen gas into the porous compact. Recently, through a sophisticated manipulation of experimental variables (including the diluent content, initial sample density, and nitrogen pressure), Yeh and Chen [17] successfully obtained stoichiometric titanium carbonitrides with different [C]/([C] + [N]) ratios (including $TiC_{0.3}N_{0.7}$, $TiC_{0.5}N_{0.5}$, and $TiC_{0.7}N_{0.3}$) by self-propagating combustion synthesis.

Due to the lack of a comprehensive database associated with the direct formation of niobium carbonitride Nb(C,N) by SHS, the objective of this experimental study aimed at investigating the combustion characteristics of the powder compacts made up of elemental niobium and carbon black in a nitrogen environment. Effects of initial sample composition and nitrogen pressure on the dynamics of combustion wave, namely, the propagation mode of combustion front, flame-front velocity, and combustion temperature profile were explored in detail. In addition, the degree of conversion was evaluated and the final composition of synthesized products was examined.

2. Experimental

2.1. Test samples

Test samples used in this study were prepared using niobium (Strem Chemicals, −325 mesh, 99.8% purity) and carbon black (Showa Chemical Co., 22 nm) powders, which were dry mixed in a ball mill for 10 h with the molar ratio according to the stoichiometry of the following reaction:

$$\mathrm{Nb} + x\mathrm{C} + \frac{y}{2}\mathrm{N}_2 \rightarrow \mathrm{NbC}_x\mathrm{N}_y \qquad (1)$$

where NbC_xN_y represents the niobium carbonitride. A stoichiometric phase of carbonitride has a composition with the sum of x and y values in NbC_xN_y equal to unity (i.e., $x + y = 1$).

Homogenous powder blends with three different molar compositions of Nb + 0.3C, Nb + 0.5C, and Nb + 0.7C were prepared in this study. The mixed powders were then cold-pressed into cylindrical compacts with a diameter of 7 mm and a height of 12 mm. To retain high permeability and rigidity of the powder compact, the density of green samples was set at 45% theoretical maximum density (TMD) of the powder mixture.

As reported in previous studies on the synthesis of Ti(C,N), the addition of TiN powders in the sample effectively improved the nitrogen content in the final products [16,17]. The influence of nitride addition was explored in this study by adopting the NbN-added sample with a composition of 0.9Nb + 0.3C + 0.1NbN in comparison to the undiluted sample composed of Nb + 0.3C.

2.2. Experimental setup and instrumentation

The SHS reaction of powder compacts was conducted in a stainless-steel windowed combustion chamber under a nitrogen pressure ranging from 0.27 to 1.65 MPa. The nitrogen gas used in this study had a purity of 99.999%. The detailed description of experimental setup and measurement approach was previously given [15]. However, it was found that the ignition of test samples containing niobium and carbon black powders was difficult to achieve by the heated tungsten coil, which was formerly used to initiate the self-sustained combustion of powder compacts made up of niobium only to produce NbN in gaseous nitrogen. Therefore, in order to ensure the successful ignition a compacted pellet (2 mm in height and 7 mm in diameter) of solely niobium powders was placed on the top of the test sample to serve as an ignition enhancer. In addition, a very thin layer of boron nitride (BN) powders was applied on the interface between the test sample and the enhancer pellet to facilitate their separation after combustion. It should be noted that according to the stoichiometry in Eq. (1) the amount of Nb which is in excess with respect to that of carbon is considered as the available niobium to react with nitrogen [16,17]. The degree of conversion to carbonitride was evaluated basing upon the amount of nitrogen uptake calculated from the measurement of weight change of the sample compacts after combustion [16,17].

3. Results and discussion

3.1. Observation of combustion characteristics

Experimental observations of this study indicate that the combustion behavior and the propagation mode of flame front associated with the Nb(C,N) synthesis depend strongly on the content of carbon in the sample compact. Fig. 1(a) presents a sequence of recorded combustion images illustrating the propagation of flame front along a powder compact with the composition of Nb + 0.3C under a nitrogen pressure of 0.62 MPa. As shown in Fig. 1(a), combustion of the test sample attached underneath the ignition enhancer was successfully initiated by the heat released from the nitridation of the pure Nb pellet, which was ignited by a heated tungsten coil. It is evident in Fig. 1(a) that a planar and self-sustained combustion front travels downward from the ignited top plane, and transforms the cold reactant into an incandescent combustion product. Under a steady propagation, the combustion front reaches the bottom of the sample at about $t = 3.17$ s, beyond which at first the luminosity on the burned sample slightly fades, but subsequently from $t = 3.73$ s the luminous glow turns stronger and remains intense for a duration comparable to the flame-propagation period. This implies the occurrence of afterburning combustion, which means the reaction taking place in bulk after the passage of the flame front. The afterburning

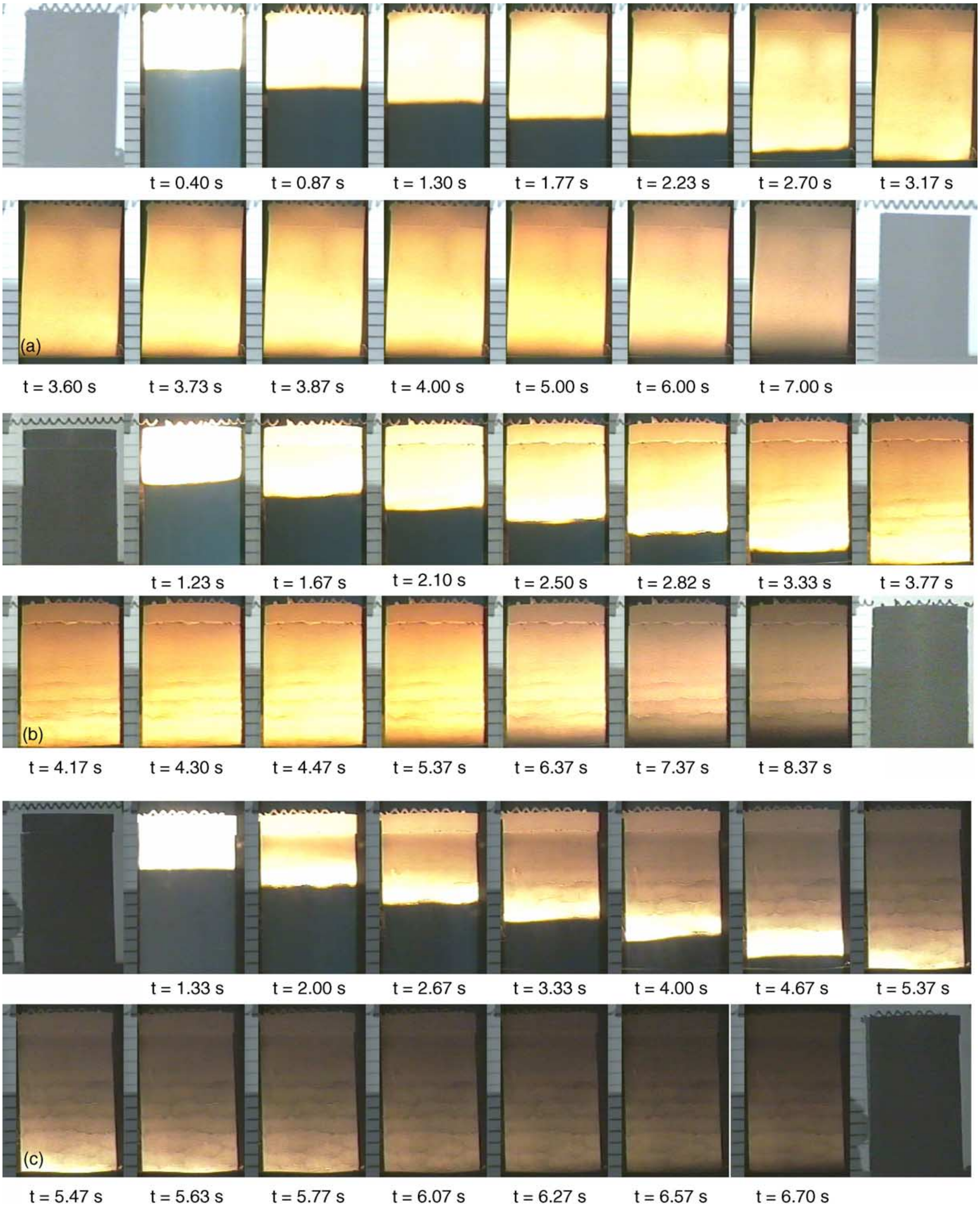

Fig. 1. Recorded burning images illustrating combustion behavior associated with: (a) a sample of Nb + 0.3C in 0.62 MPa N_2, (b) a sample of Nb + 0.5C in 1.65 MPa N_2, and (c) a sample of Nb + 0.7C in 1.31 MPa N_2.

combustion is typical of the combustion synthesis involving gaseous reagents, since conversion in the combustion front is always incomplete [11,15]. As a result, the continuous filtration of nitrogen gas into the porous sample to react with the solid reactant was responsible for the afterburning glow observed in Fig. 1(a).

As the carbon content in the green sample increases to a composition as Nb + 0.5C, the SHS process under nitrogen is presented in Fig. 1(b). Similar to those observed in Fig. 1(a), Fig. 1(b) indicates that upon ignition a distinct flame front forms and propagates along the sample, resulting in a glaring luminosity on the burned sample. Moreover, a

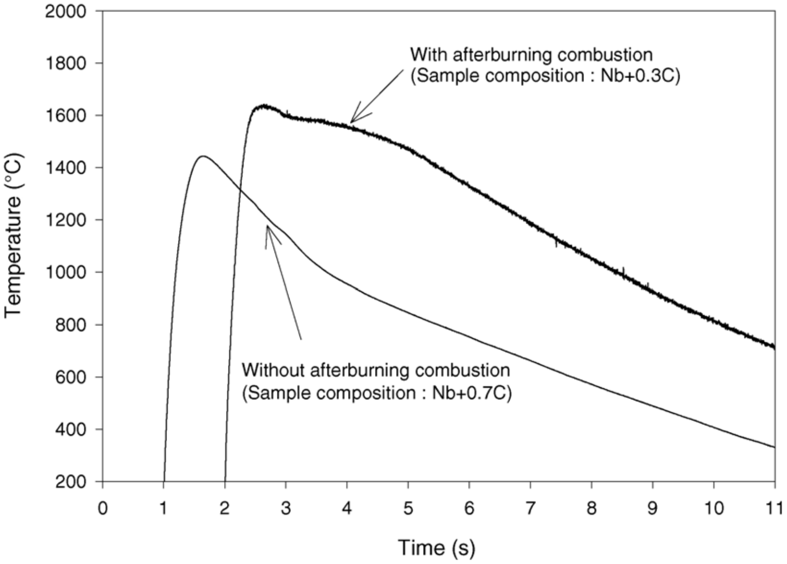

Fig. 2. Typical combustion temperature profiles illustrating SHS processes with and without afterburning combustion.

luminous glow stemming from afterburning reaction evidently emerges, as shown between $t = 4.30$ and 6.37 s, in succession to the arrival of combustion front at the bottom of the sample. Despite these similarities, it is interesting to note that the self-sustained combustion front shown in Fig. 1(b) is found to travel in a pulsating manner from approximately $t = 2.10$ s; namely, the combustion wave becomes oscillatory. This pulsating combustion (also called self-oscillation combustion) was reported to be caused by thermal instability in the combustion front [4,5]. Additionally, the pulsating combustion wave frequently results in end products with a laminated structure [7], which is consistent with the observation that several laminated marks left on the sample surface are clearly visible in Fig. 1(b) after the propagation of oscillatory flame front.

For the sample with the highest carbon content (i.e., the composition of Nb + 0.7C) in this study, the combustion characteristic in nitrogen is shown in Fig. 1(c), in which the oscillatory propagation of flame front and the resulting multilayered structure on the burned sample are similar to those shown in Fig. 1(b). It is believed that the development of the oscillatory combustion wave in the samples of Nb + 0.5C and Nb + 0.7C is a consequence of the increase of the solid-solid reaction (i.e., Nb and C) in the combustion front, which is less exothermic and with a slower reaction rate in comparison to the reaction between Nb and nitrogen. However, an obvious difference between Fig. 1(b) and (c) is that after the passage of the pulsating combustion front, the brightness on the burned sample of Fig. 1(c) vanishes relatively fast and no afterburning luminosity is further noticed. The absence of afterburning combustion in the sample of Fig. 1(c) is most likely caused by the fact that the amount of available niobium in the Nb + 0.7C compact to react with nitrogen is comparatively less than those contained in the samples of Nb + 0.3C and Nb + 0.5C.

3.2. Measurement of combustion temperature

Fig. 2 shows two typical temperature profiles corresponding to the powder compacts with and without afterburning combustion during the entire SHS process, respectively. The abrupt increase of temperature shown in both curves signifies the rapid arrival of the flame front. The temperature curve subjected to the presence of afterburning combustion (i.e., the Nb + 0.3C sample) descends at a very slow rate within a time period of about 2.5 s after reaching the maximum value, indicating the occurrence of prolonged bulk combustion behind the flame front. On the contrary, under the case with the absence of afterburning combustion (i.e., the Nb + 0.7C sample), as expected, a substantial drop in temperature after the passage of the flame front is observed.

Maximum combustion temperatures measured in this study under different test conditions are plotted in Fig. 3, which indicates that the temperature is nearly independent of the nitrogen pressure, but varies with the initial sample composition. In general, the peak combustion temperature decreases with an increase in the carbon content of the sample, implying that the reaction between Nb and nitrogen is more exothermic than that of Nb and carbon. As can be seen in Fig. 3, the combustion temperature reached on the samples of Nb + 0.3C ranges approximately between 1650 and 1800 °C, in comparison to the temperature of about 1250–1450 °C measured in the compacts of Nb + 0.7C. Fig. 3 also reveals that the addition of NbN to the compact results in a significant decrease in combustion temperature, mainly due to the dilution effect during the combustion.

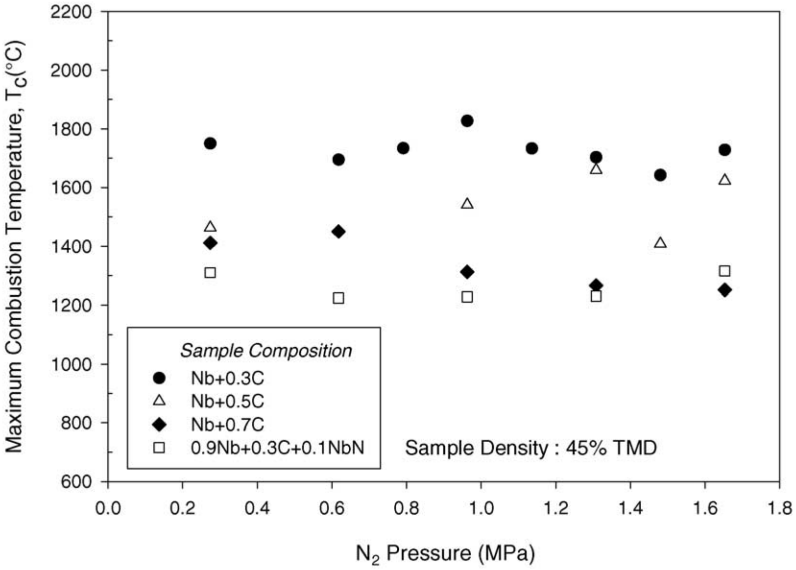

Fig. 3. Effects of nitrogen pressure, carbon content, and NbN addition on maximum combustion temperature in synthesis of Nb(C,N) by SHS.

3.3. Measurement of flame-front trajectory and propagation velocity

Two flame-front trajectories, which were deduced from the recorded images, respectively representing the steady and oscillatory modes of propagation are depicted in Fig. 4. The trajectory associated with the sample of Nb + 0.3C is quite straight, except for the very early region where the heat input from the igniter enhancer favorably affects the flame speed. The straight trajectory signifies the steady propagation of self-sustained flame front at a constant velocity. On the other hand, the flame-front trajectory belonging to the sample of Nb + 0.7C exhibits a progressing motion periodically interrupted by a stationary moment. This cyclic pattern of motion indicates the oscillatory propagation of the flame front. It should be noted that for the combustion front traveling in an oscillatory manner, the average flame-front velocity was calculated and reported in this study.

The dependence of average flame-front propagation velocity (V_f) on the nitrogen pressure, carbon content, and NbN addition is shown in Fig. 5. For the compacts with a composition of Nb + 0.3C, Fig. 5 indicates that the flame-front velocity increases with increasing nitrogen pressure, implying the dominancy of the reaction between Nb and nitrogen in the combustion front. However, the influence of nitrogen pressure appears to be less pronounced on the compact of Nb + 0.5C, for which the flame velocity increases only slightly with nitrogen pressure. Further

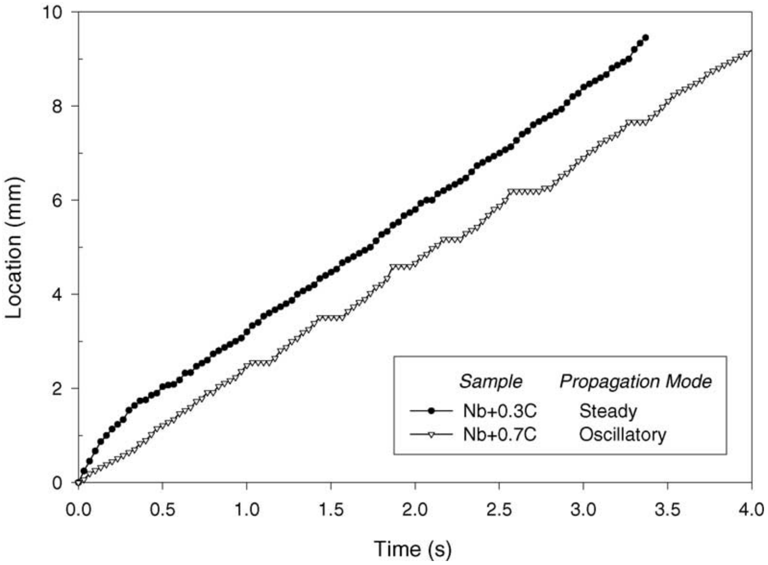

Fig. 4. Flame-front trajectories associated with steady and oscillatory modes of flame propagation.

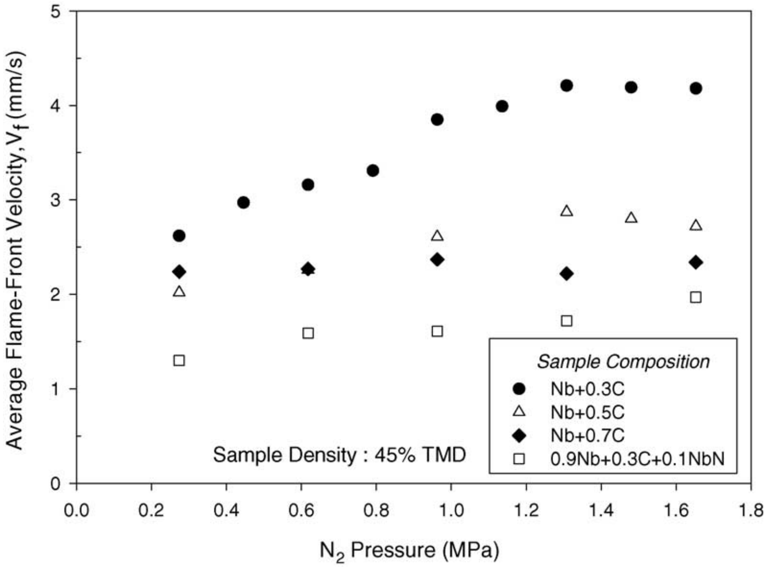

Fig. 5. Effects of nitrogen pressure, carbon content, and NbN addition on average flame-front propagation velocity in synthesis of Nb(C,N) by SHS.

increase in the carbon content, as for the sample of Nb + 0.7C, the flame-front velocity is essentially not affected by the variation of nitrogen pressure. This suggests that the reaction of Nb and carbon is dominant in the combustion front of the Nb + 0.7C sample. In addition, the flame-front velocity is found to decrease as the carbon content increases on account of the increase of Nb and carbon reaction, which lowers the combustion temperature and results in an oscillatory motion of the flame front. Fig. 5 also indicates that in agreement with the influence on combustion temperature, the addition of NbN powders to the green sample leads to a significant decrease in the flame-front velocity.

3.4. Composition analysis of final products

The nitridation percentage of powder compacts is shown in Fig. 6 as a function of the sample composition and nitrogen pressure. First of all, it was found that for all of the samples the amount of nitrogen uptake was insufficient to yield the stoichiometric niobium carbonitride NbC_xN_y (with $x + y = 1$). For the samples of Nb + 0.3C under nitrogen pressures above 0.45 MPa, the degree of nitridation is almost independent of the nitrogen pressure and reaches as high as about 80%. No influence of nitrogen pressure on the degree of conversion is attributed to the presence of afterburning combustion, in which the nitridation continues after the

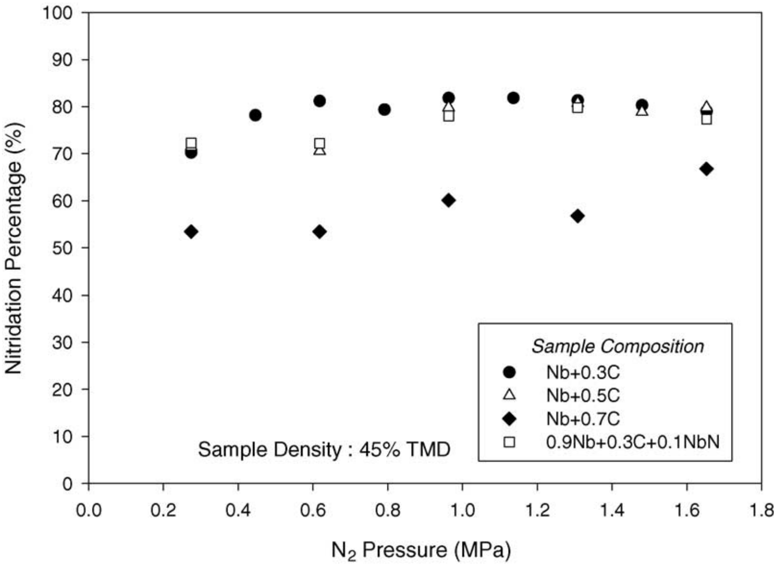

Fig. 6. Effects of nitrogen pressure, carbon content, and NbN addition on degree of conversion in synthesis of Nb(C,N) by SHS.

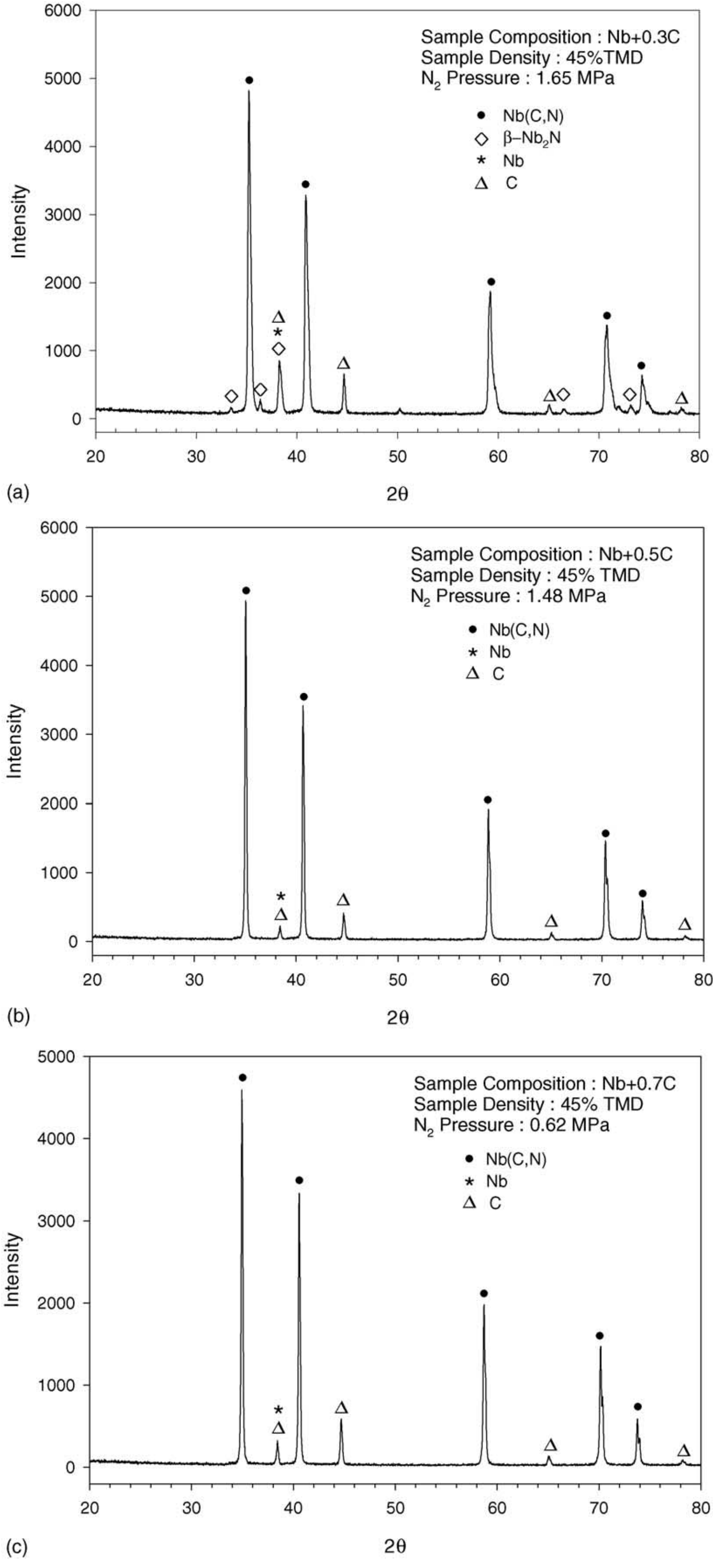

Fig. 7. XRD spectra of combustion products obtained from: (a) a sample of Nb + 0.3C in 1.65 MPa N_2, (b) a sample of Nb + 0.5C in 1.48 MPa N_2, and (c) a sample of Nb + 0.7C in 0.62 MPa N_2.

passage of the flame front. As shown in Fig. 6, the nitridation percentage achieved in the sample of Nb + 0.5C is comparable to that of the Nb + 0.3C samples in nitrogen of 0.96 MPa and above. However, due to the lack of afterburning reaction in the sample of Nb + 0.7C, the degree of nitridation was considerably decreased and ranged from 53 to 67% with increasing nitrogen pressure. On account of the lower combustion temperature, Fig. 6 shows that the addition of NbN to the green sample produces no improvement on the degree of conversion. Furthermore, since there is no melting of powder compacts observed in the synthesis of Nb(C,N), the role played by the TiN additive in the Ti(C,N) synthesis to suppress the melting and thereby to enhance the nitrogen uptake is inapplicable to the NbN adopted in the Nb(C,N) synthesis.

The XRD spectra of combustion products obtained from the samples with different initial compositions are presented in Fig. 7(a)–(c). As shown in Fig. 7(a), the final product synthesized from an Nb + 0.3C sample consists of a carbonitride of Nb(C,N), a nitride phase of β-Nb_2N, as well as some elemental Nb and C. It is obvious that the niobium carbonitride Nb(C,N) is the dominant phase in the final composition. The formation of β-Nb_2N arises from insufficient nitrogen especially in the central portion of the sample [15]. The presence of elemental Nb and C indicates that not only the nitridation of available niobium, but also the reaction between niobium and carbon are incomplete. For the samples of Nb + 0.5C and Nb + 0.7C, as shown in Fig. 7(b) and (c), the XRD analysis identifies the formation of Nb(C,N) as the dominant phase, together with small amounts of Nb and carbon. In contrast to the spectrum in Fig. 7(a), no existence of β-Nb_2N is detected in Fig. 7(b) and (c), probably because the amount of available niobium to react with nitrogen is comparatively less in the samples of Nb + 0.5C and Nb + 0.7C when compared with that in the Nb + 0.3C sample.

4. Summary and conclusions

This study represents a comprehensive investigation on the preparation of niobium carbonitride by combustion synthesis of Nb–C powder compacts in gaseous nitrogen. The carbon content in the green sample produces a significant effect on the combustion behavior as well as on the degree of completeness of the reaction.

Generally, the combustion process to produce niobium carbonitride is characterized by the self-sustained combustion wave propagating along the sample and prolonged afterburning combustion taking place in bulk after the passage of the flame front. The propagation mode of the flame front on the sample of Nb + 0.3C is shown to be steady and the propagation velocity is increased by increasing the nitrogen pressure, implying that the reaction between Nb and nitrogen dominates in the combustion front. In addition, the reaction continues lengthily in the afterburning stage. As a result, the degree of nitridation is nearly independent of the nitrogen pressure and the nitridation percentage as high as about 80% is achieved in the sample of Nb + 0.3C. However, no enhancement in the nitridation percentage was observed for the sample with the NbN additive, because of a considerable decrease in the combustion temperature.

Due to the increase of Nb and carbon reaction in the combustion front, for the samples of Nb + 0.5C and Nb + 0.7C the self-sustained combustion wave was found to travel in an oscillatory manner, yielding the burned samples with a laminated structure. After the passage of the pulsating flame front, the afterburning combustion is clearly observed in the sample of Nb + 0.5C, but is not present in the Nb + 0.7C compact. Moreover, the influence of nitrogen pressure on the flame-front velocity is gradually diminished as the carbon content in the green sample increases. It was found that the flame-front velocity of the Nb + 0.7C samples is essentially independent of the nitrogen pressure, with an implication that the reaction between Nb and carbon dominates in the combustion front. Under the presence of afterburning combustion, the nitridation percentage of the Nb + 0.5C sample reaches about 80% at nitrogen pressures of 0.96 MPa and higher. On the other hand, due to the lack of afterburning reaction, the degree of nitridation is noticeably decreased to between 53 and 67% in the samples of Nb + 0.7C.

For all samples tested in this study, the carbonitride phase Nb(C,N) was identified as the dominant composition in the final products. Small amounts of Nb and carbon left unreacted were also detected by the XRD analysis. An intermediate nitride phase of β-Nb_2N was found only in the products obtained from the sample of Nb + 0.3C.

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