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Combustion synthesis of vanadium carbonitride from V-C powder compacts under nitrogen pressure

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Abstract

An experimental investigation on the preparation of vanadium carbonitrides by self-propagating high-temperature synthesis (SHS) was conducted using compacted samples of the vanadium and carbon powder mixture ignited in gaseous nitrogen. Effects of the initial sample stoichiometry, nitrogen pressure, and dilution by vanadium nitride (VN) on the combustion characteristics and the degree of conversion were studied. Experimental observation shows that upon initiation the combustion process is characterized by the steady propagation of a self-sustained reaction front. The flame-front propagation velocity was found to decrease with an increase in the carbon content of the compact, due to the decrease of combustion temperature with increasing carbon content. For the reactants composed of V + 0.3C and V + 0.5C, after the passage of the flame front the nitridation continued lengthily in an afterburning stage. Because of a less amount of available vanadium to react with nitrogen, the compact of V + 0.5C achieved a higher degree of nitridation than did the V + 0.3C sample. However, the nitridation percentage of the V + 0.7C sample was lower than that of the V + 0.5C sample, mainly due to the absence of afterburning reaction in the V + 0.7C powder compact. Moreover, it was found that diluting the V + 0.3C sample by a small amount of VN as the sample of 0.9V + 0.3C + 0.1 VN effectively enhanced the degree of nitridation, but a further increase in the diluent concentration provided no additional improvement. The XRD analysis indicates the formation of single-phase carbonitrides V(C,N) slightly rich with vanadium from the reactant compacts of V + 0.5C, V + 0.7C, and 0.9V + 0.3C + 0.1VN. For the sample of V + 0.3C, due to the low degree of nitridation there exists an intermediate nitride phase of V_2N in addition to the dominant phase of V(C,N).

Keywords: Vanadium carbonitride; SHS; Carbon content; Afterburning combustion; Dilution

1. Introduction

Transition-metal carbides and nitrides, commonly referred to as refractory compounds, possess a unique combination of chemical and physical properties [1–3] which make them attractive from both fundamental and technological aspects. In general, they are extremely hard, have high melting points, have good electrical and thermal conductivity, have good corrosion resistance, and some of them have gained interest as potential catalysts [1–3]. Additionally, many of transition-metal carbides and nitrides are capable of forming unlimited solid solution (known as the carbonitride) with each other [4]. The physical and chemical properties of such solid solutions were demonstrated to be dependent on their composition; for example, as a function of the [C]/([C] + [N]) ratio of carbonitrides [4–6].

Khyzhun and Kolyagin [4] indicated that substitution of carbon atoms for nitrogen atoms in the cubic and rhombohedral tantalum carbonitrides, Ta(C,N), led to the increase of metallic and ionic components and the decrease of the covalent component in the chemical bonding. The microhardness of titanium carbonitride, Ti(C,N), was found to increase monotonously with increasing [C]/([C] + [N]) ratio under a load of 0.98 N, but the electrical and thermal conductivity generally increased with nitrogen content [5]. Due to the fact that the hardness of vanadium nitride (VN) is well below that of vanadium carbide, Chicco et al. [6] showed a gradual decrease in the hardness of a vanadium carbonitride coating with the decrease of the carbon content away from the surface towards the interface with the substrate.

However, it is known that conventional methods of the powder metallurgy do not allow producing some of the

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continuous single-phase carbonitrides from their carbides and nitrides [4]. As a promising alternative to the conventional methods, combustion synthesis or self-propagating high-temperature synthesis (SHS) has been employed to produce a variety of advanced materials, including borides, carbides, nitrides, hydrides, silicides, carbonitrides, intermetallics, etc. [7–10]. Even though the preparation of carbides [10–12] and nitrides [13–18] of many transition metals (especially in groups of IVB and VB) by SHS has been extensively investigated, research on direct formation of the carbonitrides of transition metals through combustion synthesis is comparatively lacking and has focused largely on the synthesis of titanium carbonitrides [19,20]. In addition to the Ti(C,N), Yeh and coworkers [20–22] recently conducted a series of experimental studies on the formation of Nb(C,N) and Ta(C,N) by SHS using compacted samples from the powder mixture of metal and carbon black under nitrogen pressure.

As an extension of previous studies [20–22], the present investigation performing the combustion synthesis of vanadium carbonitride, V(C,N), was motivated with the aim of achieving a comprehensive understanding on this category of materials produced by SHS. Effects of the initial composition of reactant compacts, nitrogen pressure, and dilution by vanadium nitride on the combustion characteristics as well as the product conversion were studied. In addition, flame-front propagation velocity and combustion temperature were measured as a function of experimental variables. After combustion, synthesized products were recovered and examined by the XRD analysis to identify their final composition.

2. Experimental procedure

Test samples used in this study were prepared by vanadium (Aldrich Chemicals, −325 mesh, 99.5% 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:

$$V + xC + \frac{y}{2}N_2 \rightarrow VC_xN_y \quad (1)$$

where VC_xN_y represents the vanadium carbonitride. A stoichiometric phase of carbonitride has a composition with the sum of x and y values in VC_xN_y equal to unity (i.e., $x + y = 1$). Homogenous powder blends containing different amounts of carbon, including the x values equal to 0.3, 0.4, 0.5, 0.6, and 0.7 in Eq. (1), 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% of theoretical maximum density (TMD) of the powder mixture.

To explore the influence of dilution by an inert reactant on the completeness of phase conversion, vanadium nitride powders were selected as the diluent in the case of synthesizing $VC_{0.3}N_{0.7}$. Owing to the inert nature of VN in the formation of V(C,N) by SHS, it was anticipated to improve the overall nitrogen uptake of the V + 0.3C compact which requires the largest amount of nitrogen to achieve the complete conversion among all test samples. Therefore, the VN-diluted samples with two compositions of 0.9V + 0.3C + 0.1VN and 0.8V + 0.3C + 0.2VN were employed in this study.

The SHS reaction of powder compacts was conducted in a stainless-steel windowed combustion chamber under a nitrogen pressure ranging from 0.45 to 1.82 MPa. The nitrogen gas used in this study had a purity of 99.999%. The detailed description of experimental setup and measurement approach was given previously [16–18]. It should be noted that according to the stoichiometry in Eq. (1) the amount of vanadium, which is in excess with respect to that of carbon, is considered as the available vanadium to react with nitrogen [19–22]. The degree of nitridation was evaluated on the basis of the amount of nitrogen uptake, which was calculated from the measurement of weight change of the sample compact after combustion [19–22]. The final composition of burned products was identified by an X-ray diffractometer (Shimadzu XRD-6000) with Cu Kα radiation operating at 40 kV. The scanning rate and sampling pitch set on the XRD analyzer were 4.0° $\min^{-1}$ and 0.02°, respectively.

3. Results and discussion

3.1. Observation of combustion characteristics

Two types of combustion processes observed in this study corresponding to the reactant compacts with different starting compositions are illustrated in Fig. 1(a), Fig. 1(b), respectively. As shown in Fig. 1(a), reaction between the powder mixture of V + 0.5C and gaseous nitrogen of 0.96 MPa is self-sustaining after ignition. It is evident that the flame front travels steadily and reaches the bottom of the sample at about $t = 2.47$ s, behind which the luminosity on the burned sample remains intense for a duration comparable to the flame-propagating period. This observation suggests that after the passage of the flame front phase conversion continues lengthily in bulk; namely, the occurrence of afterburning combustion which is typical of the combustion synthesis involving gaseous reagents. It was believed that nitridation in the combustion front was always incomplete, due to both insufficient reaction time caused by the rapid propagation of combustion wave and inadequate nitrogen in the reaction front. As a result, continuous infiltration of nitrogen gas into the porous compact to react with the solid reactant led to the appearance of afterburning glow on the burned sample. It should be noted that as is the case shown in Fig. 1(a), pronounced afterburning combustion is also observed on the samples with initial compositions of V + 0.3C and V + 0.4C.

For the reactant with a starting stoichiometry of V + 0.7C, a sequence of combustion images is presented in Fig. 1(b), where a self-sustained combustion wave traveling along the sample is clearly seen. However, in contrast to those observed in Fig. 1(a), Fig. 1(b) shows that after the combustion wave has traversed the entire sample the brightness on the burned sample fades away rapidly and no afterburning glow is noticed. The absence of

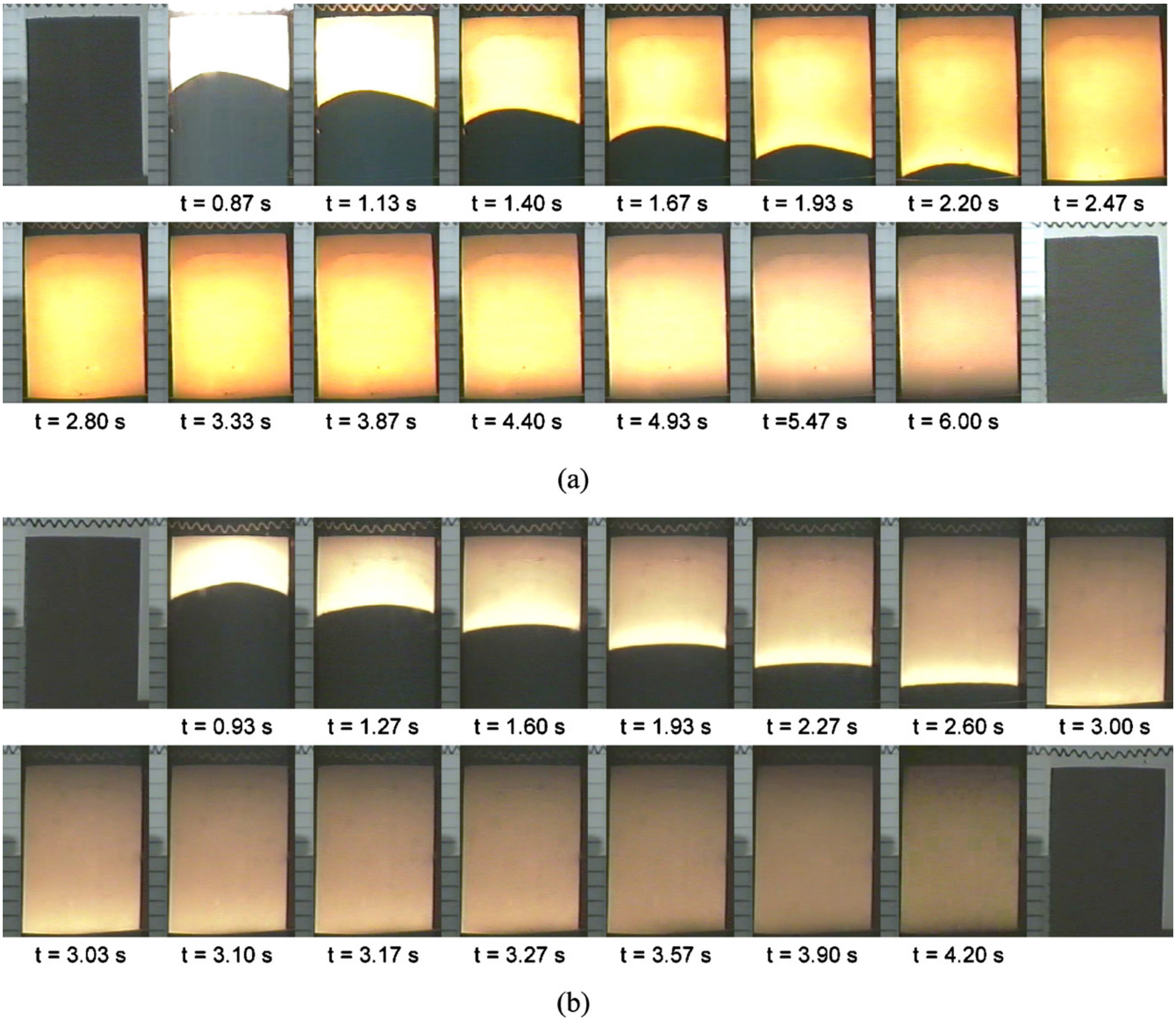

Fig. 1. Recorded burning images illustrating combustion behavior of 45% TMD powder compacts with different compositions of (a) $V + 0.5C$ and (b) $V + 0.7C$ in 0.96 MPa N_2.

afterburning combustion in the sample of $V + 0.7C$ is most likely caused by the fact that the amount of available vanadium in the $V + 0.7C$ compact to react with nitrogen is comparatively less than those contained in the reactant compacts of $V + 0.3C$, $V + 0.4C$, and $V + 0.5C$. The dependency of the occurrence of afterburning reaction on the starting stoichiometry of V-C powder compacts is consistent with those reported in the combustion synthesis of Nb(C,N) and Ta(C,N) [21,22].

3.2. Measurement of combustion temperature

Fig. 2 shows three temperature profiles corresponding to the samples with three different initial compositions of $V + 0.3C$, $V + 0.5C$, and $V + 0.7C$, respectively. The abrupt rise of temperature in all three curves signifies the rapid arrival of the flame front. As shown in Fig. 2, after the passage of combustion front the temperature measured on the $V + 0.7C$ sample

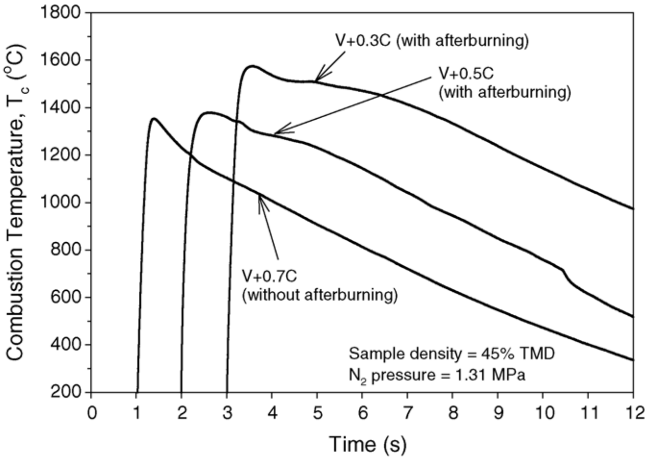

Fig. 2. Typical temperature profiles showing SHS processes with and without afterburning combustion as a function of initial composition of sample compacts.

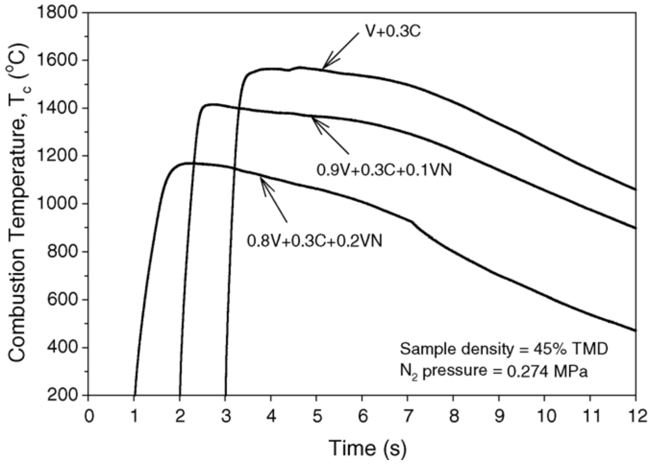

Fig. 3. Effect of diluent (VN) content on combustion temperature of powder compacts in 0.274 MPa N_2.

decreases almost linearly with time, primarily due to the lack of afterburning reaction in this sample. In contrast, because of the presence of afterburning combustion the temperature profiles associated with the reactant compacts of V + 0.3C and V + 0.5C decline slowly after the maximum value and then reach an approximately flat plateau region before going to a downward slope.

In addition to the time variation of temperature, Fig. 2 also indicates that the reaction temperature decreases with an increase in the carbon content of the sample. This might imply that the reaction between vanadium and nitrogen is more exothermic than that of vanadium and carbon. This postulation is further substantiated by the fact that the reaction temperature (~1780 °C) of a 50% TMD compact made up of solely vanadium powders burning in gaseous nitrogen of 1.14 MPa [17] is about 200–400 °C higher than the combustion front temperatures shown in Fig. 2.

Due to the dilution effect, Fig. 3 reveals that the addition of vanadium nitride in the green compact leads to a significant decrease in the reaction temperature. Moreover, it is obvious that three temperature profiles shown in Fig. 3 are all characterized by a pronounced plateau region at the elevated temperature close to that of combustion front, indicating the occurrence of prolonged afterburning combustion on account of the large amounts of available vanadium contained in all three samples.

3.3. Measurement of flame-front propagation velocity

The dependence of flame-front propagation velocity (V_f) on the nitrogen pressure as well as on the starting composition of reactant compacts is presented in Fig. 4. Firstly, it was found the increase of flame-front velocity with increasing nitrogen pressure for all three types of samples, since the concentration of nitrogen both in the reaction front and within the porous compact was increased. Secondly, Fig. 4 indicates that the flame-front velocity decreases as the carbon content of the compact increases. This is attributed to the fact that the higher content of carbon in the sample, the lower the combustion temperature. Furthermore, in agreement with the decrease of reaction temperature, the addition of diluent VN reduces the flame-front velocity, as shown in Fig. 5.

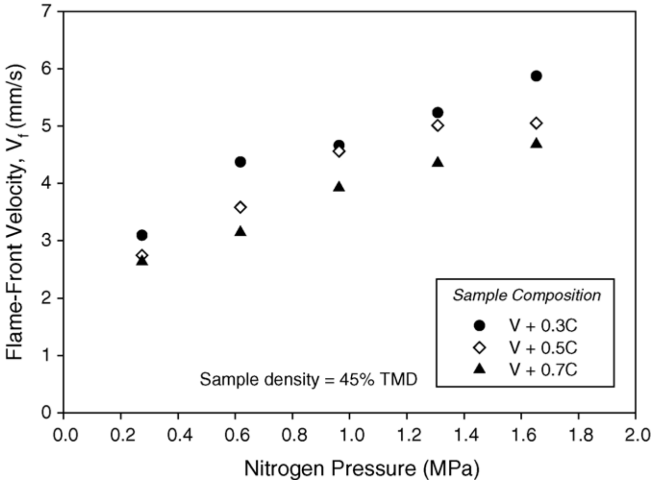

Fig. 4. Effects of nitrogen pressure and initial sample composition on flame-front propagation velocity in synthesis of V(C,N) by SHS.

3.4. Composition analysis of final products

The nitridation percentage of powder compacts is presented in Fig. 6 as a function of the initial sample composition and nitrogen pressure. First of all, it is evident that for all of the samples the amount of nitrogen uptake was insufficient to yield the stoichiometric vanadium carbonitride VC_xN_y (with $x + y = 1$). Moreover, the degree of nitridation increases only slightly with increasing nitrogen pressure. For the samples of V + 0.3C and V + 0.5C, the modest contribution to the nitridation percentage with increasing nitrogen pressure

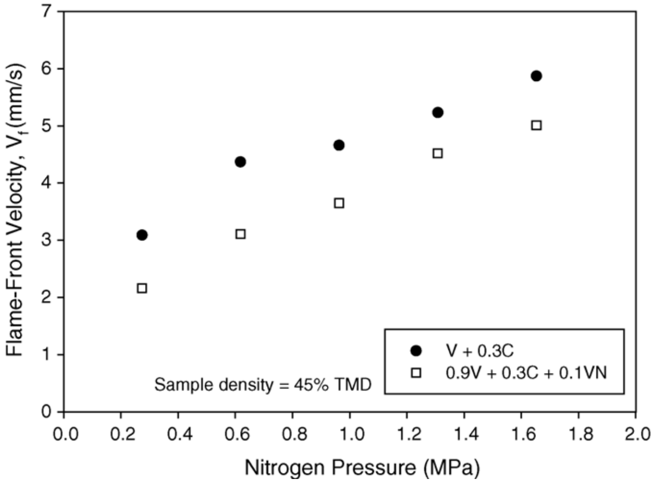

Fig. 5. Effect of dilution by VN on flame-front propagation velocity in synthesis of V(C,N) by SHS.

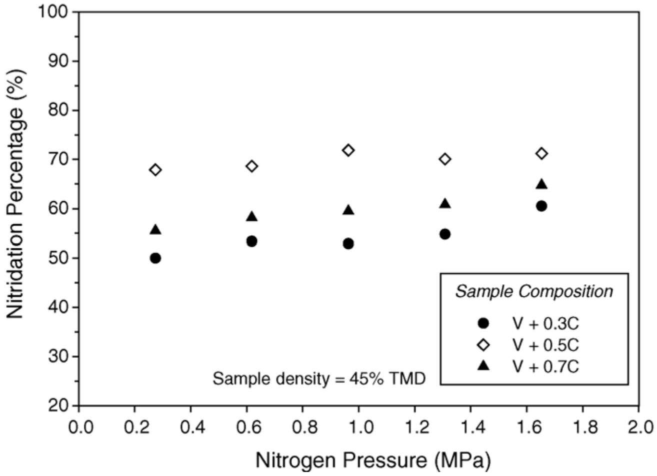

Fig. 6. Effects of nitrogen pressure and initial sample composition on degree of nitridation in synthesis of V(C,N) by SHS.

could be a consequence of the presence of afterburning reaction, during which additional nitrogen uptake took place. However, for the case without afterburning combustion as the V + 0.7C compact, this is probably because the interaction between vanadium and carbon is dominant in the combustion front.

Secondly, Fig. 6 shows that under a constant pressure of nitrogen the reactant compact with a starting stoichiometry of V + 0.5C achieves the highest nitridation percentage, followed by the compact of V + 0.7C and then that of V + 0.3C. As mentioned above, both of the V + 0.3C and V + 0.5C compacts carried on further nitridation in an afterburning stage. The finding that the V + 0.5C compact arrives at a higher degree of nitridation than does the V + 0.3C sample is mainly caused by the fact that the V + 0.5C sample possesses a less amount of available vanadium. On the other hand, the lack of afterburning reaction in the powder compact of V + 0.7C resulted in a lower nitridation percentage when compared to that of the V + 0.5C sample.

Variation of nitridation percentage with the starting stoichiometry of powder compacts at 1.31 MPa of nitrogen gas is shown in Fig. 7. As the molar ratio of carbon to vanadium (the x value in $V + xC$) in the green compact increases from 0.3 to 0.5, Fig. 7 indicates that the extent of nitridation increases from 55 to 70% on account of a decrease in the amount of available vanadium to react with nitrogen. When the carbon content was augmented to $x = 0.6$ and 0.7, the reaction between vanadium and carbon became dominant in the combustion front, thus causing the decrease of reaction temperature and the diminution of afterburning reaction. Accordingly, Fig. 7 reveals a maximum nitridation percentage of about 70% at $x = 0.5$ and a decrease in nitridation percentages to 67.6 and 60.8% in the cases of $x = 0.6$ and 0.7, respectively.

A substantial increase in the degree of nitridation by diluting the samples with VN is observed in Fig. 8. As indicated in Fig. 8, the VN-diluted compacts of 0.9V + 0.3C + 0.1VN achieve a nearly constant nitridation percentage as high as about 75%, while the nitridation percentages of undiluted compacts are in the range from 50 to 60%. The increase of nitridation percentage by the addition of VN is attributed to the fact that VN as a diluent is inert and thus consumes no nitrogen during the reaction. However, it was found that the increase of diluent content from the composition of 0.9V + 0.3C + 0.1VN to that of 0.8V + 0.3C + 0.2VN provided no further improvement in the extent of nitridation, because reaction temperature was considerably decreased by increasing the diluent concentration.

XRD patterns of the combustion products synthesized from the samples of V + 0.3C and 0.9V + 0.3C + 0.1VN under a nitrogen pressure of 1.31 MPa are illustrated in Fig. 9(a) and (b), respectively. Due to the poor nitridation percentage of about 55% for the V + 0.3C compact, Fig. 9(a) indicates the formation of a nitride phase V_2N in addition to the carbonitride phase V(C,N), implying that the uptake of nitrogen is not totally corresponding to the production of V(C,N). On the other hand, Fig. 9(b) shows the production of

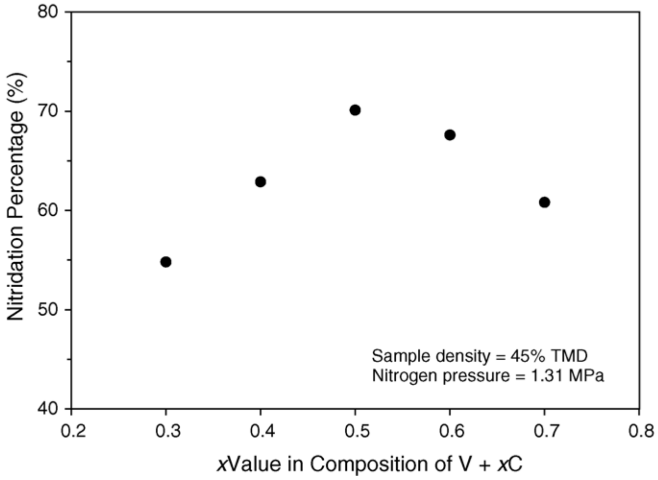

Fig. 7. Variation of nitridation percentage with carbon content of powder compacts in 1.31 MPa N_2.

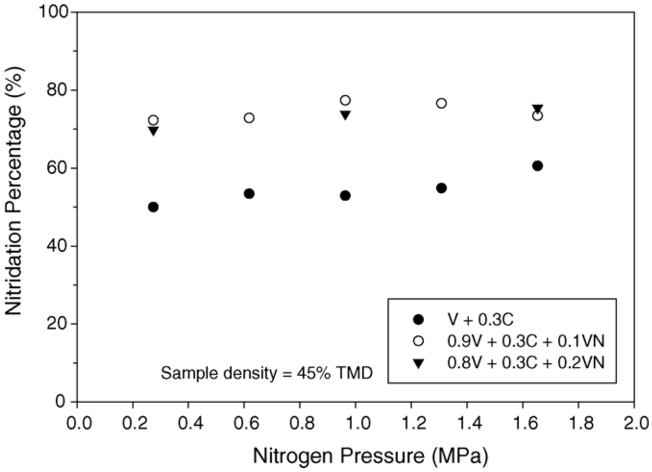

Fig. 8. Effect of dilution by VN on degree of nitridation in synthesis of V(C,N) by SHS.

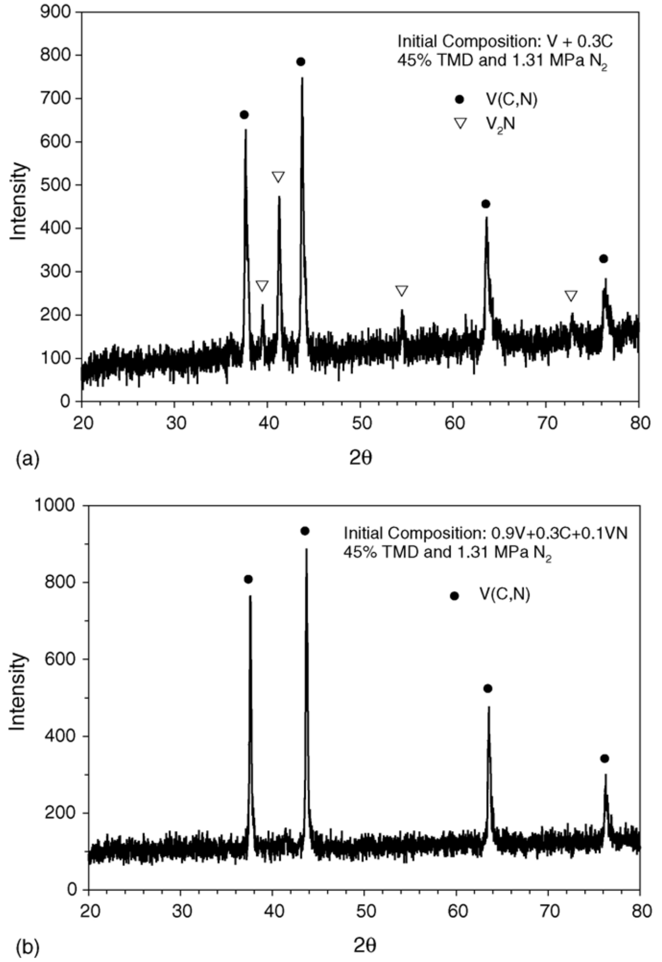

Fig. 9. XRD patterns of combustion products obtained from 45% TMD powder compacts with different initial compositions of (a) V + 0.3C and (b) 0.9 V + 0.3C + 0.1 VN in 1.31 MPa N_2.

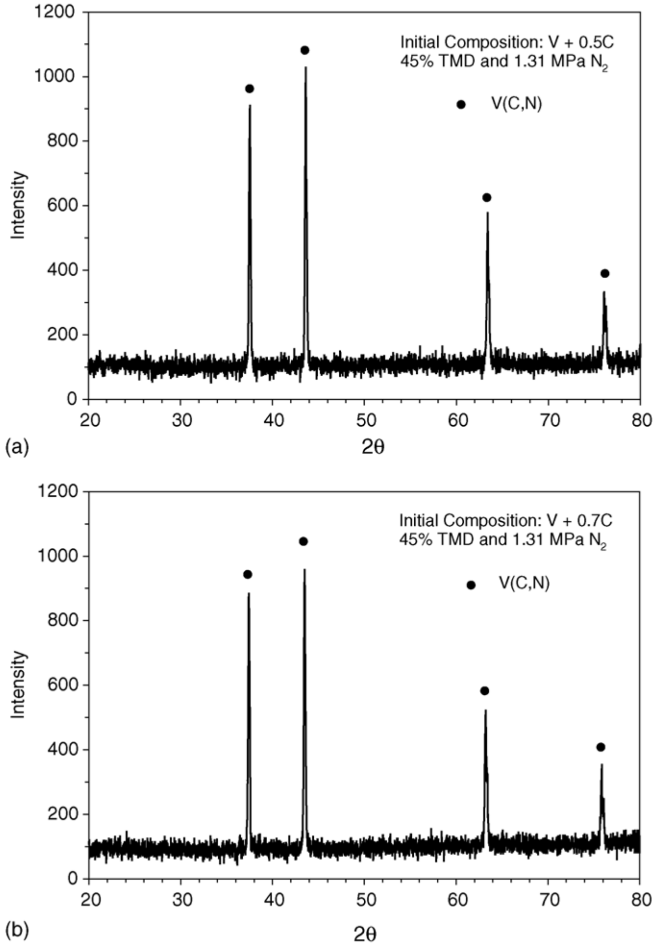

Fig. 10. XRD patterns of combustion products obtained from 45% TMD powder compacts with different initial compositions of (a) V + 0.5C and (b) V + 0.7C in 1.31 MPa N_2.

V(C,N) with almost no traces of V_2N and other intermediate species from a VN-diluted sample of 0.9V + 0.3C + 0.1VN, which has a nitridation percentage of 76.6%. Therefore, it is suggested that the XRD pattern shown in Fig. 9(b) signifies a single-phase solid solution with a composition of $VC_{0.3}N_{0.56}$, which is considered as a homogeneous vanadium carbonitride slightly rich with vanadium. Similar to that observed in Fig. 9(b), XRD patterns of the burned products synthesized from the reactant compacts of V + 0.5C and V + 0.7C demonstrate the formation of single-phase carbonitrides, as shown in Fig. 10(a) and (b). Moreover, on the basis of the calculated nitridation percentages the XRD patterns depicted in Fig. 10(a) and (b) should represent vanadium-rich carbonitrides of $VC_{0.5}N_{0.35}$ and $VC_{0.7}N_{0.18}$, respectively. Based upon the above observations, it is suggested that for vanadium in this study the completeness of carbonization appears to be better than that of nitridation. Moreover, the formation of single-phase solid solution V(C,N) was strongly dependent on the nitrogen content of the nitride phase. The intermediate nitride phase V_2N was shown to be insoluble with the carbide phase, due to the low nitrogen content.

4. Summary and conclusions

This study represents a comprehensive investigation on the preparation of vanadium carbonitride by combustion synthesis of V-C powder compacts in gaseous nitrogen. Experimental parameters, such as the initial sample stoichiometry, nitrogen pressure, and dilution by VN, were found to affect the combustion characteristics as well as the degree of completeness of the reaction.

Experimental observations indicate that the combustion process of V-C powder compacts under nitrogen pressures is characterized by a self-sustained combustion front traversing the entire sample. For the reactant compacts of V + 0.3C and V + 0.5C, after the passage of the flame front the nitridation continued in an afterburning stage. However, no afterburning reaction was observed for the V + 0.7C sample, due to a less amount of available vanadium to react with nitrogen in this composition. The combustion temperature was decreased by increasing the carbon content of the powder compact, implying that the reaction between vanadium and nitrogen is more exothermic than that of vanadium and carbon As a result, the flame-front propagation velocity decreased correspondingly with increasing carbon content of the sample.

The degree of nitridation increases with the molar ratio of carbon to vanadium in the reactant compact and reaches a maximum at the composition of V + 0.5C. Further increase of the carbon content, such as the compositions of V + 0.6C and V + 0.7C, decreases the nitridation percentage, due primarily to the lack of afterburning reaction. In this study, the samples of V + 0.3C attained the lowest nitridation percentage of about 55%. However, it was found that the addition of a proper amount of vanadium nitride as a diluent in the green compact of V + 0.3C effectively enhanced the degree of nitridation, because of the inert nature of the diluent VN that consumed no nitrogen during the reaction. Results showed that an increase of about 20% in nitridation was achieved by the reactant compact of 0.9V + 0.3C + 0.1VN, as compared to the undiluted sample.

For the samples of V + 0.5C, V + 0.7C, and 0.9V + 0.3C + 0.1VN, the XRD analysis identifies the formation of single-phase vanadium carbonitrides V(C,N) that are homogeneous solid solutions slightly rich with vanadium. However, the burned product obtained from the V + 0.3C sample contains not only the carbonitride V(C,N) as the dominant phase, but also the nitride V_2N as an intermediate phase on account of the low degree of nitridation.

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