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Preparation of tantalum carbonitride by self-propagating high-temperature synthesis of Ta-C system in nitrogen

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Abstract

An experimental investigation on the preparation of tantalum carbonitrides by self-propagating high-temperature synthesis (SHS) was conducted using compacted samples of tantalum and carbon powders ignited in gaseous nitrogen. Effects of the carbon content and nitrogen pressure on the combustion characteristics and the degree of nitridation were studied. Experimental observation shows that the SHS process is characterized by the steady propagation of a self-sustained combustion front. The flame-front propagation velocity was found to increase with an increase in the carbon content of the compact. For the samples of Ta + 0.3C and Ta + 0.5C, after the passage of the combustion front the reaction continues lengthily in an afterburning stage, leading to a moderate increase in the nitridation percentage with nitrogen pressure and a comparable degree of nitridation for these two types of samples. However, due to the lack of afterburning combustion, the degree of nitridation of the Ta + 0.7C sample was greatly affected by the pressure of nitrogen. The XRD analysis of final products indicates that in addition to the dominant phase of Ta(C,N), there exists a small amount of Ta left unreacted.

Keywords: Tantalum carbonitride; SHS; Carbon content; Afterburning combustion

1. Introduction

Carbides and nitrides of transition metals of groups IVB and VB are of great interest in both fundamental investigations and practical applications, mainly because these compounds possess a unique combination of chemical and physical properties [1,2]. They have high melting points, high hardness, good thermal and chemical stability, good corrosion resistance, and low electric resistance [1,2]. In addition, many of carbides and nitrides of transition metals are capable of forming unlimited solid solution (known as the carbonitride) with each other [3]. Physical and chemical properties of such solid solutions depend greatly on their composition; for example, as a function of the [C]/([C] + [N]) ratio of carbonitrides [3–6]. Khyzhun and Kolyagin [3] 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 heat conductivities generally increased with nitrogen content [4]. Zheng et al. [6] recently pointed out that the increase of carbon content in Ti(C,N)-based cermets reduced the dissolution of tungsten, titanium and molybdenum in the binder phase.

However, it is known that conventional methods of the powder metallurgy do not allow synthesizing a continuous cubic single-phase TaC–TaN solid solution using the hexagonal form of TaN and the cubic TaC [3]. 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 carbides, nitrides, borides, hydrides, silicides, carbonitrides, intermetallics, etc [7–10]. Among these compounds, so far the preparation of carbonitrides of transition metals by SHS has not been

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broadly reported in the literature. Relevant studies were focused largely on the synthesis of titanium carbonitrides [11,12]. There has been a lack of comprehensive study on the production of tantalum carbonitrides by SHS, even though the combustion synthesis of TaC [13,14] and TaN [15,16] was investigated to a great extent.

The objective of this study was to experimentally investigate the direct formation of tantalum carbonitride by SHS in gaseous nitrogen using the sample compact prepared by the mixture of elemental tantalum and carbon black powders. Combustion characteristics, such as the propagation mode of combustion wave, afterburning phenomenon, and reaction temperature profile, were studied to establish a fundamental understanding of the subject in question. Effects of initial sample composition and nitrogen pressure were explored on the flame-front propagation velocity, combustion temperature, and the degree of conversion. In addition, the final composition of synthesized products was identified by the XRD analysis.

2. Experimental procedure

Test samples used in this study were prepared by tantalum (Aldrich Chemical, −325 mesh, 99.9% 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:

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

where $\mathrm{TaC}_x\mathrm{N}_y$ represents the tantalum carbonitride. A stoichiometric phase of carbonitride has a composition with the sum of x and y values in $\mathrm{TaC}_x\mathrm{N}_y$ equal to unity (i.e., $x + y = 1$). Homogenous powder blends with three different molar compositions of Ta + 0.3C, Ta + 0.5C, and Ta + 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 30% of theoretical maximum density (TMD) of the powder mixture.

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 set-up and measurement approach was previously given [16,17]. It should be noted that according to the stoichiometry in Eq. (1) the amount of Ta, which is in excess with respect to that of carbon, is considered as the available tantalum to react with nitrogen [11,12]. The degree of nitridation was evaluated based upon the amount of nitrogen uptake calculated from the measurement of weight change of the sample compact after combustion [11,12].

3. Results and discussion

3.1. Observation of combustion characteristics

Typical combustion processes of the samples with different compositions are illustrated in Fig. 1a through Fig. 1c. As shown in Fig. 1a, where a Ta + 0.3C sample reacts under nitrogen of 0.79 MPa, upon ignition a planar and self-sustained combustion front propagates downward from the ignited top plane. The flame front travels steadily and speedily. It took only about 0.57 s for the combustion wave to spread throughout the sample and to transform the cold reactant into an incandescent combustion product. After the propagation of combustion front, Fig. 1a shows that at first the brightness on the burned sample slightly fades, but shortly from $t = 1.20$ s the luminosity turns stronger and remains intense for more than 3 s. This observation suggests prolonged reaction taking place in bulk after the passage of the flame front; namely, the occurrence of afterburning combustion, which is typical of the combustion synthesis involving gaseous reagents. It was believed that the conversion in the combustion front was incomplete, due to both insufficient reaction time caused by the rapid propagation of the flame front and inadequate nitrogen in the reaction front. As a result, the continuous infiltration of nitrogen gas into the porous sample to react with the solid reactant led to the appearance of the afterburning glow on the burned sample.

With an increase in the carbon content as the composition of Ta + 0.5C, a sequence of combustion images under nitrogen is shown in Fig. 1b. Similar to those observed in Fig. 1a, Fig. 1b reveals that upon ignition a distinct flame front forms and propagates along the sample in a self-sustained mode, resulting in a glaring brightness on the burned sample. After the arrival of combustion front at the bottom of the sample, a luminous glow stemming from the afterburning reaction clearly emerges on the sample at $t = 1.43$ s.

In the case of further increasing the carbon content, the combustion process is shown in Fig. 1c, in which the rapid propagation of combustion front and the resulting incandescent luminosity are observed on a Ta + 0.7C compact. However, in contrast to Fig. 1a and b, Fig. 1c indicates that after the passage of the flame front the brightness on the burned sample rapidly fades away and no afterburning luminosity is noticed. The absence of afterburning combustion in the sample of Ta + 0.7C is most likely caused by the fact that the amount of available tantalum in the Ta + 0.7C compact to react with nitrogen is comparatively less than those contained in the samples of Ta + 0.3C and Ta + 0.5C.

3.2. Measurement of combustion temperature

Fig. 2 shows three temperature profiles corresponding to the samples with three different compositions of Ta + 0.3C,

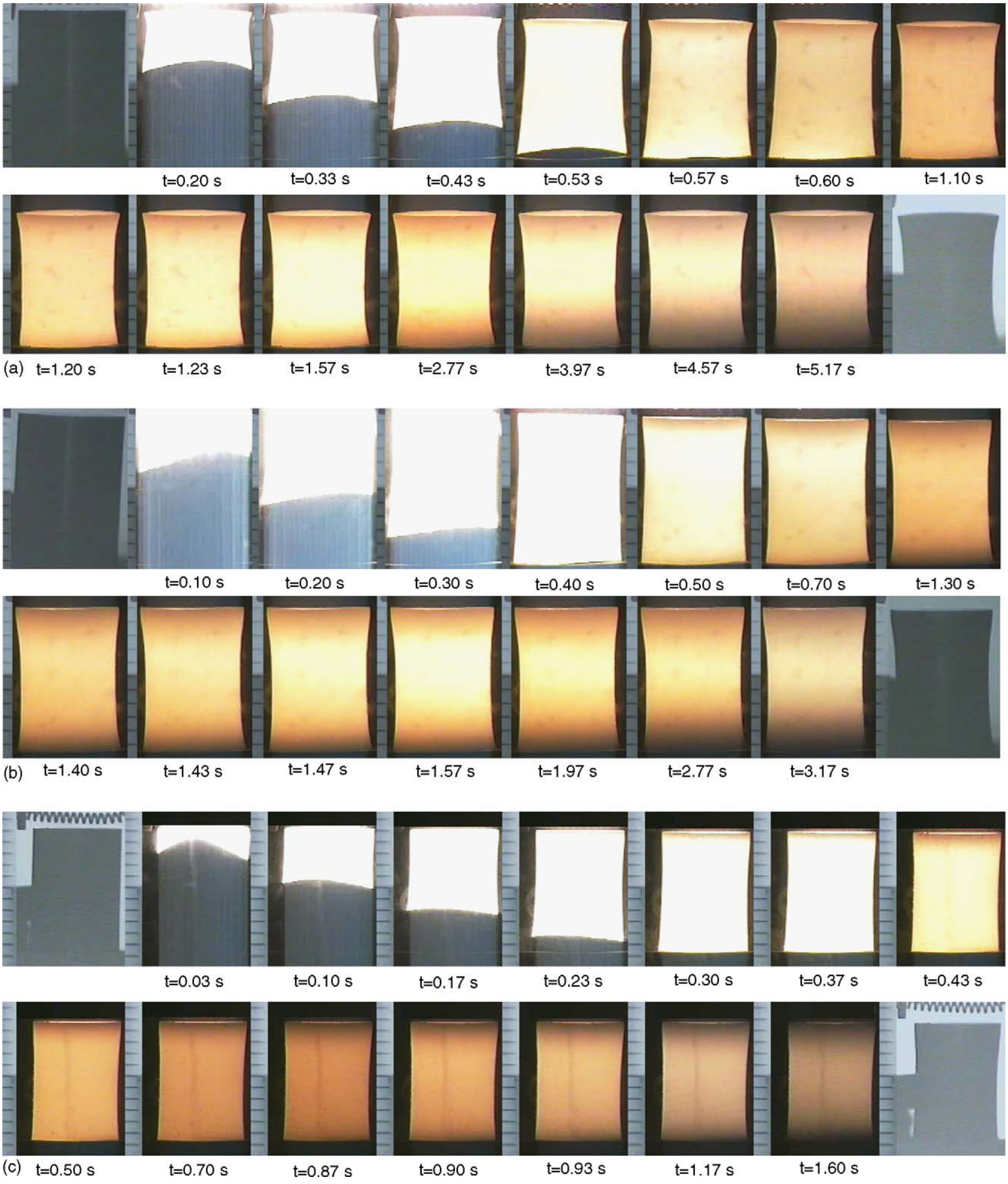

Fig. 1. Recorded burning images illustrating combustion behavior of 30% TMD sample compacts in 0.79 MPa N_2 with different compositions: (a) Ta + 0.3C; (b) Ta + 0.5C; and (c) Ta + 0.7C.

Ta + 0.5C, and Ta + 0.7C, respectively. The abrupt rise of temperature in all three curves represents the rapid arrival of the flame front. After reaching the peak temperature, Fig. 2 indicates that the sample of Ta + 0.7C experiences a quite different temperature variation from those of Ta + 0.3C and Ta + 0.5C. For the Ta + 0.3C and Ta + 0.5C samples, the profiles exhibit an approximately flat plateau region at the temperatures close to the peak value for about 2 s; that is, the samples remain at elevated temperatures after the passage of the flame front. Obviously, the prolonged afterburning combustion on the samples of Ta + 0.3C and Ta + 0.5C was responsible for the high sample temperature behind the

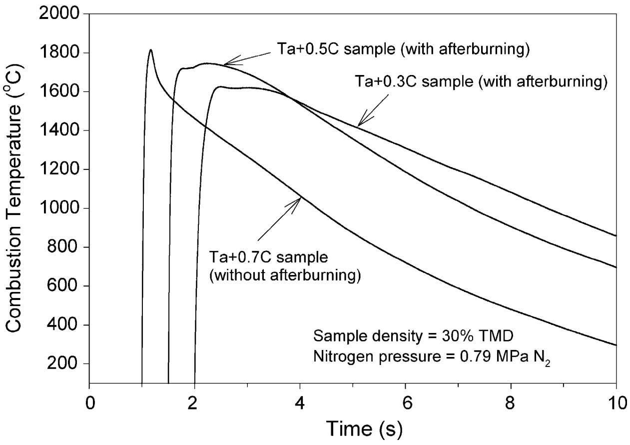

Fig. 2. Typical temperature profiles illustrating SHS processes with and without afterburning combustion.

flame front. On the contrary, due to the absence of afterburning reaction, the temperature curve detected from the sample of Ta + 0.7C reveals a substantial drop after reaching the maximum value.

In addition to the time variation of temperature, Fig. 2 also points out that the temperature of combustion front increases with an increase in the carbon content of the sample. It is important to note that in this study measured sample temperatures during both flame-propagating and afterburning stages are considerably lower than the melting points of carbon black, Ta (2996 °C) and Ta(C,N) (around 3000–3800 °C, depending upon the composition). As a result, there was no tendency to melt the reactant and burned product during the SHS reaction.

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 sample composition is presented in Fig. 3. As shown in Fig. 3, under constant nitrogen pressure the flame-front velocity increases with increasing carbon content of the compact, mainly because of the increase of combustion temperature. This discrepancy of flame-front velocity caused by the sample composition was found to diminish gradually as the nitrogen pressure increased. As shown in Fig. 3, for the Ta + 0.3C and Ta + 0.5C samples the flame-front velocity increases with increasing nitrogen pressure. However, the flame-front velocity of the Ta + 0.7C sample was found to be nearly independent of the nitrogen pressure, implying that the reaction between Ta and carbon dominates in the combustion front of the Ta + 0.7C sample.

3.4. Composition analysis of final products

The nitridation percentage of powder compacts is shown in Fig. 4 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 tantalum carbonitride $\mathrm{TaC}_x\mathrm{N}_y$ (with $x + y = 1$). In general, the nitridation percentage increases with increasing nitrogen pressure. Due to the presence of afterburning combustion on the samples of Ta + 0.3C and Ta + 0.5C, the increase of nitridation percentage with increasing nitrogen pressure was not very significant and a comparable degree of nitridation was obtained for these two types of samples. That is, the nitridation percentage increases from 76% at 0.45 MPa of nitrogen to about 89% at 1.82 MPa. On the other hand, the influence of nitrogen pressure on the extent of nitridation was quite pronounced for the Ta + 0.7C compact, mainly because of the lack of afterburning reaction. As shown in Fig. 4, the nitridation percentage of the Ta + 0.7C sample increases from 45% to 81% with the increase of nitrogen pressure from 0.45 to 1.14 MPa; however, further increase of nitrogen pressure produces almost no additional enhancement on the degree of nitridation. Moreover, due to the absence of afterburning reaction, Fig. 4 indicates that the nitridation percentage of

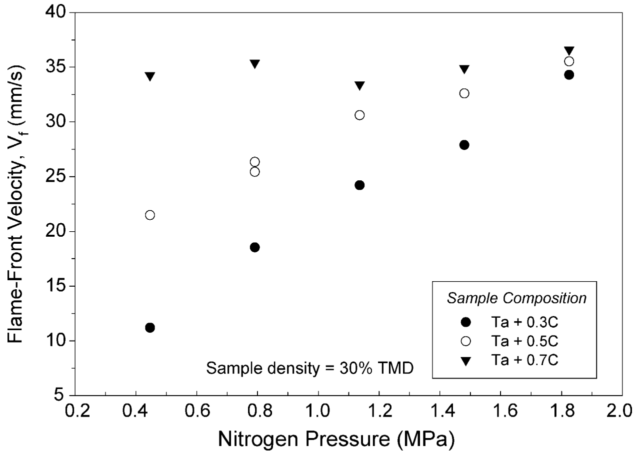

Fig. 3. Effects of nitrogen pressure and carbon content on flame-front propagation velocity in synthesis of Ta(C,N) by SHS.

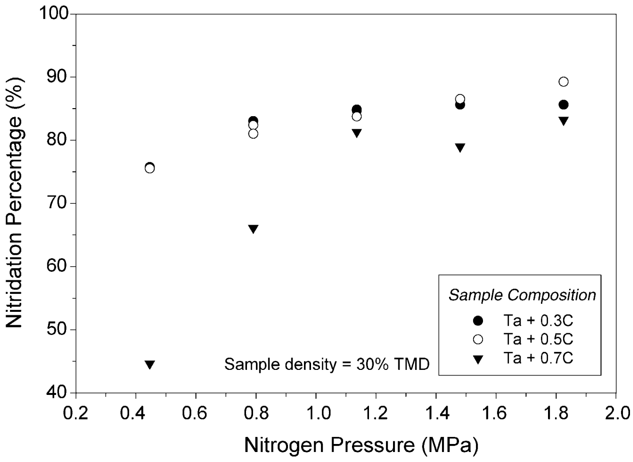

Fig. 4. Effects of nitrogen pressure and carbon content on degree of nitridation in synthesis of Ta(C,N) by SHS.

the Ta + 0.7C compact is lower than those of the Ta + 0.3C and Ta + 0.5C samples, especially under the conditions with low pressures of nitrogen.

The XRD spectra of combustion products obtained from the samples with different initial compositions are presented in Fig. 5a through Fig. 5c. As shown in Fig. 5a, the final product synthesized from a Ta + 0.3C sample consists of a carbonitride of Ta(C,N), a nitride phase of Ta_2N, as well as some elemental Ta. Evidently, the tantalum carbonitride Ta(C,N) is the dominant phase in the final composition. The formation of Ta_2N was believed to arise from insufficient nitrogen especially in the central portion of the sample [16]. For the samples of Ta + 0.5C and Ta + 0.7C, Fig. 5b and c show that the formation of Ta(C,N) as the dominant phase, together with a small amount of unreacted Ta. However, no existence of Ta_2N was detected in Fig. 5b and c, because the amount of available tantalum to react with nitrogen was relatively less in the samples of Ta + 0.5C and Ta + 0.7C when compared with that in the Ta + 0.3C sample.

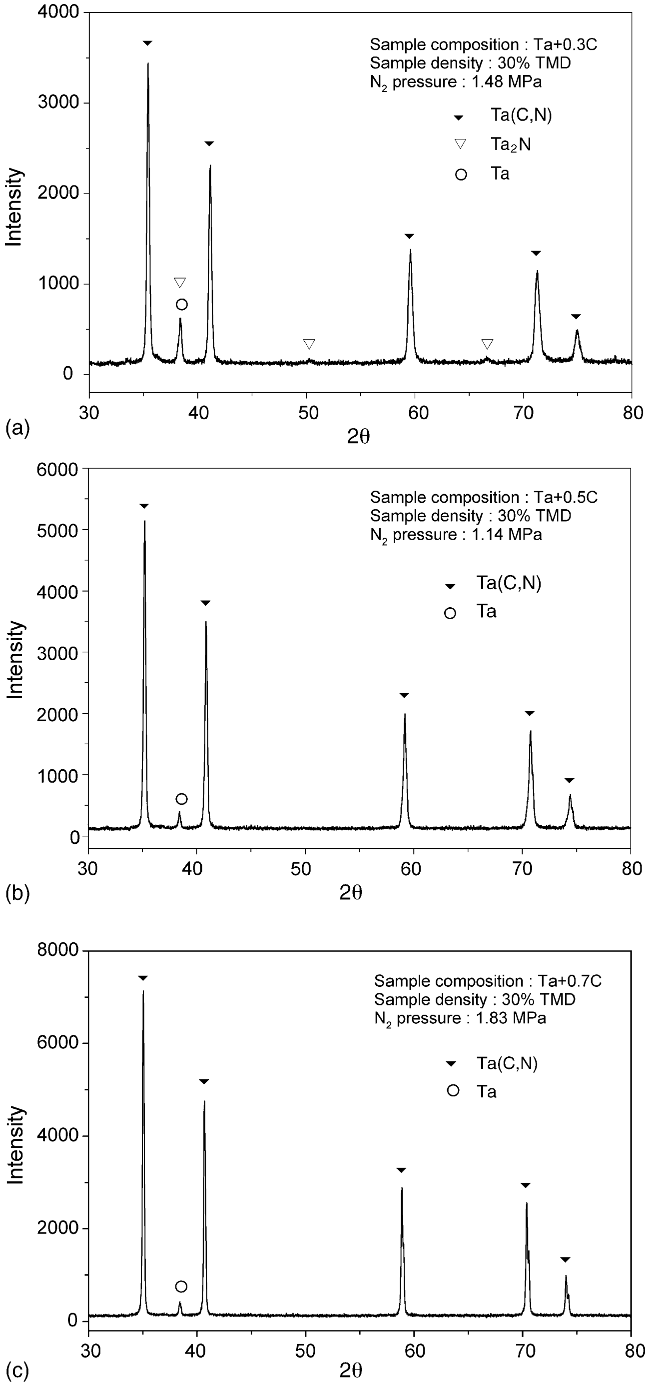

Fig. 5. XRD spectra of combustion products obtained from: (a) a sample of Ta + 0.3C in 1.48 MPa N_2; (b) a sample of Ta + 0.5C in 1.14 MPa N_2; and (c) a sample of Ta + 0.7C in 1.83 MPa N_2.

4. Summary and conclusions

This study represents a comprehensive investigation on the preparation of tantalum carbonitride by combustion synthesis of Ta-C powder compacts in gaseous nitrogen. Experimental parameters, such as the carbon content in the green compact and nitrogen pressure, were found to have significant effects on the combustion characteristics as well as on the degree of completeness of the reaction.

For the samples composed of Ta + 0.3C and Ta + 0.5C, in general, the combustion process 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. Moreover, the propagation velocity is increased by increasing the nitrogen pressure.

For the sample of Ta + 0.7C, the afterburning combustion is not present, due to a less amount of available tantalum to react with nitrogen in this composition. Additionally, the flame-front velocity of the Ta + 0.7C sample is essentially independent of the nitrogen pressure, with an implication that the reaction between Ta and carbon dominates in the combustion front. When compared with the samples of Ta + 0.3C and Ta + 0.5C under a constant pressure of nitrogen, the Ta + 0.7C sample has a higher flame-front velocity. The increase of flame-front velocity with increasing carbon content of the sample is attributed to the increase of combustion temperature.

Due to the presence of prolonged afterburning reactions in the Ta + 0.3C and Ta + 0.5C compacts, the increase of nitrogen pressure from 0.45 to 1.82 MPa produces simply a moderate increase in the nitridation percentage from 76 to 89%. However, the increase of nitrogen pressure contributes significantly to the degree of nitridation of the Ta + 0.7C sample, because of the lack of afterburning combustion. The nitridation percentage of Ta + 0.7C samples increases substantially from 45 to 81% within the pressure range conducted. For all samples tested in this study, the carbonitride phase Ta(C,N) was identified as the dominant composition in the final products. An intermediate nitride phase of Ta_2N was found only in the product obtained from the sample composed of Ta + 0.3C.

Acknowledgements

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