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# Direct formation of titanium carbonitrides by SHS in nitrogen

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## Abstract

An experimental investigation of direct formation titanium carbonitrides by self-propagating high-temperature synthesis (SHS) was conducted using compacted samples of titanium and carbon powders ignited in gaseous nitrogen. Effects of sample green density, nitrogen pressure, and diluent content on the degree of conversion and flame-front velocity were studied. For the undiluted samples, a low degree of nitrogen uptake was obtained, primarily due to the excessive melting of titanium during the reaction. Results indicated that the addition of diluent TiN was required in order to achieve the complete conversion. Three stoichiometric carbonitrides with the compositions of $TiC_{0.7}N_{0.3}$, $TiC_{0.5}N_{0.5}$, and $TiC_{0.3}N_{0.7}$ were synthesized in this study. The required diluent content and nitrogen pressure were found to increase with the increase of nitrogen content in the final product. For the $TiC_{0.7}N_{0.3}$, complete conversion was achieved by using a sample made up of 0.9Ti + 0.7C + 0.1TiN under nitrogen pressures of 0.62 MPa and above. More diluents and higher nitrogen pressure were necessary in the synthesis of $TiC_{0.5}N_{0.5}$ and $TiC_{0.3}N_{0.7}$, which were synthesized from the 0.75Ti + 0.5C + 0.25TiN sample at 1.14 MPa of nitrogen and the 0.6Ti + 0.3C + 0.4TiN sample at 1.65 MPa of nitrogen, respectively.

*Keywords:* Titanium carbonitride; SHS; Diluent; Afterburning; Nitrogen uptake

## 1. Introduction

Titanium carbonitride, Ti(C,N), has been of practical interest because of its outstanding and unique combination of physical properties, such as high melting point, high hardness, good thermal and chemical stability, excellent electrical and thermal conductivities, and metallic luster [1]. Titanium carbonitride exists as a solid solution between the boundary phase titanium carbide (TiC) and titanium nitride (TiN), and the stoichiometric phase can be expressed as $TiC_xN_y$ (with $x + y = 1$). When combined with metal binders (i.e., Ni, Co, Mo), Ti(C,N)-based cermets have been widely used in the field of cutting tools and wear-resistance materials [1–4]. Furthermore, the addition of different metal carbides (i.e., WC, $Mo_2C$, TaC, NbC) into Ti(C,N)-based mixtures has become a standard procedure of the manufacturing route to adjust and to improve specific properties [4–7].

Physical properties of Ti(C,N), such as microhardness, electrical and heat conductivities, molar heat capacity, and shear modulus, have been reported as a function of the [C]/([C] + [N]) ratio of the carbonitride [8,9]. The microhardness of Ti(C,N) was found to increase monotonously with increasing [C]/([C] + [N]) ratio under a load of 0.98 N [8]. On the contrary, the electrical and heat conductivities generally increase with increasing nitrogen content [8]. For the stoichiometric $TiC_xN_y$, the shear modulus exists a maximum of 196 GPa at $[C]/([C] + [N]) \approx 0.6–0.7$ [9].

Raw Ti(C,N) powders have been typically produced by the carbothermal reduction of titanium oxide ($TiO_2$) in nitrogen [10–12]. However, the final products obtained from the chemical reduction process usually have the drawback of low purity. On the other hand, production routes associated with the thermal decomposition [13] and chemical vapor deposition [14,15] to synthesize Ti(C,N) are costly. Besides the above-mentioned approaches, self-propagation high-temperature synthesis (SHS) or combustion synthesis with

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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, hydrides, carbonitrides, and intermetallics, etc. [16–19]. In addition to the economic benefits, the formation of high-purity products from the SHS process is also widely acknowledged [16–19]. The preparation of TiC [19–21] and TiN [22–25] by SHS has been extensively studied, but research on the combustion synthesis of Ti(C,N) is still limited. Holt and Munir [21] indicated that the SHS reaction between titanium and carbon black powders to form TiC is highly exothermic with an adiabatic temperature of 3210 K, and the process is featured by the steady propagation of a planar combustion front. However, controversy has existed regarding the reaction mechanism associated with the combustion synthesis of TiC [19]. During the SHS process related to the formation of TiN, due to the excessive melting of titanium samples, the porosity of test compacts provided nearly no influence on the flame-front velocity and the degree of nitride conversion [25]. The addition of TiN as a diluent in the titanium sample was found to reduce the melting of test compacts, thus leading to a substantial increase in the nitride conversion percentage [23,25]. The TiN powders were also employed as the diluent in the sample compacts of titanium and carbon black powders in order to directly produce titanium carbonitride ($TiC_{0.5}N_{0.5}$) by SHS in gaseous nitrogen [26]. Reaction mechanism with respect to the combustion synthesis of $TiC_{0.5}N_{0.5}$ was proposed by Eslamloo-Grami and Munir [26], which involves the formation of the carbide phase $TiC_{0.5}$ followed by the incorporation of nitrogen in the defect-structure carbide to form the carbonitride solid solution.

The objective of this study was to experimentally investigate the direct formation of stoichiometric titanium carbonitride Ti(C,N) by SHS in gaseous nitrogen with the sample compacts prepared by the mixture of titanium and carbon powders. Apart from identifying the conditions necessary for the synthesis of Ti(C,N) with different [C]/([C] + [N]) ratios, combustion characteristics associated with the SHS process were studied, including flame-front propagation velocity, sample melting phenomenon, and afterburning reaction. In addition, effects of experimental parameters consisting of the sample green density, nitrogen pressure, and diluent content on the degree of conversion to carbonitride were addressed.

## 2. Experimental

### 2.1. Test samples

Titanium (Strem Chemicals, 325 mesh, 99% purity) and carbon black (Showa Chemical Co., 22 nm) powders were used as the reactants in this study. For the undiluted sample, titanium and carbon powders were dry mixed in a ball mill for 10 h with the molar ratio according to the stoichiometry of the following reaction:

$$Ti + xC + \frac{y}{2}N_2 \rightarrow TiC_xN_y \quad (1)$$

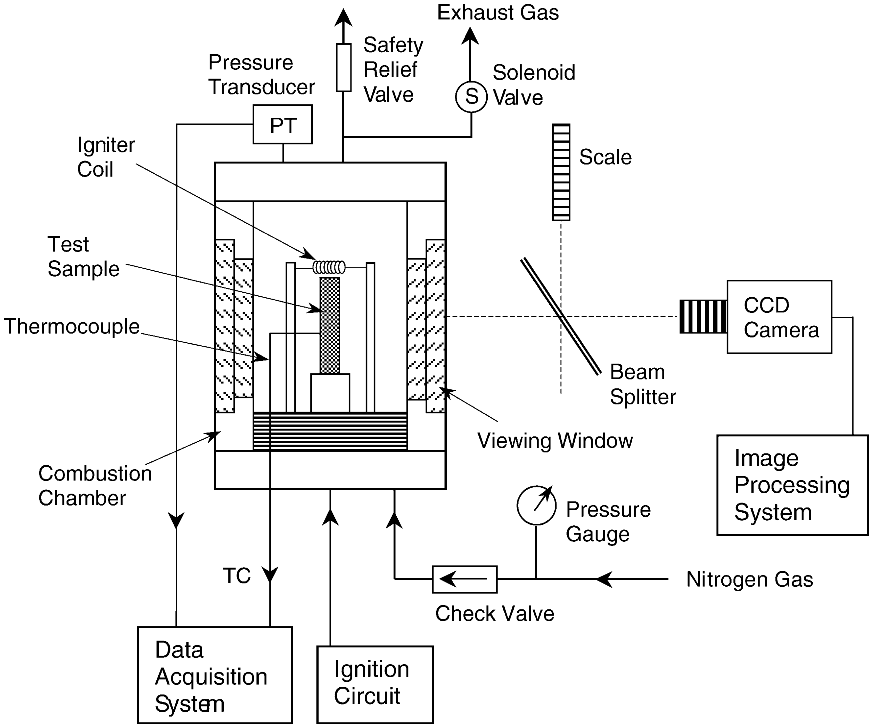

Fig. 1. Schematic diagram of experimental setup to study SHS of titanium carbonitride.

Homogenous powder blends with three different molar compositions of Ti + 0.3C, Ti + 0.5C, and Ti + 0.7C were prepared for the synthesis of carbonitrides $TiC_{0.3}N_{0.7}$, $TiC_{0.5}N_{0.5}$, and $TiC_{0.7}N_{0.3}$, respectively. The mixed powders were then cold-pressed into cylindrical samples with a diameter of 7 mm and a height of 12 mm. In order to obtain test samples with different porosities, the powder compacts were formed with the initial packing densities ranged from 40% to 60% of the theoretical maximum density (TMD) of the powder mixture. For the preparation of test samples containing titanium nitride, TiN (Strem Chemicals, 325 mesh, 99% purity) as the diluent, the composition of TiN-diluted samples was based upon the following reaction:

$$(1-z)\mathrm{Ti} + x\mathrm{C} + z\mathrm{TiN} + \frac{(y-z)}{2}\mathrm{N}_2 \rightarrow \mathrm{TiC}_x\mathrm{N}_y \qquad (2)$$

The diluent content required in the powder mixture was affected by the composition of the desired product. The coefficient $z$ in reaction (2) representing the degree of dilution was varied from 0.1 to 0.4 in this study. Dilution of the reactant mixture with the nitride product was suggested as an effective means to improve the extent of nitridation, especially for the case with the formation of

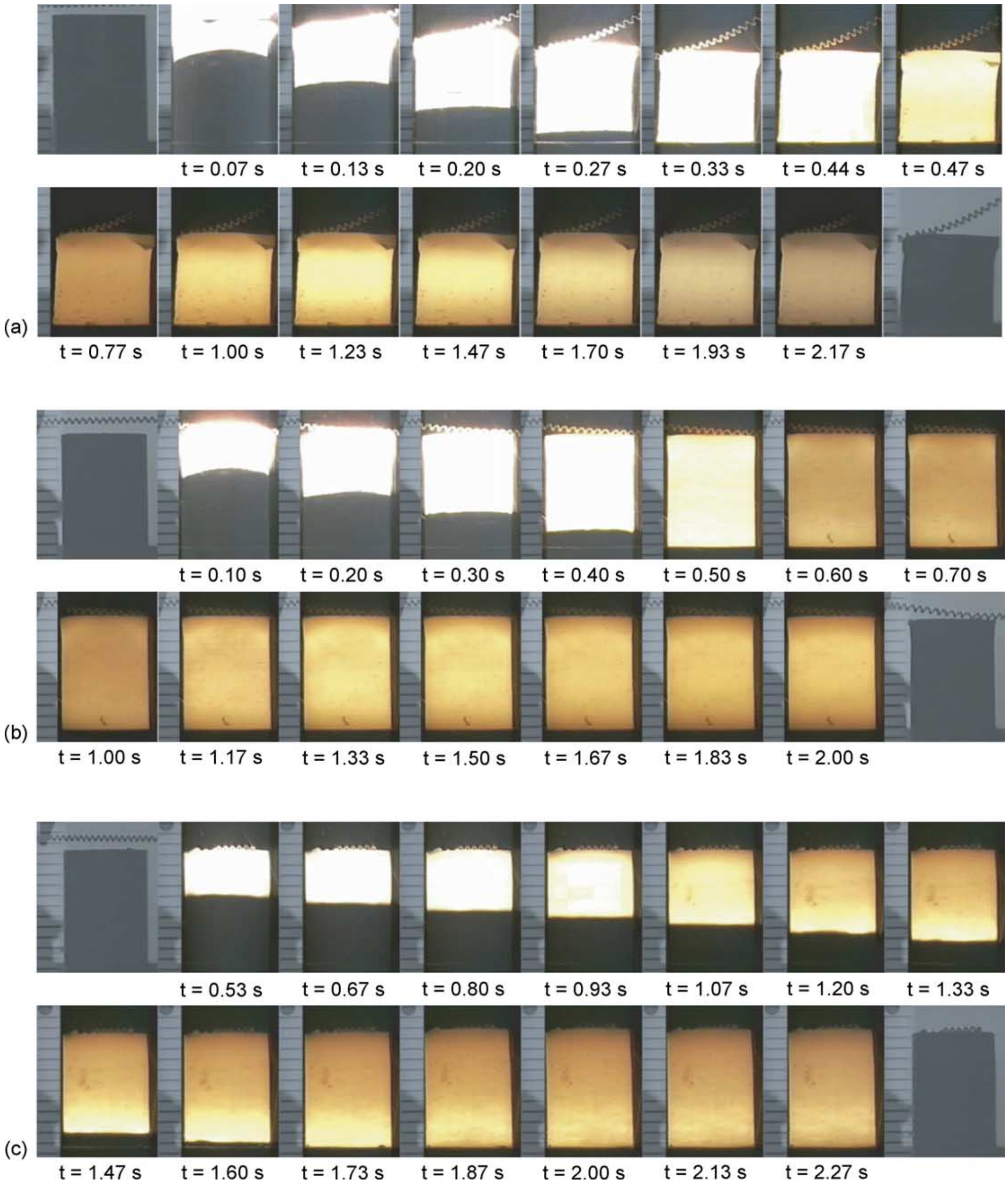

Fig. 2. Recorded burning images indicating flame-front propagation and afterburning reaction associated with: (a) a 50% TMD sample of Ti + 0.5C in 0.62 MPa $N_2$; (b) a 50% TMD sample of 0.8Ti + 0.5C + 0.2TiN in 0.62 MPa $N_2$; and (c) a 50% TMD sample of 0.65Ti + 0.5C + 0.35TiN in 1.31 MPa $N_2$.

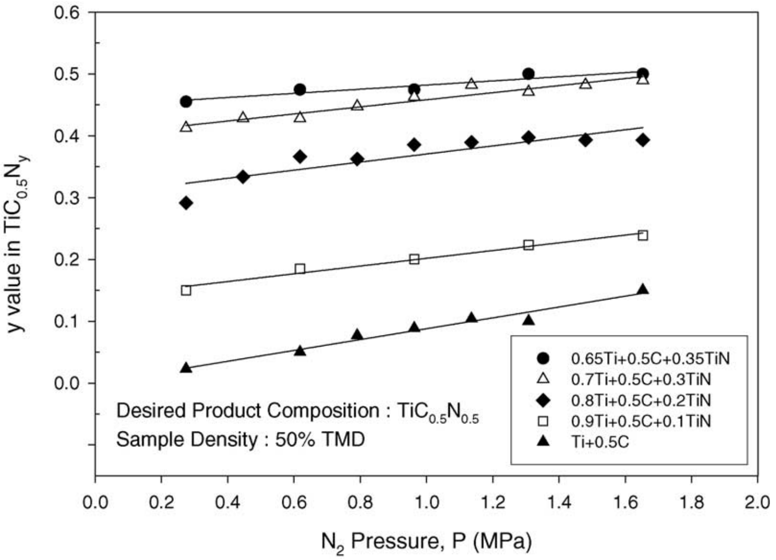

Fig. 3. Effects of nitrogen pressure and diluent content on degree of conversion in synthesis of $TiC_{0.5}N_{0.5}$.

liquid phase during the SHS reaction [23–26]. The reaction between Ti and C in the sample was assumed to be complete; therefore, the remaining elemental Ti was considered as the available titanium to react with nitrogen [26].

### 2.2. Experimental setup and instrumentation

The SHS reaction of Ti/C or Ti/C/TiN powder compacts was conducted in a stainless steel windowed combustion chamber (as shown in Fig. 1) under a nitrogen pressure ranging from 0.27 to 1.65 MPa. The nitrogen gas used in this study has a purity of 99.999%. The detailed description of experimental setup and measurement approach was previously given [25,27]. The burned samples were recovered and weighed after combustion. The amount of nitrogen uptake was calculated from the measurement of weight change of the sample compact, and the degree of conversion to carbonitride was considered based upon the assumption that nitrogen reacts with available titanium to form stoichiometric products [26].

## 3. Results and discussion

### 3.1. Observation of combustion characteristics

Fig. 2(a) shows a series of recorded images illustrating the propagation of the flame-front associated with the

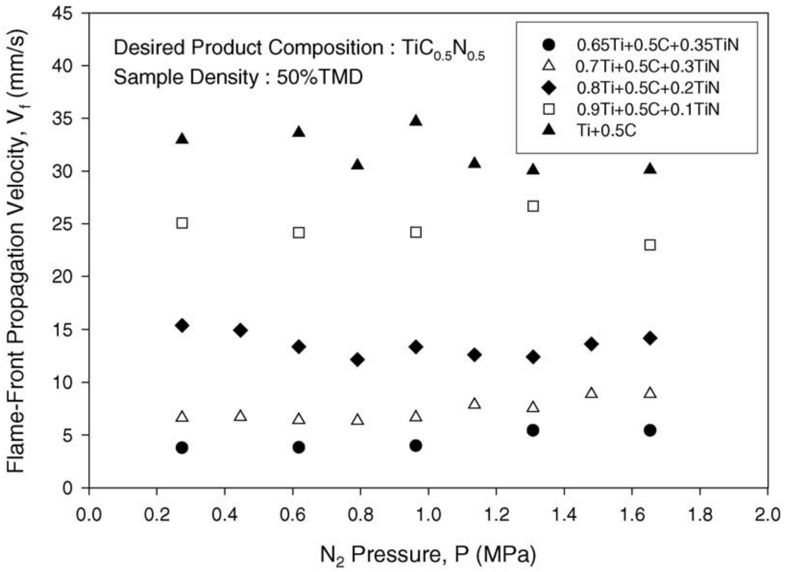

Fig. 4. Effects of nitrogen pressure and diluent content on flame-front propagation velocity of samples prepared for synthesis of $TiC_{0.5}N_{0.5}$.

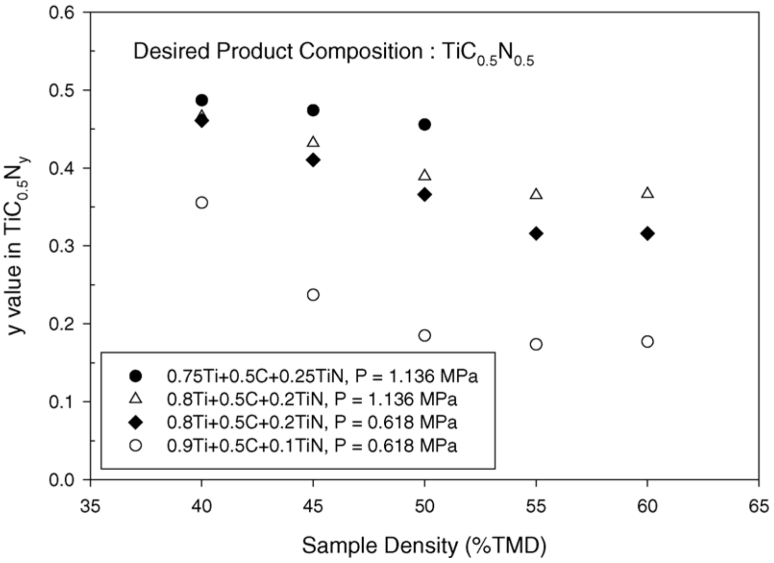

Fig. 5. Effects of sample green density on degree of conversion in synthesis of $TiC_{0.5}N_{0.5}$.

nitridation of an undiluted sample (having a composition of Ti + 0.5C and a density of 50% TMD) in nitrogen of 0.62 MPa. It is evident in Fig. 2(a) that upon ignition a distinct and self-sustained flame-front propagates downward as a nearly parallel combustion wave from the ignited top plane, and transforms the cold reactant into an incandescent combustion product. According to the flame-front trajectory constructed upon the recorded film images, the combustion front was found to propagate in a steady mode. Fig. 2(a) indicates as well that the propagation of the flame-front is accompanied by a significant melting of the test sample, resulting in a considerable shrinkage of the final product. Based upon the results reported by Eslamloo-Grami and Munir [26], the melting was caused by the fact that the combustion temperature of Ti + 0.5C samples in nitrogen was higher than the melting point of titanium (1660 °C). Moreover, the substantial melting could result in the reduction of sample porosity, which in turn impeded the filtration of nitrogen gas into the sample compact. As a result, it is very likely that the amount of nitrogen uptake in the sample of Fig. 2(a) during the reaction would be insufficient to yield the desired composition.

As also shown in Fig. 2(a), the flame-front rapidly reaches the bottom of the sample and the whole sample glows in white at about $t = 0.44$ s, beyond which the brightness gradually vanishes from the sample. However, at $t = 1.0$ s the recurrence of luminosity on the sample is noticed, implying the occurrence of an afterburning reaction

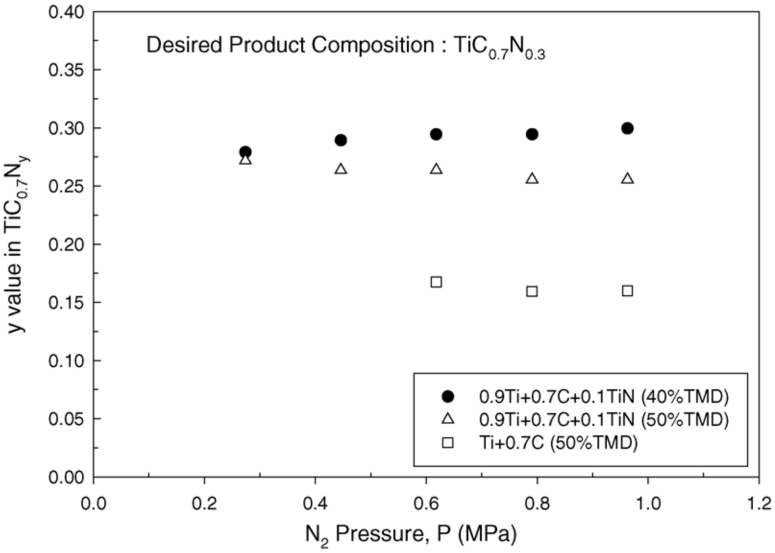

Fig. 6. Effects of nitrogen pressure, diluent content, and sample green density on degree of conversion in synthesis of $TiC_{0.7}N_{0.3}$.

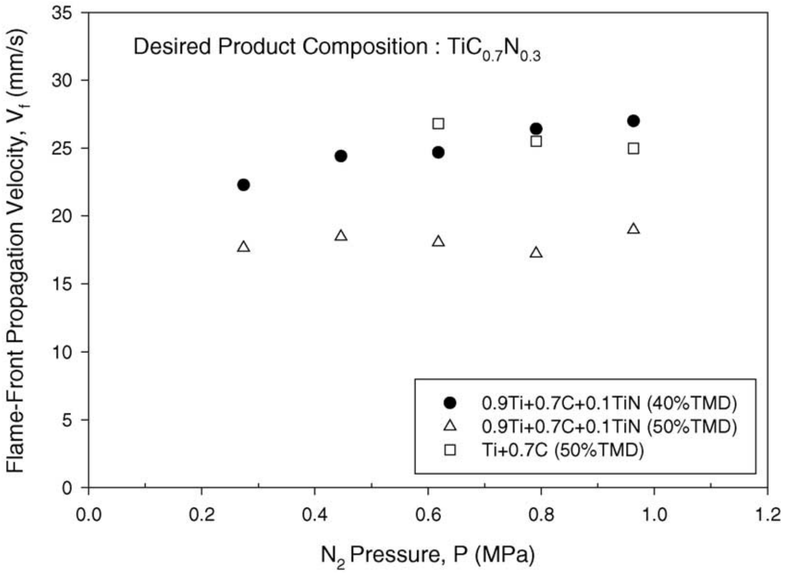

Fig. 7. Effects of nitrogen pressure, diluent content, and sample green density on flame-front propagation velocity of samples prepared for synthesis of $TiC_{0.7}N_{0.3}$.

which means the reaction taking place after the passage of the flame-front. The afterburning luminosity on the sample is clearly observable during the time period of 1.0–1.7 s in Fig. 2(a). This observation also implies that due to the high propagation rate the reaction in the combustion front was incomplete and further conversion proceeded in bulk during the afterburning stage.

All undiluted samples (including the compositions of Ti + 0.3C, Ti + 0.5C, and Ti + 0.7C) employed in this study exhibited combustion characteristics similar to those presented in Fig. 2(a). In addition, the sample with a low degree of dilution (such as, the composition of 0.9Ti + 0.5C + 0.1TiN) also experienced significant melting and showed noticeable shrinkage during the combustion. However, the melting of sample compacts was effectively reduced by increasing the TiN content in the sample. As shown in Fig. 2(b), a TiN-diluted sample with the composition of 0.8Ti + 0.5C + 0.2TiN reveals only slight contraction of about 0.3 mm in height after reaction. Consistent with those shown in Fig. 2(a), the combustion process illustrated in Fig. 2(b) is characterized by both the fast propagation of a self-sustained combustion front reaching the sample bottom at $t = 0.50$ s and a subsequent afterburning reaction starting at approximately $t = 1.17$ s.

Further increase in the diluent content contributed to a greater reduction of combustion temperature, and hence no

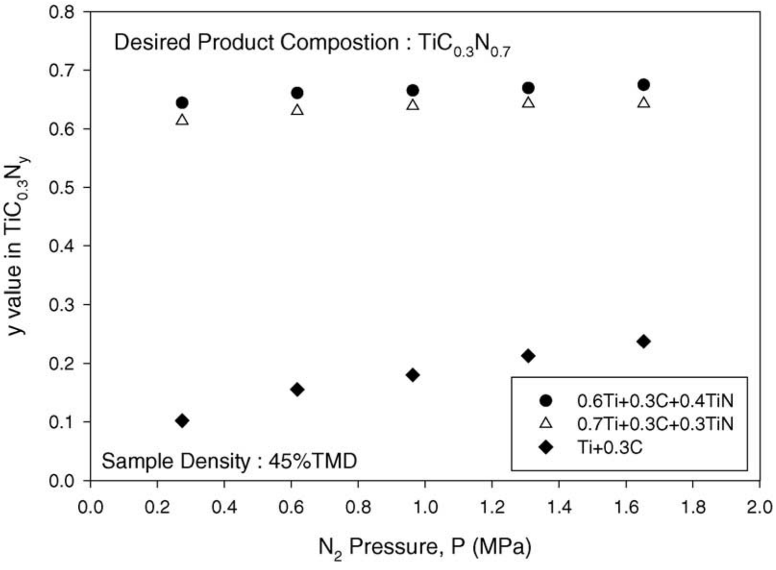

Fig. 8. Effects of nitrogen pressure and diluent content on degree of conversion in synthesis of $TiC_{0.3}N_{0.7}$.

melting of the test sample was observed. As shown in Fig. 2(c), the SHS process of a 0.65Ti + 0.5C + 0.35TiN sample under a nitrogen pressure of 1.31 MPa is presented. It was found that the sample essentially retained its original shape and porosity after combustion. Moreover, due to the high degree of dilution, the flame-front propagation velocity of the sample in Fig. 2(c) is much lower than those shown in Fig. 2(a) and (b). It took approximately 1.87 s for the combustion front to arrive at the bottom of the sample. After the passage of the flame-front, the luminosity on the burned sample gradually faded away without any re-emergence. It was believed that since the flame velocity was sufficiently slow, the afterburning reaction occurred in the burned region while the flame-front was still in progress. This explains the absence of the re-glowing luminosity after the passage of the flame-front for the highly diluted compacts, such as the samples made up of 0.65Ti + 0.5C + 0.35TiN and 0.7Ti + 0.5C + 0.3TiN.

### 3.2. Combustion synthesis of $TiC_{0.5}N_{0.5}$

Fig. 3 shows the effects of nitrogen pressure and diluent content on the degree of conversion of 50% TMD powder compacts, which were intended to yield the stoichiometric carbonitride $TiC_{0.5}N_{0.5}$. As shown in Fig. 3, it was found that the nitrogen uptake of undiluted samples (with $y$ values between 0.02 and 0.15) is far less than the stoichiometric value ($y = 0.5$). According to the two-stage reaction mechanism of the carbonitride proposed by Eslamloo-Grami and Munir [26], the first stage, taking place in the combustion front, yields the non-stoichiometric carbide phase, which further reacts with nitrogen to form carbonitride solid solution during the afterburning stage. The low degree of conversion for the undiluted samples in this study was primarily caused by the fact that the filtration of nitrogen into the compacted sample was hindered by the melting of titanium particles, resulting in a lack of nitrogen in the inner portion of the sample. Even though the extent of nitridation is anticipated to be enhanced by increasing the nitrogen pressure, Fig. 3 shows that the improvement is limited. On the contrary, the addition of TiN in the reactant mixture was found to appreciably increase the degree of conversion. The introduced TiN not only contributed nitrogen to the final product, but also served as a diluent to reduce the melting of samples and thereby to increase the amount of nitrogen uptake. For the samples with a green density of 50% TMD as shown in Fig. 3, complete conversion to form the stoichiometric carbonitride $TiC_{0.5}N_{0.5}$ was accomplished by using TiN-diluted samples with a composition of 0.65Ti + 0.5C + 0.35TiN under nitrogen pressures higher than 1.3 MPa.

The corresponding variation of flame-front propagation velocities ($V_f$) of undiluted and TiN-diluted samples of 50% TMD with nitrogen pressure is shown in Fig. 4. In general, the velocity of flame-front was almost independent of the nitrogen pressure. This implies that the reaction between titanium and carbon dominates in the combustion front. It should be noted that due to the significant melting and shape deformation of undiluted samples during the combustion, a relatively large scattering on the deduced flame velocity was observed for undiluted samples. In addition, Fig. 4 shows that the flame-front velocity is noticeably decreased by increasing the diluent content.

The dependence of the extent of nitridation of TiN-diluted samples on the sample green density is presented in Fig. 5. It was found that the decrease of initial compact density from 60% to 55% TMD produced nearly no effect on the nitrogen uptake, but further decrease in the sample green

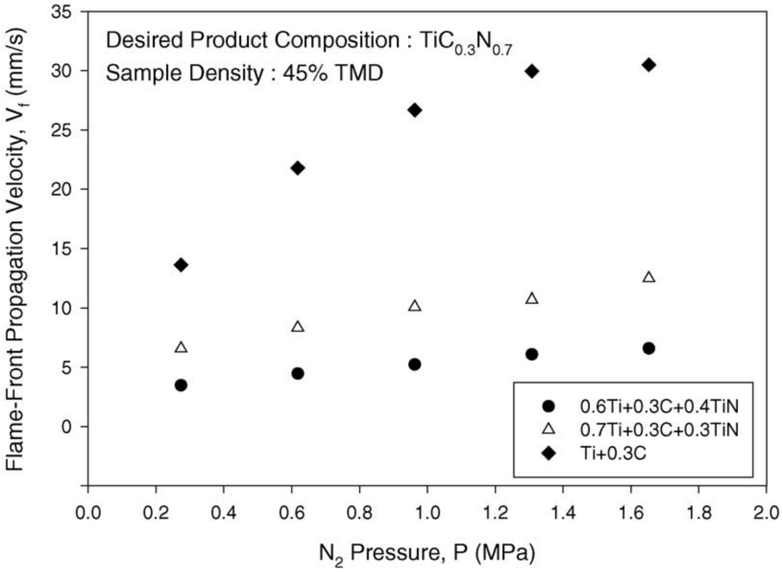

Fig. 9. Effects of nitrogen pressure and diluent content on flame-front propagation velocity of samples prepared for synthesis of $TiC_{0.3}N_{0.7}$.

density brought about an obvious increase in the degree of conversion. This is because the compacted sample with a lower density not only possesses a larger amount of nitrogen within the porous structure, but also provides higher permeability for the filtration of nitrogen. Effects of diluent concentration and nitrogen pressure on the nitrogen content of final products are also shown Fig. 5. However, their influences became less pronounced as the green density of samples was decreased. Above observations suggest that besides the addition of diluent, the decrease of sample green density contributes significantly to the enhancement of the nitrogen uptake as well. These findings also imply that in order to synthesize the carbonitride $TiC_{0.5}N_{0.5}$ under the condition with less diluent and at lower nitrogen pressure than those shown in Fig. 3, the green density of samples has to decrease. This postulation was further verified and it was shown in Fig. 5 that the desired carbonitride $TiC_{0.5}N_{0.5}$ was obtained from a 0.75Ti + 0.5C + 0.25TiN sample with a green density of 40% TMD ignited in nitrogen gas of 1.14 MPa.

### 3.3. Combustion synthesis of $TiC_{0.7}N_{0.3}$

Fig. 6 shows the influence of nitrogen pressure, diluent content, and sample green density on the degree of conversion of sample compacts prepared for the synthesis of $TiC_{0.7}N_{0.3}$. In agreement with the above observations, the nitrogen uptake for the undiluted samples is less than the stoichiometric value ($y = 0.3$) due to the melting of the sample during the reaction. The addition of TiN as the

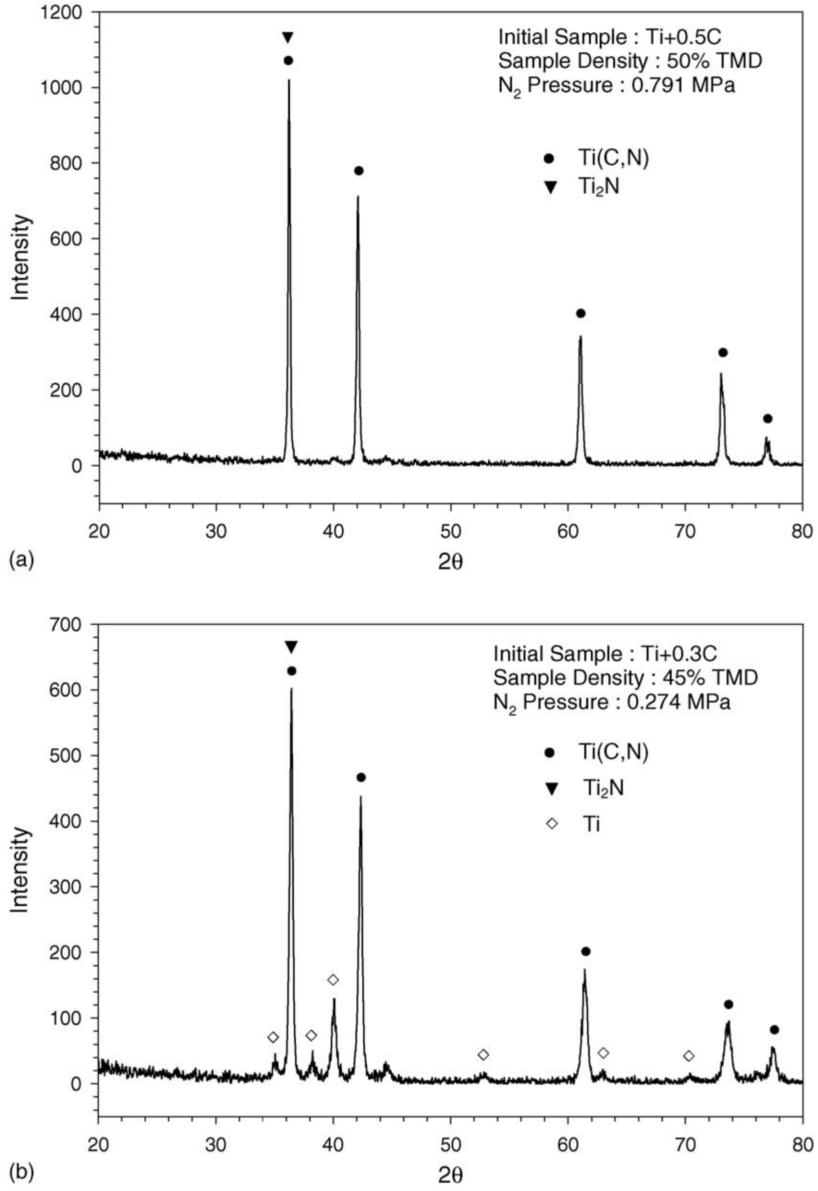

Fig. 10. XRD spectra of combustion products obtained from (a) a 50% TMD sample of Ti + 0.5C in 0.79 MPa $N_2$ and (b) a 45% TMD sample of Ti + 0.3C in 0.27 MPa.

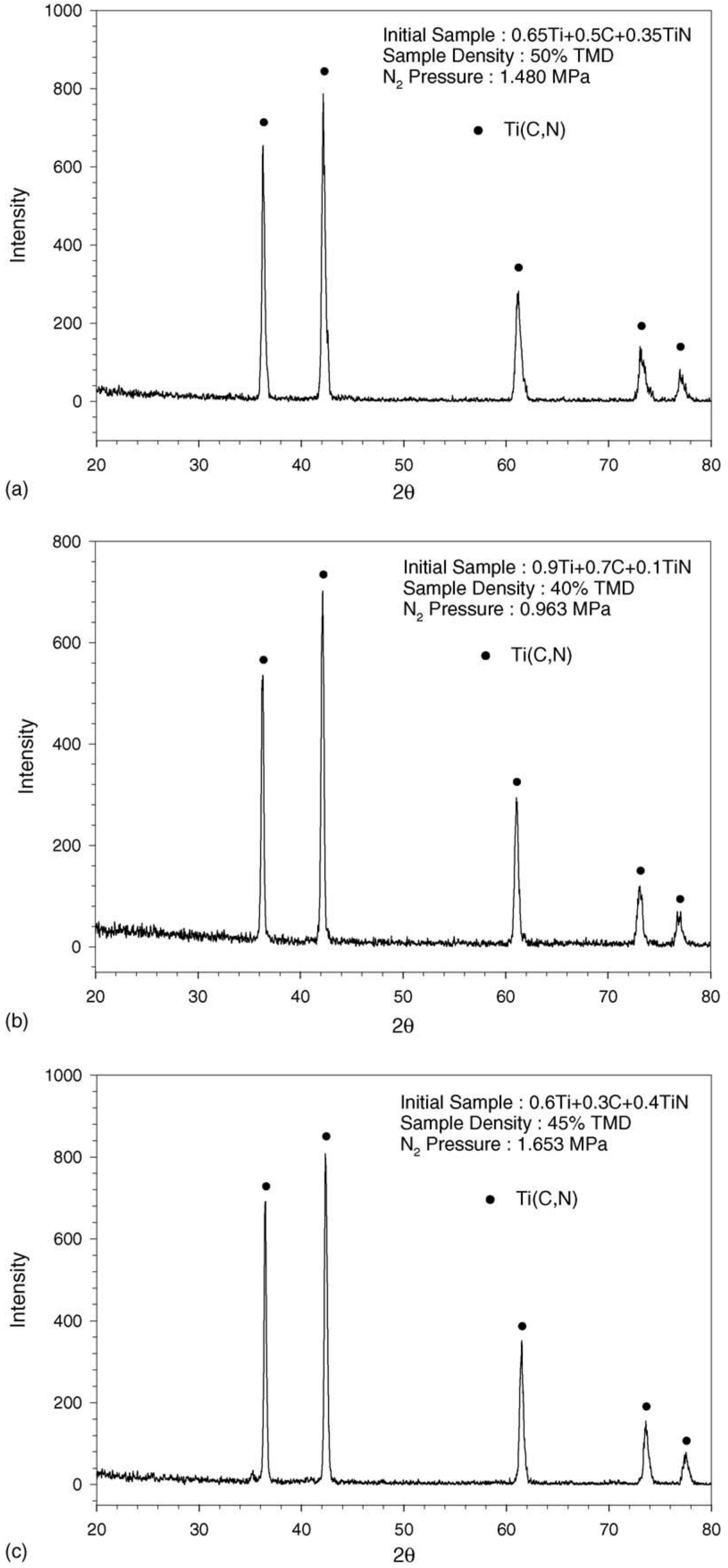

Fig. 11. XRD spectra of combustion products obtained from: (a) a 50% TMD sample of 0.65Ti + 0.5C + 0.35TiN in 1.48 MPa $N_2$; (b) a 40% TMD sample of 0.9Ti + 0.7C + 0.1TiN in 0.96 MPa $N_2$; and (c) a 45% TMD sample of 0.6Ti + 0.3C + 0.4TiN in 1.65 MPa $N_2$.

diluent was found to increase the extent of nitridation and to achieve full conversion in the formation of $TiC_{0.7}N_{0.3}$ from 40% TMD samples with an initial composition of 0.9Ti + 0.7C + 0.1TiN under nitrogen pressures of 0.62 MPa and above. Since the amount of the available titanium to react with nitrogen for the samples prepared to produce $TiC_{0.7}N_{0.3}$ (shown in Fig. 6) was less than those used to synthesize $TiC_{0.5}N_{0.5}$ (shown in Fig. 4), the effect of nitrogen pressure on the synthesis of $TiC_{0.7}N_{0.3}$ was found to be less significant as compared with that of $TiC_{0.5}N_{0.5}$. Fig. 5 indicates that the degree of conversion is nearly independent of nitrogen pressure for the 50% TMD samples, and increases slightly with increasing nitrogen pressure for the 40% TMD samples.

The flame-front propagation velocity of sample compacts prepared for the synthesis of $TiC_{0.7}N_{0.3}$ is shown in Fig. 7 as a function of nitrogen pressure. The effect of nitrogen pressure on the flame-front velocity was in a manner consistent with that on the degree of conversion. The addition of diluent TiN led to a decrease in the flame-front velocity. Fig. 7 also shows that the decrease of the sample green density results in an increase in the flame-front velocity. Because the propagation velocity of the flame-front is mainly governed by the nature of the reaction in the combustion front, the above observation implies that for the sample with a lower green density there is more nitrogen gas participating in the reaction of combustion front, leading to an increase in the flame-front velocity.

### 3.4. Combustion synthesis of $TiC_{0.3}N_{0.7}$

The degree of conversion and the corresponding flame-front velocity of sample compacts prepared to produce $TiC_{0.3}N_{0.7}$ in nitrogen are shown in Figs. 8 and 9, respectively. Similar to the observations presented above, Fig. 8 shows poor conversion with the $y$ value between 0.1 and 0.24 for the undiluted samples. The TiN-diluted samples of 0.7Ti + 0.3C + 0.3TiN yielded a significant increase in the nitrogen content of final products reaching a $y$ value of about 0.64 under nitrogen of 0.96 MPa and above. However, further increase in the diluent content from the composition of 0.7Ti + 0.3C + 0.3TiN to that of 0.6Ti + 0.3C + 0.4TiN resulted in only slight increase of the nitrogen content in the final product, which has a maximum $y$ value of 0.68. This means that the end product with a composition very close to the desired $TiC_{0.3}N_{0.7}$ was synthesized by using the 0.6Ti + 0.3C + 0.4TiN samples under nitrogen pressure of 1.65 MPa. In fact, the amount of nitrogen uptake from the surroundings during the reaction for the 0.6Ti + 0.3C + 0.4-TiN compact was not as much as that for the 0.7Ti + 0.3C + 0.3TiN sample. This was likely because of the decrease of combustion temperature with the increase of diluent content, resulting in the reduction of the degree of nitridation.

Fig. 9 shows that the flame-front velocity of sample compacts for the synthesis of $TiC_{0.3}N_{0.7}$ increases with increasing nitrogen pressure. It is useful to point out that the flame-front velocity of the Ti + 0.3C samples increases considerably from about 13.6 to 30.5 mm/s with nitrogen pressure from 0.27 to 1.65 MPa. This pronounced increase was believed to be the result of the high content of the available titanium to react with nitrogen in the compact of Ti + 0.3C.

### 3.5. XRD analysis of combustion products

Fig. 10(a) and (b) present the XRD spectra of the combustion products obtained from undiluted samples of Ti + 0.5C and Ti + 0.3C, respectively. According to the results shown in Figs. 3 and 8, the conversion to carbonitride was always incomplete for the undiluted samples. The spectrum shown in Fig. 10(a) indicates that in addition to the titanium carbonitride Ti(C,N) there exists a nitride phase $Ti_2N$ in the end product. Based upon the intensity of characteristic peaks, the first and second strongest XRD peaks signifying the Ti(C,N) phase are at $2\theta = 42.1^\circ$ and $36.3^\circ$, respectively. However, the XRD spectrum of Fig. 10(a) exhibits the peak with the strongest intensity at $2\theta = 36.3^\circ$. This was caused by the superimposition of the signal of $Ti_2N$ with that of Ti(C,N). The $Ti_2N$ phase was considered as an intermediate compound during the SHS reaction, because of insufficient nitrogen especially in the central portion of the sample. On the other hand, the XRD spectrum of Fig. 10(b) represents a combination of three species, including the titanium carbonitride Ti(C,N), intermediate nitride phase $Ti_2N$, as well as the unreacted titanium. The presence of elemental titanium in Fig. 10(b) was attributed to the fact that the sample of Ti + 0.3C contained more available titanium than did the Ti + 0.5C sample. Therefore, some titanium remained unreacted under a low degree of nitridation.

Results of XRD analysis of combustion products with complete conversion to form the desired compositions of $TiC_{0.5}N_{0.5}$, $TiC_{0.7}N_{0.3}$, and $TiC_{0.3}N_{0.7}$ are presented in Fig. 11(a)–(c), respectively. The XRD patterns shown in Fig. 11(a)–(c) are identical and match perfectly with that of the stoichiometric titanium carbonitride Ti(C,N).

## 4. Summary and conclusions

This study represents the first attempt to comprehensively investigate the direct synthesis of stoichiometric carbonitrides with different [C]/([C] + [N]) ratios by SHS in gaseous nitrogen. The initial sample density and the addition of diluent TiN were demonstrated to greatly affect the final composition of combustion products.

The SHS process to produce titanium carbonitride was characterized by both the planar combustion front propagating in a steady manner and the afterburning reaction after the passage of the flame-front. For the undiluted samples, the propagation of the flame-front was accompanied by a significant melting of the test sample. However, the addition of TiN as a diluent in the reactant mixture effectively reduced the melting of samples and thus enhanced the extent of conversion substantially. In the synthesis of $TiC_{0.5}N_{0.5}$ and $TiC_{0.7}N_{0.3}$, the flame-front propagation velocity was almost independent of the nitrogen pressure, implying that the reaction between titanium and carbon was dominant in the combustion front and nitridation took place largely in the afterburning stage. Because there was more available titanium in the samples used to produce $TiC_{0.3}N_{0.7}$, the flame-front velocity increased with nitrogen pressure, suggesting that the participation of nitrogen in the reaction of combustion front became important.

In the synthesis of $TiC_{0.5}N_{0.5}$, XRD analysis indicated that the undiluted samples of $Ti + 0.5C$ yielded final products containing a large amount of the intermediate nitride phase $Ti_2N$. Complete conversion to produce $TiC_{0.5}N_{0.5}$ was achieved by using TiN-diluted samples of $0.65Ti + 0.5C + 0.35TiN$ with a green density of 50% TMD under nitrogen pressures higher than 1.3 MPa. Due to the increase of nitrogen uptake by decreasing the sample green density, the carbonitride $TiC_{0.5}N_{0.5}$ was also produced from a 40% TMD sample with a less diluent content (i.e., $0.75Ti + 0.5C + 0.25TiN$) and at a lower nitrogen pressure (i.e., 1.14 MPa), as compared with those conditions required for the 50% TMD sample. For the stoichiometric carbonitride with a $[C]/([C] + [N])$ ratio higher than 0.5, such as $TiC_{0.7}N_{0.3}$, the required diluent content and nitrogen pressure were further reduced. Experimental results reported that the final product of $TiC_{0.7}N_{0.3}$ was successfully synthesized from the 40% TMD sample with an initial composition of $0.9Ti + 0.7C + 0.1TiN$ under nitrogen pressures of 0.62 MPa and above.

In the synthesis of $TiC_{0.3}N_{0.7}$, the unreacted titanium and intermediate nitride phase $Ti_2N$ were found in the end product obtained from the undiluted sample with the composition of $Ti + 0.3C$. Owing to the high nitrogen content in the $TiC_{0.3}N_{0.7}$, the amount of diluent in the reactant mixture plays an important role in the degree of conversion. Synthesized products with a composition very close to the desired composition of $TiC_{0.3}N_{0.7}$ were yielded by using the $0.6Ti + 0.3C + 0.4TiN$ samples in nitrogen of 1.65 MPa.

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