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Combustion characteristics of SHS process of titanium nitride with TiN dilution

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Abstract

An experimental investigation of self-propagating high-temperature synthesis (SHS) of titanium nitride (TiN) was conducted using titanium compacts with TiN dilution in gaseous nitrogen. The objective of this study was to study the effect of diluent content on the combustion temperature, flame-front propagation velocity, and product morphology and composition. In addition, SHS characteristics, such as the melting and afterburning phenomena, associated with the titanium/nitrogen system were photographically presented. It was found that all undiluted titanium samples showed a considerable melting of titanium powders during the SHS process and thus led to a low degree of nitride conversion about 20–30%. The dilution of TiN in the reactant mixtures decreased the combustion temperature and reduced the melting of titanium. As a result, the TiN-diluted sample retained its porosity for the continuous filtration of nitrogen gas, hence leading to a prolonged afterburning stage where the nitridation continued. With the TiN dilution, the final product consisting of more than 90% of TiN was obtained in this study.

Keywords: Titanium nitride; SHS; Combustion; Dilution; Afterburning

1. Introduction

Metal nitrides, especially those of transition metals, have received increasing attention in recent years because of their unique chemical and physical properties. Among such materials, titanium nitride (TiN) is particularly interesting, due to its superior hardness, good thermal stability, high wear resistance, excellent corrosion resistance, and relatively high electrical conductivity [1]. Titanium nitride is also an outstanding candidate as a binding phase in the sintering of boron nitride to improve the mechanical properties [2].

Besides the traditional method of direct reaction between titanium and nitrogen gas or ammonia at near 1200 °C for extended periods of time, TiN could also be produced by the self-propagating high-temperature synthesis (SHS) in a time scale of seconds. Due to the sufficiently exothermic reaction between titanium and nitrogen, the reaction initiated at one end of the sample by a heat source generates a self-sustained combustion wave traveling through the sample. SHS has been recognized as an attractive alternative to the conventional methods of producing advanced materials [3–6]. More than 500 kinds of materials, including carbides, borides, silicides, nitrides, sulfides, selenides, hydrides, oxides, intermetallics, and complex composites have been synthesized by applying the SHS process not only for solid–solid systems, but also for solid–gas and/or solid–liquid systems [4,5].

Combustion synthesis of titanium nitride has been conducted with high-pressure gaseous nitrogen [7–9]. Eslamloo-Grami and Munir [7,8] investigated the effects of sample porosity, nitrogen pressure, and diluent content on the combustion synthesis of titanium nitride with the use of compacted titanium samples in the form of cylindrical pellets. The melting of titanium powders during the combustion was observed, resulting in a reduction of the continuous porosity and a low degree of conversion to the nitride [7]. In order to lower the filtration resistance of compacted samples, Agrafiotis et al. [9] conducted the synthesis of titanium nitride using loosely packed powders in the form of porous beds. At a 40 atm nitrogen pressure and for a bed depth up to 3 cm, it was found that the nitrogen was available at the bottom of the sample bed and the final product was completely nitrided [9]. For the purpose

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of achieving high conversion, the synthesis of titanium nitride with liquid nitrogen was performed by Shibuya et al. [10], and the product identified as $TiN_{0.87}$ was shrunk and densified, due to the drastic increase in chamber pressure.

The objective of the present study was to experimentally investigate the synthesis of titanium nitride by SHS using compacted titanium samples diluted with TiN in gaseous nitrogen. The dynamics of combustion wave, i.e. flame-front trajectory, propagation velocity and combustion temperature, as well as the composition and morphology of final products obtained under different nitrogen pressures and diluent contents were studied. In particular, the observation of solid-flame structures and burning characteristics, such as the melting and afterburning phenomena, was performed.

2. Experimental

2.1. Test samples

Titanium (Ti) powders (Strem Chemicals, −325 mesh) of 99% purity were used as the reactant in this study and were pressed into cylindrical specimens having a diameter of 7 mm and a height of 12.5 mm. In order to obtain test samples with different porosities, the titanium compacts were formed with the green packing densities equal to 45, 50, and 55% of the theoretical maximum density (TMD) of titanium (4.5 g/cm^3).

In order to avoid the melting of titanium compacts, the combustion product was suggested to serve as a diluent to lower the sample temperature and then to increase the conversion percentage [8]. The addition of TiN powders as an inert material in the reactant mixture did not cause any variation in the homogeneity of the combustion product. For the preparation of samples that contained the final product TiN as a diluent, both Ti and TiN powders (Strem Chemicals, −325 mesh) were dry mixed in a ball mill for 10 h. The diluent content was ranged from 20 to 50% by weight of the total powder mixture. The density of sample compacts containing the diluent, TiN, was set at 55% TMD of the powder mixture. It is useful to note that since the sample diluted with 50 wt.% TiN was too fragile to handle at 55% TMD, it was prepared to have the density equal to 60% TMD in this study. After the combustion, the conversion percentage of titanium to TiN was calculated from the measurement of weight change of sample compacts assuming a stoichiometric nitride as the final product [7–9].

2.2. Experimental setup and instrumentation

The reaction between the titanium sample and nitrogen gas was carried out in a stainless-steel windowed combustion chamber (Fig. 1) under a nitrogen pressure ranging from 0.27 to 1.5 MPa. The nitrogen gas used in this study had a purity of 99.999%. The ignition of titanium samples was accomplished by a heated tungsten coil with a voltage of 60 V and a current of 1.5 A. Two windows on the combustion chamber provided visual monitoring, as well as optical diagnostics. Before the experiment, the chamber was evacuated down to 0.01 Torr and then flushed with the nitrogen gas for 2–3 min. After that, the chamber was filled with nitrogen up to the desired pressure.

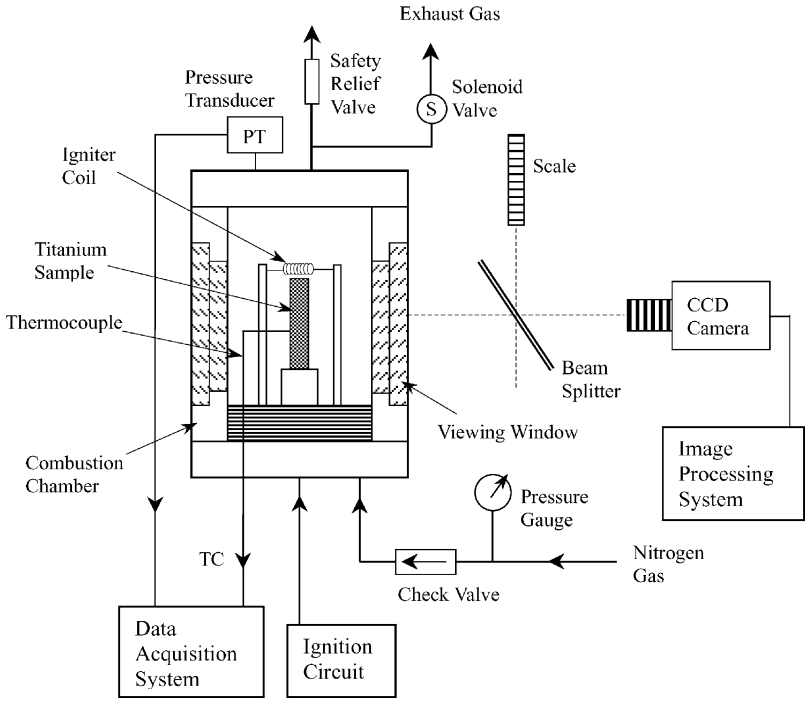

Fig. 1. Schematic diagram of experimental setup to study SHS of titanium nitride.

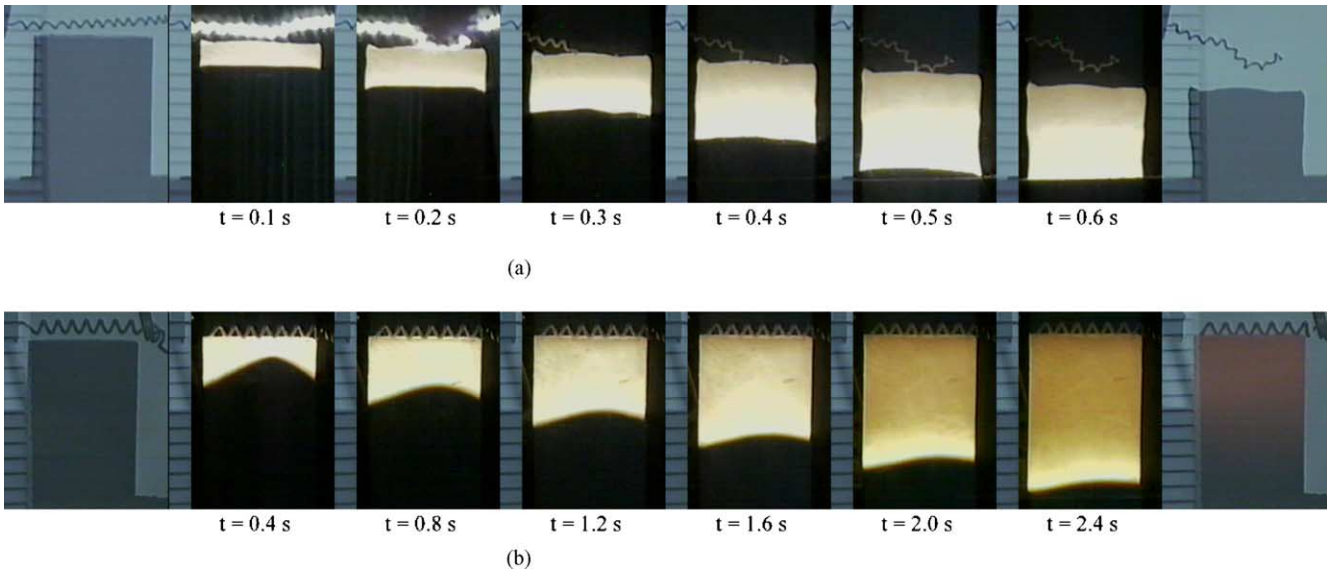

Fig. 2. Recorded images of SHS process indicating propagation of flame-front associated with (a) an undiluted sample with 45% TMD in 0.62 MPa N_2 and (b) a 40 wt.% TiN-diluted sample with 55% TMD in 0.27 MPa N_2.

The propagation rate of combustion wave was measured by the recording of the whole combustion event with a color CCD video camera (Pulnix TMC-7) at 30 frames/s. Due to the extremely high intensity of light emission during the reaction between titanium and nitrogen, the exposure time of each recorded image was set at 0.1 ms. To facilitate the accurate measurement of instantaneous locations of the combustion front, a beam splitter (Rolyn Optics), with a mirror characteristic of 75% transmission and 25% reflection, was used to optically superimpose a scale onto the image of the titanium compact. The combustion temperature of titanium sample was measured by a fine-wire (125 μm) Pt/Pt–13%Rh thermocouple (Omega Inc.) attached on the sample surface. The variation of chamber pressure during the test was monitored by a pressure transducer.

The burned samples were recovered and weighed. The microstructure of combustion product was examined under a scanning electron microscope (SEM). The chemical composition of burned samples was identified by an X-ray diffractometer (Mac Science MXP) with Cu Kα radiation operating at 40 kV.

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 of an undiluted titanium sample nitrided in nitrogen of 0.62 MPa. It is evident in Fig. 2(a) that 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 to an incandescent combustion product. The scale image

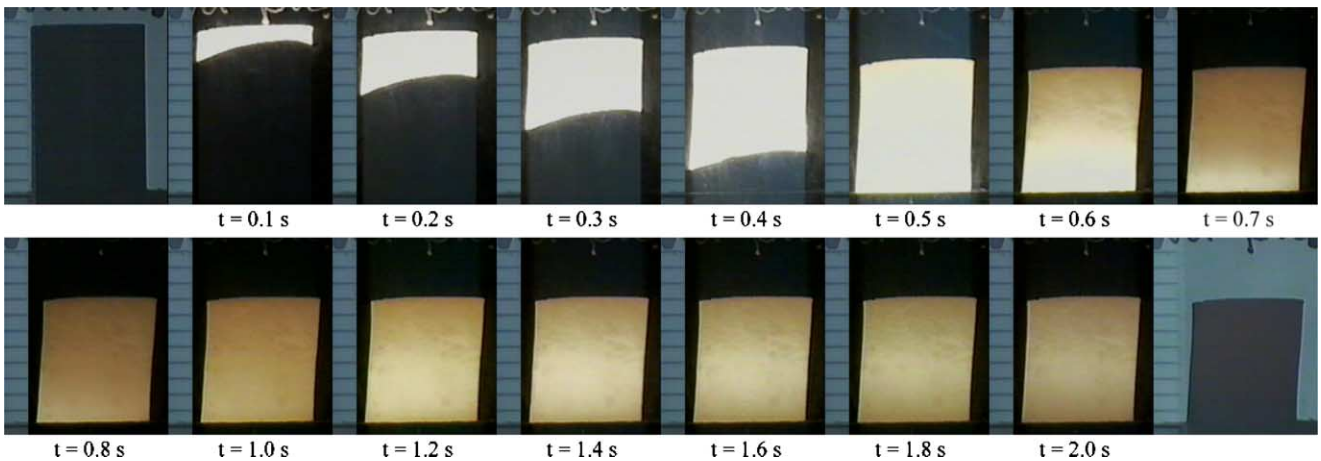

Fig. 3. Recorded burning images indicating afterburning phenomenon on a 20 wt.% TiN-diluted sample with 55% TMD in 1.14 MPa N_2.

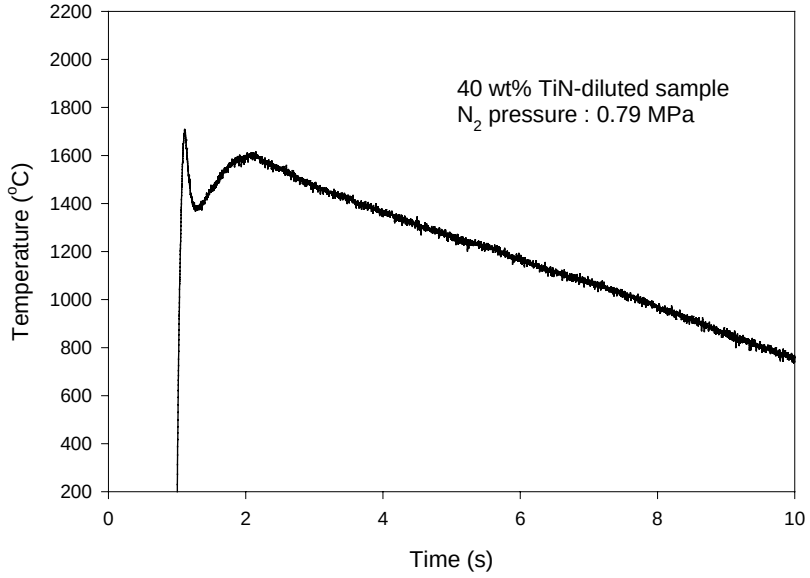

Fig. 4. Measured temperature profile of a 40 wt.% TiN-diluted sample reacted in 0.79 MPa N_2.

appeared on the left-hand side of each picture is the optically superimposed reflection described above. It is important to note that when compared with the initial dimension of the test sample the end product was apparently shrunk in height, indicating that a significant melting of titanium powders occurred during the SHS process. This also suggests the combustion temperature higher than the melting point of titanium (1660 °C). The shrinkage and/or irregular deformation were clearly observed for all of the undiluted samples after SHS in this study.

On the contrary, as shown in Fig. 2(b), the recorded images of a test sample diluted with 40 wt.% TiN indicate no shrinkage and deformation during the SHS process. The burned sample almost retained its original shape and porosity. As also shown in Fig. 2(b), after the passage of the flame-front the upper portion of the sample was gradually cooled down and revealed the yellow–gold color of titanium nitride. Within the pressure range tested in this study, both 40 and 50 wt.% TiN-diluted samples exhibited no observable deformation after the SHS process. The deformation of final products for samples initially diluted with 20 and 30 wt.% TiN was still observed.

Besides the melting of titanium, the other characteristic of titanium compacts reacted in nitrogen is the afterburning phenomenon, which means that the reaction takes place after the passage of the flame-front. Recorded images illustrating

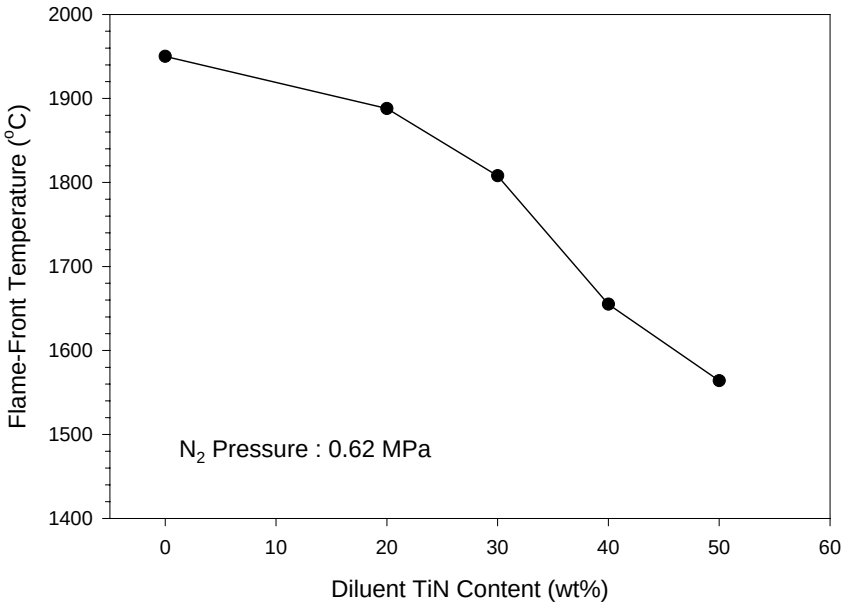

Fig. 5. Effect of diluent content on flame-front temperature of SHS of titanium nitride.

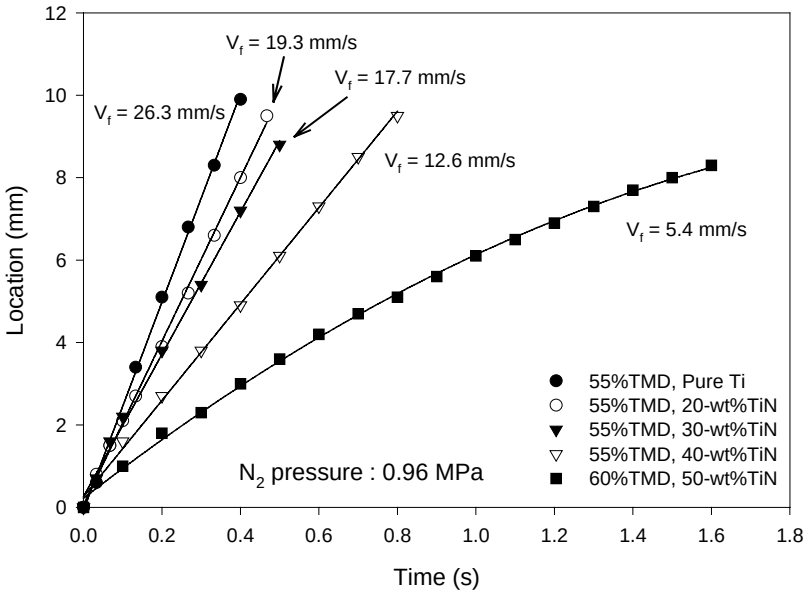

Fig. 6. Flame-front trajectories of test samples diluted with different amounts of TiN in 0.96 MPa N_2.

the afterburning reaction are presented in Fig. 3. As shown in Fig. 3, at $t = 0.5$ s the flame-front reaches the bottom of the sample and the whole sample is glowing in white. Then, the luminosity starts to fade from the top of the sample and the brightness nearly all vanishes on the sample at $t = 0.8$ s. However, at $t = 1.0$ s the sample appears to reglow, implying that the reaction resumes. The luminosity on the sample is clearly observed during the time period of 1.2–1.8 s, beyond which the brightness fades away gradually. This observation provides a visual evidence of the afterburning stage, where a prolonged bulk post-combustion occurs. It is useful to note that the sample shown in Fig. 3 was diluted with 20 wt.% TiN and experienced a noticeable shrinkage during the nitridation at 1.14 MPa of nitrogen.

In addition to the recorded burning images, the afterburning reaction was demonstrated by the measured temperature profile. Fig. 4 represents a typical temperature profile of the burning sample in this study. As shown in Fig. 4, the appearance of the abrupt peak signifies the arrival of the flame-front and the subsequent temperature rise followed by a gradual decline represents a prolonged post-combustion stage; that is, an afterburning region. Moreover, the temperature in the afterburning stage is usually lower than the peak temperature of the flame-front. It was suggested by the above

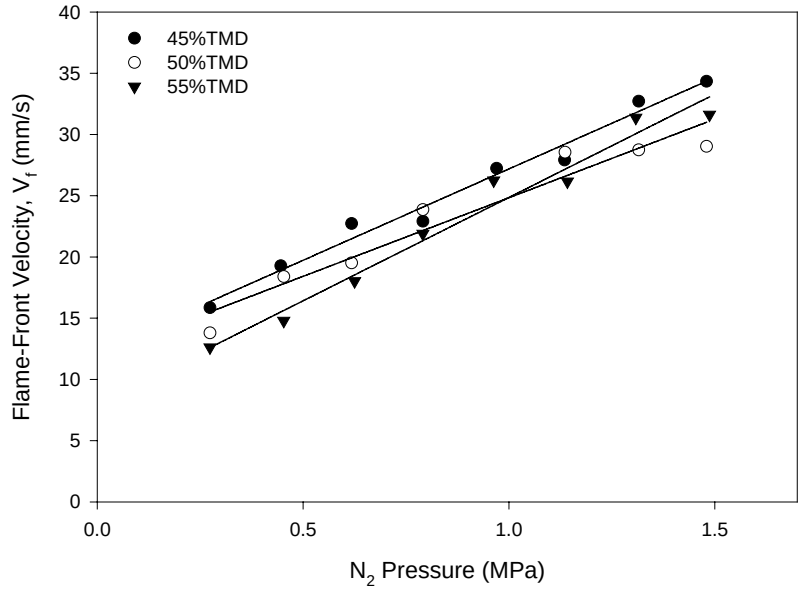

Fig. 7. Effect of nitrogen pressure on flame-front propagation velocity of undiluted titanium samples with different compacted densities.

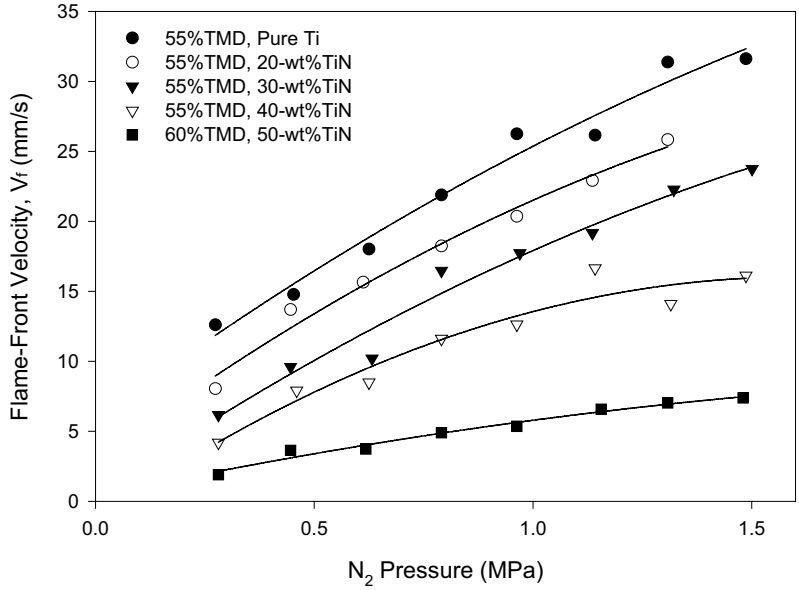

Fig. 8. Effect of nitrogen pressure on flame-front propagation velocity of test samples diluted with different amounts of TiN.

observations that the conversion of titanium to nitride at the combustion front was always incomplete and a significant part of nitridation occurred during the afterburning stage. As reported by Eslamloo-Grami and Munir [7], some of the solid solution further reacts with nitrogen to form TiN in the afterburning period. The decrease of flame-front temperature with increasing diluent content is shown in Fig. 5. It is apparent that together with the undiluted sample, combustion temperatures of samples diluted with 20 and 30 wt.% TiN are higher than the melting point of titanium (1660 °C). This further confirms the observation of sample melting for undiluted and 20 and 30 wt.% TiN-diluted samples during the SHS process.

3.2. Measurement of flame-front trajectory and propagation velocity

The flame-front propagation velocity (V_f) was determined in this study from the measured flame-front trajectory, which was constructed upon the recorded film images. Fig. 6 shows a plot of flame-front trajectories of test samples diluted with different amounts of TiN. Except for the 50 wt.% TiN-diluted sample, the linearity of the time derivative of trajectories indicates that the propagation of flame-front can be treated as a constant-velocity event. For the sample diluted with 50 wt.% TiN, the flame-front propagation velocity was slightly higher in the early stage right after the ignition,

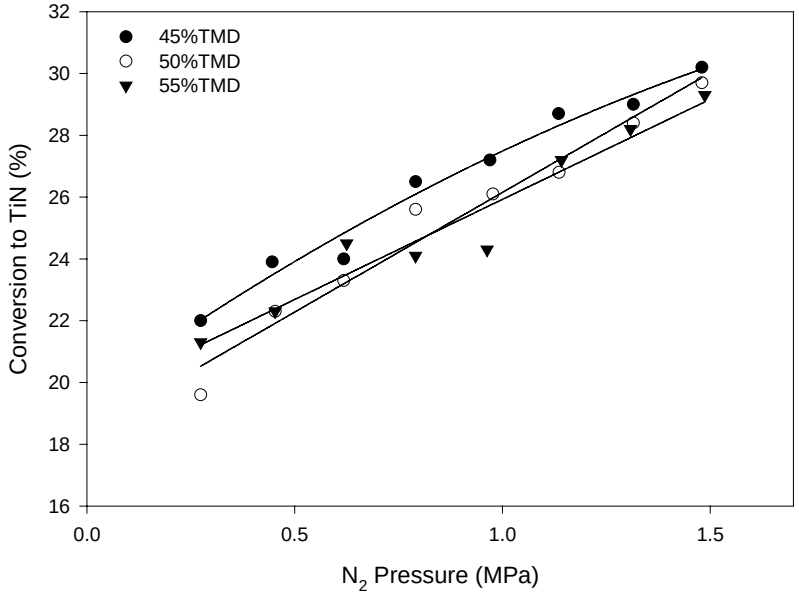

Fig. 9. Effect of nitrogen pressure on conversion percentage of undiluted samples with different compacted densities.

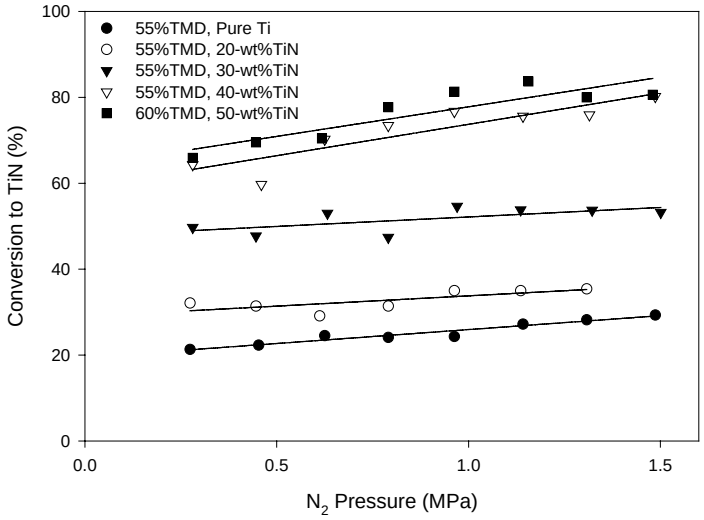

Fig. 10. Effect of nitrogen pressure on conversion percentage of test samples diluted with different amounts of TiN.

and then the velocity decelerated, finally reaching a nearly constant value. The relatively high propagation velocity in the beginning was attributed to the thermal energy supplied by the igniter, and the constant velocity in the later stage represents the self-sustained propagation of flame-front. As can be seen in Fig. 6, the flame-front propagation velocity was decreased by increasing the diluent concentration.

Fig. 7 shows the effect of nitrogen pressure on the flame-front propagation velocity (V_f) of undiluted titanium samples with different compacted densities. The flame-front propagation velocity increases substantially with increasing nitrogen pressure, due to an increase of the initial nitrogen concentration within the porous sample. In addition, the flame-front propagation velocities of the sample with a density of 45% TMD were slightly higher than those of 50 and 55% TMD samples, which have very close front propagation velocities. It is believed that in the absence of the melting of compacted powders, the sample porosity should play an important role in the nitrogen filtration, which affects the flame-front propagation rate and the subsequent conversion percentage. As shown in Fig. 7, the effect of sample density on the flame-front propagation velocity is not very pronounced for undiluted titanium samples, largely because of the considerable melting of titanium powders during the SHS process.

The effect of diluent content on the flame-front propagation velocity is shown in Fig. 8. It was found that the propagation velocity became noticeably slower when the diluent concentration was increased. Similar to undiluted samples, the front propagation velocity of diluted samples increases with increasing nitrogen pressure.

3.3. Analysis of product composition and morphology

The molar conversion percentage of titanium to nitride for the undiluted samples under different nitrogen pres-

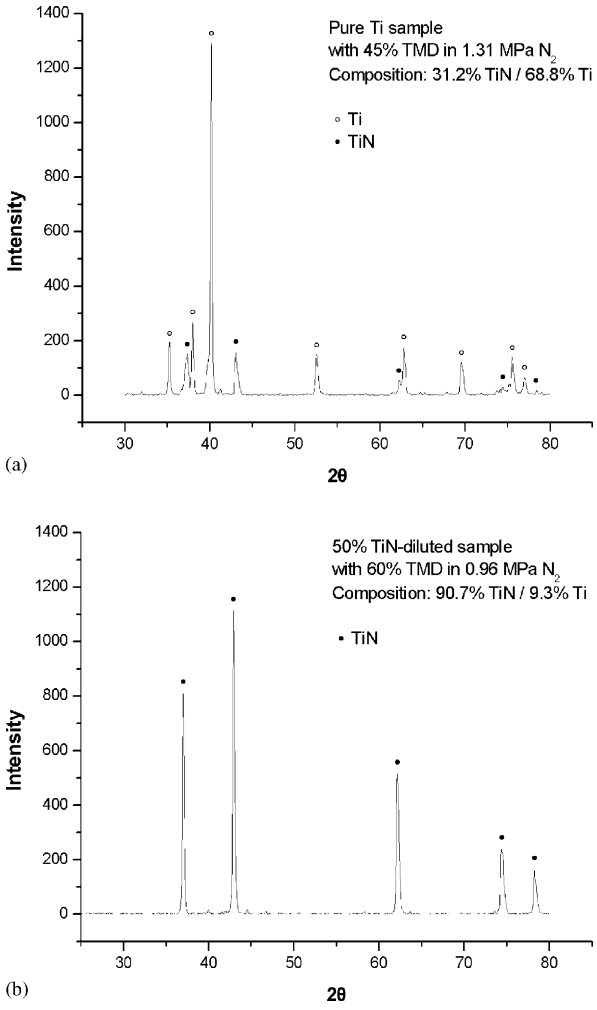

Fig. 11. XRD spectra of products obtained from (a) an undiluted sample reacted in 1.31 MPa N_2 and (b) a 50 wt.% TiN-diluted sample reacted in 0.96 MPa N_2.

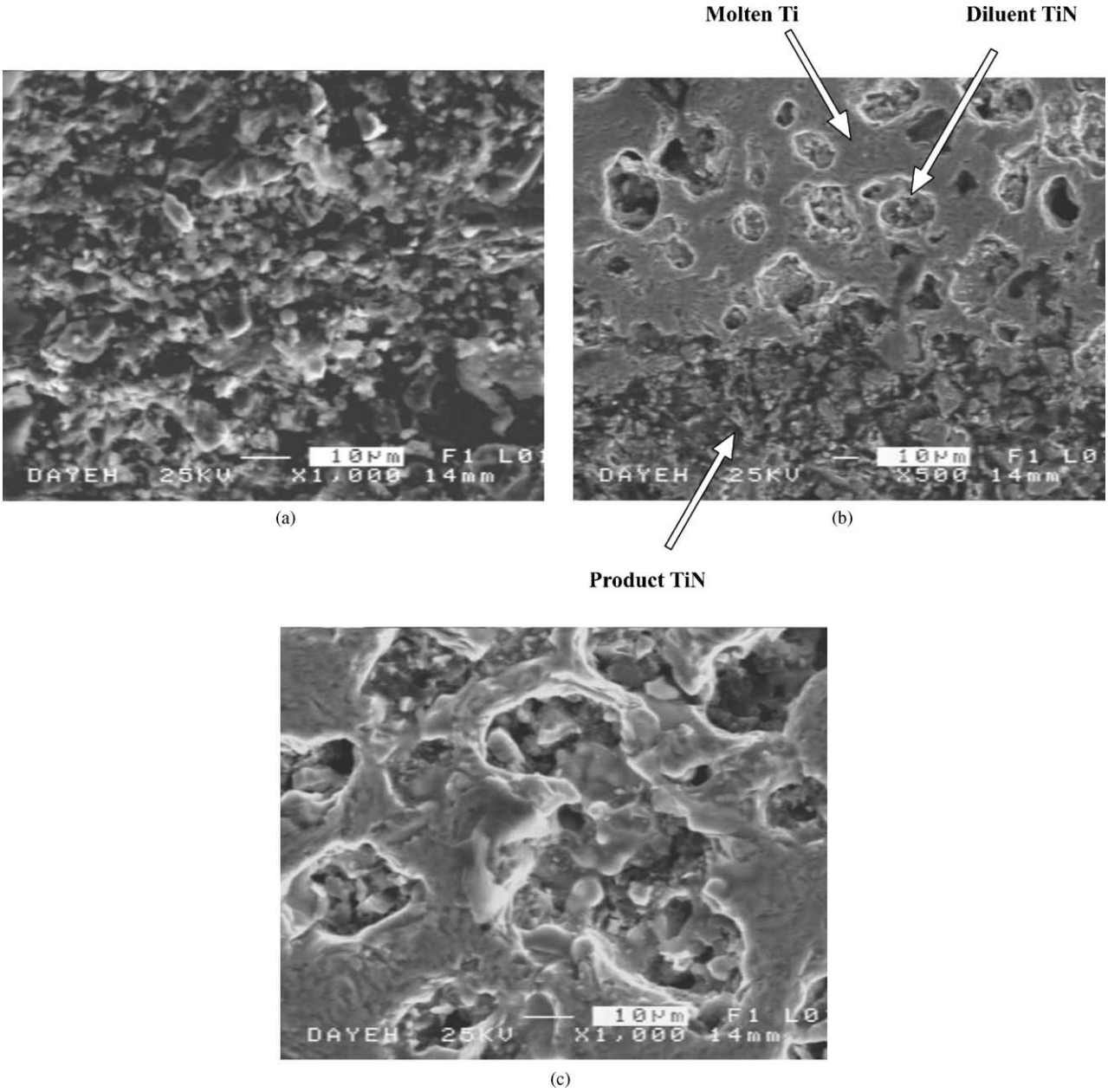

Fig. 12. SEM micrographs of a 30 wt.% TiN-diluted sample in 0.45 MPa nitrogen: (a) near surface of sample, (b) halfway to center of sample, and (c) near center of sample.

sures is shown in Fig. 9. The conversion percentage increases with increasing nitrogen pressure. As indicated in Fig. 9, the sample porosity produced nearly no influence on the nitride conversion percentage of undiluted samples. The 45% TMD sample exhibits slightly higher nitride conversion than the 50 and 55% TMD samples, whose conversion percentages were quite close. Generally speaking, low conversions of around 20–30% were obtained for all undiluted samples. This was because that the filtration of nitrogen into the compacted sample was hindered by the melting of titanium powders, resulting in a lack of nitrogen in the inner portion of the sample. The similarity between nitride conversion percentage (Fig. 9) and front propagation velocity (Fig. 7) of the undiluted sample with respect to nitrogen pressure and sample density implies that the main nitridation occurs at the combustion front for the undiluted sample, for which the afterburning reaction contributes no significance to the conversion percentage due to the melting of titanium in the undiluted sample.

Fig. 10 shows the molar conversion percentage as a function of nitrogen pressure and diluent content. It was found that the conversion percentage was greatly enhanced by the dilution with the TiN powders. The conversion percentage

over 80% was achieved for the 50 wt.% TiN-diluted sample. The nitride conversion increases with the increase in either the diluent concentration or the nitrogen pressure. This implies that the penetration of gaseous nitrogen through the pores of the compacted sample maintained the local availability of nitrogen, since the melting of titanium was reduced by the addition of TiN. However, as shown in Fig. 10, the increase of TiN dilution content from 40 to 50 wt.% produced no obvious improvement in the nitride conversion percentage. This was partly caused by the lower combustion temperature for the 50 wt.% TiN-diluted sample. In part, this was due to the higher sample density (60% TMD), i.e. lower sample porosity, for the 50 wt.% TiN-diluted sample.

The composition of burned samples, which exhibited a bright gold color of TiN rather than the gray titanium color, was determined by the X-ray diffraction (XRD) analysis. Fig. 11(a) shows the XRD spectrum of the product obtained from an undiluted sample reacted in 1.31 MPa nitrogen. It is evident to see in Fig. 11(a) that the XRD pattern represents a combination of two spectra signifying titanium and TiN, respectively. This confirms that titanium did not react completely with nitrogen to form titanium nitride for undiluted samples. Fig. 11(a) also reveals a great amount of titanium left unreacted, because the intensity of XRD characteristic peaks of TiN is relatively low when compared with that of Ti signals. Based upon the weight calculation, the conversion percentage of the sample presented in Fig. 11(a) was only about 31.2%.

The XRD spectrum shown in Fig. 11(b) corresponds to the burned product obtained from a 50 wt.% TiN-diluted sample under 0.96 MPa nitrogen. As indicated in Fig. 11(b), the XRD spectrum matches the pattern of TiN, implying that the TiN is the dominant component and the amount of Ti is trivial. According to the conversion calculation, the conversion percentage was about 82% for the sample shown in Fig. 11(b). In other words, with the consideration of the diluent concentration, the final composition of this burned sample was made up of about 91% TiN.

The morphology of a partially-molten sample initially diluted with 30 wt.% TiN was examined by SEM and shown in Fig. 12(a)–(c). Fig. 12(a) shows the microstructure at locations near the surface of the sample, where the titanium powders were almost totally converted to TiN and no evidence of melting was observed due to the high melting point of TiN (2950 °C). The microstructure at locations about halfway between the surface and the center of the sample is shown in Fig. 12(b). A molten layer formed by the melting of titanium was clearly observed in the upper portion of Fig. 12(b). There exist some individual particles surrounded by the molten titanium layer. Those particles were believed to be the diluted TiN powders. The microstructure shown in the lower portion of Fig. 12(b) is similar to that shown in Fig. 12(a) and represents the product TiN. Fig. 12(c) representing the microstructure at locations near the center of the sample shows the molten titanium, diluted TiN particles, and some remaining pores.

4. Conclusions

Combustion characteristics, including flame-front velocity and combustion temperature, and product composition and morphology of titanium nitride produced by SHS are greatly affected by the addition of TiN as the diluent. Based upon the experimental observations and measurements of this study, several important results are summarized below.

The observation of the SHS process associated with titanium in nitrogen to form titanium nitride clearly indicates the propagation of a self-sustained flame-front. Both the melting of titanium compacts during the SHS process and the occurrence of afterburning reaction following the passage of combustion front were observed photographically. Moreover, measured temperature profiles indicated the appearance of an abrupt peak signifying the fast propagation of the flame-front, and a subsequent temperature rise representing the prolonged afterburning period.

All undiluted titanium samples in this study showed a considerable melting of titanium powders during the SHS process and thus led to a low degree of nitride conversion about 20–30%. Due to the melting of undiluted samples, the porosity of test compacts did nearly not contribute to the flame-front velocity and nitride conversion. The addition of TiN as a diluent in the titanium sample decreased the combustion temperature; as a result, the melting of test compacts was reduced and the nitride conversion percentage was greatly enhanced. The final product consisting of more than 90% of TiN was obtained from TiN-diluted samples.

The XRD analysis of burned products identified the formation of TiN and the existence of unreacted Ti. The molten titanium in the interior of test sample was clearly observed in the SEM micrograph. Moreover, the synthesized TiN at locations near the sample surface exhibited a totally different microstructure from the molten titanium.

Acknowledgements

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References

[1] L.E. Toth, Transition Metal Carbides and Nitrides, Academic Press, New York, 1971.
[2] E. Benko, A. Wyczesany, T.L. Barr, CBN—metal/metal nitride composites, Ceram. Int. 26 (6) (2000) 639–644.
[3] A.G. Merzhanov, Solid flames: discoveries, concepts, and horizons of cognition, Combust. Sci. Technol. 98 (1994) 307–336.
[4] A.G. Merzhanov, History and recent development in SHS, Ceram. Int. 21 (5) (1995) 371–379.
[5] J.J. Moore, H.J. Feng, Combustion synthesis of advanced materials: Part I. Reaction parameters, Prog. Mater. Sci. 39 (1995) 243–273.
[6] J.J. Moore, H.J. Feng, Combustion synthesis of advanced materials: Part II. Classification, application and modeling, Prog. Mater. Sci. 39 (1995) 275–316.

[7] M. Eslamloo-Grami, Z. Munir, Effect of porosity on the combustion synthesis of titanium nitride, J. Am. Ceram. Soc. 73 (1990) 1235–1239.
[8] M. Eslamloo-Grami, Z. Munir, Effect of nitrogen pressure and diluent content on the combustion synthesis of titanium nitride, J. Am. Ceram. Soc. 73 (1990) 2222–2227.
[9] C.C. Agrafiotis, J.A. Puszynski, V. Hlavacek, Experimental study on the synthesis of titanium and tantalum nitrides in the self-propagating regime, Combust. Sci. Technol. 76 (1991) 187–218.
[10] M. Shibuya, J.F. Despres, O. Odawara, Characteristic sample temperature and pressure during processing of titanium nitride combustion synthesis with liquid nitrogen, J. Mater. Sci. 33 (1998) 2573–2576.