

# Effects of dilution and preheating on SHS of vanadium nitride

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## Abstract

An experimental investigation of self-propagating high-temperature synthesis (SHS) of vanadium nitride (VN) was conducted with vanadium powder compacts in gaseous nitrogen. Effects of sample density, nitrogen pressure, diluent content, and sample preheating on the degree of conversion, flame-front velocity, and combustion temperature were studied. Experimental observations showed that the SHS process of the vanadium/nitrogen reaction was characterized by the steady propagation of a planar combustion front, followed by a prolonged afterburning reaction. The flame-front velocity increased with nitrogen pressure, but decreased with sample density. For the undiluted samples, a low degree of nitride conversion between 45 and 55% was obtained, primarily due to the formation of a liquid phase at nitrogen pressures higher than 0.79 MPa. The dilution of vanadium compacts with the nitride product VN powders suppressed the liquid formation, leading to a substantial increase in the degree of conversion. In addition, the conversion percentage of VN-diluted samples was further increased by properly preheating the sample prior to ignition. Under the condition with 30 wt.% dilution and preheating at 100–200 °C, it was found that a conversion over 90% was achieved. Based upon the XRD analysis, the  $\delta$ -VN was identified as the dominant nitride phase synthesized in this study.

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## 1. Introduction

Nitrides of transition metals have received increasing attention in recent years due to their unique chemical and physical properties, such as high melting point, chemical inertness, superior hardness, metallic electrical conductivity, and low work function [1]. In addition, some nitrides and carbides of early transition metals are known to be catalytically active materials with the catalytic properties similar to those of noble metals [2,3]. Among the nitrides of early transition metals, vanadium nitride (VN) has been proved to be a highly effective catalyst for many hydrogen transfer reactions, such as the synthesis and decomposition of  $\text{NH}_3$  [3], the dehydrogenation of *n*-butane [4], and the hydrodeoxygenation of benzofuran [5]. Galesic and Kolbesen [6] studied the preparation of vanadium nitride of 200 nm thick by the rapid thermal processing and indicated at 800–850 °C only the formation of a nitrogen-lean phase  $\beta$ - $\text{V}_2\text{N}$ , which converted into a nitrogen-rich phase  $\delta$ -VN at 900–1100 °C. However, no formation of vanadium nitride was observed

in a conventional furnace at 1100 °C [6]. According to the vanadium–nitrogen phase diagram, both hexagonal  $\beta$ - $\text{V}_2\text{N}$  and cubic  $\delta$ -VN are stable phases [7].

Because of the highly exothermic nature of the reaction involving transition metals (especially in groups IVB and VB) with nitrogen, some transition metal nitrides can be synthesized by means of the self-propagating combustion. In the self-propagating high-temperature synthesis (SHS), once initiated the combustion front becomes self-sustained traveling through the sample due to the sufficient liberation of reaction heat and the final product is formed progressively without requiring additional heat [8–10]. Combustion synthesis has been recognized as an attractive alternative to the conventional methods of producing advanced materials, such as carbides, borides, silicides, nitrides, hydrides, intermetallics, and many complex composites [8–10]. The energy savings and economic benefits with the SHS process are widely acknowledged [8–10]. Among the transition metals of groups IVB and VB, the titanium–nitrogen system has been extensively investigated by SHS [11–13]. The production of niobium nitride with SHS has also been broadly studied [14–16]. Other metal nitrides, including zirconium, hafnium, and tantalum nitrides, produced using the SHS

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technique, were demonstrated by Merzhanov and Borovinskaya [17]. However, there has been a lack of SHS studies associated with the vanadium–nitrogen system.

The objective of this research was to experimentally study the synthesis of vanadium nitride by SHS using compacted vanadium samples in gaseous nitrogen. Combustion characteristics, such as combustion wave propagation, afterburning reaction, and liquid phase formation, were investigated to establish a fundamental knowledge on the vanadium–nitrogen SHS reaction. Effects of the sample density, nitrogen pressure, diluent concentration, and sample preheating temperature on the degree of conversion, combustion temperature, and flame-front propagation velocity were studied. In addition, the composition and morphology of final products obtained under different test conditions were examined.

## 2. Experimental

### 2.1. Test samples

Vanadium (V) powders (Aldrich Chemicals, –325 mesh) of 99.5% 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 prepare test samples with different porosities, the vanadium compacts were formed with the green packing densities equal to 50, 55, and 60% of the theoretical maximum density (TMD) of vanadium ( $6.1 \text{ g/cm}^3$ ).

For the preparation of test samples that contained the final nitride product as a diluent, both V and VN powders were dry mixed in a ball mill for 10 h. Dilution of the metal reactant with the final nitride product was suggested as an effective means to improve the degree of conversion, especially for the case with the formation of liquid phase during the reaction [11–13]. Moreover, the addition of product nitride powders in the reactant mixture will not cause any variation in the homogeneity of the combustion product. The diluent concentrations adopted in this study were 20 and 30% by weight of the total powder mixture. The density of VN-diluted samples was set at 50% TMD of the powder mixture. After the combustion, the conversion percentage of vanadium to nitride was calculated from the measurement of weight change of sample compacts assuming a stoichiometric nitride as the final product [11–15].

### 2.2. Experimental setup and instrumentation

The SHS reaction between the vanadium sample and nitrogen gas was carried out in a stainless-steel windowed combustion chamber (as shown in Fig. 1) under a nitrogen pressure ranging from 0.27 to 1.5 MPa. The nitrogen gas used in this study has a purity of 99.999%. Two windows on the combustion chamber provide visual monitoring, as well as optical diagnostics. The test sample was mounted in a sample holder, which was equipped with a 600 W cartridge heater used to preheat the sample prior to ignition. The main purpose of preheating in this study was to facilitate the igni-

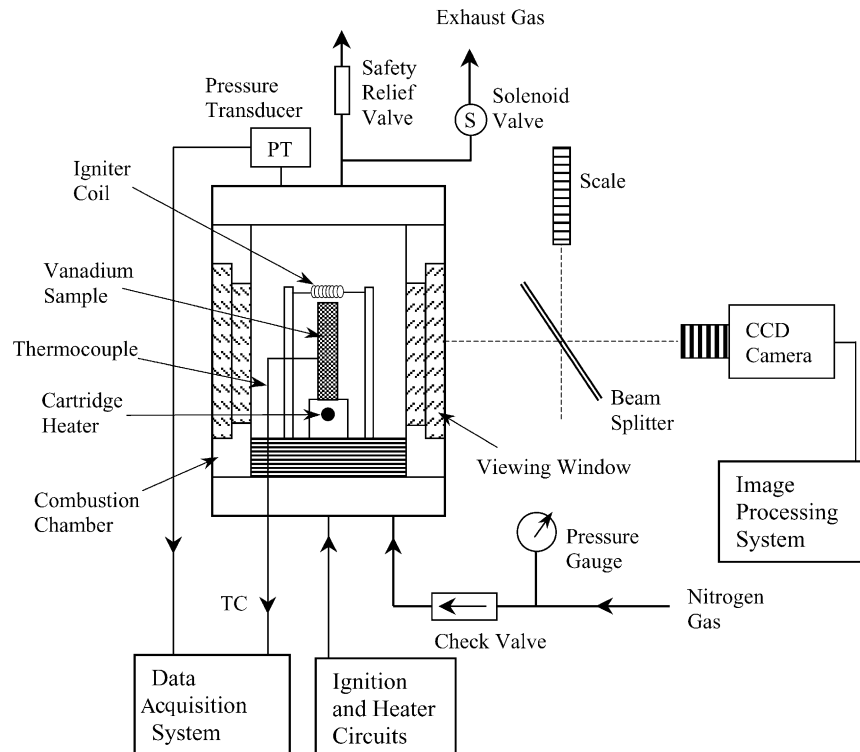


Fig. 1. Schematic diagram of experimental setup to study SHS of vanadium nitride.

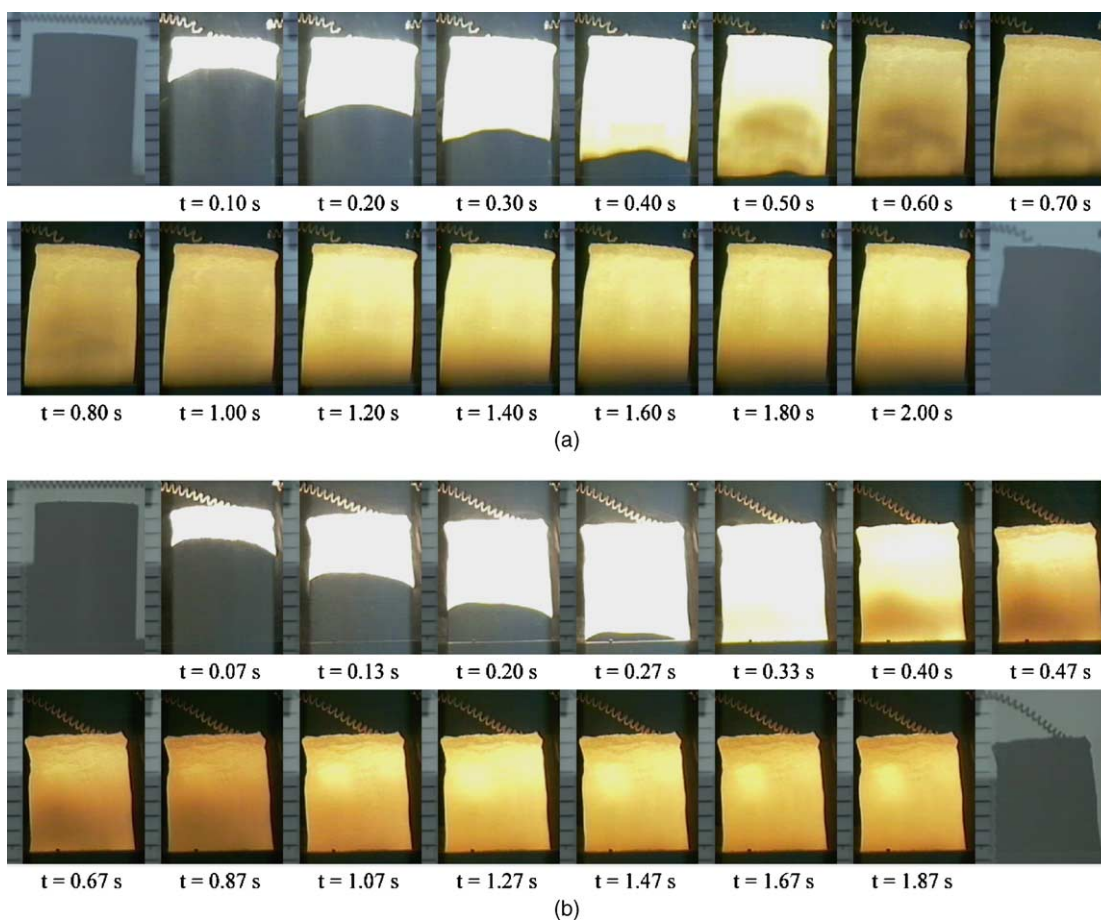


Fig. 2. Recorded burning images indicating flame-front propagation and afterburning reaction of 50% TMD undiluted samples in 1.14 MPa  $N_2$ : (a) without preheating, and (b) with preheating at 200 °C.

tion of VN-diluted samples. The effect of sample preheating on the SHS process of undiluted samples was also examined. The ignition of test samples was accomplished by a heated tungsten coil with a voltage of 60 V and a current of 1.5 A. 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.

The propagation rate of combustion wave was measured by recording the whole combustion event with a color CCD video camera (Pulnix TMC-7) at 30 frames per second. Due to the extremely high intensity of light emission during the SHS reaction between vanadium and nitrogen, the exposure time of each recorded image was set at 0.1 ms. To ensure the accurate measurement of instantaneous locations of the combustion front, a beam splitter (Rolyon

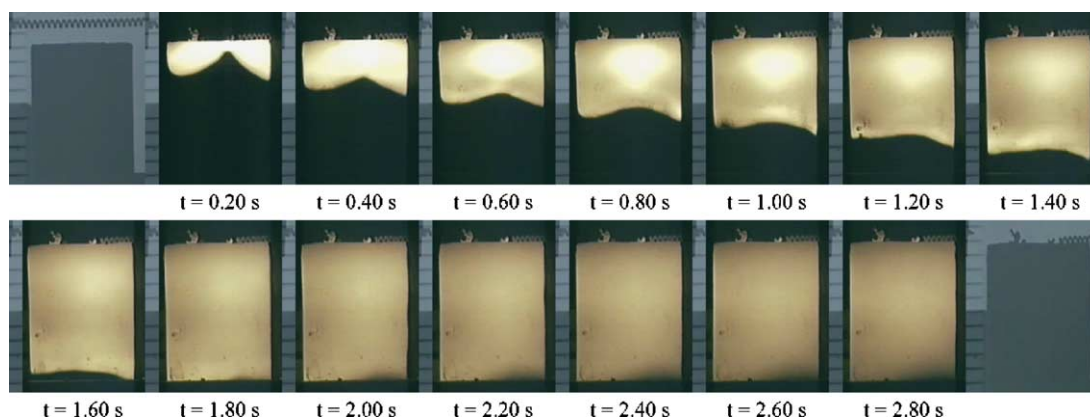


Fig. 3. Recorded burning images of a 30-wt.% VN-diluted sample with a preheating temperature of 200 °C in 1.14 MPa  $N_2$ .

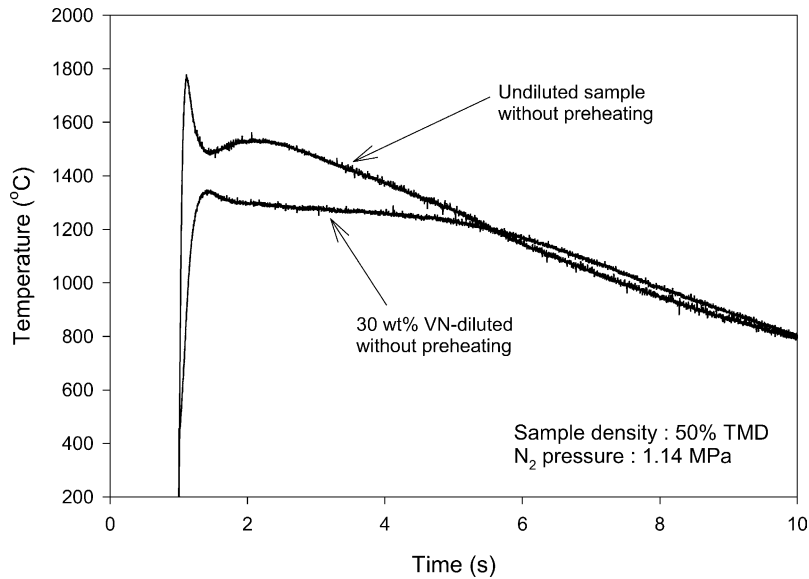


Fig. 4. Combustion temperature profiles of undiluted and VN-diluted samples without preheating in 1.14 MPa  $N_2$ .

Optics), with a mirror characteristic of 75% transmission and 25% reflection, was used to optically superimpose a scale onto the image of the vanadium compact. The combustion temperature of vanadium sample was measured by a fine-wire (125  $\mu\text{m}$ ) 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  $K\alpha$  radiation operating at 40 kV.

### 3. Results and discussion

#### 3.1. Observation of SHS characteristics

Fig. 2a and b shows two sets of recorded images illustrating the SHS processes of undiluted vanadium samples without and with preheating, respectively, in nitrogen of 1.14 MPa. It is evident in Fig. 2a and b that upon ignition a distinct and self-sustained flame front travels downward from the ignited top plane. Moreover, the self-sustained combustion wave forms a nearly planar front propagating in a steady manner, and transforms the cold reactant into an incandescent combustion product. It was found that the combustion product in Fig. 2a was slightly deformed, while the

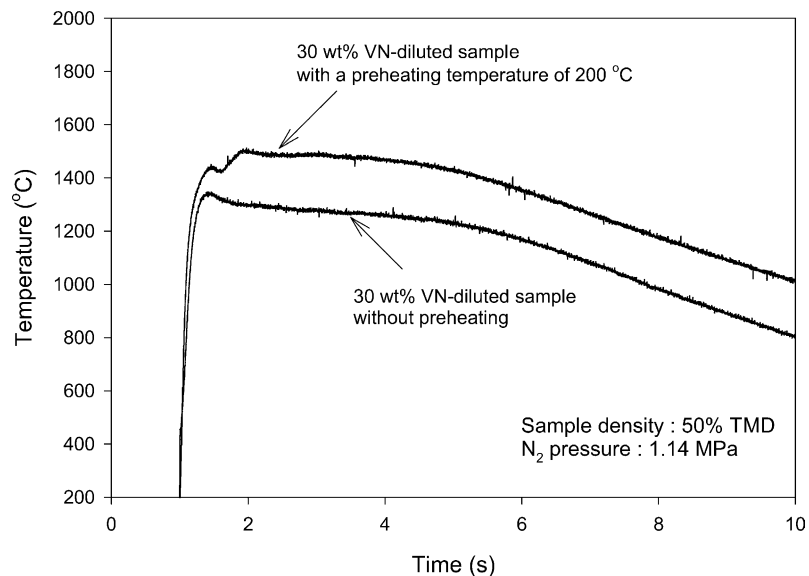


Fig. 5. Combustion temperature profiles of 30-wt.% VN-diluted samples with and without preheating in 1.14 MPa  $N_2$ .

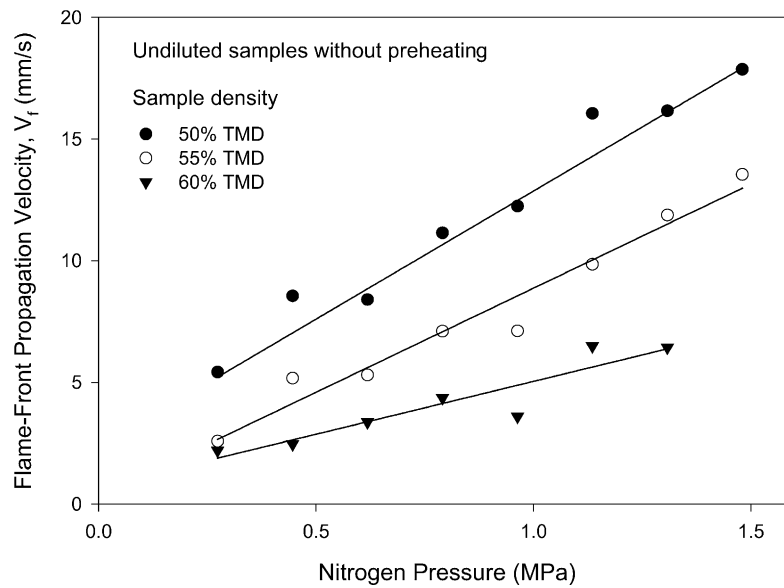


Fig. 6. Effects of nitrogen pressure and sample density on flame-front propagation velocity of undiluted samples without preheating.

end product in Fig. 2b was appreciably shrunk. This implies the formation of a liquid phase during the SHS process. In addition, it is obvious that preheating the sample prior to ignition could enhance the liquid formation, most probably due to an increase in combustion temperature. The presence of a liquid phase during the reaction improved the transfer of heat flux from the burned to the unburned region, thus leading to the increase of the propagation rate of combustion front. However, it was believed that the substantial melting might diminish the sample porosity and hence could inhibit the filtration of nitrogen gas. As a result, the nitride conversion percentage would be reduced.

Another important SHS characteristic of the vanadium–nitrogen system is the afterburning phenomenon, which rep-

resents that the reaction takes place after the passage of the flame front. As shown in Fig. 2a, the flame front reaches the bottom of the sample at about  $t = 0.5$  s, beyond which the brightness gradually vanishes from the sample. The burned sample becomes very dim at around  $t = 0.7$  s. However, at  $t = 1.0$  s the test sample appears to reglow, implying that the reaction resumes. The afterburning luminosity on the sample is clearly observable during the time period of 1.2–2.0 s in Fig. 2a. This observation provides a visual evidence of the afterburning stage, where a prolonged bulk post-combustion occurs. Similarly, the afterburning reaction was apparently seen from  $t = 1.07$  to 1.87 s in Fig. 2b.

Fig. 3 shows the SHS process of a 30-wt.% VN-diluted sample with a preheating temperature ( $T_p$ ) of 200 °C at

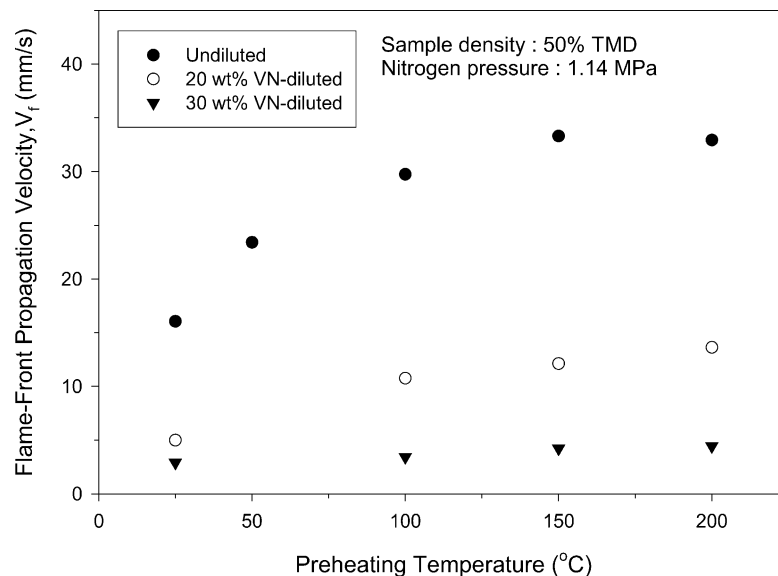


Fig. 7. Effects of sample preheating temperature and diluent concentration on flame-front propagation velocity of 50% TMD samples in 1.14 MPa  $N_2$ .

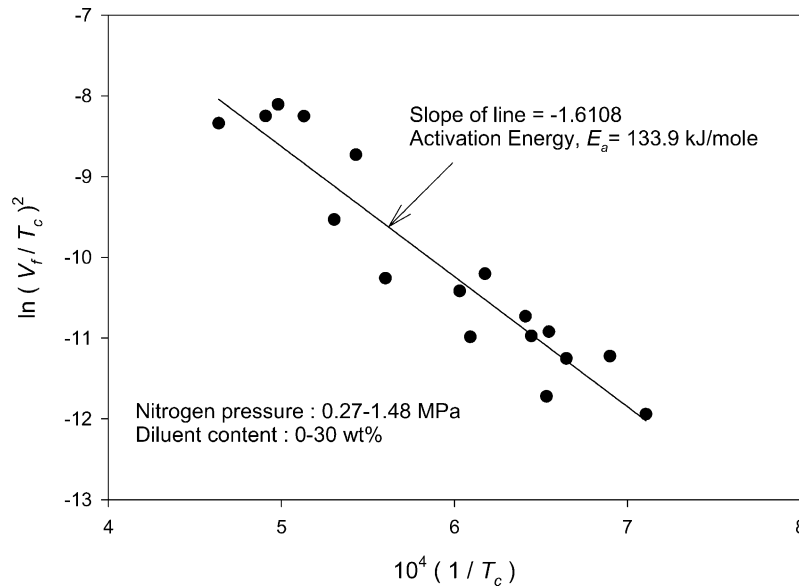


Fig. 8. Relation between flame-front velocity and combustion temperature for determination of activation energy of V/N<sub>2</sub> SHS system.

1.14 MPa of nitrogen. It is interesting to note that no shrinkage and/or deformation of the end product were found; that is, the burned sample basically retained its original shape and porosity. Moreover, when compared with the undiluted samples, the luminosity on the burning VN-diluted sample is less intense and the flame-front propagation rate is much lower. These observations could be largely attributed to the decrease of combustion temperature by the addition of VN powders as a diluent in the test sample.

### 3.2. Measurement of combustion temperature

In addition to the recorded burning images, the SHS characteristics can also be demonstrated by the measured

temperature profile. Fig. 4 presents typical temperature profiles of burning samples with and without VN dilution. It is obvious that the combustion temperature ( $T_c$ ) of VN-diluted sample is significantly lower than that of undiluted sample. As shown in Fig. 4, for the undiluted sample the appearance of an abrupt peak signifies the arrival of the flame front propagating at a high speed. The subsequent temperature rise followed by a gradual decline represents a prolonged post-combustion stage; that is, an afterburning period. In contrast, the absence of a sharp rise in temperature was noticed for the 30-wt.% VN-diluted sample, mostly due to the relatively low flame-front propagation velocity. After the passage of the flame front, the temperature profile of VN-diluted sample reveals a fairly flat plateau region at

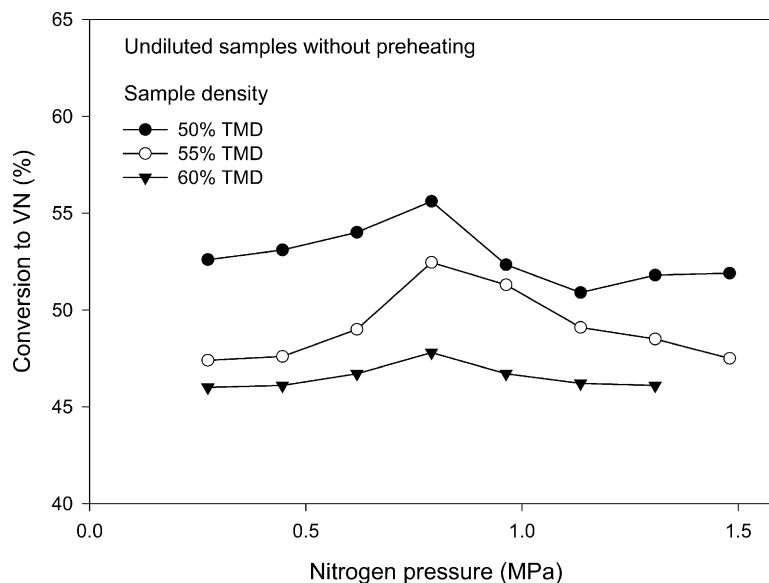


Fig. 9. Effects of nitrogen pressure and sample density on nitride conversion percentage of undiluted samples without preheating.

high temperatures for about 3 s, implying that the reaction continues behind the combustion front.

The effect of sample preheating on the combustion temperature is shown in Fig. 5. Although preheating VN-diluted samples was essentially used to facilitate the ignition, it still contributed an increase in combustion temperature, as shown in Fig. 5. Even with preheating the combustion temperature of VN-diluted sample was found to be lower than that of undiluted sample under the same nitrogen pressure. It is important to note that the preheating temperature employed in this study was properly controlled at within 200 °C, so that during the SHS process the VN-diluted sample did not produce a liquid phase, which might reduce the sample porosity and hence lower the degree of conversion.

### 3.3. Measurement of flame-front propagation velocity

Fig. 6 shows the effects of nitrogen pressure and sample density on the flame-front propagation velocity ( $V_f$ ) of undiluted samples. It was found that the flame propagation velocity was increased by increasing the nitrogen pressure, due to the increase of the initial nitrogen concentration within the porous sample. As also shown in Fig. 6, the propagation velocity increases with decreasing sample density, since the sample with a lower density offers a better permeability for nitrogen gas to penetrate.

Effects of diluent content and sample preheating temperature on the flame-front propagation velocity are presented in Fig. 7. For the undiluted samples, the flame-front propagation velocity increases substantially with sample preheating temperature, primarily due to the excessive melting of the test sample, as shown in Fig. 2b. Under the condition without preheating ( $T_p = 25$  °C in Fig. 7), the addition of diluent to the sample results in a considerable decrease in

the flame velocity. The flame-front velocity of VN-diluted samples was also increased by the preheating. However, the influence of sample preheating on the flame velocity was found to be less pronounced as the diluent concentration was increased.

A typical approach to the investigation of the mechanism of self-sustained reactions is through a determination of the dependence of the flame-front velocity on combustion temperature. Such a dependence is expressed in the following simplified form [12,15].

$$\left(\frac{V_f}{T}\right)^2 = K(R/E_a) \exp(-E_a/RT_c)$$

where  $V_f$  is the velocity of the combustion wave,  $T_c$  is the combustion temperature,  $E_a$  is the activation energy of the process,  $R$  is the gas constant, and  $K$  is a constant which includes the heat capacity and density of the product and the heat of reaction. Fig. 8 is a plot of  $\ln(V_f/T_c)^2$  versus  $1/T_c$  for samples reacted under nitrogen pressures in the range from 0.27 to 1.48 MPa. From the slope of the best-fit line of all the data in Fig. 8, an activation energy,  $E_a$ , of 134 kJ/mol was calculated for the vanadium–nitrogen reaction.

### 3.4. Analysis of product composition and morphology

Fig. 9 shows the nitride conversion percentage of undiluted samples as a function of nitrogen pressure and sample density under the condition without preheating. It is evident that the conversion percentage increases with decreasing sample density. This is because compacted samples with a lower density not only possess a larger amount of nitrogen within the porous structure, but also provide a higher permeability for the filtration of nitrogen. As far as the variation of conversion percentage with nitrogen pressure

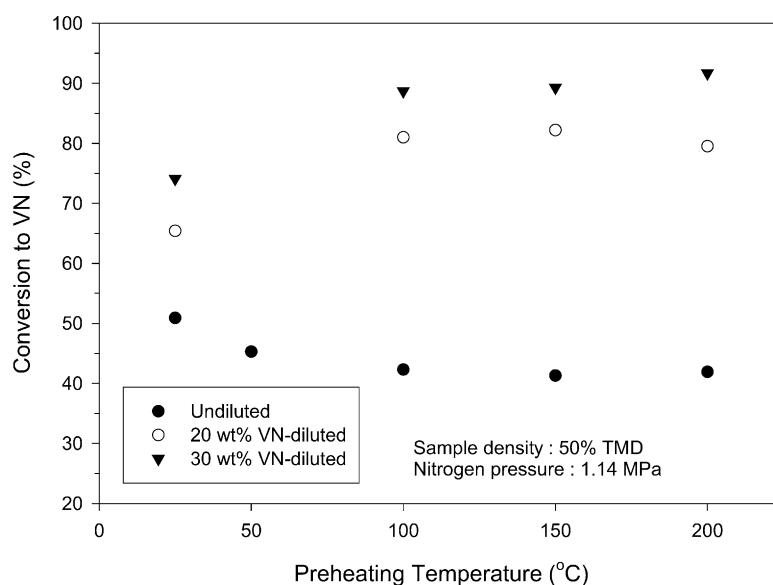


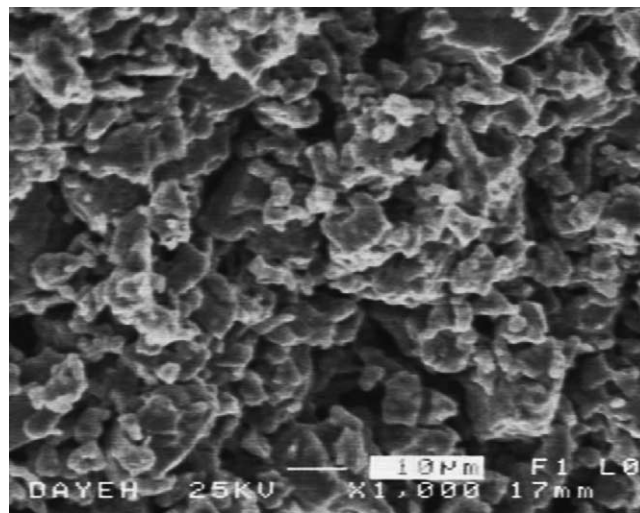
Fig. 10. Effects of sample preheating temperature and diluent concentration on nitride conversion percentage of 50% TMD samples in 1.14 MPa  $N_2$ .

was concerned, an interesting trend was observed. That is, a slight increase in the conversion percentage was found with nitrogen pressures from 0.27 to 0.79 MPa, beyond which the degree of conversion decreased. This was believed to be caused by the fact that at nitrogen pressures above 0.79 MPa, a liquid phase formed in the central portion of the sample; therefore, the continuous penetration of nitrogen gas into the sample was hindered by the formation of liquid phase, resulting in the decrease of the conversion percentage. Generally speaking, a low degree of conversion between 45 and 55% was yielded for the undiluted samples.

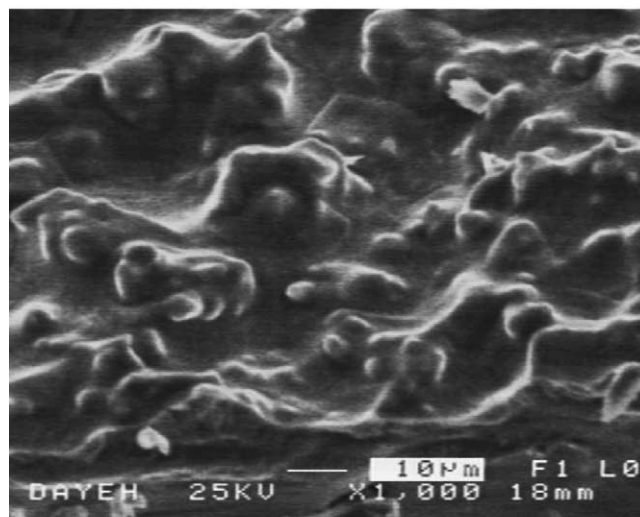
The dependence of nitride conversion percentage on preheating temperature and diluent content is shown in Fig. 10. The addition of VN powders as a diluent in the sample was found to be very effective in increasing the degree of conversion. As shown in Fig. 10, the conversion percentage of samples without preheating ( $T_p = 25^\circ\text{C}$ ) increases from around 51% for the undiluted sample to about 74% for the 30-wt.% VN-diluted sample. Preheating the undiluted sample led to a decrease in conversion percentage because of the formation of excessive liquid phase during the reaction. On the contrary, preheating enhanced the conversion percentages of VN-diluted samples, primarily due to the increase of combustion temperature. A nitride conversion over 90% was obtained from a 30-wt.% VN-diluted sample under preheating at 100–200 °C.

Fig. 11a and b shows the microstructure of combustion products obtained from undiluted samples without preheating in nitrogen of 0.62 and 0.96 MPa, respectively. Fig. 11a indicates that the burned sample at 0.62 MPa of nitrogen remains in solid phase. When compared to the reactant powders, the particle morphology did not change after the SHS reaction. This not only suggests no melting of the vanadium particle or product nitride, but also implies without formation of any liquid phase during the SHS process at 0.62 MPa of nitrogen. However, the presence of a liquid phase is clearly observed in Fig. 11b. This finding further verifies that the decrease of nitride conversion percentage at nitrogen pressures higher than 0.79 MPa was caused by the formation of liquid phase during the reaction. Moreover, it was believed that the liquid layer was composed of certain intermediate products, rather than vanadium nitride (VN) or unreacted vanadium. This was because the combustion temperatures obtained in this study for unpreheated samples are lower than the melting points of vanadium (1917 °C) and its nitride (2177 °C).

Results of XRD analyses of burned samples under different test conditions are presented in Fig. 12a–c. Fig. 12a indicates the composition of the final product obtained from an undiluted sample without preheating at 1.14 MPa of nitrogen. The XRD pattern in Fig. 12a represents a combination of three species, including two nitride phases of  $\delta$ -VN and  $\beta$ -V<sub>2</sub>N, as well as the elemental vanadium. The  $\beta$ -V<sub>2</sub>N phase was considered as an intermediate compound during the SHS reaction, because of insufficient nitrogen especially in the central portion of the sample. The strong intensity of



(a)



(b)

Fig. 11. SEM micrographs of combustion products obtained from 50% TMD undiluted samples without preheating in (a) 0.62 MPa N<sub>2</sub> and (b) 0.96 MPa N<sub>2</sub>.

vanadium peaks signifies a large amount of vanadium left unreacted in the product.

Fig. 12b shows the XRD spectrum of the final product obtained from a 20-wt.% VN-diluted sample with preheating at 100 °C. The existence of  $\delta$ -VN,  $\beta$ -V<sub>2</sub>N, and elemental vanadium was found in Fig. 12b. As compared with Fig. 12a, the intensity of the peaks associated with the nitride phase  $\delta$ -VN was noticeably increased, implying a significant increase in the conversion percentage, while the amounts of  $\beta$ -V<sub>2</sub>N and elemental vanadium were decreased. This also suggests that the  $\delta$ -VN is the dominant nitride phase synthesized in this study. With a further increase in the diluent content up to 30 wt.%, the combustion product was found to be made up largely of  $\delta$ -VN with a negligible amount of  $\beta$ -V<sub>2</sub>N and V, as shown in Fig. 12c.



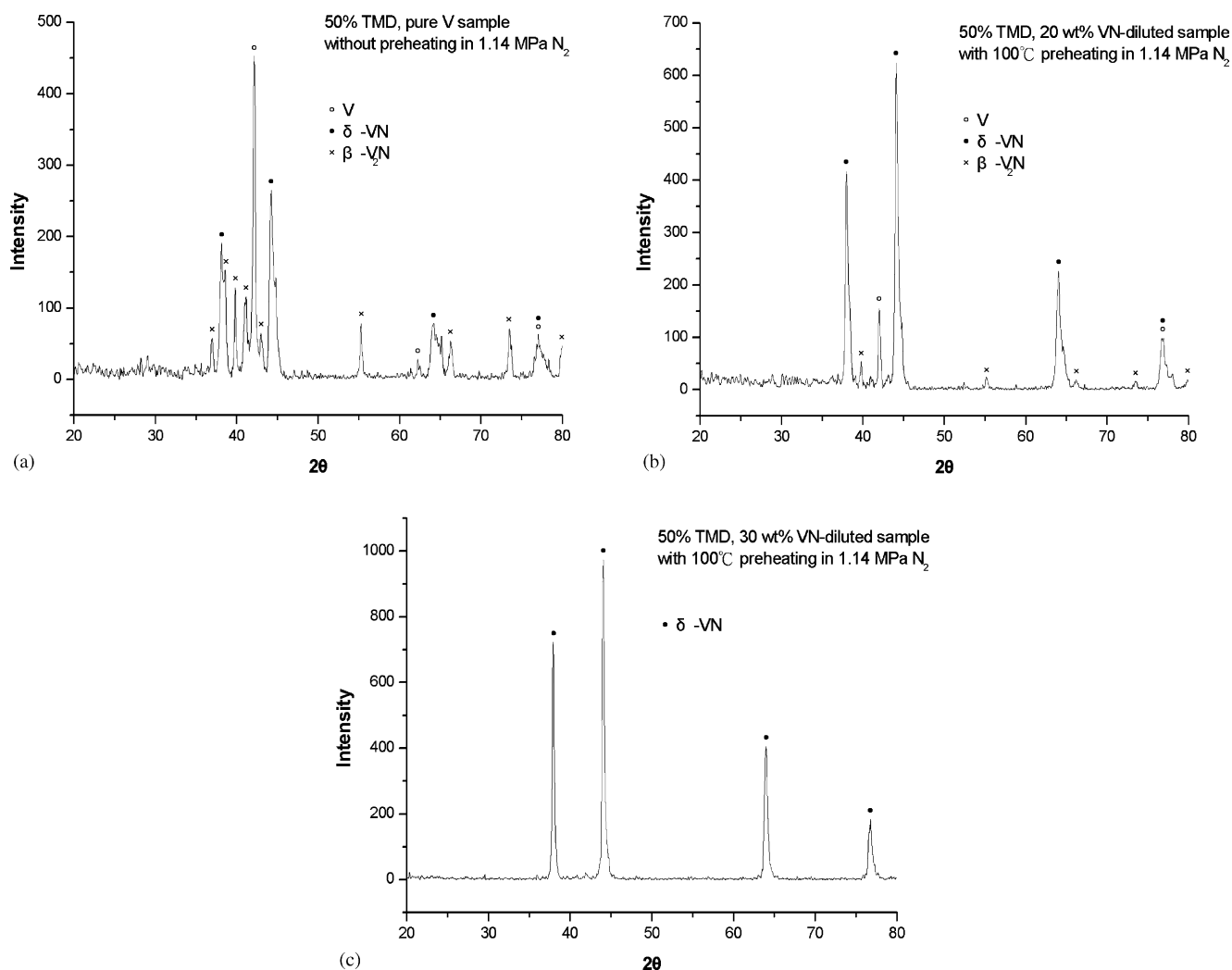


Fig. 12. XRD spectra of combustion products obtained in 1.14 MPa N<sub>2</sub> from (a) an undiluted sample without preheating, (b) a 20-wt.% VN-diluted sample with preheating at 100°C, and (c) a 30-wt.% VN-diluted sample with preheating at 100°C.

#### 4. Summary and conclusions

The SHS process associated with vanadium compacts in nitrogen to form vanadium nitride was experimentally investigated. Dilution of metal reactants with the final nitride product and preheating the samples prior to ignition were demonstrated to greatly affect the flame-front velocity, combustion temperature, and product composition.

The flame propagation mode of the V/N<sub>2</sub> SHS system was characterized by the planar combustion front propagating in a steady manner. After the passage of flame front, the occurrence of afterburning reaction was clearly observed. Flame-front propagation velocity increased with nitrogen pressure, but decreased with sample density. In agreement with the visual observation, the measured temperature profile of undiluted samples showed an abrupt peak signifying the arrival of the combustion front, and a subsequent temperature rise representing the afterburning reaction. For the undiluted samples, the conversion percentage increased

slightly with nitrogen pressure from 0.27 to 0.79 MPa and then decreased with a further increase in nitrogen pressure, due to the formation of a liquid phase at high pressures. In this study, a low degree of conversion between 45 and 55% was obtained for the undiluted sample.

The dilution of sample compacts with VN powders decreased the combustion temperature and thus suppressed the liquid formation, consequently leading to a considerable increase in nitride conversion. An increase in the conversion by more than 20% was achieved by the addition of 30 wt.% diluent in the sample. The conversion percentage of VN-diluted samples was further increased by properly preheating the sample prior to ignition. Under preheating temperatures of 100–200°C, a nitride conversion over 90% was obtained from a 30-wt.% VN-diluted samples in this study. Based upon the XRD analysis, the dominant nitride phase synthesized was identified as δ-VN. Both the secondary nitride β-V<sub>2</sub>N and the unreacted vanadium were significantly reduced in the final products of VN-diluted

samples with preheating. In addition, an activation energy of 134 kJ/mol was deduced for the V/N<sub>2</sub> reaction.

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