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Journal of the European Ceramic Society 24 (2004) 3807–3815

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Effect of preheating on synthesis of tantalum nitride by self-propagating combustion

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Received 30 September 2003; received in revised form 18 December 2003; accepted 27 December 2003

Abstract

An experimental investigation of self-propagating high-temperature synthesis (SHS) of tantalum nitride (TaN) was conducted with tantalum compacts in nitrogen of 0.27–1.82 MPa. Effects of sample density, nitrogen pressure, and preheating temperature on the flame-front propagation velocity, combustion temperature, degree of conversion, and product composition were studied. Results showed that the SHS process of the tantalum/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. Preheating the sample prior to ignition contributed higher combustion temperatures, thus leading to an increase in the conversion percentage. For the unpreheated samples, the conversion increased significantly with nitrogen pressure and reached around 80% at 1.82 MPa of N_2. With preheating temperatures between 150 and 300 °C, the conversion was increased by about 15% when compared with that without preheating. The nitride phase TaN was identified by XRD as the dominant composition in the combustion product.

Keywords: SHS; TaN; Combustion front; Preheating; Afterburning

1. Introduction

Transition metal nitrides have received considerable 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] Among these nitrides, tantalum nitrides (TaN and Ta_2N) have been successfully applied as a stable thin-film resistor,[2,3] and an excellent diffusion barrier between silicon and metal overlayers.[4,5] In addition, Leng et al.[6] demonstrated that the blood compatibility of tantalum nitride is better than that of low-temperature isotropic pyrolytic carbon (LTIC), a most widely accepted biomedical material for artificial heart valves.

Because of the high heat of reaction between transition metals (especially in groups IV and V) and nitrogen, nitrides of some transition metals can be obtained by means of the combustion synthesis, or self-propagating high-temperature synthesis (SHS), in which a sufficiently exothermic reaction generates a self-sustained combustion wave traveling through the sample.[7–9] Combustion synthesis has been recognized as an attractive alternative of producing advanced materials to the conventional methods, which, in general, are time-consuming and energy intensive.[8,9] Among the nitrides of early transition metals, the titanium nitride (TiN) has been extensively investigated by SHS.[10–14] The synthesis of niobium nitride (NbN) by SHS has also been broadly studied.[15–17] However, much less SHS study associated with the tantalum/nitride system has been reported in the literature. Agrafiotis et al.[13] conducted the combustion synthesis of tantalum nitride (TaN) in nitrogen of 3–100 atm using loosely packed tantalum powders in the form of porous beds. With this configuration at pressures higher than 55 atm, almost complete conversion of Ta to TaN was achieved under the solid-phase dilution with 10–30 wt.% TaN in the reactant mixture. Agrafiotis et al.[13] also indicated that combustion temperatures were significantly lower than the melting points of Ta (2996 °C) and TaN (3090 °C).

The objective of this research was to experimentally study the synthesis of tantalum nitride by SHS using compacted tantalum samples in gaseous nitrogen. Combustion characteristics, such as flame-front propagation mode, afterburning

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doi:10.1016/j.jeurceramsoc.2003.12.032

phenomenon, and combustion temperature profile were investigated to establish a fundamental knowledge of the SHS process for the production of tantalum nitride. In addition to the influence of sample density and nitrogen pressure, an attempt was made to explore the effect of sample preheating temperature on the flame-front propagation velocity, combustion temperature, and degree of conversion. In this study, preheating the sample prior to ignition was to achieve higher combustion temperatures, and thereby to enhance the nitride conversion. Finally, the combustion products were analyzed for their microstructure and chemical composition.

2. Experimental procedure

Elemental tantalum (Ta) powders (Aldrich Chemical, −325 mesh) with a mean particle diameter of 45 μm and a purity of 99.9% 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 tantalum compacts were prepared with the green packing densities equal to 45 and 50% of the theoretical maximum density (TMD) of tantalum (16.65 g/cm^3).

The SHS reaction between the tantalum sample and nitrogen gas was carried out in a stainless-steel windowed combustion chamber (shown in Fig. 1) under a nitrogen pressure ranging from 0.27 to 1.82 MPa. The nitrogen gas used in this study had a purity of 99.999%. 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. In order to control the sample initial temperature prior to ignition, the sample holder was equipped with a 600 W cartridge heater. In this study, the sample initial temperature was preheated up to 300 °C. 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.

The propagation rate of combustion front was measured by the recording of 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 reaction between tantalum 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 tantalum compact. The temperature of tantalum sample was measured by a fine-wire (125 μm) Pt/Pt–13% Rh thermocouple (Omega Inc.) attached on the sample surface.

After the combustion, burned samples were recovered and weighed. The conversion percentage of metal to nitride was calculated from the measurement of weight change of sample compacts assuming a stoichiometric nitride (TaN) as the final product.[11–13] The microstructure of combustion product was examined under a scanning electron microscope (SEM). The chemical composition was identified by an X-ray diffractometer (Mac Science MXP) with Cu Kα radiation operating at 40 kV.

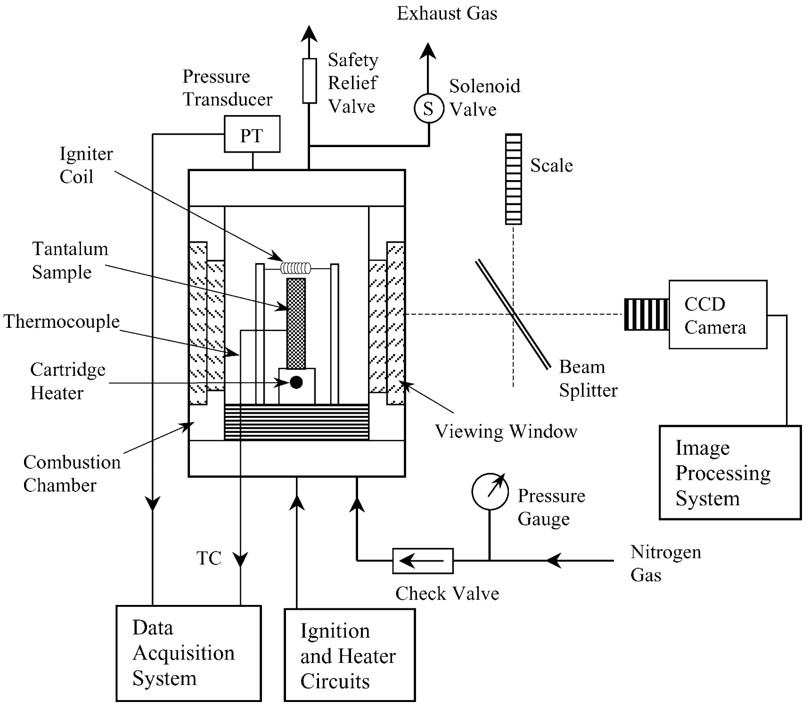


Fig. 1. Schematic diagram of experimental setup to study SHS of tantalum nitride.

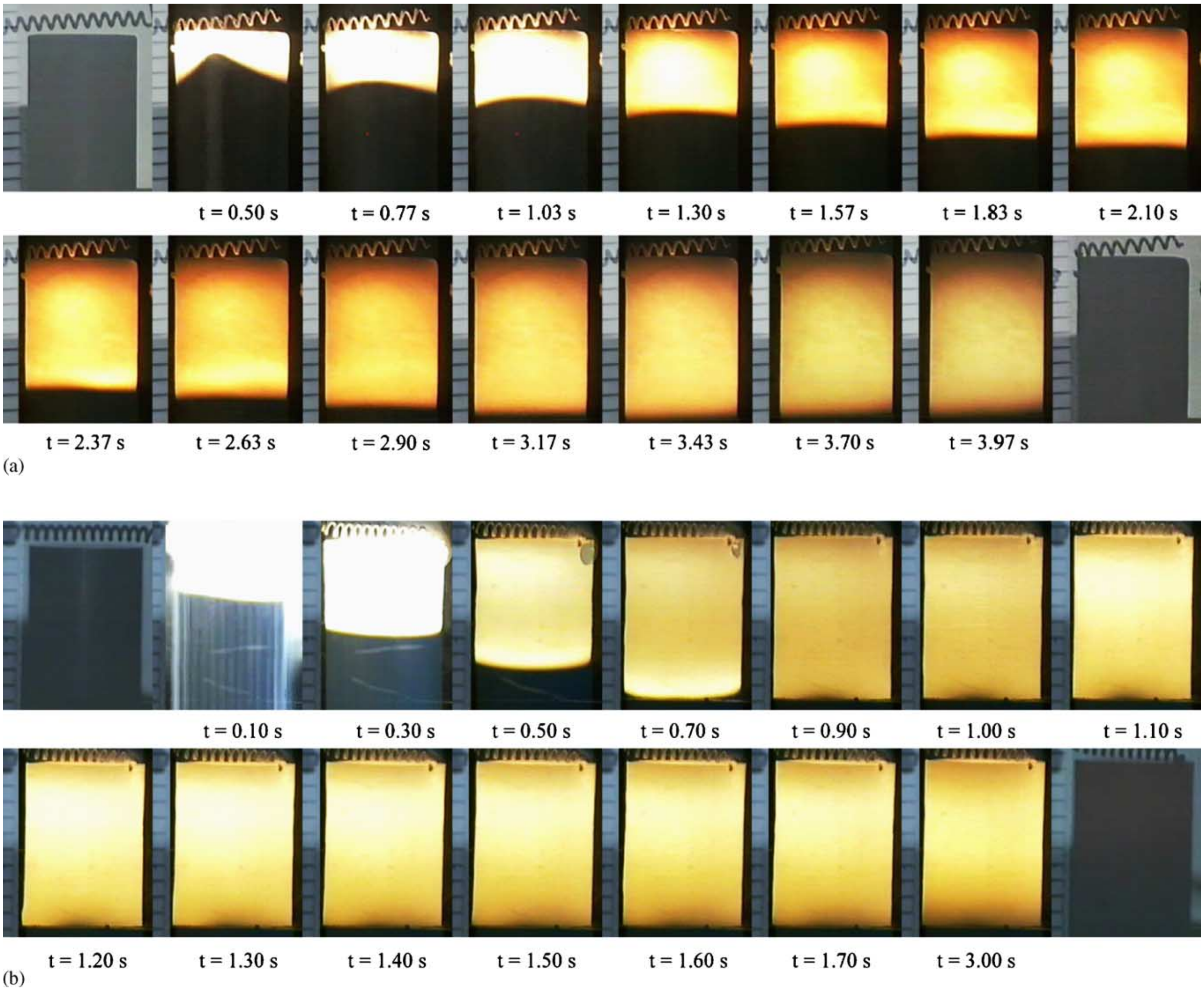


Fig. 2. Recorded burning images indicating steady flame-front propagation and afterburning reaction of (a) an unpreheated 45% TMD Ta sample in 0.45 MPa N_2, and (b) a 250 °C-preheated 50% TMD Ta sample in 1.48 MPa N_2.

3. Results and discussion

3.1. Observation of combustion characteristics

Fig. 2a shows a series of recorded images illustrating the propagation of the flame front associated with an unpreheated tantalum sample reacted in nitrogen of 0.45 MPa. It is evident that upon ignition a distinct combustion front travels downward from the ignited top plane, and transforms the cold reactant into an incandescent combustion product. The self-sustained combustion wave forms a nearly planar front propagating in a steady manner. The scale image on the left-hand side of each picture is the optically superimposed reflection described above. As shown in Fig. 2a, the region behind the flame front remains glowing for a period of time, indicating that the nitridation continues after the passage of the flame front; namely, the occurrence of the so-called afterburning reaction.[11–13]

The SHS process of the preheated tantalum compact was also featured by the steady propagation of a planar combustion front, as shown in Fig. 2b. It is useful to note that due to a faster propagation rate of the flame front, as compared with the one without preheating, the preheated sample exhibits a more obvious afterburning phenomenon. As shown in Fig. 2b, the flame front reaches the bottom of the sample at about $t = 0.7$ s, beyond which the brightness gradually fades away from the sample. However, at $t = 1.1$ s the sample appears to reglow, implying that the reaction resumes. The afterburning luminosity on the sample shown in Fig. 2b is clearly observable during the time period of 1.1–3.0 s. This observation provides a visual evidence of the afterburning stage, where a prolonged bulk post-combustion takes place. It was also found that the burned samples basically retained their original shape and porosity.

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

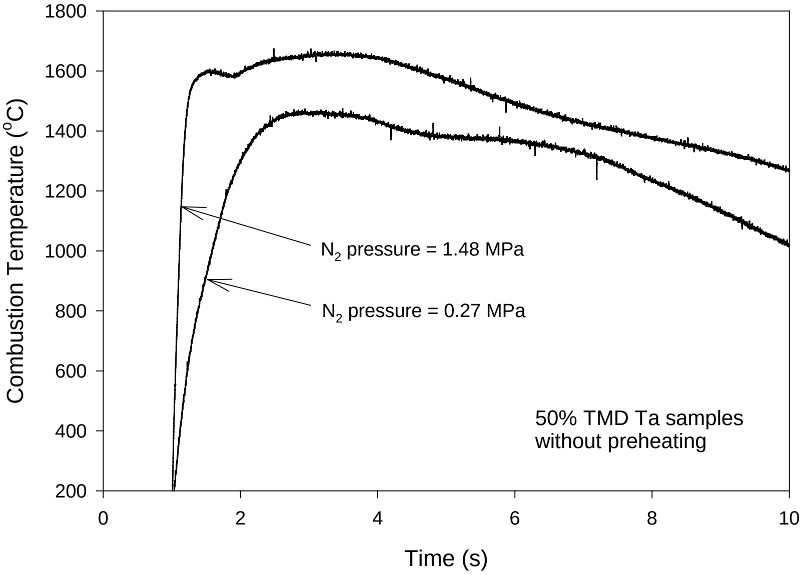


Fig. 3. Typical temperature profiles of burning Ta samples without preheating in nitrogen.

temperature profile. Fig. 3 presents typical temperature profiles of burning samples without preheating in this study. As shown in Fig. 3, the abrupt increase of temperature signifies the arrival of the flame front. After the passage of the flame front, the sample remains at high temperatures for about 2–3 s, representing a prolonged afterburning phase. Fig. 3 also indicates that the combustion temperature increases with an increase in nitrogen pressure. The effect of sample preheating temperature on the combustion temperature is shown in Fig. 4. It was found that the combustion temperature was increased by increasing the sample preheating temperature. It is important to note that in this study measured sample temperatures during both flame propagating and afterburning stages are considerably below the melting points of Ta (2996 °C) and TaN (3090 °C), which is consistent with the observation by Agrafiotis et al.[13] As a result, there was no tendency to melt the metal reactant and nitride product during the tantalum/nitrogen SHS reaction.

3.2. Measurement of flame-front propagation velocity

The flame-front propagation velocity (V_f) was determined from the measured flame-front trajectory, which was constructed upon the recorded film images. Fig. 5 shows the effect of nitrogen pressure on the flame-front propagation velocity of unpreheated tantalum samples with different compacted densities. The flame-front propagation velocity increased with increasing nitrogen pressure, due to

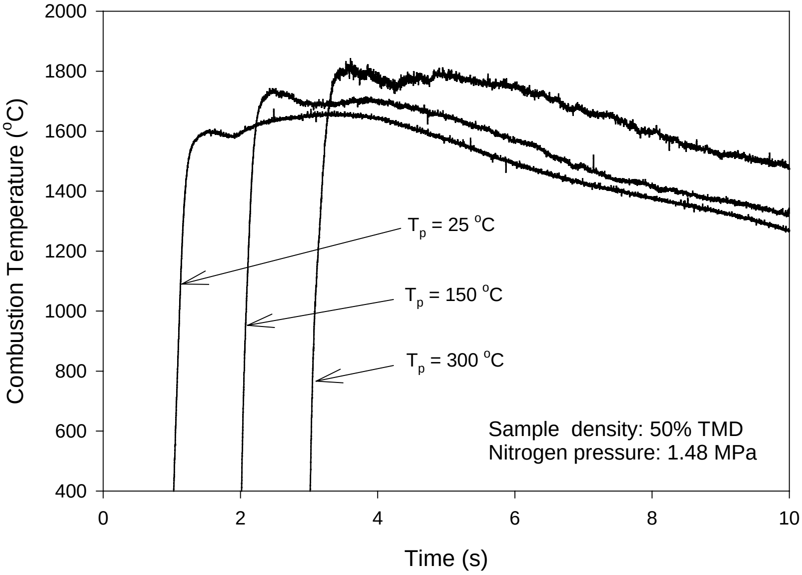


Fig. 4. Effect of sample preheating temperature on combustion temperature of Ta samples in 1.48 MPa N_2.

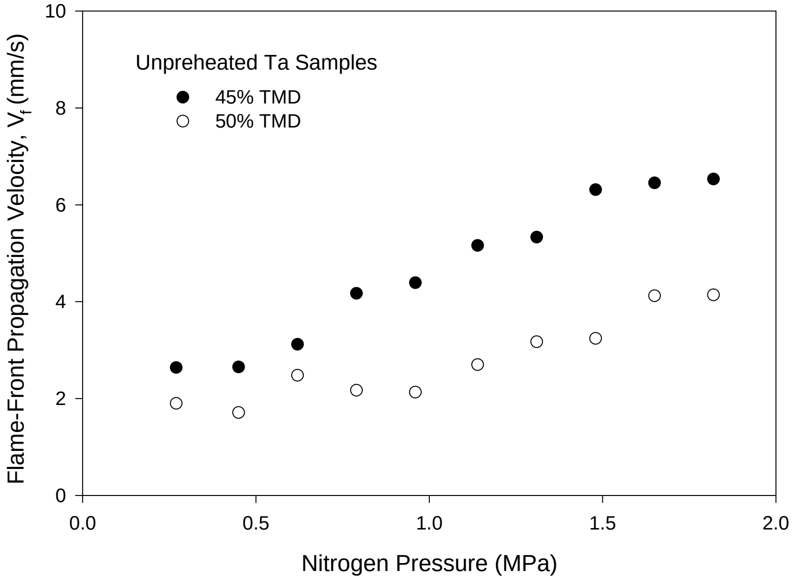


Fig. 5. Effects of nitrogen pressure and sample density on flame-front propagation velocity of unpreheated Ta samples.

an increase in the initial nitrogen concentration within the porous sample. The propagation velocity was also found to increase with decreasing sample density, since a better permeability for nitrogen gas to infiltrate was provided by a sample compact with a lower green density. Fig. 6 indicates that preheating the sample leads to a considerable increase in the front propagation velocity. This was attributed to the fact that combustion temperature was increased by increasing the sample preheating temperature.

According to the study by Agrafiotis et al.,[13] the expression for the dependence of flame propagation velocity on combustion temperature can be simplified as:

$$\left(\frac{V_\mathrm{f}}{T_\mathrm{c}}\right)^2 F(\eta_\mathrm{s}) = K\left(\frac{R}{E_\mathrm{a}}\right)\exp\left(\frac{-E_\mathrm{a}}{RT_\mathrm{c}}\right)$$

where V_f is the velocity of the combustion wave, T_c is the combustion temperature, $F(\eta_\mathrm{s})$ is a function describing the conversion reached at the passage of the flame front, E_a is the activation energy of the process, R is the gas constant, and K is a constant which includes the heat of reaction, product density, effective thermal conductivity, and concentration of gaseous reactant. The expressions for the function, $F(\eta_\mathrm{s})$, under chemical kinetics- and filtration-controlled cases were given in detail by Agrafiotis et al.[13] In order

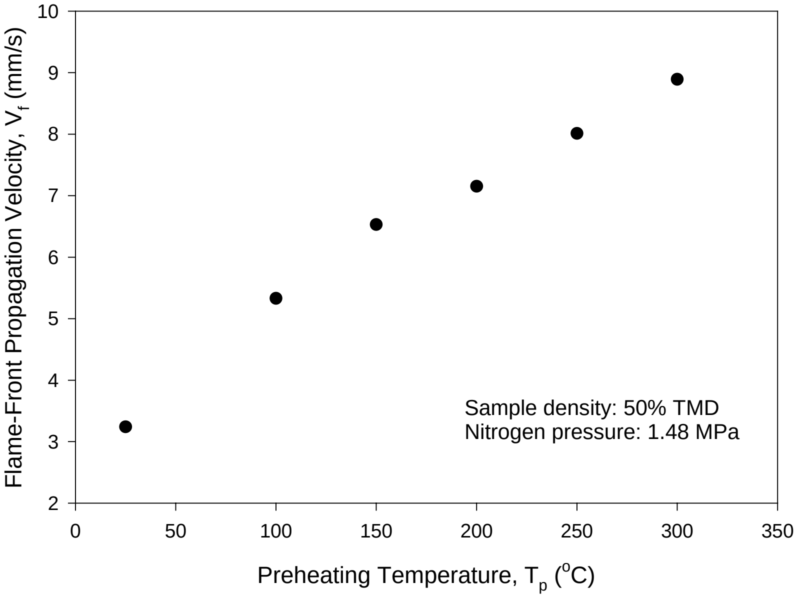


Fig. 6. Effect of sample preheating temperature on flame-front propagation velocity of Ta samples in 1.48 MPa N_2.

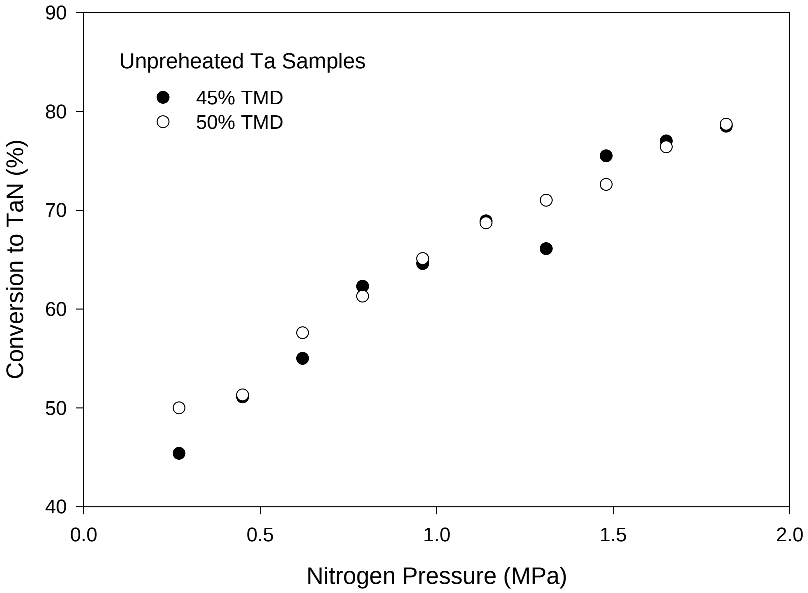


Fig. 7. Effects of nitrogen pressure and sample density on conversion percentage of unpreheated Ta samples.

to determine the activation energy from the combustion measurement, the combustion parameter must reach a pressure-independent value; that is, a kinetically-controlled regime.[13,16] Based upon the results obtained in this paper, however, the combustion parameters, such as the flame propagation velocity, combustion temperature, and nitride conversion percentage (to be discussed in the next section), increase as the nitrogen pressure is increased. This implies a filtration-controlled combustion. As a result, the activation energy cannot be deduced from the present investigation.

3.3. Analysis of product morphology and composition

The molar conversion percentage of tantalum to nitride for the unpreheated samples under different nitrogen pressures is shown in Fig. 7. It was found that the degree of conversion increased substantially with increasing nitrogen pressure. A conversion of about 80% was obtained at 1.82 MPa of nitrogen. In addition, no dependence of the conversion percentage on the sample density was observed. This is mainly because of the afterburning reaction, in which the continuous nitridation takes place after the passage of

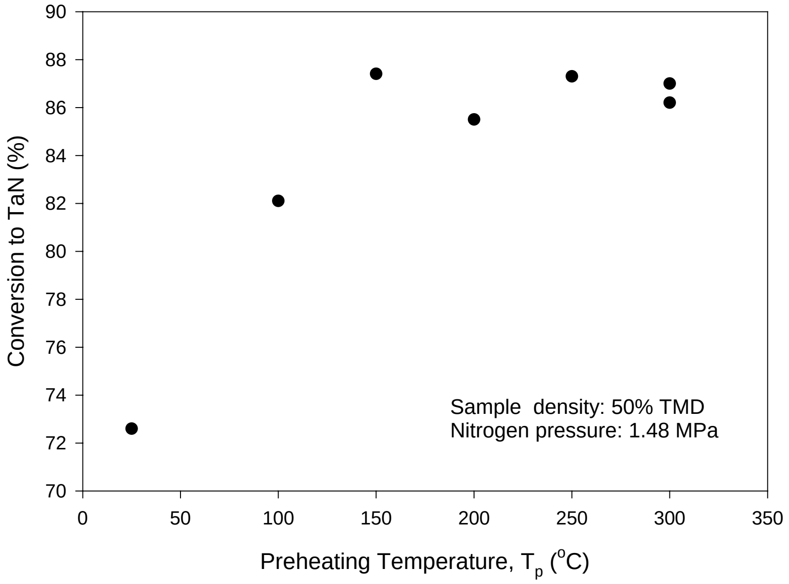
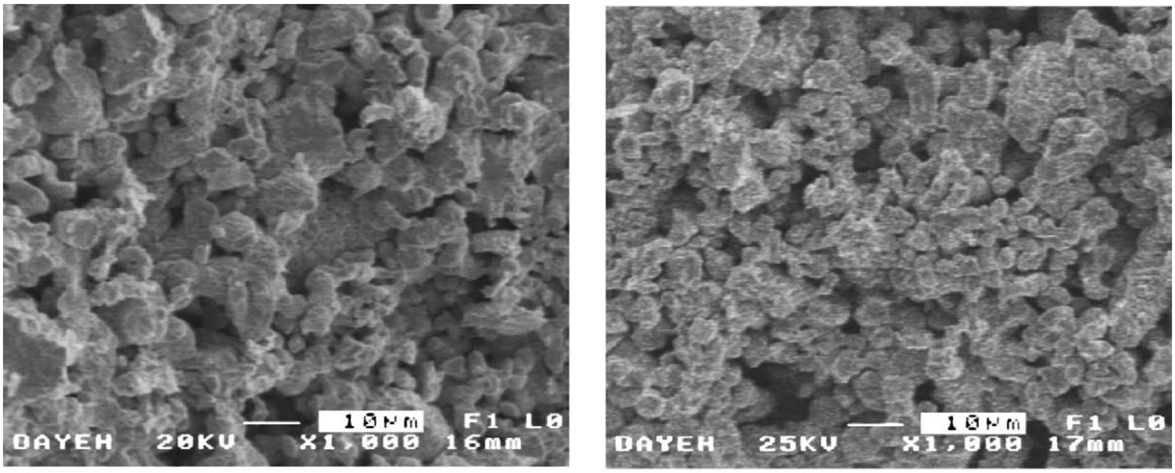


Fig. 8. Effect of sample preheating temperature on conversion percentage of Ta samples in 1.48 MPa N_2.



(a) (b)

Fig. 9. SEM micrographs of combustion products obtained from (a) an unpreheated 50% TMD Ta sample in 1.48 MPa N_2, and (b) a 300 °C-preheated 50% TMD Ta sample in 1.48 MPa N_2.

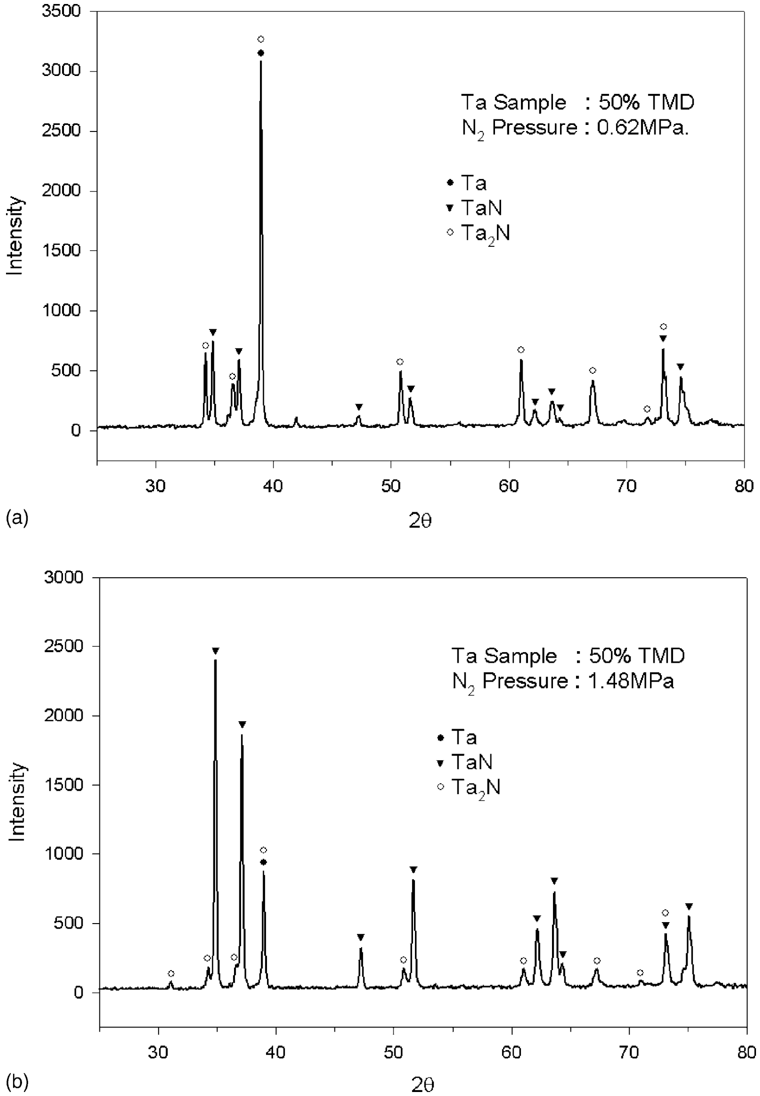


Fig. 10. XRD spectra of combustion products obtained from (a) an unpreheated 50% TMD Ta sample in 0.62 MPa N_2, (b) an unpreheated 50% TMD Ta sample in 1.48 MPa N_2, and (c) a 200 °C-preheated 50% TMD Ta sample in 1.48 MPa N_2.

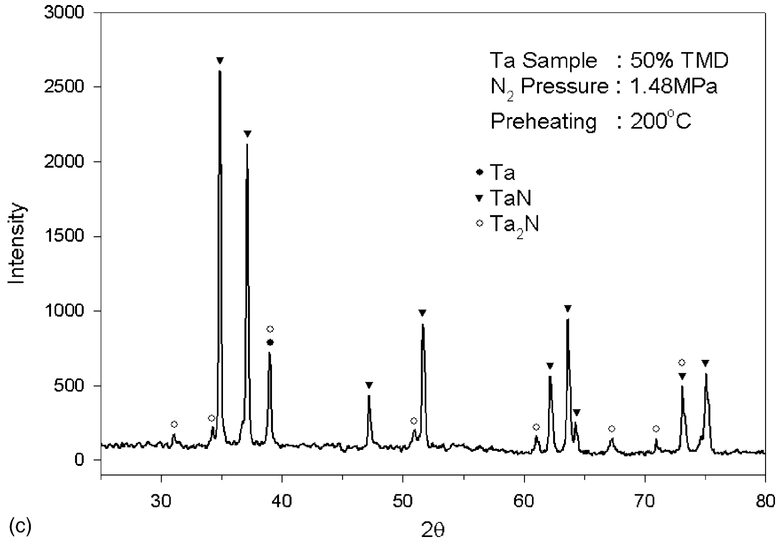


Fig. 10. (*Continued*).

the flame front. The effect of sample preheating on the conversion percentage under a nitrogen pressure of 1.48 MPa is shown in Fig. 8. A considerable increase in the conversion by about 15% was achieved as the sample initial temperature increased from 25 to 150 °C. However, further increase in the preheating temperature up to 300 °C produced no additional increase in the degree of conversion. This might be caused by the fact that the combustion front velocity increased significantly with the sample preheating temperature, resulting in a shorter retention time of high temperatures behind the flame front for the nitridation to proceed.[10]

SEM micrographs illustrating the morphologies of combustion products obtained from samples without and with preheating are displayed in Fig. 9a and b, respectively. SEM micrographs first revealed that the microstructure shown in Fig. 9b was very similar to that in Fig. 9a. Secondly, as compared with the reactant powder, no change in the particle morphology was observed after the SHS reaction. This further verifies the absence of any liquid phase formation during the SHS process even with sample preheating. Therefore, the test sample was able to retain its porosity for the continuous filtration of nitrogen gas, leading to an afterburning stage observed above.

Typical X-ray diffraction (XRD) spectra of combustion products obtained under three different test conditions are shown in Fig. 10a–c. XRD analysis indicated that the presence of three species in the final product, including two nitride phases of TaN and Ta_2N, as well as the unreacted Ta. Due to the low degree of conversion of about 57% at 0.62 MPa of nitrogen, Fig. 10a shows a great amount of the Ta left unreacted. In comparison with Fig. 10a, a significant increase in the TaN phase at 1.48 MPa of nitrogen was observed in Fig. 10b, which confirmed a substantial increase in the conversion with nitrogen pressure. It should be noted that besides elemental Ta, the peak intensity of the nitride Ta_2N decreased with increasing nitrogen pressure. This suggests that TaN is the dominant nitride phase at high pressures of nitrogen. The formation of the secondary nitride phase Ta_2N was because of insufficient nitrogen. Fig. 10c presents the XRD spectrum of the combustion product with a preheating temperature of 200 °C. Even though the XRD pattern shown in Fig. 10c was quite close to that in Fig. 10b, it was found that the peak intensity associated with TaN was higher in Fig. 10c. This was attributed to an enhancement of the degree of conversion by preheating the sample.

4. Conclusions

The SHS process associated with tantalum compacts in nitrogen to form tantalum nitride was experimentally investigated in this study. Preheating the test samples prior to ignition was demonstrated to greatly affect the flame-front velocity, combustion temperature, and product composition. Based upon the experimental observations and measurements of this study, several important results are summarized below.

The flame propagation mode of the Ta/N_2 SHS system is 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. In agreement with the visual observations, measured temperature profiles showed a sharp increase signifying the arrival of the combustion wave, and a subsequent high-temperature region representing the prolonged afterburning reaction. Measured combustion temperatures together with SEM micrographs verified the absence of any liquid phase formation during the SHS process of tantalum/nitrogen system. This suggests that after the passage of the flame front the sample still retains its porosity for nitrogen to penetrate, thus resulting in the afterburning reaction. Flame-front propagation velocity was found to increase with nitrogen pressure, but decrease with sample density. An increase in sample preheating temperature led to the increase of flame propagation velocity, because the combustion temperature was increased.

The nitride conversion percentage of unpreheated samples was substantially increased by increasing the nitrogen pressure. A relatively high conversion of about 80% was achieved at 1.82 MPa of nitrogen. Due to the continuous nitridation in the afterburning stage, the degree of conversion was found to be independent of the sample density. Preheating the sample prior to ignition was demonstrated to enhance the conversion by about 15% optimally. The dominant nitride phase synthesized in this study was identified as TaN by the XRD analysis. Both the secondary nitride Ta_2N and the unreacted Ta were significantly reduced by increasing either the nitrogen pressure or the sample preheating temperature.

Acknowledgements

This research was sponsored by the National Science Council of Taiwan, ROC, under grants of NSC 91-2212-E-212-020 and NSC 92-2212-E-212-003.

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