

Gradient microstructure of titanium nitride fabricated by combustion synthesis with liquid nitrogen

M. Shibuya*, J.F. Despres¹

Department of Electron Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

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Abstract

Titanium nitride has been fabricated by combustion synthesis from a titanium powder compact and liquid nitrogen in a closed vessel. This method drastically increases the pressure around the sample, resulting in combustion propagation. The products obtained in this system are non-homogeneous in morphology and composition along the propagation direction. The nitridation and densification of the products have improved with the increase of the maximum pressure or pressure gradient. With a pressure gradient of 9.5 MPa s^{-1} , the first combustion part of the product is almost unreacted titanium, but the main product at the last combustion part is titanium nitride ($\text{TiN}_{0.75}$) with a dense body. The Vickers micro-hardness of the product (at 0.98 N force) along the propagation direction is gradually increased from 9.7 to 17.3 GPa. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Titanium nitride is an important technological material for many applications in which a high melting point, extreme hardness, high electric conductivity and high chemical stability are required.¹ Recently, titanium nitride has been used in composite materials and as a coating material for improving the fracture toughness, strength and corrosion characteristics.^{2,3} Combustion synthesis^{4,5} is a conventional method for the synthesis of titanium nitride. Titanium nitride produced by combustion synthesis should be better than that produced by conventional method because of the short time reaction propagation at higher temperatures that results in a high purity product.

High conversion ratio to titanium nitride, however, has not been achieved by the combustion synthesis between pure

titanium and gaseous nitrogen through a self-sustaining reaction because the molten titanium in front of the propagating combustion wave prevented the nitrogen penetration into the reactant. In order to achieve a high conversion ratio of the products, high pressure of gaseous nitrogen,^{6,7} sodium azide⁸ and liquid nitrogen⁹ have been required. Recently, other simple techniques such as microwave activation have successfully achieved a very high conversion ratio during the combustion synthesis of nitrides.¹⁰ The conversion ratio in the case used liquid nitrogen as nitrogen source was less than 70%. In contrast, a dense product with a conversion ratio of 89% has been fabricated by the nitriding reaction in a closed vessel filled with liquid nitrogen, and this product has been densified up to 99% of the theoretical density¹¹ in spite of the difficulty for densification of titanium nitride with a high melting temperature and covalent bonding. The increase of the conversion ratio and the densification of the product occurred because the pressure drastically increased during the combustion synthesis. A drastic increase of the pressure around the reactant is produced by utilizing liquid nitrogen in a closed system, according to its gasification by heat generation during the combustion synthesis. The structural process following the combustion process plays an important role

* Corresponding author. Present address: Venture Business Laboratory, Yamagata University, 4-3-16 Jonan Yonezawa, Yamagata 992-8510, Japan. Tel.: +81 238 26 3486; fax: +81 238 26 3499.

E-mail address: mshibuya@yz.yamagata-u.ac.jp (M. Shibuya).

¹ Present address: IMRA-Europe, 220 rue Albert Caquot 06904 Sophia-Antipolis, France.

in the final product.^{12,13} Products fabricated under increasing pressure during the combustion reaction show differences in conversion ratio, formation of the metastable phase, and densification. From the thermodynamic point of view, the increase of pressure in a solid–gas reaction increases the driving force of the reaction and is expected to enhance the conversion into the final product.¹⁴

In the present work, we investigated the effects of pressure change during combustion synthesis just after the initiation of the reaction on microstructural and mechanical properties in order to clarify the reaction mechanisms of TiN combustion synthesis with liquid nitrogen in closed system. Functionally graded materials like products fabricated by this method have different composition and structure in one direction.

2. Experimental procedure

Titanium powder with an average particle size of 30 μm (Nakarai Inc., Tokyo, Japan) was used. The packing density of the powder compact, compressed uniaxially in a cylindrical stainless steel die (diameter 15 mm) with double-acting rams, was about 50%. At a packing density of 58%, the conversion ratio of TiN combustion synthesis using liquid nitrogen is at maximum.⁹ In this study, however, the packing density was about 50% because it is difficult to melt the Ti particles with a combustion initiation of Ti powder compact over 50%. The powder compact was placed in a combustion synthesis apparatus as shown in Fig. 1. The vessel with an inner volume of 785 cm^3 was filled with liquid nitrogen and hermetically closed after cooling of inner closed vessel. A tungsten ignition wire (0.5 mm in diameter) was in contact with the bottom surface of the titanium powder compact. After ignition, the reaction propagation occurred from the bottom to the top of the sample. This configuration had been selected because the combustion propagating upward was more effective for higher conversion than the combustion propagating downward.⁹ The combustion temperature

was measured by using W–Re_{5%}/W–Re_{26%} thermocouples located inside the compact. The pressure inside the vessel was measured by a strain gauge transducer (PH-B, Kyowa Inc., Tokyo, Japan) with a dynamic strain amplifier (DPM-711B, Kyowa Inc., Tokyo, Japan). The temperature and pressure data were recorded with a data logger (sampling time 50 ms). The combustion velocity was calculated with data of two thermocouples. The phases of the products were identified by X-ray diffraction ($K_{\alpha 1} = 0.15402 \text{ nm}$) (RINT2500, Rigaku Inc., Tokyo, Japan). The fracture surface of the products was observed by scanning electron microscopy (SEM) (JSM-220, JEOL Inc., Tokyo, Japan). The hardness of each product was determined by the Vickers micro-hardness apparatus (HMV-2000, Shimadzu Inc., Kyoto, Japan) at 0.98 N force for 10 s.

3. Results and discussion

3.1. Effects of simultaneous combustion reaction and pressure increase on the product

The pressure inside a closed vessel fully filled with liquid nitrogen increases from 0.1 to 65 MPa when the temperature in the vessel changes from -196 to 0°C according to the volumetric expansion of nitrogen (the density of liquid nitrogen is 808 kg m^{-3} at -196°C , which is about 650 times greater than the nitrogen density at 0°C). With regard to the possibility of combustion synthesis of titanium nitride using liquid nitrogen, the heat formation of $\text{TiN}_{1.0}$ is 336 kJ mol^{-1} and the heat of liquid nitrogen evaporation is 5.6 kJ mol^{-1} . The adiabatic temperature of $\text{TiN}_{1.0}$ using liquid nitrogen as the nitrogen source is 4527°C . This is almost the same as the adiabatic temperature of $\text{TiN}_{1.0}$ using gaseous nitrogen (i.e. 4827°C). The maximum pressure in the closed vessel depends on the heat generation of the reaction increasing the evaporation of the liquid nitrogen with the sample weight and conversion ratio. Titanium nitride is a typical material with

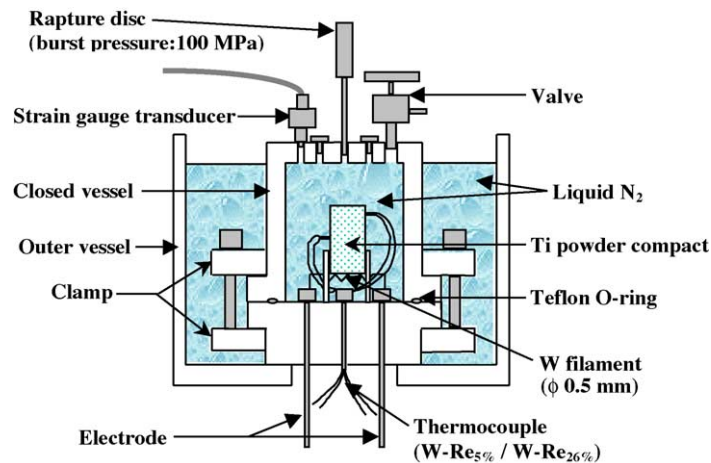


Fig. 1. Schematic illustration of an apparatus with a closed vessel used in the present work.

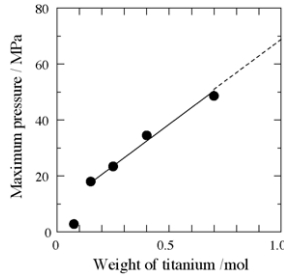


Fig. 2. Relationship between weight of titanium as reactant and maximum pressure in the present vessel.

a wide range of stoichiometry symbolized with the formula TiN_x , where x ranges from 0.6 to 1.0.¹⁵ The dominant defect in TiN_x is vacancies at the nitrogen site.

The maximum pressure in the vessel could be measured up to 50 MPa by a strain gauge transducer. Fig. 2 shows the relationship between the weight of titanium as a reactant and the maximum pressure in the present vessel. For a sample weight less than 0.1 mol, the pressure did not increase because the heat generation from the titanium nitride synthesis was not sufficient. The strong cooling of the inner vessel by the outer vessel quickly prevents the pressure increase by the condensation of nitrogen gas at -196°C . The critical size has been estimated at around 0.15 mol, from which the maximum pressure was coarsely increased in proportion to the sample weight. With a 0.7 mol sample, the maximum pressure reached was approximately 50 MPa and the pressure took about 20 s to increase from 0.1 to 50 MPa. Seventy seconds after the maximum pressure, the pressure had decreased to 0.1 MPa due to the cooling of the surrounding liquid nitrogen.

Products fabricated under changing pressure have different shapes in the combustion propagation direction. The first part of the product was a porous body, but the last part was a dense body due to the shrinkage of the sample. In combustion synthesis, the structural process occurs just after the combustion process; accordingly, the pressure evolves during the structural process, providing a variable density along the propagation direction.

Typical different phases in the combustion propagating direction of the product were identified by X-ray diffraction. Fig. 3 shows X-ray powder diffraction patterns in the first (a) and last (b) combustion parts of the product. This prod-

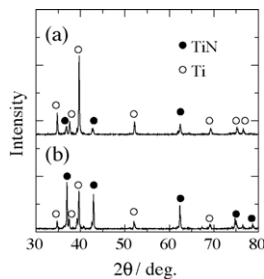


Fig. 3. X-ray diffraction patterns in first (a) and last (b) combustion parts of the product (maximum pressure: 34.5 MPa).

uct was fabricated while the nitrogen pressure changed from 0.1 to 34.5 MPa. The composition in both parts of the product was identified as unreacted titanium and titanium nitride. The sample displays an increase in the titanium nitride between the first and the last part. The lattice constant of the titanium nitride in the last combustion part calculated from X-ray diffraction peaks is 0.420 nm and corresponds to $\text{TiN}_{0.65}$. The x value of TiN_x can be estimated from data of relationship between lattice constant and TiN_x . However, the titanium did not react completely with the nitrogen in either part. Actually, the maximum combustion temperature in this case was 2142°C , more than 400°C higher than the melting point of titanium. Consequently, the molten titanium prevented the penetration of nitrogen into the sample and the titanium nitride synthesis was inhibited.

Fig. 4 shows scanning electron micrographs in the first (a) and last (b) combustion parts of a cross section of the same product. It is clear that the first combustion part of the product is a porous body and the last combustion part is a dense body. In general, the rate of densification of the sample decreases with the increase of the nitrogen content.¹⁶ In our case, densification occurred at the last part because the liquid nitrogen served as a pressure source.

As indicated in experimental procedure, the temperature and the velocity of the combustion were measured by W–Re thermocouples in order to consider a model of combustion

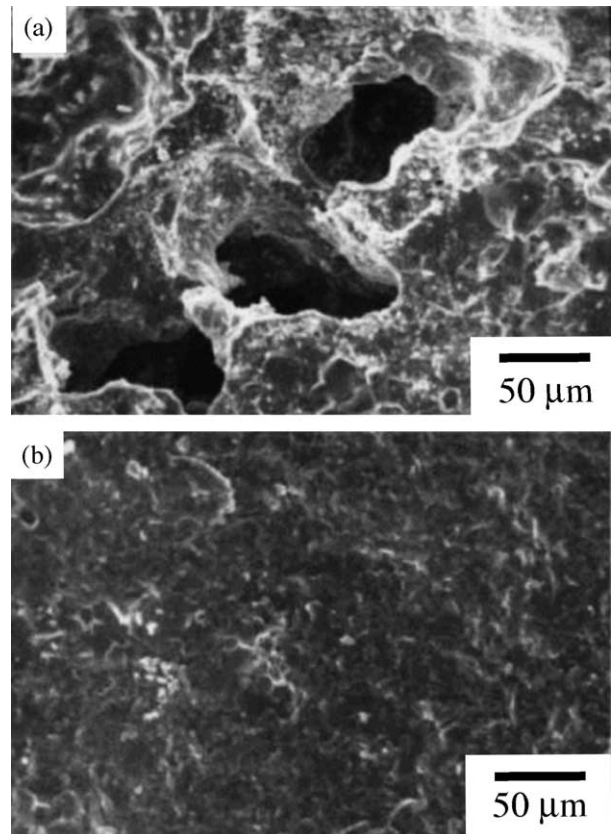


Fig. 4. Scanning electron micrographs in first (a) and last (b) combustion parts of the fracture surface of the product (maximum pressure: 34.5 MPa).

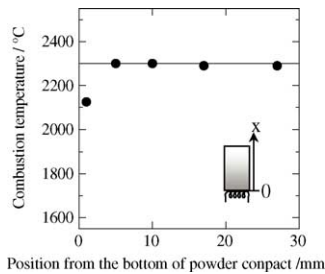


Fig. 5. Combustion temperature at several positions from the sample bottom.

synthesis and densification in this system. Fig. 5 shows the combustion temperature at several points of the sample. At a distance of 1 mm from the bottom, the combustion temperature was about 2060 °C. That was almost the same as the maximum temperature (1947 °C) of the combustion synthesis between the titanium and liquid nitrogen in an open vessel. In general, the maximum combustion temperature increased with pressure.⁶ Therefore, the temperature in the initial stage of the combustion synthesis indicated that the pressure in the vessel did not increase owing to the heat consumption of the liquid nitrogen around the reactant. However, the combustion temperature reached about 2230 °C at distances exceeding 5 mm from the initiation point. This high combustion temperature indicates the high conversion ratio. Thus, as the pressure increase because of heat generation (which is directly proportional to the conversion ratio), the conversion ratio and pressure are associated. The measured combustion velocities were 6.17 mm s⁻¹ at 5–10 mm from the initiation point, 6.59 mm s⁻¹ at 10–17 mm, and 7.46 mm s⁻¹ at 17–27 mm. The combustion velocity increased because of expansion in the reaction zone during the combustion process. This expansion is due to the intensified convection of gaseous nitrogen at the non-reacted part of the sample according to the increase of pressure. In general, it has been reported that combustion velocity does not depend on gaseous pressure for combustion synthesis involving solid–solid reactions.⁵ For reactions with fluid phases, however, the combustion velocity depends on the gaseous supply or the gaseous pressure. The combustion velocities in the combustion synthesis of Ta–N system¹⁷ and TiN–TiB₂ composite¹⁸ increased with nitrogen pressure. The higher combustion velocity at higher nitrogen pressure is thought to be related to the increase of the maximum combustion temperature with nitrogen pressure.¹⁹

Consequently, the conversion ratio and densification of the product increased with pressure in the vessel. Next, we considered the relationship between the combustion temperature, environmental pressure and sample shape during the reaction. Fig. 6 depicts combustion temperature profiles of the sample, pressure profiles in the vessel and sample shape modifications obtained from this project. A–E indicate the modified shape of the sample at several reaction times. T₁ and T₂ profiles represent the combustion temperature of the several parts as shown in the sample shape A. As shown in Fig. 6, the combustion propagation terminates in C. The structural stage of

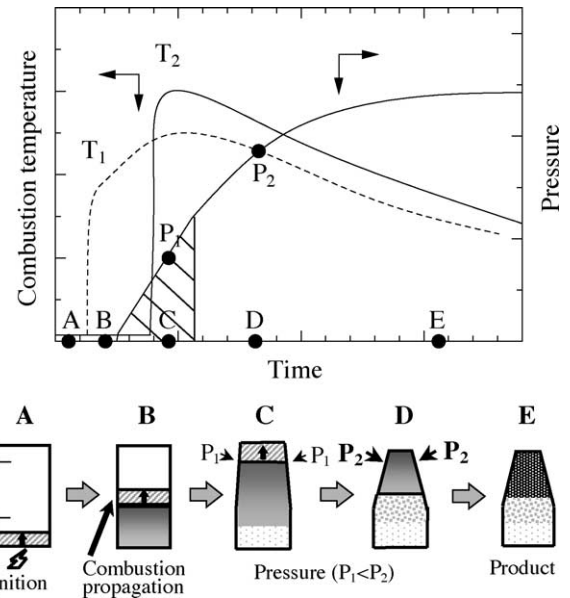


Fig. 6. Combustion temperature profiles of the sample, pressure profiles in the vessel and sample shape modifications.

the product occurs after combustion propagating as shown in sample shape D. The structural stage in combustion synthesis with titanium nitride continues until about 1230 °C.¹³ The conical shape of the sample as it is illustrated on “E” in Fig. 6 results from the increasing pressure during and after the combustion propagation. Of course, the pressure measured by the strain gauge transducer is the average pressure in the vessel, it is not the real environmental pressure around the reactant on a microscopic scale. Therefore, it is clear that the pressure gradient in the linear part that is called the initial stage is a very important parameter as a determining factor of the conversion ratio and the densification of the final product. Moreover, the pressure gradient increased in proportion to the maximum pressure as shown in Fig. 7.

3.2. Effect of pressure gradient on the structure of the product

The maximum pressure and pressure gradient increased with the heat generation (according to the weight of titanium powder compacts) in the combustion synthesis of titanium nitride with liquid nitrogen in a closed vessel. Fig. 2 plots the

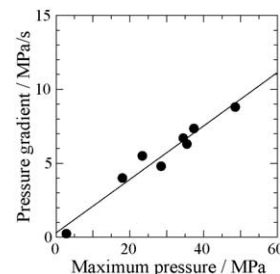


Fig. 7. Relationship between maximum pressure and pressure gradient.

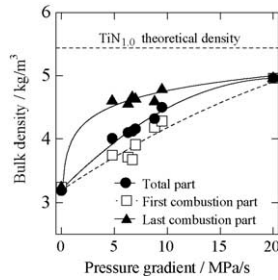


Fig. 8. Relationship between the bulk densities of samples along the direction of propagation and the pressure gradient.

maximum pressure against the sample weight. The conversion ratio increases with the pressure caused by the reaction starting, and consequently produces a greater amount of heat. This heat warms the nitrogen in the closed vessel and the pressure is gradually increased. This phenomenon continues until heat generation stops due to a lack of reactant.

The bulk density of the products increased with the pressure gradient. Fig. 8 shows the relationship between the bulk densities of samples along the direction of propagation and the pressure gradient. The three ranks of dots represent the bulk density of the total, first, and last combustion synthesis parts. The bulk density of the products was assessed as $4.6 \times 10^3 \text{ kg m}^{-3}$ for a pressure gradient of 9.5 MPa s^{-1} and $5.0 \times 10^3 \text{ kg m}^{-3}$ for a pressure gradient of 20 MPa s^{-1} . The bulk densities of the products in the last combustion part are clearly higher than at the first combustion part. The differences in the bulk density in the direction of propagation, however, are small in the presence of high-pressure gradients. With a pressure gradient of 20 MPa s^{-1} , there is no difference in the bulk density between sample parts. This may be because the combustion synthesis of titanium nitride with liquid nitrogen as well as gaseous nitrogen is initiated at a temperature above the melting point of titanium ($1670 \text{ }^\circ\text{C}$).²⁰ The structural stage of the product occurs during high-temperature term just after combustion propagation (i.e. after burn).⁶ In the case of a pressure gradient of 20 MPa s^{-1} , the effect of the pressure during the structural stage of the product was approximately constant.

We investigated different morphologies of the products in the propagating direction. Fig. 9 shows X-ray diffraction patterns in the first (a) and last (b) combustion parts of the

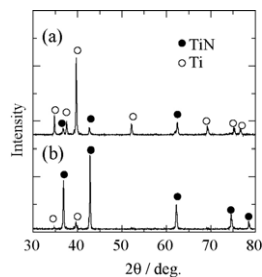


Fig. 9. X-ray diffraction patterns in first (a) and last (b) combustion parts of the product (pressure gradient: 9.5 MPa s^{-1}).

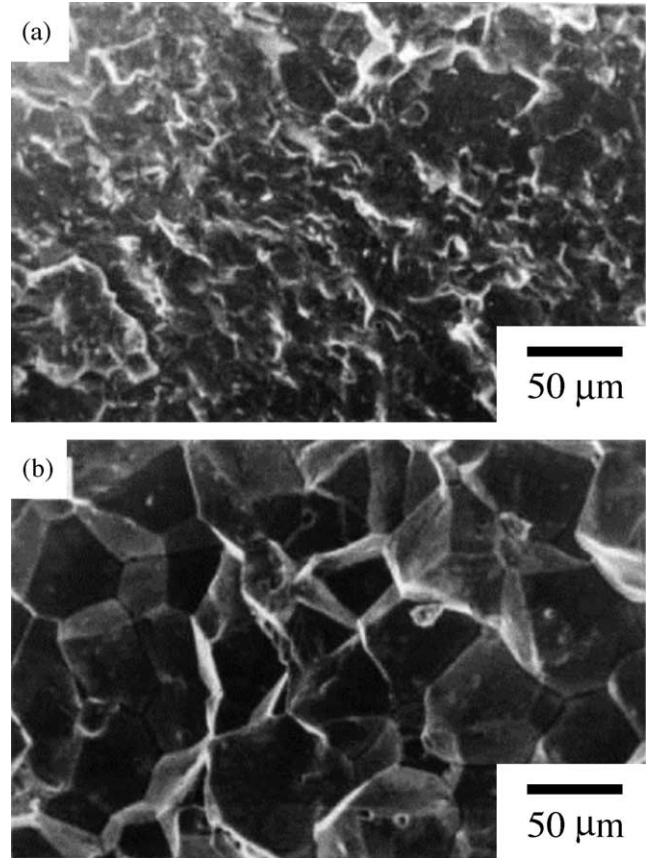


Fig. 10. Scanning electron micrographs of the fracture surface in first (a) and last (b) combustion parts of the product (pressure gradient: 9.5 MPa s^{-1}).

product fabricated at a pressure gradient of 9.5 MPa s^{-1} . The main product in the first (last) combustion parts was identified as titanium (titanium nitride). The lattice constant of the product in the last combustion part, calculated from the X-ray diffraction peaks, is 0.422 nm , which corresponds to $\text{TiN}_{0.75}$. This value has been calculated from the reported dependence of the lattice constant on deviation from stoichiometry for titanium nitride.¹⁵ According to conventional combustion synthesis, the maximum conversion of the reaction of nitridation of pure titanium using gaseous^{12,13,21} and liquid nitrogen⁹ was lower than 70%. However, we could produce titanium nitride with a high conversion ratio because we supplied liquid nitrogen into the titanium compact at high density and high pressure.

Fig. 10 shows scanning electron micrographs of the fracture surface in the first (a) and last (b) combustion parts of the product fabricated at a pressure gradient of 9.5 MPa s^{-1} . Both parts of the first and last are produced dense bodies, but the morphologies are clearly different. In the first part, the penetration of gaseous nitrogen into the space of the molten reactant was interrupted by the effect of reducing the surface area of the reactant. In the last combustion part, the product was titanium nitride with a mean particle size of approximately $50 \text{ } \mu\text{m}$. In this case, the heat of formation increased

owing to the high conversion in the last combustion part, but the maximum combustion temperature was 2457 °C, lower than the melting point of titanium nitride. The melting point of TiN_x , however, decreases with a lower content of nitrogen (i.e. less than 2947 °C). Therefore, the particle growth occurred by volume diffusion which should allow transport of matter from the grain boundaries to the neck regions.

We measured the Vickers micro-hardness (at 0.98 N) of the products fabricated in a pressure gradient of 9.5 MPa s^{-1} . The hardness in the product varied along the combustion propagating direction. The hardness is 9.7 GPa for the first and 17.3 GPa for the last combustion part. We found that the hardness increases with the conversion ratio and densification of the product as shown in the XRD patterns and SEM photographs. Complete nitrides were synthesized by combustion synthesis by lowering the combustion temperature according to the addition of a product to dilute the reactant powder.⁶

4. Conclusions

In this work, we investigated the effect of pressure changes during combustion synthesis of titanium nitride with liquid nitrogen in a closed vessel on the conversion ratio, the microstructure, and mechanical properties of the products in order to clarify the reaction mechanisms. A drastic increase of the pressure, just after the combustion initiation of the sample, stimulated the conversion ratio and densification of the products. The morphology of the product has been observed as non-homogeneous along the propagating direction for large pressure gradient (the increasing rate of pressure). With a pressure gradient of 9.5 MPa s^{-1} , the first combustion part of the product was mainly titanium, but the last combustion part of the product was almost all titanium nitride ($\text{TiN}_{0.75}$) with a dense body. The product exhibited the Vickers micro-hardness ranging from 9.7 to 17.3 GPa.

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