JOURNAL OF MATERIALS SCIENCE 33 (1998) 2573–2576

Characteristic sample temperature and pressure during processing of titanium nitride combustion synthesis with liquid nitrogen

M. SHIBUYA, J. F. DESPRES, O. ODAWARA
Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan
E-mail: odawara@materia.titech.ac.jp

Titanium nitride synthesis has been investigated by sustaining a nitriding reaction of titanium powder compacts set in a closed vessel filled with liquid nitrogen. The characteristic features of the present combustion synthesis technology are the accelerating pressure in the vessel following sample heating through its combustion propagation, which results in a specific structure formation of the products. It has been confirmed in the present work that the pressure in the closed vessel was drastically increased (ca. 20 MPa s^{-1}) by propagating the nitriding reaction. The product was shrunk and densified up to 99%. The product was identified as $TiN_{0.87}$ without any trace of elemental titanium.

1. Introduction

Titanium nitride is a typical material with a wide range of stoichiometry, TiN_x, where x varies from 0.6–1.0 [1]. TiN_x has advantageous properties such as hardness, chemical stability and electrical conductivity [2, 3]. Combustion synthesis [4, 5] has been applied to TiN synthesis, which is conventionally performed with gaseous nitrogen [6–8]. At an atmospheric pressure of gaseous nitrogen, the conversion ratio was, at most, 40%. For the purpose of achieving high conversion, a reaction method in gaseous nitrogen at high pressure has been proposed [9, 10]. Liquid nitrogen [11] and sodium azide [12] have been used as densified nitrogen sources and performed successfully in combustion synthesis with a rather high conversion ratio.

In the case of utilizing liquid nitrogen, its gasification by the reaction heat during combustion synthesis would affect the environment around the reacting sample, especially the pressure, which would increase in the closed system.

In the present work, the combustion synthesis of TiN with liquid nitrogen in a closed system was investigated in order to assess the potential of its technical advantage in certain material processing. The pressure change following the reaction propagation is considered to affect not only the propagation phenomenon itself, but also the product characteristics of structure and properties.

2. Experimental procedure

2.1. Design of the closed vessel

The density of liquid nitrogen at 77 K is 808 kg m^{-3}, which is almost 650 times larger than that of gaseous nitrogen (1.25 kg m^{-3}). In the case of a closed vessel fully filled with liquid nitrogen, the pressure in the vessel reaches 70 MPa at 298 K according to gasification of liquid nitrogen as follows

$$\left[\frac{V_{N_2(g)}}{V_{N_2(l)}}\right]_P = \left[\frac{P_{N_2(g)}}{P_{N_2(l)}}\right]_V \approx 180 \times \frac{T}{77} \qquad (1)$$

Therefore, the vessel should be designed to be mechanically resistive to at least 100 MPa high pressure. The vessel should also be adequate for use at the low temperature of liquid nitrogen. A vessel was designed to be suitable for use at a pressure of more than 100 MPa at 77 K. The inner volume was chosen equal to 785 cm^3 (diameter 100 mm × 100 mm). The choice of structural material was determined by its high resistance to the induced inner pressure. In the present work, the SNCM439 alloy (C 0.4%, Ni 1.8%, Cr 0.8%, Mo 0.23%, tensile strength >980 MPa) was used as the structural material for the vessel, which was 30 mm thick. Fig. 1 shows a schematic design of the present apparatus.

2.2. Procedure

Titanium powder with an average particle size of 30 μm was used. It was compressed uniaxially in a cylindrical shape (approximately 25 mm diameter and 43 mm long) at 2 MPa using a stainless steel die with double-acting rams. The packing density was about 50% theoretical. Each compact was placed in the central part of vessel, as shown in Fig. 1a.

A tungsten wire (diameter 0.5 mm), attached to the bottom surface of sample compact, was used for ignition by passage of an electric current. The upper part

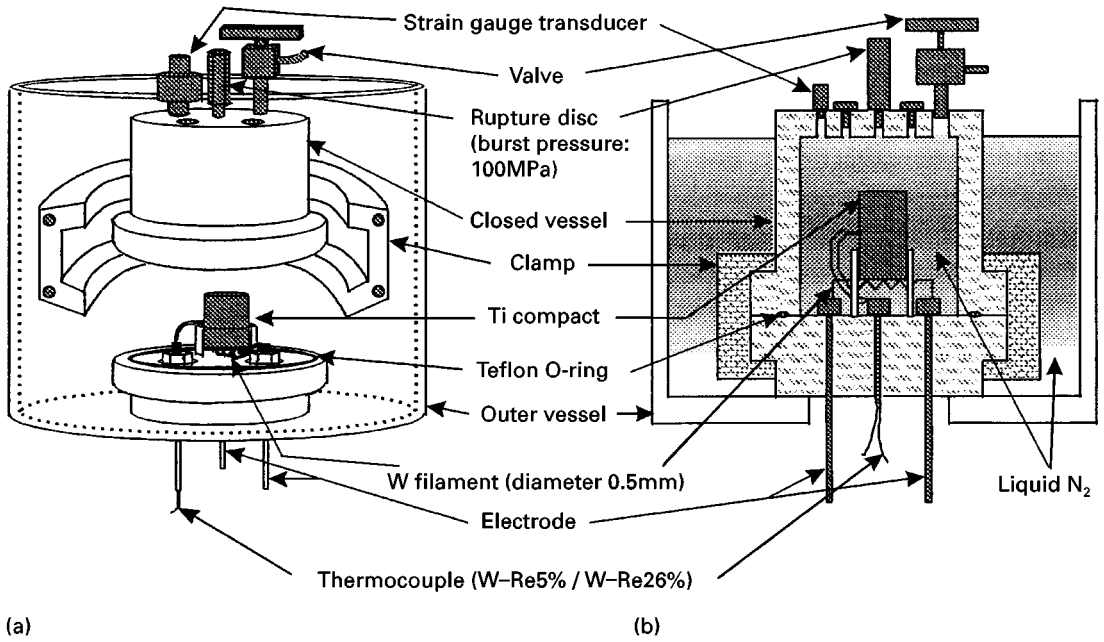

Figure 1 Schematic illustration of an apparatus with a closed vessel used in the present work: (a) perspective view, (b) sectional view.

of the vessel and the clamps were positioned as in Fig. 1b. The vessel was hermetically closed after filling with liquid nitrogen. The sample temperature and pressure in the vessel were measured using a W–Re thermocouple and a strain gauge transducer with a dynamic strain amplifier, respectively. These data were recorded with a data logger (sampling time 50 ms). The fracture surface of the products was observed by scanning electron microscopy (SEM) and the phases were identified by X-ray diffraction.

3. Results and discussion

The reaction between titanium and nitrogen gas is as follows

$$Ti + 1/2N_2 \rightarrow TiN + 336\,kJ \qquad (2)$$

The adiabatic temperature is calculated to be 5100 K. When using liquid nitrogen, the combustion reaction could be sustained because its heat of reaction is sufficient to compensate for the heat of liquid nitrogen evaporation (5.6 kJ mol^{-1}). The adiabatic temperature of this reaction with liquid nitrogen is calculated to be 4800 K, which is a little lower than that with gaseous nitrogen.

When titanium reacts with nitrogen through combustion synthesis in a closed vessel fully filled with liquid nitrogen, the pressure in the vessel increases as in Equation 1. Fig. 2 shows the relationship between the amount of titanium reacted and the change in pressure. For example, in the case of the reaction with 1 mol titanium, the pressure change reaches about 77 MPa (vessel volume 785 cm^3, conversion from titanium to TiN: 100%).

In order to perform the present experiments, two practical problems needed to be solved. The first was how to maintain the vessel at a low temperature at which liquid nitrogen would not evaporate in the initial stage. The bubbling caused by evaporation of liquid nitrogen could produce some unstable contact between the sample and the tungsten wire. In order to keep the vessel at low temperatures, the experiment was carried out with the vessel surrounded by liquid nitrogen. The second problem was the selection of a hermetic seal joint between the parts of vessel which could withstand the rapid increase of pressure. A Teflon o-ring was used in the present work, which is ductile even at cryogenic temperature.

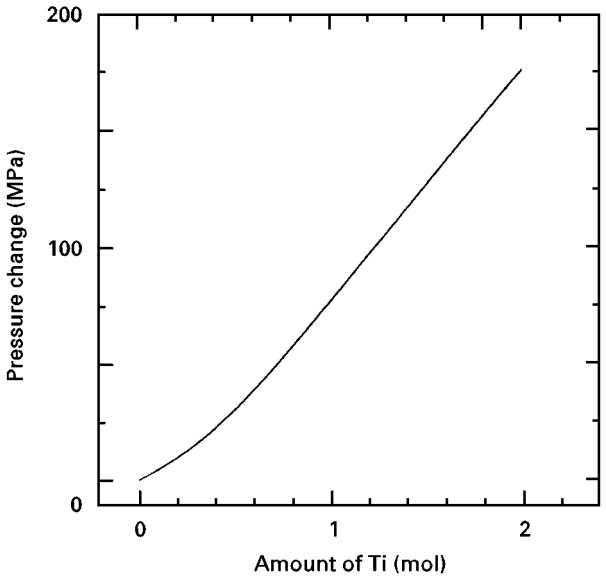

Figure 2 Calculated pressure change following TiN complete combustion synthesis in the present vessel (785 cm^3 inner volume) fully filled with liquid nitrogen.

The typical temperature and pressure changes in the present experiments are shown in Fig. 3. As seen, the pressure in the closed vessel drastically increased (approximately 20 MPa s^{-1}) after induction of the

reaction because of increasing sample temperature (temperature reached more than 2000 K within 5 s after ignition).

The synthesized product was shrunk and densified by the present reaction. The bulk density of the product was approximately 4.96×10^3 kg m^{-3}. Fig. 4 shows scanning electron micrographs of the fracture surface of the products obtained (a) under atmospheric pressure and (b) in the present closed vessel. The latter was found to be more densified than the former, the grain size of which was more than 100 μm. During the combustion propagation, the temperature in the reaction system greatly exceeded the melting point of titanium (1943 K). The densification mechanism can be explained as follows [9]. (1) Titanium melts around the combustion front, (2) the molten titanium forms closed pores which include gaseous nitrogen, (3) the gaseous nitrogen trapped inside reacts with the molten titanium, (4) the inner gas pressure subsequently becomes relatively lower than that outside, and (5) the densification can occur. Fig. 5 shows X-ray diffraction patterns of the products obtained under atmospheric pressure and in a closed vessel. The present product was identified as TiN with no trace of elemental titanium. Its lattice constant was calculated from the X-ray diffraction pattern, and the value ($a =$ 0.4230 nm) was found to correspond to $TiN_{0.87}$, which is shown in Fig. 6. Thus, the density of the present product (4.96×10^3 kg m^{-3}) is considered to be about 99% densified $TiN_{0.87}$.

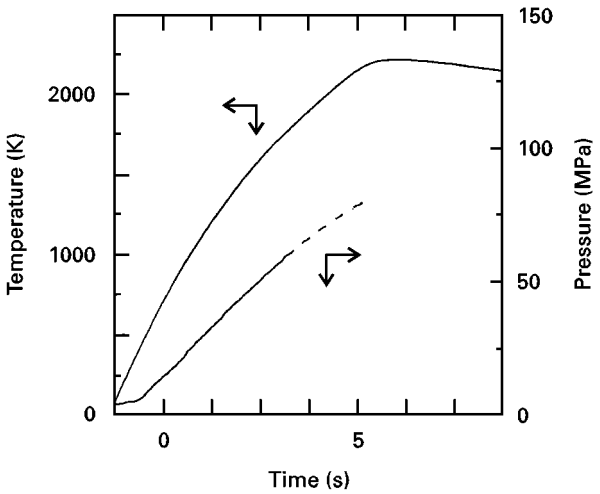

Figure 3 Typical results of temperature and pressure changes during TiN combustion synthesis in the present work.

Because the pressure around the sample increases following reaction propagation, it may be expected that the change in structure will occur in the direction of the reaction propagation, because the structure steps behind the combustion front would proceed differently according to the gradual pressure change in the propagation direction. However, the morphology of the present sample was found to be uniform in every way with the data of SEM observation and X-ray analysis for several positions in the direction of propagation. Because the initiation of TiN combustion synthesis occurs above the melting point of titanium (1943 K) [13], the change in structure takes place during the reaction after the maximum temperature is reached (i.e. in the "after-burn" region [7]). In the after-burn region, the pressure increase during the process plays an important role in densification. As shown in Fig. 3, the pressure gradient dp/dt is constant

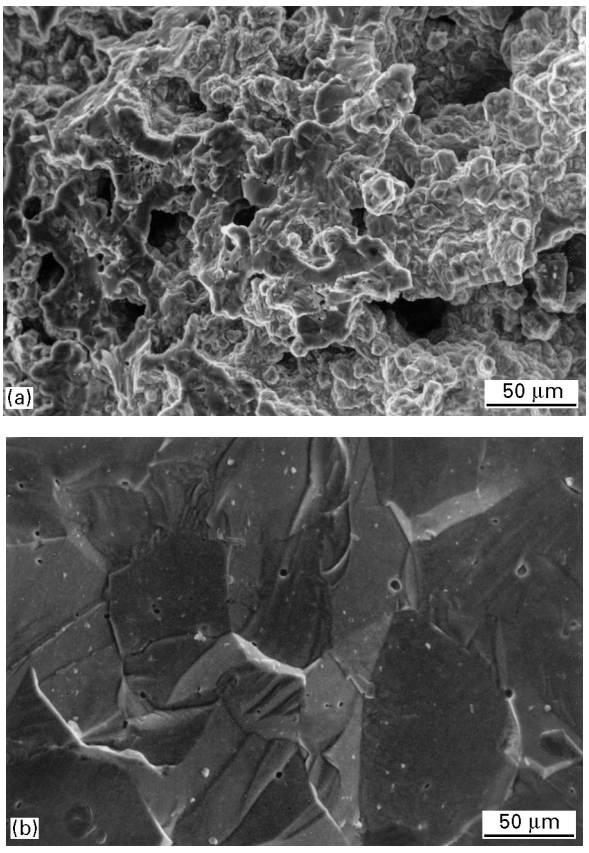

Figure 4 Scanning electron micrographs of the fracture surfaces of the products obtained by combustion synthesis under (a) atmospheric pressure and (b) closed conditions.

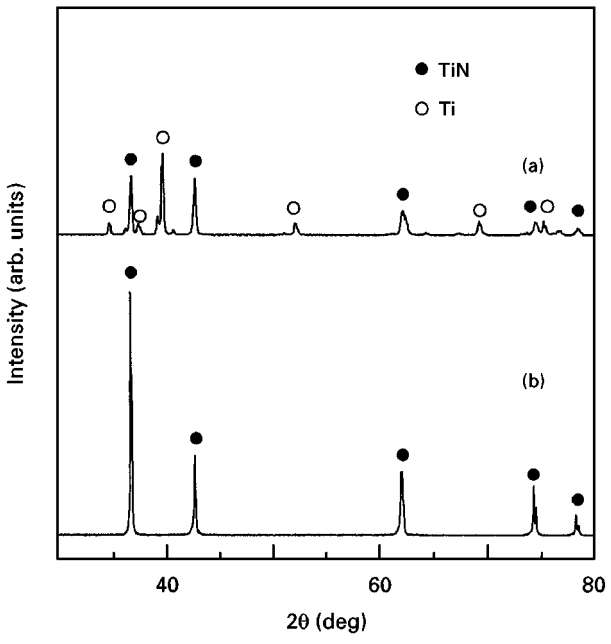

Figure 5 X-ray diffraction patterns of the products obtained by combustion synthesis under (a) atmospheric pressure and (b) closed conditions.

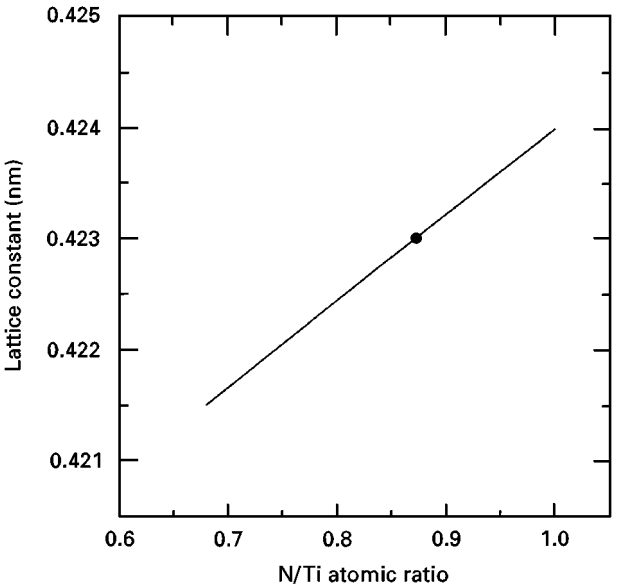

Figure 6 Variation of lattice constant with composition for TiN_x: (●) present work, (—) after Wriedt *et al.* [1].

in the present case. Therefore, the effect of pressure on product densification would be the same in the direction of propagation. To check this hypothesis, it is important to investigate the behaviour of the combustion wave velocity under increasing pressure.

4. Conclusions

TiN synthesis was carried out by sustaining the reaction between titanium metal and nitrogen in a closed vessel filled with liquid nitrogen. The following results have been confirmed.

1. The pressure in the closed vessel drastically increased by more than 60 MPa within 3 s with increasing sample temperature after its reaction induction.

2. The obtained product was densified up to more than 99%.

3. The lattice constant of the product was measured as 0.4230 nm by X-ray diffraction and the value corresponds to a compound of $TiN_{0.87}$.

4. The morphology of the product was uniformly distributed in the direction of the reaction propagation.

The present results reveal that some new phase could be formed following the gradual pressure increase in combustion synthesis technology such as this in a closed vessel filled with liquid nitrogen.

References

1. H. A. WRIEDT and J. L. MURRAY, *Bull. Alloy Phase Diagr.* **8** (1987) 378.
2. L. E. TOTH, "Transition Metal Carbides and Nitrides" (Academic Press, New York, London 1971).
3. P. T. B. SHAFFER, "Materials Index No. 1" (Plenum Press, New York, 1964).
4. A. G. MERZHANOV and I. P. BOROVINSKAYA, *Dokl. Chem.* **204** (1972) 429.
5. *Idem.*, *Combust. Sci. Technol.* **10** (1975) 195.
6. Z. A. MUNIR, *High Temp. High Press.* **20** (1988) 19.
7. M. E-GRAMI and Z. A. MUNIR, *J. Am. Ceram. Soc.* **73** (1990) 1235.
8. H. KUDO and O. ODAWARA, *J. Mater. Sci.* **24** (1989) 4030.
9. M. SHIBUYA, O. ODAWARA, M. OHYANAGI and M. KOIZUMI, *Int. J. SHS* **5** (1996) 77.
10. M. E-GRAMI and Z. A. MUNIR, *J. Am. Ceram. Soc.* **73** (1990) 2222.
11. O. ODAWARA and H. WU, *Int. J. Mater. Product Technol.* **10** (1995) 493.
12. J. B. HOLT and D. D. KINGMAN, *Mater. Sci. Res.* **17** (1984) 167.
13. M. SHIBUYA, J. F. DESPRES and O. ODAWARA, *Mater. Res. Bull.* **32** (1997) 1341.

Received 9 June 1997
and accepted 13 February 1998