

## Properties and rapid consolidation of binderless titanium nitride by pulsed current activated sintering

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A nanopowder of TiN was fabricated by explosion of Ti wire under a nitrogen pressure of 1 atmosphere. A dense pure TiN hard material with a relative density of up to 97% theoretical was produced with the simultaneous application of 80 MPa pressure and a pulsed current within 2 minutes. The hardness and fracture toughness of TiN sintered at 1600°C under 80 MPa pressure and 2800A are 1650 kg·mm<sup>-2</sup> and 6 MPa·m<sup>1/2</sup>.

**Key words:** Sintering, Nanopowder, Hardness, TiN.

### Introduction

Nitrides have many applications because of their hardness, their properties at high temperature and their wear resistance. Titanium nitride among the nitrides is particularly interesting for its high wear resistant coatings for cutting-tool materials and high corrosion resistance [1]. Titanium nitride can be produced by a self-propagating high temperature synthesis (SHS) process. The SHS developed by Merzhanov and coworkers [2, 3] in the late 1960 s, refers to a process in which materials with sufficiently high heat of formation are synthesized in a combustion wave, which after ignition, spontaneously propagates throughout the reactants and converts them into the products. SHS is extremely attractive, giving a high-purity product due to the volatilization of low boiling point impurities at elevated temperature, and high productivity due to very high reaction rates. The combustion synthesis of titanium nitride has mainly been conducted under nitrogen gas pressures ranging from 0.1 to 10 MPa. The effects of the nitrogen pressure, the pressed sample porosity and diluent additions on the material stoichiometry have been investigated [4-7].

Dense TiN bodies can be sintered from micrometric powders by conventional sintering at high temperature (above 2000 °C) [8]. The use of nanometric starting powders allows specimens to be sintered at lower temperatures (1300 °C to 1500 °C) [9] but these powders present a high oxygen affinity which could be an obstacle to the densification stage

[10]. In recent days, pulsed current activated sintering equipment can make dense material within two minutes which are difficult to sinter without additives because of their high melting point and strong covalent bonding [11].

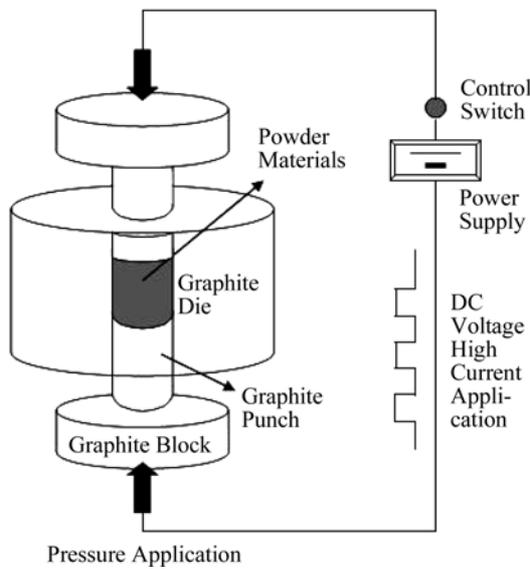
In this study, we investigated the production of nanopowder and dense binderless TiN hard material by pulsed current activated sintering. In addition, we also studied the mechanical properties of binderless TiN.

### Experimental Procedure

Pure Ti wire of 0.3 mm  $\Phi$  was used for the explosion experiment. The capacitance of the exploding circuit was 3.5  $\mu$ F. The applied voltage across the 2 cm-long wire was 11.4 kV. The wire was exploded under a nitrogen pressure of 1 atmosphere. After the explosion, the powders were stabilized overnight and filtered through a 120 mesh sieve to remove some misfired portions.

The powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the pulsed current activated sintering (PCAS) apparatus shown schematically in Fig. 1. The PCAS apparatus includes a 30 kW power supply which provides a pulsed current (on time; 20  $\mu$ s, off time; 10  $\mu$ s) through the sample, and a 50 kN uniaxial press. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. A pulsed current was then activated and maintained until the densification rate was negligible, as indicated by the real-time output of the shrinkage of the sample. The shrinkage was measured by a linear gauge measuring the vertical displacement. Temperatures were measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the pulsed current was turned off

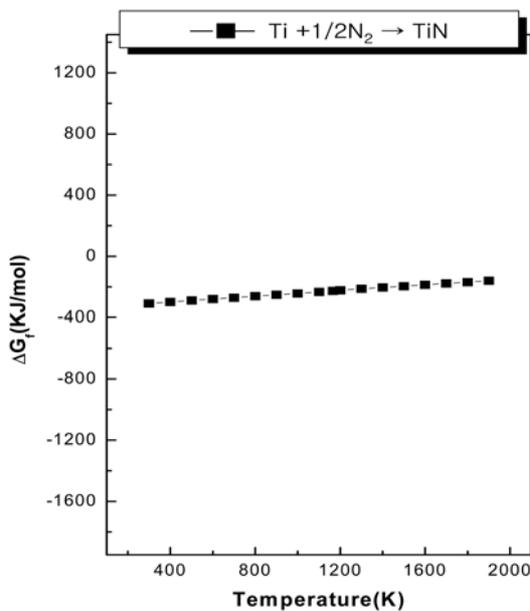
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**Fig. 1.** Schematic of Pulsed-Current Activated Sintering Set up.

and the sample cooled to room temperature. The process was carried out under a vacuum of  $4 \times 10^{-2}$  Torr (5.33 Pa).

The relative density of the sintered sample was measured by the Archimedes method. Microstructural information was obtained from product samples, which had been polished and etched using a solution of HF (10 vol.%), HNO<sub>3</sub> (40 vol.%) and H<sub>2</sub>O (50 vol.%) for 1-2 minutes at room temperature. Compositional and microstructural analyses of the powder and the products were made through X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), a field emission scanning electron microscope (FE-SEM) and a field emission transmission electron microscope (FE-TEM).



**Fig. 2.** Temperature dependence of the Gibbs free energy for the interaction between Titanium and Nitrogen.

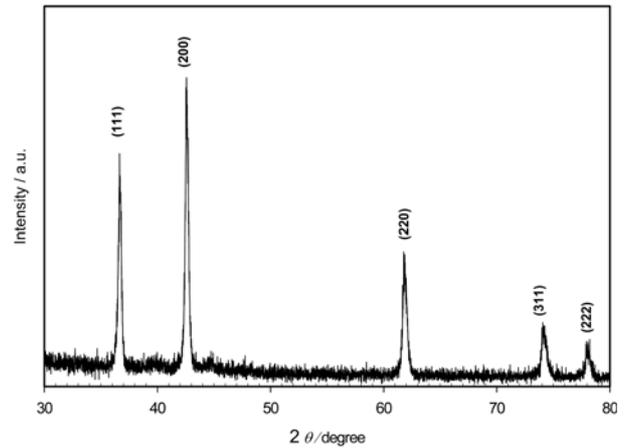
Vickers hardness was measured by performing indentations at a load of 20 kg<sub>f</sub> and a dwell time of 15 s.

### Results and Discussion

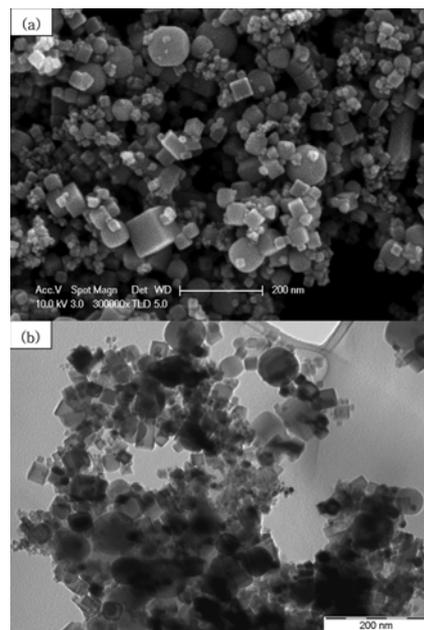
The interaction between Ti and N<sub>2</sub> :



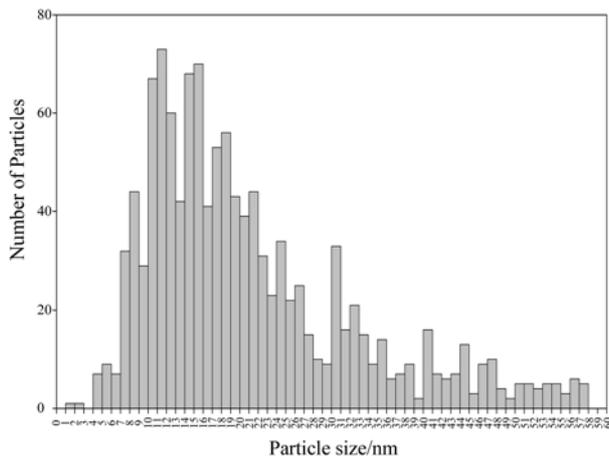
is thermodynamically feasible as shown in Fig. 2 [12]. Fig. 3 shows X-ray diffraction pattern of the TiN nanoparticles synthesized by explosion of Ti wire under 1 atm N<sub>2</sub>. All peaks are TiN. So, TiN is synthesized from Ti and N<sub>2</sub>. FE-SEM and TEM images of TiN synthesized nanoparticles are shown in Fig. 4. The TiN particles have a well-defined cubic shape or a round shape. Fig. 5 shows particle size distribution of TiN particles. Many particles are distributed in



**Fig. 3.** X-ray diffraction pattern of TiN nanoparticles synthesized by explosion of Ti wire under 1 atm N<sub>2</sub>.



**Fig. 4.** FE-SEM and TEM micrograph of TiN nanoparticles synthesized by explosion of Ti wire under 1 atm N<sub>2</sub>.



**Fig. 5.** Particulate size distribution of TiN particles prepared by electrical wire explosion under 1 atm N<sub>2</sub>.

**Table 1.** TiN nanoparticles synthesized in this study

| Average particle size (nm) | Nitrogen content (wt.%) | Oxygen content (wt. %) | Lattice parameter (nm) | BET (m <sup>2</sup> /g) |
|----------------------------|-------------------------|------------------------|------------------------|-------------------------|
| 25                         | 25                      | 4-6                    | 0.4243                 | 28.5                    |

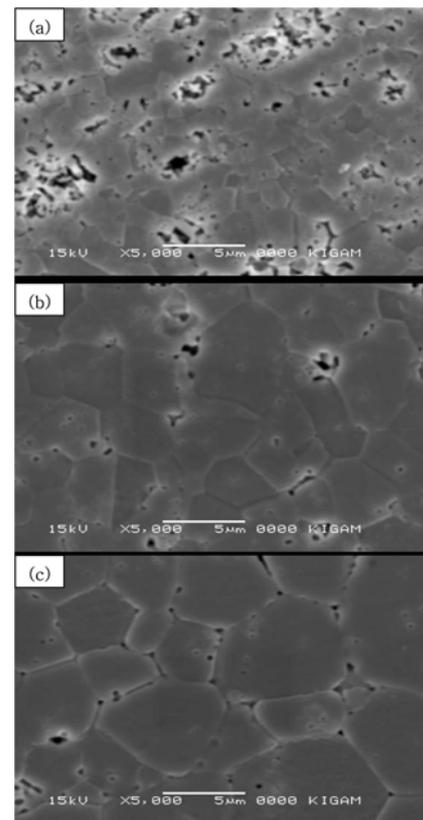
the range of 7 and 26 nm. Table 1. shows the characteristics of TiN powder. The average particle size, lattice parameter and BET are 25 nm, 0.4243 nm, and 28.5 m<sup>2</sup>/g, respectively. SEM micrographs of the cross section and the fracture surface of TiN compacts sintered at 1350, 1450 and 1600 °C are shown in Fig. 6 and 7. As expected, the amount of pores decreased and the grain size increased with an increase in the sintering temperature. The grain size of TiN increased from 1.5 μm to 7.1 μm with the sintering temperature as shown in Fig. 8. Fig. 9 shows an X-ray diffraction pattern of TiN sintered at 1600 °C. All the peaks are from TiN. The relative densities and Vickers hardness of TiN sintered at 1350, 1450, and 1600 °C are 95, 96 and 97% theoretical, 1100, 1300 and 1650 kg·mm<sup>-2</sup>, respectively. The increase in the hardness of TiN is due to the increase of the density.

Indentations with large enough loads produced median cracks around the indent. From the length of these cracks, fracture toughness values can be determined using Anstis *et al.* [13] equation :

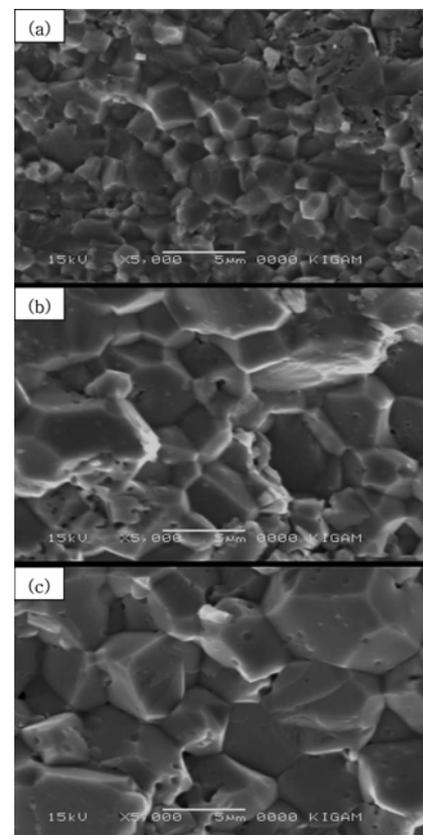
$$K_{IC} = 0.016 (E/H)^{1/2} \cdot P/C^{3/2} \quad (2)$$

where E is Young's modulus, H the indentation hardness, P the indentation load, and C the trace length of the crack measured from the center of the indentation. The modulus of TiN has been reported as 251 GPa [14]. The fracture toughnesses of TiN sintered at 1350, 1450, and 1600 °C are 3, 4, and 6 Mpa·m<sup>1/2</sup>, respectively. The increase of toughness of TiN is due to the increase of the density.

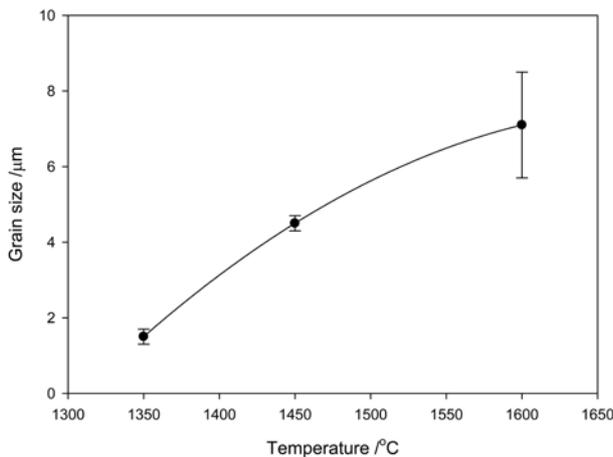
Highly dense TiN was sintered within two minutes by pulsed current activated heating. The role of the pulsed current in sintering has been the focus of several attempts



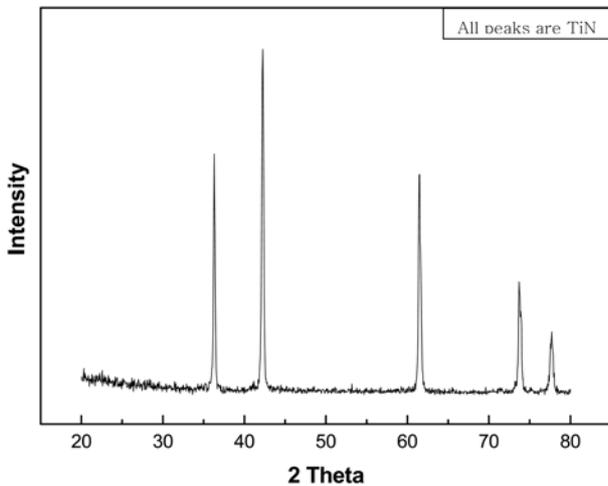
**Fig. 6.** SEM micrographs of the cross section of TiN compacts sintered at (a) 1350 °C (b) 1450 °C (c) 1600 °C.



**Fig. 7.** SEM micrographs of the fracture surface of TiN compacts sintered at (a) 1350 °C (b) 1450 °C (c) 1600 °C.



**Fig. 8.** Effect of sintering temperature on the grain size of TiN compacts.



**Fig. 9.** X-ray diffraction pattern of TiN compact sintered at 1600 °C.

aimed at providing an explanation of the observed enhancement of sintering and the improved characteristics of the products. The role played by the current has been variously interpreted, the effect being explained in terms of the fast heating rate due to Joule heating, the presence of a plasma in the pores separating powder particles [15], and the intrinsic contribution of the current to mass transport [16-18].

### Summary

Nanopowder of TiN was fabricated by the explosion of Ti wire under anitrogen pressures of 1 atmosphere. Highly dense TiN was sintered using the rapid sintering method,

PCAS within two minutes. The average grain sizes, the fracture toughnesses and the Vickers hardnesses of the TiN were about 1.5, 4.5, 7.1 μm, and 3, 4, 6 Mpa·m<sup>1/2</sup> and 1100, 1300, 1650 kg·mm<sup>-2</sup>, for the samples sintered at 1350, 1450, and 1600 °C and their corresponding densities were approximately 95, 96 and 97%, respectively.

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### References

1. K. Vandierendonck and M. Van Stapen, *Surface and Coatings Technology* 97 1-3 (1997) 218-223.
2. I.P. Borovinskaya, A.G. Merzhanov, N.P. Novikov and A.K. Filonenko, *Combust. Explos. Shock Waves* 10 (1974) 2-10.
3. A.G. Merzhanov, G.G. Karyuk, I.P. Borovinskaya, V.A. Prokudina and E.G. Dyad, *Powder Metall. Met Ceram.* 20 (1981) 709-715.
4. M. Eslamloo-Grami and Z.A. Munir, *J. Am. Ceram. Soc.* 73[8] (1990) 2222-2227.
5. M. Eslamloo-Grami and Z.A. Munir, *J. Am. Ceram. Soc.* 73[5] (1990) 1235-1239.
6. H. Kudo, O. Odawara, *J. Mater. Sci.* 24 (1989) 4030-4033.
7. C.L. Yen and H.C. Chuang, *Ceram. Int.* 30-5 (2004) 705-714.
8. M.A. Kuzenkova and P.S. Kislyi, *Poroshk Metall* 98[2] (1971) 125-132.
9. R.A. Andrievski, *Nanostruct. Mater.* 9 (1997) 607-10.
10. O.B. Zgalat-Lozinskii, A.V. Ragulya and V.V. Skorokhod, Tomila TVm Timofeeva II, Klochkov LI, Garbuz VV, *Powder Metall Met Ceram* 40[9-10] (2001) 471-477.
11. H.C. Kim, I.J. Shon, J.E. Garay and Z. A. Munir, *International Journal of Refractory Metals & Hard Materials* 22 (2004) 257-264.
12. O. Knake, O. Kubaschewski and K. Hesselmann, in "Thermochemical Properties of Inorganic Substances" (Springer-Verlag press 1991).
13. G.R. Anstis, P. Chantikul, B.R. Lawn and D.B. Marshall, *J. Am. Ceram. Soc.* 64 (1981) 533-538.
14. D.S. Stone, K.B. Yoder and W.D. Sproul, *Journal of Vacuum Science and Technology A* 9[4] (1991) 2543-2547.
15. Z. Shen, M. Johnsson, Z. Zhao and M. Nygren, *J. Am. Ceram. Soc.* 85 (2002) 1921-1926.
16. J.E. Garay, U. Anselmi-Tamburini, Z.A. Munir, S.C. Glade and P. Asoka-Kumar, *Appl. Phys. Lett.* 85 (2004) 573-580.
17. J.R. Friedman, J.E. Garay, U. Anselmi-Tamburini and Z.A. Munir, *Intermetallics.* 12 (2004) 589-596.
18. J.E. Garay, J.E. Garay, U. Anselmi-Tamburini and Z.A. Munir, *Acta Mater.*, 51 (2003) 4487-4493.