



Effect of compacting pressure, powder degassing and thermobaric treatment on densification and properties of nanocrystalline titanium nitride

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Abstract

The effects of compacting pressure, powder degassing and high pressure sintering temperature and time on the densification and properties of nanocrystalline titanium nitride have been investigated. For this reason, TiN powder with a mean particle size of 55 nm was pressed in the range of compacting pressure from 0.2 to 1.0 GPa and sintered under static pressure of 3.5 GPa in the temperature range of 900–1600°C for 45–120 s. Some of green bodies were degassed in vacuum before sintering. It was shown that samples compacted in the pressure range of 0.2–0.6 GPa have the highest density after the thermobaric treatment. The maximum density (about 97.3 %TD) was obtained with degassed samples. Microhardness and microstructure investigations have shown that recrystallization of the TiN nanopowder begins at the sintering temperatures of 1100–1200°C and sintering time less than one minute. The maximum microhardness obtained was 23.2±1.0 GPa and the maximum Young modulus was 370 GPa.

Keywords: titanium nitride, nanopowder, densification, high pressure sintering

1. Introduction

Titanium nitride (TiN) is a high-melting-point compound with high hardness, low electric resistance and good thermal stability [1,2]. Usually, TiN is used in coatings and there is virtually no information about its usage as a bulk material. The main reason for that is a low density of the sintered material which results in poor mechanical properties. Pure TiN powders are very difficult to fully densify because of covalent bonding, very low self-diffusion coefficient and tendency to decompose at high temperatures [3]. The use of nanosized powders shows great promise for producing dense TiN parts at lower temperatures and improving the mechan-

ical properties of sintered compacts [4]. Consolidation of TiN nanopowders has been attempted using several sintering techniques: Spark Plasma Sintering (Field-Assisted Sintering) [4,5] and Gas Pressure Sintering [6]. Dense ceramics on the basis of TiN having nanocrystalline structure and increased hardness have been obtained using High Pressure Sintering (HPS) [7–9]. HPS is especially effective for fabricating nanoceramics based on high-melting point compounds because dense materials can be produced without any additives while duration of sintering can be reduced [10–15].

HPS of TiN nanopowders under pressures of 3 and 4 GPa was investigated in work [8]. It was shown that the density and hardness of samples sintered from TiN powder with a mean particle size of 40 nm at pressure of 4 GPa are much higher than at pressure of 3 GPa. These

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results had demonstrated that value of applied pressure plays an import role in the densification process of TiN nanopowders during HPS.

However, there is virtually no information about how the green density of the compacts affects the final density of the sintered samples based on TiN nanopowder. The primary objective of the present work was to investigate the effect of all stages of thermobaric treatment on densification of titanium nitride nanopowder. For this reason, we have studied densification of TiN green bodies prepared at different compacting pressures. Furthermore, we have investigated the role of degassing in the densification process of TiN nanopowder. The basic features of the sintering process and their effect on the resulting physical and mechanical properties of the sintered material are examined.

II. Experimental

Pure TiN powder (Institute of Problems of Chemical Physics RAS, Russia) with a specific surface of 20.5 m²/g and a mean particle size of 55 nm was used as starting material for the experiments. X-ray diffraction analysis of investigated powder had identified only one phase (Fig. 1): the face-centered cubic (FCC) modification of TiN with lattice parameter $a = 4.2361 \pm 0.0007$ Å. According to [16] N/Ti ratio in this case is about 0.9.

Cylindrical green compacts, 11 mm in diameter and 5 mm high, were formed in a stainless steel die in the range of compacting pressures of 0.2 to 1.0 GPa. Some of green bodies were previously degassed in a vacuum furnace at the temperature of 300°C for 30 min and then at temperature of 800°C for 60 min. A modified high pressure anvil-type apparatus [17] was used for HPS. The samples were subjected to the pressure of 3.5 GPa at room temperature and then heated to 900–1600°C (at the same pressure) and sintered for 45–120 s. The sintering process was controlled and monitored using previously developed automated control system for thermobaric sintering [18].

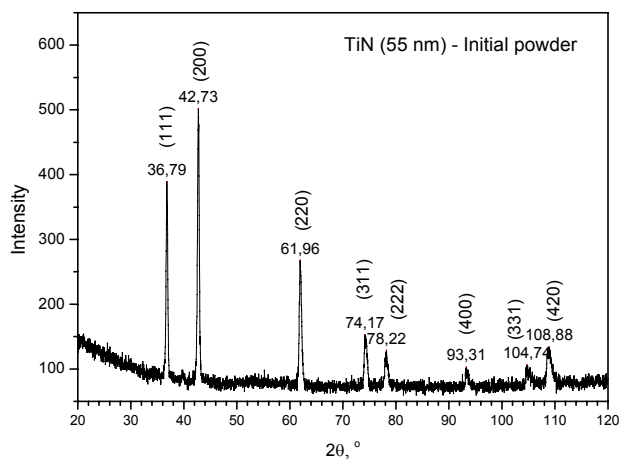


Figure 1. X-Ray data for initial TiN nanopowder

Density of the sintered specimens was measured using the Archimedes principle by weighing them in carbon tetrachloride at room temperature. The accuracy of this method is about ± 0.01 g/cm³. Relative density was calculated in accordance to the theoretical density of 5.388 g/cm³. The microhardness measurements were carried out at a load of 100 g and indentation time of 10 s. Young's modulus of the sintered samples was obtained by measured the velocity of the ultrasonic waves transition through the sample [19]. The accuracy of calculated Young's modulus could be estimated to be 2 %. Microstructure investigations were carried out using Leica DM IRM metallurgical microscope and JSM-6490 (JEOL Ltd., Tokyo, Japan) scanning electron microscope. The average grain size was measured using linear intercept method.

III. Results and discussion

At the first stage of the investigation green samples have been prepared from TiN nanopowder under five compacting pressures: 0.2, 0.4, 0.6, 0.8 and 1.0 GPa. Then the samples were sintered under the pressure of 3.5 GPa in the temperature range of 900–1600°C for 60 s. Fig. 2 shows the relative densities of the sintered samples as a function of compacting pressure and sintering temperature. As one can see, the final relative density of the sintered samples depends on their green density and HPS temperature. Obtained results indicate that the higher sintering temperature is applied the lower compacting pressure is needed for maximum densification of the powder. Thus, under low sintering temperatures (900–1100°C) density of the sintered samples increases with raising the compacting pressure up to 0.6 GPa. At the same time, after sintering at higher temperatures (1400–1600°C) the specimens compacted in the pressure range of 0.2–0.4 GPa have the highest relative densities. It is known that there is a formation of cracks in powder compacts if deformation degree exceeds limiting value [20]. This process is accompanied by poros-

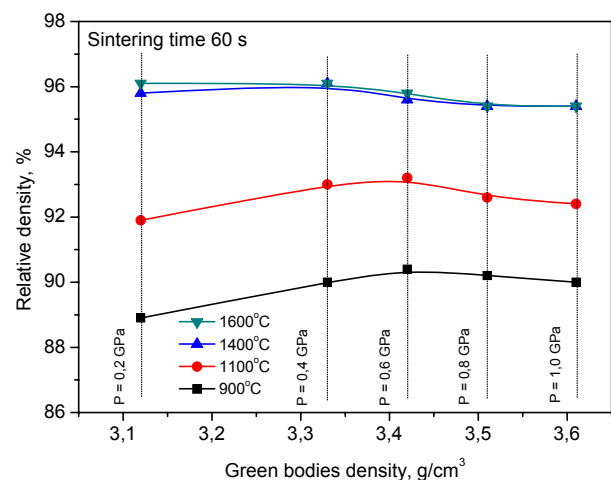


Figure 2. Density of sintered TiN samples vs. green bodies' density

ity increase. Most likely, this is the main reason why the use of very high compacting pressure leads to a decrease in the relative density of the sintered material. Accelerated recrystallization in the samples whose particles are in stronger contact might be the second reason, on which the density goes down.

At the second stage we have investigated the effect of powder degassing on densification during HPS. For this reason, we used green bodies compacted under the pressure of 0.2 GPa and degassed in a vacuum furnace. After degassing the samples were sintered under the pressure of 3.5 GPa in the temperature range of 900–1600°C for 60 s. The obtained results are presented in Fig. 3. It has been shown that samples sintered after vacuum annealing have the relative density about 1–2 % higher than before. This means that initial investigated nanopowder contains adsorbed gases that complicate its densification during the sintering. In all cases the most intensive powder densification is observed in the temperature range of 1100–1400°C while the maximum values of density are achieved at the sintering temperatures of 1400–1600°C. At the same time decrease of microhardness above 1100°C demonstrates that recrystallization begins at temperatures above 1100–1200°C (Fig. 4).

The results of microstructure investigations are presented in Figs. 5–7. As one can see, investigated powder has bimodal particle size distribution (Fig. 5a). As a result, all SEM micrographs demonstrate that sintered material also has bimodal grain size distribution – smaller submicrometer grains and much larger grains of few to several tens of micrometers (Fig. 5b–5f). Optical micrographs (Fig. 6) also indicate presence of two phases in the sintered material: small grains (matrix) and big round grains. Small grains have yellow to orange colouring meanwhile the colour of big round grains is grey. So, in accordance with [16] the matrix has N/Ti ratio about 0.8–1.0 meanwhile big grey particles have N/Ti ratio about 0.5 or less. It is to be noticed that at sintering temperatures of 900°C, 1100°C

and 1250°C clear boundaries between the big particles and the matrix are observed (Fig. 6a). At the same time, at sintering temperatures of 1400°C and 1600°C these boundaries become washed away (Fig. 6b). It is very likely that free titanium located inside big particles diffuses into the matrix and dissolves in it. Thus, the material becomes more homogeneous. At that matrix colour becomes brighter which means that N/Ti ratio of matrix is reduced. It is possible, that this is one of the reasons why the samples sintered at temperatures of 1400–1600°C possess the lowest microhardness.

A mean particle size of the initial powder and a mean grain size in the samples sintered at temperatures of 900–1100°C are in a range of 40–100 nm (Fig. 5a–5c and 7) while in the sample sintered at temperature of 1250°C this range extends up to 200 nm (Fig. 5d and 7). In the samples sintered at temperatures of 1400 and 1600°C the mean crystallite sizes were in a range of 100–500 nm (Figs. 5e and 7) and 200–500 nm (Figs. 5f and 7) respectively. It is to be noted, that we did not use the sizes of big round particles for calculating the mean particles size of initial powder and average grain size of sintered material.

Finally, the effect of sintering time on the physical and mechanical properties of ceramics sintered from TiN nanopowder was investigated. For this reason, some of the degassed samples were sintered under the pressure of 3.5 GPa in the temperature range of 1100–1400°C for 45–120 s. For sintering, the same green compacts as on the second stage were used. The obtained results are presented in Figs. 8 and 9.

As is shown in Fig. 8a, optimal sintering time for the TiN nanopowder subjected to the pressure of 3.5 GPa depends on the sintering temperature. The higher sintering temperature is applied the shorter time is needed for ending powder densification. After sintering at all investigated temperatures (1100, 1250 and 1400°C) microhardness of the samples decreases with increasing the sintering time (Fig. 8b). This means that increasing the sintering

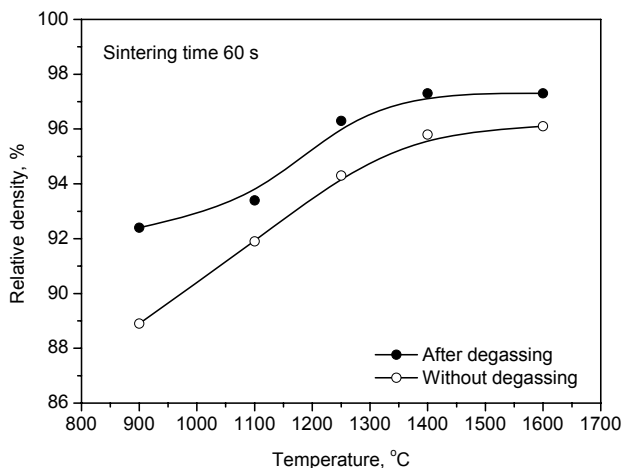


Figure 3. Density of TiN samples vs. sintering temperature

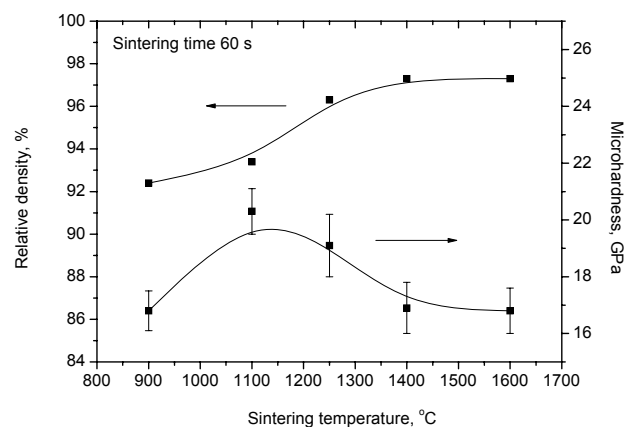


Figure 4. Relative density and microhardness of degassed TiN samples depending on sintering temperature

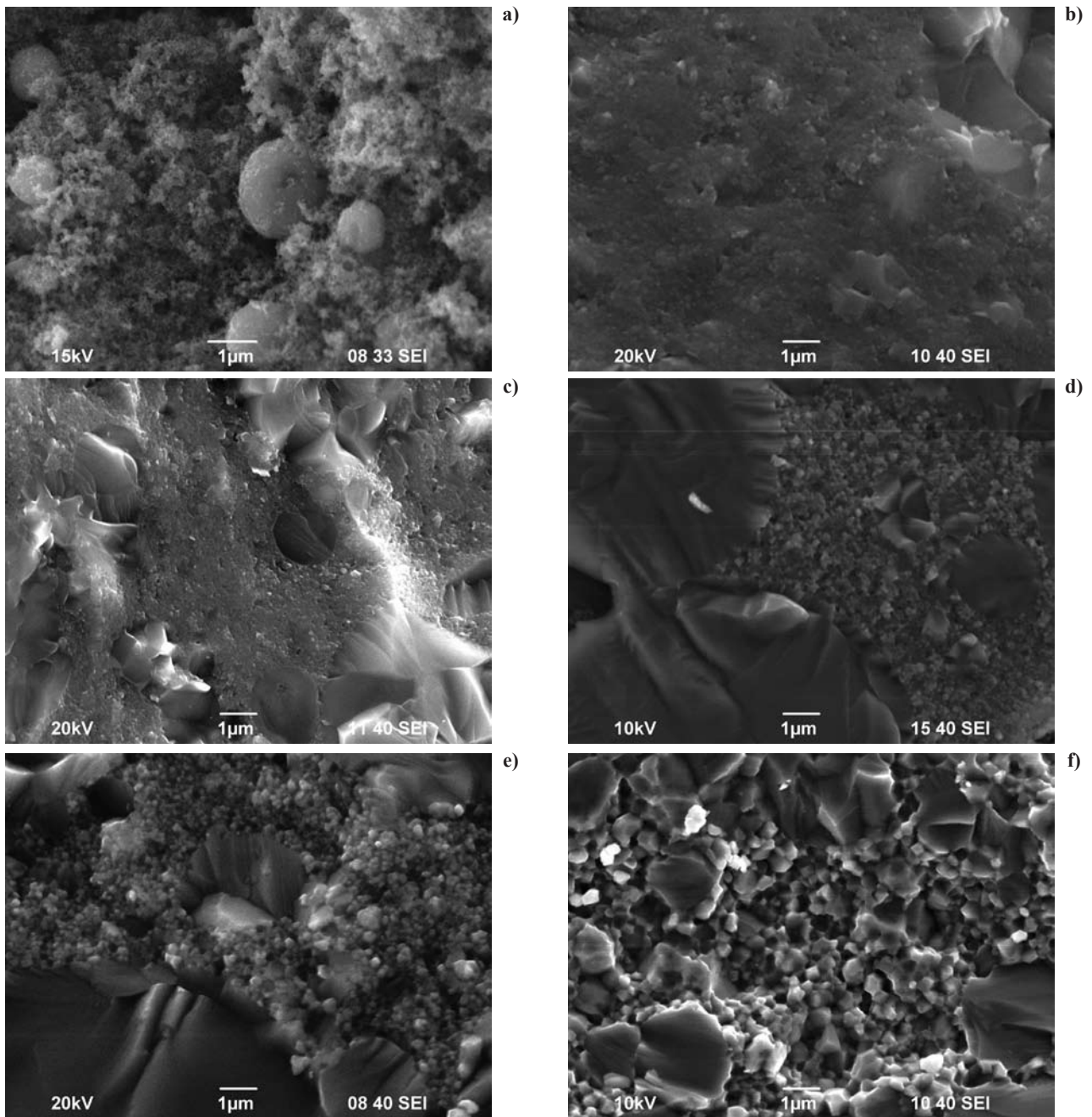


Figure 5. SEM micrographs of the initial TiN powder (a) and fracture surfaces of degassed samples sintered at different temperatures: 900°C (b), 1100°C (c), 1250°C (d), 1400°C (e) and 1600°C (f)

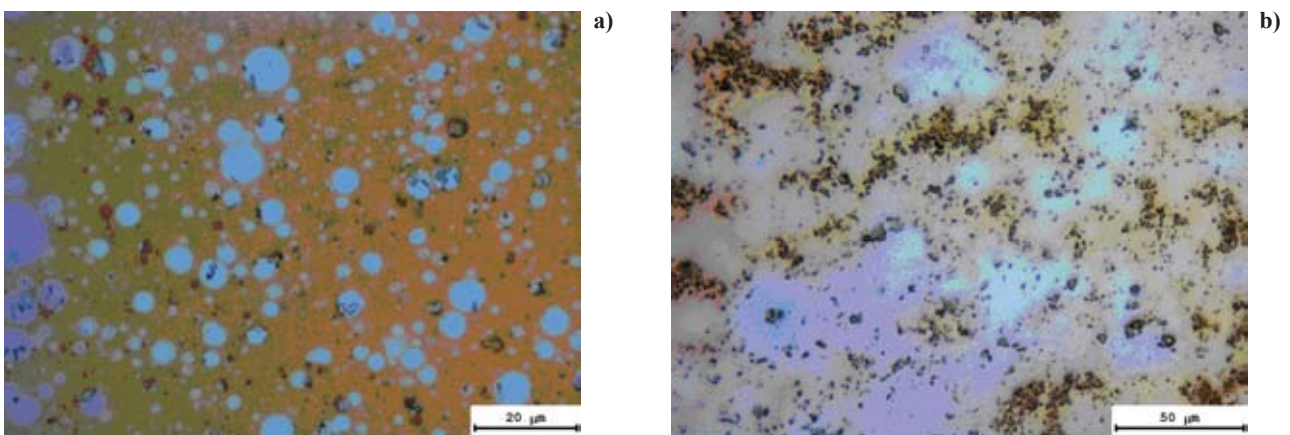


Figure 6. Optical micrographs of degassed TiN samples sintered at temperatures of 1250°C (a) and 1600°C (b)

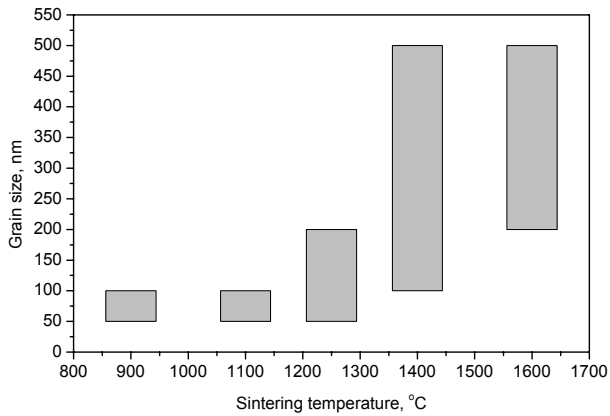
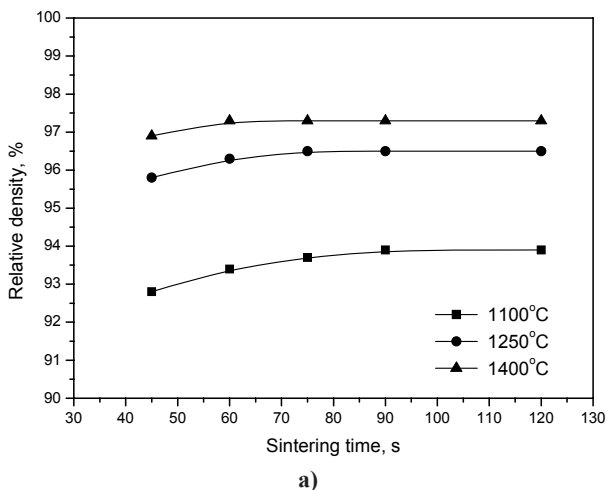
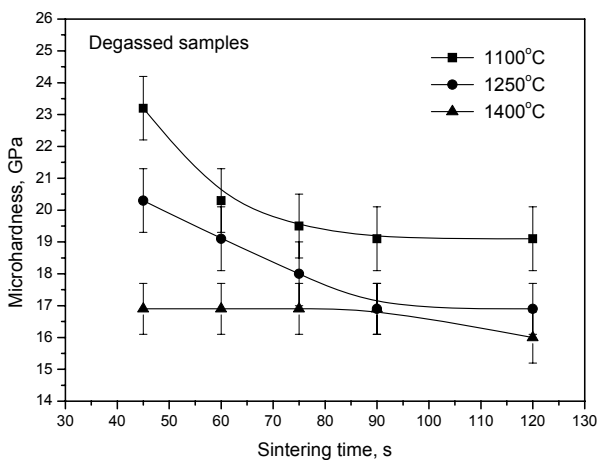


Figure 7. Average grain size of degassed TiN samples sintered at different temperatures

time and temperature intensifies the rate of recrystallization processes of nanocrystalline titanium nitride. The maximal value of microhardness obtained in current investigation (23.2 ± 1.0 GPa) is lower compared to values obtained earlier with use of TiN powder with the mean particle size of 40 nm (about 30 GPa), but it is comparable to hardness of samples sintered from TiN powder with the mean particle size of 80 nm [8].



a)



b)

Figure 8. Relative density (a) and microhardness (b) of degassed TiN samples vs. sintering time

The Young's modulus of all sintered samples was found to be proportional to their relative density (Fig. 9). Substantial improvement of the elastic properties is observed with raising the sintering temperature from 1100 to 1250°C while at a further increase in the sintering temperature (from 1250 to 1400°C) a change in both the density and elasticity modulus of the samples is insignificant. The maximal value of the Young's modulus obtained in present investigation (about 370 GPa) is lower than some of previous results [21]. Probably, this is concerned with nonstoichiometric composition of the investigated material [22].

IV. Conclusions

The effects of compacting pressure, powder degassing and high pressure sintering temperature and time on the densification and properties of nanocrystalline titanium nitride have been investigated. It has been shown that the samples compacted from TiN powder with a mean particle size of 55 nm in the pressure range of 0.2–0.6 GPa exhibit the highest relative density after thermobaric treatment under the pressure of 3.5 GPa, about 95–96 %TD. In all cases the use of compacting pressure exceeding 0.6 GPa leads to a decrease in the density of the sintered material. Powder degassing permitted raising the maximum relative density of sintered samples up to 97.3 %TD.

Microstructure investigations have shown that mean particle size of the initial powder and a mean grain size in the samples sintered at temperatures of 900–1250°C are in a range of 40–200 nm while in the samples sintered at temperatures of 1400–1600°C this range extends up to 100–500 nm. Microhardness measurements had also demonstrated that recrystallization begins in the temperature range of 1100–1200°C.

The maximum physical and mechanical properties of sintered material ($H_v = 23.2 \pm 1.0$ GPa, $E = 370$ GPa) are lower than some of known literature data. This fact can be explained by nonstoichiometric composition of investigated TiN nanopowder.

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References

1. R. Yamamoto, S. Murakami, K. Maruyama, “High-temperature mechanical properties of hot-pressed TiN with fine grain size” *J. Mater. Sci.*, **33** (1998) 2047–2052.
2. F. Zhang, W.A. Kaczmarek, L. Lu, M.O. Lai, “Formation of titanium nitrides via wet reaction ball milling”, *J. Alloy. Compd.*, **307** (2000) 249–253.
3. J.H. Won, K.H. Kim, J.H. Chae, K.B. Shim, “Sintering of attrition-milled TiN powders using a spark plasma sintering technique”, *J. Ceram. Process. Res.*, **3** [3] (2002) 166–170.

4. L. Wang, W. Jiang, L. Chen. “Consolidation of nano-sized TiN powders by Spark Plasma Sintering”, *J. Am. Ceram. Soc.*, **89** [7] (2006) 2364–2366.
5. J.R. Groza, J.D. Curtis, M. Kramer, “Field-assisted sintering of nanocrystalline titanium nitride”, *J. Am. Ceram. Soc.*, **83** [5] (2000) 1281–1283.
6. T. Rabe, R. Wasche, “Sintering behaviour of nanocrystalline titanium nitride powders”, *Nanostruct. Mater.*, **6** (2005) 357–360.
7. V.S. Urbanovich “Consolidation of nanocrystalline materials at high pressures”, pp. 405–424 in *Nanostructured materials. Science and Technology*, Kluwer Academic Publishers, Dordrecht, 1998.
8. V.S. Urbanovich “Properties of nanocrystalline titanium nitride-based materials prepared by high-pressure sintering”, pp. 169–176 in *Functional Gradient Materials and Surface Layers Prepared by Fine Particles Technology*, Kluwer Academic Publishers, Dordrecht, Netherlands, 2001.
9. A.I. Bykov, I.I. Timofeeva, L.A. Klochkov, A.V. Ragulya, I.V. Gridneva “Features of the behavior of titanium nitride nanopowders during sintering under the condition of high pressures”, Book of abstracts *X WRTS Conference*, Belgrade, 2002.
10. V.S. Urbanovich “Sintering at high pressures and properties of aluminum nitride ceramics”, pp. 112–114 in W.A. Trzeciakowski (ed.), *High Pressure Science and Technology*, World Scientific Publishing Co. Pte. Ltd, Singapore, 1996.
11. V.S. Urbanovich, Y.G. Gogotsi, K.G. Nickel et al. “Properties of highly dense α -Si₃N₄ ceramics, sintered at high static pressure”, pp. 9–10 in *British ceramic proceeding, IOM Communications Ltd*, Cambridge, No 60. Book 718, vol. 2, 1999.
12. R.A. Andrievski, V.S. Urbanovich, N.P. Kobelev, V.M. Kuchinski, “Structure, density and properties evolution of titanium nitride ultrafine powders under high pressures and high temperatures”, pp. 307–312 in *Fourth Euro Ceramics, Basic Sciences - Trends in Emerging Materials and Applications*. Ed. A. Bellosi, Faenza, Italy, 1995.
13. R.A. Andrievski, G.V. Kalinnikov, V.S. Urbanovich, “Consolidation and evolution of physical and mechanical properties of nanocomposite materials based on high-melting compounds”, pp. 413–418 in *Nanophase and Nanocomposite Materials II*. Eds. S. Komarneni, J.C. Parker, H.J. Wollenberger, MRS, Pittsburgh 1997.
14. R.A. Andrievski, Y. Ogino, V.S. Urbanovich, T. Yamasaki, “Consolidation of TiN/TiB₂ ultrafine powder composites under high pressure and properties of obtained ceramics”, pp. 435–440 in, “*Ceramics: Getting into the 2000's-Part C*”, *Advanced in Science and Technology, 15. Proc. of the World Ceramics Congress. The Ninth CIMTEC - World Ceramics Congress & Forum on New Materials*. Ed. P. Vincenzini, Techna Sri, Faenza, Florence, Italy, 1998.
15. R.A. Andrievski, V.S. Urbanovich, Y. Ogino, T. Yamasaki, “Consolidation processes in nanostructured high melting point compound-based materials”, pp. 389–390 in *British ceramic proceeding*, IOM Communications Ltd, Cambridge, No 60. Book 718, vol. 1, 1999.
16. W. Lengauer, J. Bauer, A. Guillou, D. Ansel, J.P. Bars, M. Bohn, E. Etchessahar, J. Debuigne, P. Ettmayer. “WDS-EPMA nitrogen profile determination in TiN/Ti diffusion couples using homotypic standard materials”, *Microchimica Acta*, **107** [3-6] (1992) 303–310.
17. A.M. Mazurenko, V.S. Urbanovich, V.M. Kuchinski, “High pressure apparatus for sintering ceramics based on high-melting point compounds”, *Proceedings of the Academy of Sciences of Belarus, ser. Phys.-Tech. Sciences*, **1** (1994) 42 (in Russian).
18. V.S. Urbanovich, G.G. Shkatulo, “Computerized system for the sintering of nanoceramics at high pressures”, *Powder Metall. Met. Ceram.*, **42** [1-2] (2003) 19–23.
19. P. Figiel, S. Zimowski, P. Klimczyk, T. Dziwisz, L. Jaworska, “Mechanical and tribological properties of TiC-based composites for ED machining”, *Arch. Mater. Sci. Eng.*, **33** [2] (2008) 83–88.
20. L.A. Ryabicheva, Y.N. Nikitin, “The analysis of stress-strain state in process of stamping of porous bodies”, *New Mater. Technol. in Metall. Mechanical Eng.*, **1** (2008) 63–66.
21. R.A. Andrievski, V.S. Urbanovich, N.P. Kobelev, V.I. Torbov. *Reports of RAS*, **356** [1] (1997) 39.
22. R.A. Andrievski, G.V. Kalinnikov, N.P. Kobelev, Y.M. Soyfer, D.V. Shtanski, “Structure, physical and mechanical properties of nanostructural boride and nitride films”, *Solid State Phys*, **39** [10] (1997) 1859–1964.