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Obtaining at High Pressure the TiN-TiB$_2$ Ceramic Nano-Composite

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Abstract

The process of consolidation of TiN nanopowders under a hydrostatic pressure of 3 GPa was evaluated from the evolution of substructure parameters of compacts obtained after different exposure of powder bodies under constant pressure at room temperature. It has been established that in compaction, changes in the substructure reflect deformation processes of the porous body, which are accompanied by relaxation processes and the corresponding decrease in microstresses. The sintering of consolidated 80 wt% TiN - 20 wt% TiB$_2$ powders at 3 GPa in the temperature range 1300°C - 1600°C leads to the substitution of N atoms by B atoms in TiN and possibly to the substitution of B atoms by N atoms in TiB$_2$. The presence of oxygen in powders promotes the formation of titanium oxynitride, which increases the microhardness of specimens.

Keywords

TiN, TiN-TiB$_2$, Baric Treatment, Substructure, Ceramics

1. Introduction

The physicomechanical properties of ceramics can be improved by sintering of nanosized powders with retention of nanosized grains [1]-[4]. Among efficient methods of densification of nanopowders, it is compaction under high quasihydrostatic pressures. Such baric pretreatment (BP) consists in compression of powder briquettes by high quasihydrostatic pressure (as a rule, to 5 GPa) and enables one to obtain a compact with a density to 90% [5]. The advantage of the method of baric compaction is a homogeneous distribution of the density over the volume, which increases the efficiency of subsequent sintering. BP can be combined with vacuum

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treatment of the initial powder briquette. In the absence of vacuum treatment, air remains in porous briquettes, which increases their porosity and the amount of oxynitride formed in sintering.

The aim of the present work is to analyze the kinetic features of BP of nanocrystalline titanium nitride and the influence of the method of realization of BP on the formation of the structure and properties of nanograined TiN-TiB$_2$ ceramic under the conditions of high pressures and temperatures. Interest to the given object of investigation was aroused by a number of causes. Titanium nitride is a refractory compound with a high hardness, low electric resistance, and good thermal stability [1] [3]. It can be used as a cutting tool and electro-conducting material operating at elevated temperatures.

2. Experimental Procedure

In the work, TiN nanopowder and 80 wt% TiN - 20 wt% TiB$_2$ composite nanopowder obtained by plasma-chemical synthesis (Plasma & Ceramic Technologies, Ltd., Latvia) were used. The mean particle size of the powders ranged from 40 to 60 nm. The powders contained at most 5 wt% of oxygen.

For the investigation of the compaction kinetics of the nanopowders under the isobaric conditions of a high quasihydrostatic pressure of 3 GPa, TiN nanopowder was treated in a high-pressure apparatus for 10 - 600 s. Before sintering, the composite powder was briquetted under high pressure by the following two methods: in vacuum under a pressure of 2.5×10^{-3} Hg mm (series 1) and in air (series 2) under a pressure of 3 GPa. Briquettes were sintered in the temperature range 1300°C - 1600°C under a hydrostatic pressure of 3 GPa. The time of sintering at each temperature was 180 s.

An X-ray diffraction (XRD) analysis of obtained specimens was performed on a DRON-3M diffractometer (Russia). The average size of coherent scattering regions (CSR) and microdistortions of the lattice were determined by the method of approximation from the broadening of diffraction peaks [6].

A study of the microstructure and elemental analysis of the sintered specimens were performed with a JSM-6490 scanning electron microscope (Jeol, Japan). The density was measured by the Archimedes method. The microhardness of the ceramic was determined on a Micromet microhardness tester (Buehler GmbH, Germany) with a Vickers pyramid under a load of 2 N.

3. Results and Discussion

3.1. TiN Powder Compacts

Processes of deformation of a porous powder body are accompanied by the fragmentation of particles and their rearrangement. These effects show themselves as a change in the size of crystallites that form particles and microdistortions of the lattice. This is why we analyzed the process of consolidation of TiN powder in the field of high quasihydrostatic pressure considering the evolution of the substructure parameters of compacts obtained after holding the powder under constant pressure. The change in the average size of the coherent scattering regions (CSR) D reflects both the fragmentation process and process of consolidation of particles in their approach, relative rotation, and slip [7]. The decrease in microdistortions of the lattice ($\Delta a/a$) characterizes relaxation processes at fracture of particles and the accumulated energy of crystals under plastic deformations [8].

The dependences of the parameters of the substructure of nanocrystalline TiN on the time of baric action shown in **Figure 1** indicate deformation processes proceeding in the porous body. In the initial stage of densification of the powder, the decrease in the average size of the CSR D reflects the process of fragmentation of the largest particles. Their fragmentation is accompanied by microstress relaxation, which manifests itself as a decrease in the value of $\Delta a/a$. Subsequent deformation processes proceeding in the time interval 40 s > t_{exp} > 60 s lead to an increase in D and $\Delta a/a$. The insignificant rise in $\Delta a/a$ in this stage of consolidation of the powder body can be explained by the fact that the compression of the briquette proceeds predominantly due to relative rotations and displacements of particles without their substantial deformation. In the time interval 60 s > t_{exp} > 150 s, the next stage of fragmentation with an insignificant decrease in D and, hence, a small decrease in $\Delta a/a$ proceeds. The deformation processes of densification occurring in the time interval 120 - 150 s enable us to obtain a briquette with a low level of microstresses. During baric treatment in the time interval 150 - 600 s, the average size of crystallites increases monotonically. This may be caused by the fact that the particles approach one another so that the distance between them becomes equal to the distances of interatomic interaction and by the manifestation of physicochemical effects that correspond to this situation. The dependence of microdistortions

on the exposure time in this time interval has a nonlinear character. At $t_{exp} > 300$ s, the ratio $\Delta a/a$ decreases. However, even at $t_{exp} \sim 600$ s, the value of microstresses is higher than that at $t_{exp} = 150$ s. It can be assumed that, at $t_{exp} > 300$ s, a compact in which densification is accompanied by relaxation and deformation processes forms. Some increase in D may be caused by further decrease in the distance between particles.

Thus, the process of BP of the nanopowders under constant pressure is stepwise and consists of the stage of fracture of larger particles, the stage of subsequent densification of smaller particles, etc.

The change in the density of compacts in different stages of BP agrees with the scheme of stepwise densification-fracture of crystallites decreasing in size (**Figure 1(b)**): the presence of maximums on the dependences of the density on the time of exposure under pressure (**Figure 1(b)**) correlates with the development of intensive deformation processes, which manifest themselves as decreases in D and $\Delta a/a$.

3.2. TiN-TiB$_2$ Ceramic

According to the XRD data, the main phase in the sintered ceramic is TiN (**Figure 2**).

The SEM analysis of the microstructure of the TiN-TIB$_2$ ceramic (**Figure 3**) revealed the presence of large formations based on titanium nitride (3 - 5 μm) in the nanograined matrix.

The electron-probe microanalysis (EPMA) data (**Table 1**) indicate that, depending on the sintering temperature and conditions of BP of the powders (in vacuum and in air), in the regions formed predominantly on the
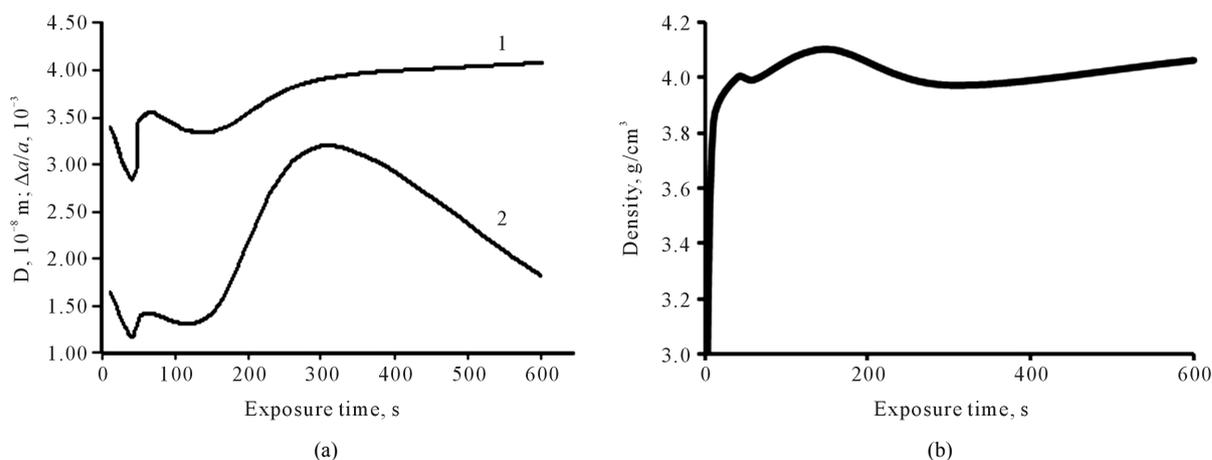

Figure 1. Change in the size of the coherent scattering regions (1) and microdistortions of the lattice (2) in titanium nitride nanopowder (a) and in the density of a compact (b) with the time of exposure under a pressure of 3 GPa.
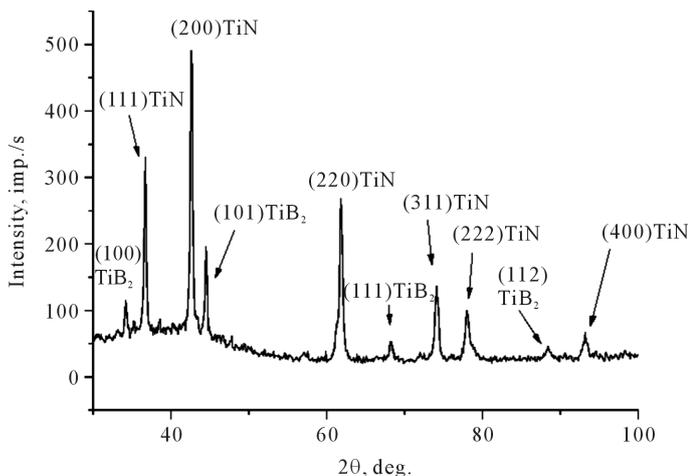

Figure 2. Fragment of an X-ray diffraction pattern of a sintered TiN-TiB$_2$ nanocomposite.
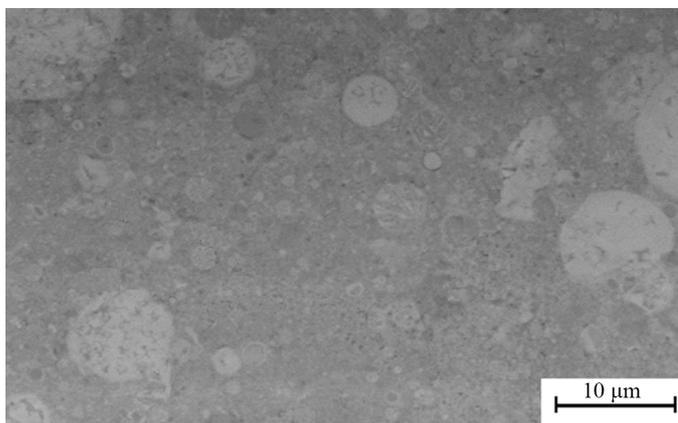
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Figure 3. SEM secondary-electron micrograph of theTiN-TIB$_2$ ceramic sintered at 1400˚C. Light gray areas correspond to aggregates of TiN grains, and dark gray areas correspond to a mixture of TiN and TiB$_2$ grains.

Table 1. Elemental composition of areas of a microsection formed on the base of TiN in the TiN-TiB$_2$ ceramic obtained the powder preliminarily subjected to vacuum treatment.

$T_{sint.}$, ˚C	Content of elements, wt%			
	Ti	N	O	B
1300	40 - 41.8	44.8 - 47.5	9.0 - 9.2	1.0 - 1.2
1400	41.6 - 42.5	41.1 - 45.4	5.0 - 6.0	1.4
1500	37 - 40	40 - 41.5	2.2 - 3.0	2.4
1600	40 - 42	45 - 46	10 - 12	2 - 2.8

base of TiN, the contents of elements vary. The simultaneous presence of oxygen and nitrogen in some specimens indicates the formation of titanium oxynitride in sintering, and the detection of boron in areas based on TiN may indicate that boron enters into the lattice of TiN.

Proceeding from the EPMA data, we should consider possible changes in the nonmetallic sublattice of TiN from the viewpoint of substitution of nitrogen atoms by oxygen and boron atoms.

The performed analysis of structural changes in the sintered ceramic was based on the approach considered in [9], according to which the scattering power of different atoms is proportional to their atomic numbers, and the square of the structural factor (*S*) of the intensity of diffraction peaks (for TiN with a NaCl lattice) with even indices is proportional to the square of the sum of the atomic scattering factors of Ti (F_{Ti}) and a nonmetal (F_n), where n is nitrogen, oxygen, or boron: $S_{\text{even}}^2 = \left(F_{Ti} + F_n\right)^2$. For reflections with odd indices, this relation has the form $S_{\text{odd}}^2 = \left(F_{Ti} - F_n\right)^2$. Thus, evaluating the relation of the intensities of lines, we can evaluate the completeness of the metallic and nonmetallic sublattices of titanium nitride and titanium oxynitride, and the features of occupation of the lattice sites influence its constant.

In the present work, we used the reflections (111) and (200). The lattice constant (*a*) was calculated from the position of the lines (111), (200), (311), (400), and (333).

As is seen in **Figure 4**, the dependence of the ratio of the intensities of the peaks (200) and (111) on the sintering time has a nonlinear character.

The decrease in the ratio $I_{(200)}/I_{(111)}$ in the ceramic of series 1, obtained at a sintering temperature $T_{sint.} \sim$ 1300˚C - 1400˚C (**Figure 4(a)**, curve 1), can be explained by the decrease in the occupancy of the sites of the nonmetallic sublattice of TiN, *i.e.*, by the formation of vacancies. This is substantiated by the EPMA data (see **Table 1**), according to which a part of the nitrogen atoms are substituted by oxygen and boron atoms, and the total content of atoms of the nonmetals is above 50 wt%. At $T_{sint.} \sim$ 1400˚C, the total content of atoms of the nonmetals decreases as a result of a decrease in the content of nitrogen and oxygen. These processes can be ac-

companied by the formation of vacancies in the sublattice of Ti. In this case, the lattice constant somewhat decreases (**Figure 4(a)**, curve 2). Further decrease in the ratio $I_{(200)}/I_{(111)}$ at $T_{sint.}$ ~ 1500˚C can be connected with the substitution of nitrogen atoms by boron atoms, which agrees with the EPMA data. Correspondingly, this is accompanied by an increase in the lattice constant of TiN. Sintering with an isothermal exposure at a temperature of 1600˚C leads to an abrupt increase in the oxygen content in the material, which results in an insignificant increase in the ratio $I_{(200)}/I_{(111)}$.

In the ceramic obtained from compacts of series 2 (BP in air), the increase in the ratio $I_{(200)}/I_{(111)}$ for specimens sintered in the temperature range 1300˚C - 1500˚C (**Figure 4(b)**, curve 1) indicates a decrease in the imperfection of the nonmetallic sublattice of TiN. The subsequent decrease in the ratio $I_{(200)}/I_{(111)}$ at $T_{sint.} > 1500$˚C may be connected with the possible substitution of a part of nitrogen atoms by boron atoms, which have a lower atomic scattering factor. The source of boron in the investigated composite material is TiB_2. In the temperature range 1300˚C - 1400˚C, the lattice constant of TiN does not change (**Figure 4(b)**, curve 2). However, at $T_{sint.} > 1400$˚C, the parameter a increases.

The change in the atomic composition of the nonmetallic sublattice of TiN influences substantially the formation of the physicomechanical properties of the ceramic. **Figure 5** illustrates the change in the microhardness (H_v) of the ceramic obtained at different sintering temperatures. At low sintering temperatures ($T_{sint.} < 1500$˚C), materials obtained with BP in air (specimens of series 2) have a higher H_v. However, among specimens sintered at $T_{sint.} \geq 1500$˚C, the ceramic obtained from compacted powders of series 1 (BP in vacuum) has a higher microhardness. Hence it follows that the conditions of BP influence the physic-mechanical properties of the ceramic. The presence of titanium oxynitride, which forms in sintering, in the composite material can be the cause of the increase in the hardness of the ceramic. The microhardness of polycrystalline materials based on TiN is about 20 GPa [10], and the microhardness of titanium oxynitride is 26 GPa [11]. At $T_{sint.} < 1500$˚C, in specimens of series 1, the oxygen content is lower, and, therefore, the amount of formed oxynitride is smaller, due to which H_v is lower. The ceramic sintered at $T_{sint.} \geq 1500$˚C after BP in vacuum is characterized by a minimum D, minimum level of microdistortions of the lattice ($\Delta a/a$), which are equal to 38 nm and 1.62×10^{-3}, respectively. Obviously, this state of the substructure of the ceramic provides its higher hardness. For the ceramic obtained with conventional BP under the same temperature-time conditions, D and $\Delta a/a$ equel 64 nm. and 2.5×10^{-3}, respectively.
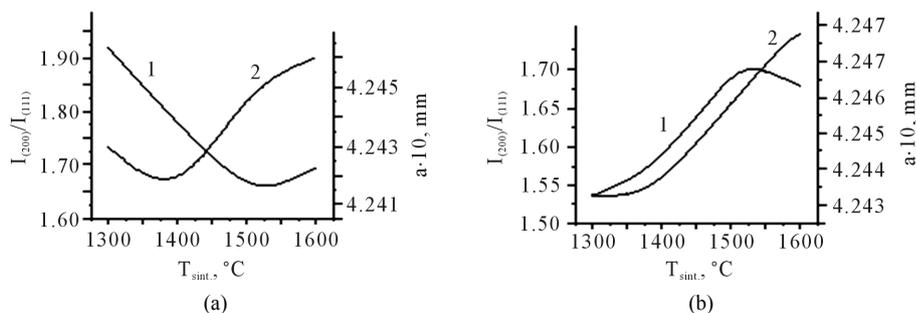

Figure 4. Change in the ratio of the intensities of the peaks (200) and (111) (curves 1) and lattice constants (curves 2) of TiN in the ceramic pretreated in vacuum (a) and in air (b) with the sintering temperature.
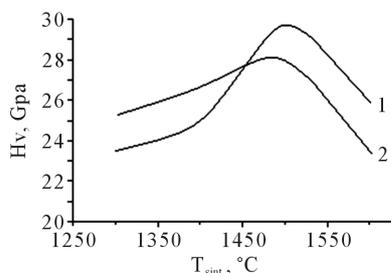

Figure 5. Change in the microhardness of the TiN-TiB_2 nanocomposite with the sintering temperature: 1) ceramic of series 1 (vacuum pretreatment); 2) ceramic of series 2 (pretreatment in air).

4. Conclusion

Under the action of constant compressive quasihydrostatic stresses, a porous compact from TiN nanopowder deforms at a small rate, which manifests itself in the character of change in D and $\Delta a/a$ with time. At a constant compression pressure, there exists an optimal time of isobaric treatment of a porous compact at which a briquette of maximum density forms. During sintering of the composite TiN-TiB$_2$ nanopowder under high pressures in the temperature range 1300°C - 1600°C, a composite in which TiN and TiB$_2$ change their atomic composition forms. The most probable processes are the formation of oxynitride on the base of TiN, substitution of nitrogen atoms by boron atoms in TiN, and possible substitution of boron atoms by nitrogen atoms in TiB$_2$.

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