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X-RAY EMISSION AND PHOTOELECTRON SPECTROSCOPY STUDIES OF INTERACTION OF NANOCRYSTALLINE TiN AND TiB₂ AFTER HIGH-PRESSURE SINTERING

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A few samples of nanocrystalline TiN–TiB₂ ceramics were synthesized by high-pressure (3.0 GPa) and high-temperature ($t = 1300–1500\text{ }^{\circ}\text{C}$) sintering a mixture of TiN and TiB₂ nanopowders (80 wt.% TiN and 20 wt.% TiB₂) and the microhardness of the samples was determined. Peculiarities of the chemical bonding of the TiN–TiB₂ ceramics possessing the highest microhardness among the samples under consideration, mainly 29.65 ± 0.90 GPa, were studied in the present work using the X-ray emission and photoelectron spectroscopy methods. The X-ray emission spectra reflecting the energy distribution of the valence electronic states of the constituents (the N K α (N 2p-like states), B K α (B 2p-like states), Ti L α (valence Ti s,d-like states) and Ti K β_5 (Ti 4p-like states) bands) were measured for the mentioned ceramics and for the initial mixture of TiN and TiB₂ nanopowders. For the above substances the X-ray photoelectron core-level binding energies were evaluated as well. It has been established that, when synthesizing the nanocrystalline TiN–TiB₂ ceramics from the initial mixture of TiN and TiB₂ nanopowders, the half-widths of the X-ray emission Ti L α and Ti K β_5 bands decrease by $(0.5–0.6) \pm 0.2$ eV.

1. Introduction

Transition metal (TM) borides and nitrides of group IVB of the Periodic Table possess a unique combination of properties such as high melting point, hardness, low electrical resistivity, high thermal conductivity, and chemical stability [1–4]. Therefore, the above compounds are of great interest both in science and in technology. The chemical bonding in TM borides and nitrides of group IVB of the Periodic Table is a superposition of the covalent, metallic and ionic components [2,3]. As a result, the interpretation of the electronic structure of the compounds is rather difficult [3,4].

Many of physical and chemical properties of the compounds can be predicted and understood by considering their electronic structure. Due to the results of band-structure calculations of TiN [3,5–12] and TiB₂ [13–17] and of experimental

studies (using either X-ray emission, absorption or photoelectron spectroscopy methods) of these compounds [2,12,18–20], the occupied part of the valence band of titanium nitride and titanium diboride is determined mainly by the energy distribution of the Ti 3*d*-, Ti 4*p*- and N(B) 2*p*-like states. Additionally, for the above compounds, charge transfer in the direction from titanium atoms to nitrogen (boron) atoms and a strong Ti 3*d*–N(B) 2*p*-hybridization are characteristic. The main difference in the chemical bonding of the compounds is the existence of direct B–B bonds in titanium diboride, while direct N–N bonds are absent in titanium mononitride [1–4].

The purpose of this work is to investigate the character of chemical bonding in a material obtained due to interaction of titanium mononitride with titanium diboride at high pressure–high temperature conditions. It is well known that TiN crystallizes in a cubic structure of NaCl-type with lattice parameter $a = 0.4244$ nm, however TiB₂ in a hexagonal structure of AlB₂-type with lattice parameters $a = 0.3028$ nm and $c = 0.3228$ nm [4,21]. For investigation of peculiarities of the chemical bonding of a material obtained as a result of high pressure–high temperature treatments of a mixture of TiN and TiB₂ nanopowders, we have employed the X-ray emission spectroscopy and X-ray photoelectron spectroscopy (XPS) methods.

2. Experimental

A mixture of ultra-fine plasmochemical powders (synthesized and certificated by «Plasma & Ceramic Technologies» Ltd, Latvia) was chosen in the ratio 80 wt.% TiN and 20 wt.% TiB₂ as a precursor for obtaining a series of nanocrystalline TiN–TiB₂ ceramics. The powder sizes were found to be in the range 20 to 40 nm [22]. The synthesis of the ceramics was carried out in two stages. On the first stage, the mentioned mixture of ultra-fine TiN and TiB₂ powders was undergone

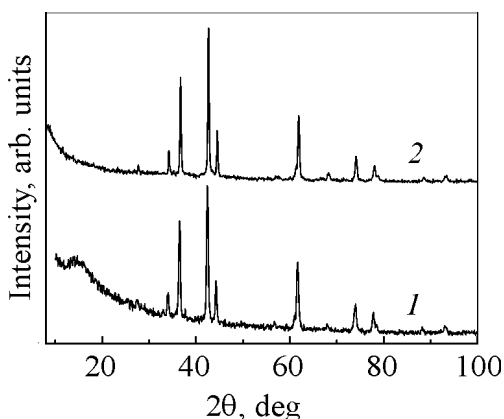


Fig. 1. Data of X-ray diffraction analysis of the pristine mixture of ultra-fine TiN and TiB₂ powders (1) and of the TK-4 ceramics obtained due to sintering the powders at 3.0 GPa and 1500°C for 3 min (2)

to high pressure (about 4 GPa, without heating) for granulating. On the second stage, the pressure was decreased to 3 GPa and the granulated mixture of TiN and TiB₂ was heated to 1300–1500°C for 1–5 min in order to obtain TiN–TiB₂ ceramics. Sintering conditions for obtaining 14 samples of TiN–TiB₂ ceramics are summarized in Table 1. As one can see from data listed in Table 1, the microhardness of the TiN–TiB₂ ceramics obtained due to the above-mentioned high pressure–high temperature treatments is within 17.48–29.65 GPa. It is well known that the hardness of solids is determined by peculiarities their chemical bonding.

Therefore, for our experimental study of chemical interaction of atoms in the TiN–TiB₂ ceramics, we have chosen the one possessing the highest microhardness among those obtained in the present high pressure–high temperature sintering, mainly the TK-4 ceramics (see Table 1). Due to the X-ray diffraction analysis carried out with a DRON-3 diffractometer using Cu *K*α radiation (Fig. 1), the TK-4 ceramics consists of two phases, mainly titanium mononitride, TiN, with a lattice constant *a* = 0.4245 nm and titanium diboride, TiB₂, with lattice constants *a* = 0.3025 nm and *c* = 0.3230 nm. The above unit-cell parameters of the TK-4 ceramics differ slightly from those of the initial powder mixture: TiN (*a* = 0.4242 nm) and TiB₂ (*a* = 0.3029 nm and *c* = 0.3236 nm). Microscopy studies of the TK-4 ceramics have revealed that its grain sizes are within 90 to 120 nm [23].

Table 1
Sintering conditions and microhardness of nanocrystalline ceramics obtained due to high pressure–high temperature treatments of the ultra-fine TiN–TiB₂ powders

Specimen	Sintering conditions			Microhardness, GPa
	pressure, GPa	temperature, °C	duration, min	
TK-1	3	1300	1	23.47 ± 1.00
TK-2	3	1400	3	24.93 ± 1.80
TK-3	3	1300	3	22.99 ± 1.20
TK-4	3	1500	3	29.65 ± 0.90
TK-5	3	1600	3	25.87 ± 1.40
TK-6	3	1300	3	25.30 ± 1.90
TK-7	3	1400	3	26.71 ± 0.50
TK-8	3	1500	3	27.98 ± 1.70
TK-9	3	1600	3	23.43 ± 0.80
TK-10	3	1300	1	25.40 ± 0.70
TK-11	3	1300	5	21.08 ± 1.00
TK-12	3	1300	5	20.89 ± 0.70
TK-13	3	1600	5	22.42 ± 1.30
TK-14	3	1600	5	17.48 ± 0.70

The ultrasoft X-ray emission N *K*α and B *K*α (*K* → *L*_{II,III} transition) and Ti *L*α (*L*_{III} → *M*_{IV,V} transition) bands reflecting the energy distribution of the N 2*p*-, B 2*p*- and valence Ti *s*,*d*-like states, respectively, in the studied mixture of the ultra-fine TiN and TiB₂ powders and in the nanocrystalline TK-4 ceramics derived by high-temperature and high-pressure treatments of the powder mixture were obtained using two RSM-500 spectrometers. The N *K*α and Ti *L*α emission bands were derived using the RSM-500 spectrometer with a diffraction grating of 600 lines/mm and a radius of curvature *R* ≈ 6 m. In the RSM-500 spectrometer used in the present work for studies of the B *K*α band, the dispersion element was a diffraction grating with 600 lines/mm and a radius of curvature *R* ≈ 2 m. In the both spectrometers, the detectors were secondary electron multipliers VEU-6 with CsI photocathodes. Operating conditions of X-ray tubes in the present experiments were the following: accelerating voltage *U*_{*a*} = 4 kV and anode current *I*_{*a*} = 10 mA

when studying the B $K\alpha$ bands and $U_a = 5$ kV and $I_a = 11$ mA when measuring the N $K\alpha$ and Ti $L\alpha$ bands.

The fluorescent X-ray emission Ti $K\beta_5$ bands ($K \rightarrow M_{IV,V}$ transition), reflecting the energy distribution of the valence Ti p -like states, in the ultra-fine TiN–TiB₂ powder mixture and in the TK-4 ceramics were derived using a DRS-2 spectrograph equipped with an X-ray BKhV-7 tube (chromium anode). The Ti $K\beta_5$ bands were measured due to reflection from the (0001) plane of a quartz crystal prepared according to Johann (see Ref. [20] for details). Operating conditions of the BKhV-7 tube in the experiments were $U_a = 35$ kV and $I_a = 70$ mA.

The spectrometer/spectrograph energy resolutions were 0.2 eV in the case of measuring the B $K\alpha$ band, about 0.3 eV in the energy regions corresponding to the positions of the N $K\alpha$ and Ti $L\alpha$ bands, and better than 0.4 eV in the case of measuring the Ti $K\beta_5$ bands.

Measurements of the XPS core-level spectra were carried out in an ion-pumped chamber of an ES-2401 spectrometer having a base pressure less than $5 \cdot 10^{-8}$ Pa. In the mentioned spectrometer, the Mg $K\alpha$ radiation ($E = 1253.6$ eV) was used as a source of spectra excitation. The binding energy (BE) of 84.00 ± 0.05 eV of the XPS Au $4f_{7/2}$ core-level spectrum was used as a reference.

3. Results and discussion

In titanium diboride, TiB₂, with the structure of AlB₂-type, boron atoms can be viewed as those inserted into interstitials of the hexagonal lattice formed by titanium atoms [4]. Therefore, similar to TiN, a typical representative of the class of interstitial phases, titanium diboride can be also considered as a representative of such phases. Additionally, the similarity exists in chemical interaction of titanium atoms with boron and nitrogen atoms in TiB₂ and TiN, respectively. As Serebryakova and co-workers stress [4], when synthesizing titanium borides the charge transfer occurs from titanium atoms to boron atoms and the B sp^2 - and B sp^3 -like hybridization with the valence Ti s,d -like states takes place. The similar effect is characteristic of titanium nitrides, however the N sp^3 - and N s^2p^6 -like hybridization with the metallic valence s,d -like states is characteristic of this compound. Certainly, when sintering titanium diboride and titanium nitride one could expect the formation of a TiB₂–TiN solid solution. Nevertheless, it is well known that interaction of TiB₂ and TiN phases is rather difficult [4,24]. Due to studies of interaction of titanium diboride and titanium nitride made by Huang and Chen [25], the formation of a TiN layer on a TiB₂ surface was observed at 1400°C, however after 11 hour exposing at the mentioned temperature, in addition to TiN, boron nitride was also synthesized. Nevertheless, changes of lattice parameters of TiB₂ during its nitriding were not studied in Ref. [25]. It is believed that, in nanocrystalline states of TiB₂ and TiN phases their interaction will increase because of increasing deflection and the surface energy of the phases in such a state [22]. Additionally, high pressure and temperature that increase lattice energy should assist this interaction. Such treatment was employed in the present work as it has been

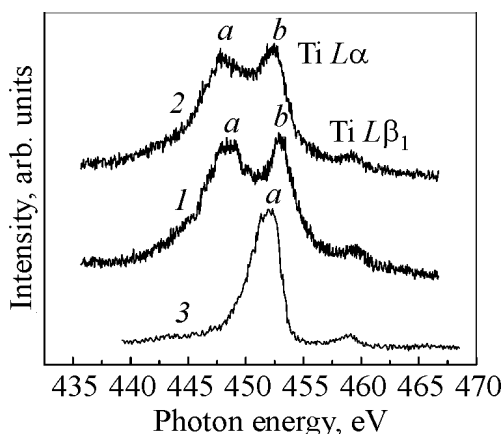


Fig. 2. X-Ray emission Ti $L\alpha$ bands of the pristine mixture of ultra-fine TiN and TiB_2 powders (1) and of the TK-4 ceramics obtained due to sintering the powders at 3.0 GPa and 1500°C for 3 min (2); for comparison, the band of pure metallic titanium is also presented (3)

bands of the pristine mixture of ultra-fine TiN and TiB_2 powders and of TK-4 ceramics, while only one feature «a» is typical of the band of pure metallic titanium (there are, certainly, a few additional features slightly resolved on the bands of the ceramics and the initial mixture of ultra-fine TiN and TiB_2 powders). Due to the results of experimental studies for the electronic structure of TiN and TiB_2 compounds summarized in monographs [2,4], the high-energy subband «b» of the Ti $L\alpha$ band is created by the Ti $3d$ -like states taking part in forming the metallic component of the chemical bonding of the above compounds, while the low-energy feature «a» of the band in titanium diboride and titanium mononitride is created by the Ti $3d$ -like states taking part in the formation of the covalent $d_{Ti}-p_{B(N)}$ bonds due to the Ti $3d$ -B(N) $2p$ -like hybridization. The relative intensities of the «a» and «b» subbands of the Ti $L\alpha$ emission band do not change significantly when sintering the pristine mixture of TiN and TiB_2 powders at high pressure–high temperature conditions and obtaining the TK-4 ceramics. However, the subband «b» of the Ti $L\alpha$ band in the pristine mixture of TiN and TiB_2 powders is positioned by about 0.5 eV towards higher photon energies as compared with that in the TK-4 ceramics. It is obvious that the Ti $L\alpha$ band of the pristine powder mixture is the superposition of the bands of constituent substances, mainly ultra-fine TiN and TiB_2 compounds. On the contrary, the Ti $L\alpha$ band of the TK-4 ceramics is the spectrum representing the energy distribution mainly of the valence Ti s,d -like states in the solid. Therefore, as data listed in Table 2 reveal, the half-width of the band decreases by about 0.6 eV when going from the pristine mixture of ultra-fine TiN and TiB_2 powders to the TK-4 ceramics obtained due to high pressure–high temperature sintering the powder mixture.

mentioned in the Experimental section. The presence of the interaction should be visible upon changes of shapes of the X-ray emission bands reflecting the energy distribution of the valence electronic states of the ceramic constituents and pristine mixture of the ultra-fine TiB_2 and TiN powders.

Fig. 2 shows results of measurements of the Ti $L\alpha$ emission bands in the two specimens under study, initial mixture of TiB_2 and TiN powders and obtained from the mixture at high pressure–high temperature conditions the nanocrystalline TK-4 ceramics. The band of pure metallic titanium, for comparison, is also presented there. From Fig. 2 it is apparent that the two-peak structure (features «a» and «b») is characteristic of the Ti $L\alpha$

Table 2

Half-widths (in eV) of the X-ray emission bands of the pristine mixture of ultra-fine TiN and TiB₂ powders and of the TK-4 ceramics obtained due to sintering the powders at 3.0 GPa and 1500°C for 3 min

Specimen	B K α band	N K α band*	Ti L α band	Ti K β_5 band**
Pristine mixture of ultra-fine TiN and TiB ₂ powders	4.5	3.3	8.7	7.0
Nanocrystalline TiN–TiB ₂ (TK-4) ceramics	4.3	3.2	8.1	6.5
Uncertainty	±0.2	±0.2	±0.2	±0.2

*The band superimposes the inner X-ray Ti L₁ line.

**Without any corrections for tails of the inner X-ray Ti K $\beta_{1,3}$ line superimposing the band.

The above results for the Ti L α band look to be in excellent agreement with those obtained when studying the Ti K β_5 band for the substances under consideration. Results of investigation of the Ti K β_5 bands in the pristine mixture of TiB₂ and TiN powders, the nanocrystalline TK-4 ceramics obtained from the mixture at high pressure–high temperature conditions and, for comparison, in pure metallic titanium are presented in Fig. 3. As Fig. 3 reveals, the main maxima «a» of the Ti K β_5 bands in the mixture of TiB₂ and TiN powders and in the TK-4 ce-

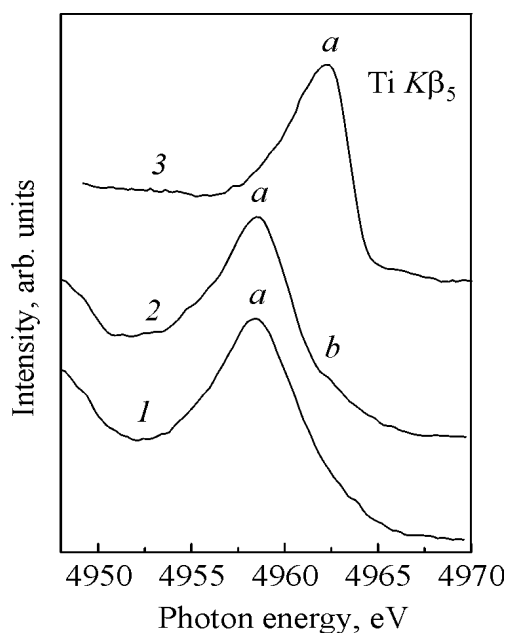


Fig. 3. X-Ray emission Ti K β_5 bands of the pristine mixture of ultra-fine TiN and TiB₂ powders (1) and of the TK-4 ceramics obtained due to sintering the powders at 3.0 GPa and 1500°C for 3 min (2); for comparison, the band of pure metallic titanium is also presented (3)

ramics are positioned by 3.8 ± 0.2 eV towards lower photon energies as compared with that of the band of pure metallic titanium. In accordance with the above results for the Ti L α band, the main maximum «a» of the Ti K β_5 band in titanium nitrides and borides is created by the Ti 4*p*-like states hybridized with the N(B) 2*p*-like states, while the high-energy feature «b», which is resolved on the spectrum of the TK-4 ceramics, is formed by the Ti 4*p*-like states taking part in the formation of the metallic Ti–Ti bonds in the TiB₂ and TiN compounds [2,4]. It is obvious that the energy position of the maximum «a» of the Ti K β_5 band does not change when going from the pristine mixture of TiN and TiB₂ powders to the TK-4 ceramics. However, the half-width of the Ti K β_5 band is higher by about 0.5 eV in the initial mixture of ultra-fine TiN and TiB₂ powders as compared with that in the

TK-4 ceramics studied (Table 2). Taking into account the same arguments as in the case for the Ti $L\alpha$ band, the above-mentioned decreasing the half-width of the Ti $K\beta_5$ band can be explained by the fact that the band of the pristine powder mixture represents the superposition of the bands of constituent compounds (TiN and TiB₂), while the band of the TK-4 ceramics is the spectrum representing the energy distribution of the Ti 4*p*-like states of a TiN–TiB₂ solid.

The investigation of the N $K\alpha$ bands in the initial mixture of ultra-fine TiN and TiB₂ powders and the TK-4 ceramics obtained from the powders after their high-pressure and high-temperature sintering reveals that the N $K\alpha$ band in the both samples superimposes the inner X-ray Ti L_1 line. This circumstance makes difficulties in determination of the true shape of the band in the samples under consideration. Results of our study reveal that the energy position of the maximum of the N $K\alpha$ band does not change when going from the pristine mixture of TiN and TiB₂ powders to the TK-4 ceramics. Our results allow to conclude that the peak intensity of the N $K\alpha$ band with respect to that of the Ti L_1 line is ca. 10% higher in the mixture of TiN and TiB₂ powders as compared to that in the TK-4 ceramics. For the two samples under study, the half-widths of the N $K\alpha$ band are similar (Table 2).

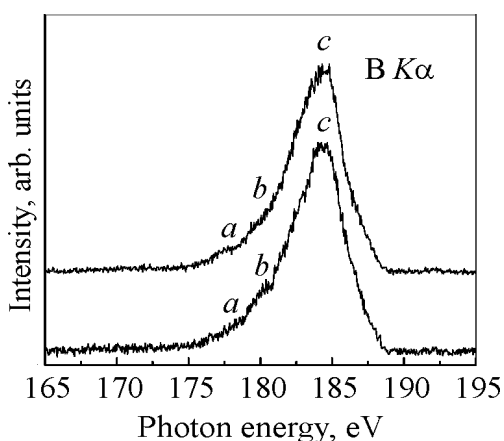


Fig. 4. X-Ray emission B $K\alpha$ bands of the pristine mixture of ultra-fine TiN and TiB₂ powders (1) and of the TK-4 ceramics obtained due to sintering the powders at 3.0 GPa and 1500°C for 3 min (2)

Nevertheless, as Fig. 4 shows, relative intensity of the low-energy feature «*b*» of the B $K\alpha$ band decreases from the value $I_b/I_c = 0.33 \pm 0.02$ to $I_b/I_c = 0.28 \pm 0.02$ and the fine-structure feature «*a*» of the band becomes more pronounced when going from the TiN and TiB₂ powder mixture to the TK-4 ceramics obtained by high-pressure and high-temperature sintering the powders.

It should be mentioned that, on the first stage of sintering, mixtures of ultra-fine TiN and TiB₂ powders were undergone to high-pressure treatment at room temperature. And only after the mentioned treatment, the samples were heated to high temperature at high pressure as listed in Table 1. The so-called cold deformation on the first stage of sintering leads to appearance in the samples under

The X-ray emission B $K\alpha$ bands of the pristine mixture of TiN and TiB₂ powders and the TK-4 ceramics under consideration are presented in Fig. 4. For the both samples under study, the energy positions of the centers of gravity and of the maxima «*c*» of the B $K\alpha$ bands remain constant within the accuracy of ± 0.2 eV, and the half-width of the band does not change when going from the powder TiN–TiB₂ mixture to the TK-4 ceramics obtained by sintering the powders (Table 2).

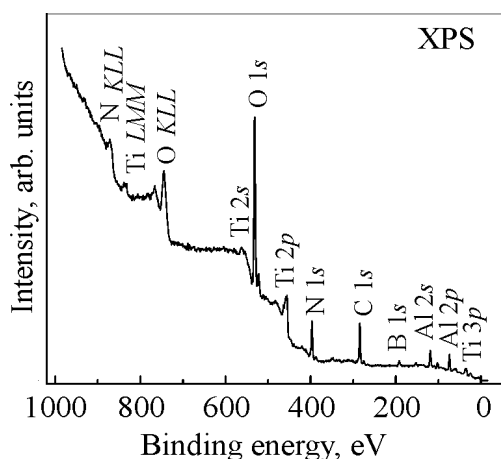


Fig. 5. Survey of X-ray photoelectron spectrum for the pristine mixture of ultra-fine TiN and TiB₂ powders (some additional signals originate from an aluminium plate in which the powders were pressed)

non-metal impurities in the bulks of TiN and TiB₂ powders and of the nanocrystalline TK-4 ceramics should be minor. In addition, as one can see from Fig. 4, the well-pronounced feature «*b*» of the B *K*α band vanishes almost completely when going from the pristine TiN and TiB₂ powder mixture to the TK-4 ceramics. As shown in Ref. [22], the feature «*b*» of the B *K*α band of TiB₂ is created by the B 2*p*-like states taking part in the formation of the B–B bonds in the compound. Therefore, decreasing the relative intensity of the feature «*b*» of the B *K*α band when synthesizing the TK-4 ceramics from the ultra-fine TiN and TiB₂ powder mixture may be an indication of the formation of new B–N bonds in the TK-4 ceramics. These phenomena can explain the rather high microhardness of the TiN–TiB₂ ceramics (17.48–29.65 GPa, Table 1). As it has been already mentioned, the existence of B–B-bonds is characteristic of transition metal diborides. Substitution of some boron atoms by nitrogen in TiB₂ should lead to the formation of B–N bonds, which are carriers of a number of very important properties, partly extremely high microhardness (close to that of diamond) and plasticity. A decrease of the lattice parameters *a* and *c* of TiB₂ when sintering the TK-4 ceramics from the TiN and TiB₂ powder mixture at high pressure–high temperature conditions (3.0 GPa, 1500°C, 3 min) may also indicate a possibility of the formation of B–N bonds in the ceramics studied. Indeed, lengths of the shortest B–B bonds in TiB₂ are equal to 0.175 nm, while those of B–N bonds in the lattice of sphalerite-like BN are about 0.157 nm. The decreasing half-widths of the Ti *L*α and Ti *K*β₅ bands when sintering the nanocrystalline TK-4 ceramics from the pristine TiN and TiB₂ powder mixture also confirms a statement about the creation of new bonds in the ceramic material.

It is necessary to mention that the present XPS studies indicate that the XPS N 1*s* and B 1*s* core-level binding energies do not change within accuracy of ±0.1 eV

treatment of a number of defects, mainly vacancies and dislocations, which can be sewers for boron and nitrogen atoms increasing their mobility. The creation of vacancies in the non-metal sublattice of titanium nitride can be considered as «traps» for boron atoms as well as for other atoms, e.g. oxygen and carbon, which are present on the surfaces of pristine TiN and TiB₂ powders as the present XPS results reveal (Fig. 5). However, when studying the X-ray emission Ti *K*β₅ bands in the substances under consideration (Fig. 3), we did not detect the presence of the so-called Ti *K*β'' subbands associated neither with titanium oxide nor with titanium carbide.

Therefore, the presence of the above

when going from the pristine TiN and TiB₂ powder mixture to the TK-4 ceramics. This fact indicates that the charge state of the nitrogen and boron atoms do not change significantly when synthesizing the TK-4 ceramics from the ultra-fine TiN and TiB₂ powder mixture. Studies of the XPS Ti 2*p* core-level binding energies are in progress now. Such studies will allow us to set on a common energy scale all the X-ray emission spectra obtained in the present paper for the pristine ultra-fine TiN and TiB₂ powder mixture and for the TK-4 ceramics and to discuss in detail the question about the formation of new bonds in the ceramics.

4. Conclusions

It has been established that, when sintering the mixture of ultra-fine TiN and TiB₂ powders (80 wt.% TiN and 20 wt.% TiB₂) at high-pressure and high-temperature conditions (3.0 GPa, 1300–1500°C), interaction of these phases is observed and nanocrystalline TiN–TiB₂ ceramics with the microhardness of 17.48–29.65 GPa are synthesized. The crystal structure of the ceramics consists of two phases, mainly of cubic TiN and hexagonal TiB₂ components. When sintering the TK-4 ceramics possessing the highest microhardness, mainly 29.65 ± 0.90 GPa, the lattice parameters *a* and *c* of the TiB₂ phase decrease but the lattice parameter *a* of the TiN phase increases somewhat. The present X-ray emission spectroscopy data indicate that the half-widths of the Ti *L*α and Ti *K*β₅ bands decrease by (0.5–0.6) ± 0.2 eV when obtaining the nanocrystalline TK-4 ceramics from the pristine mixture of TiN and TiB₂ powders. The energy positions of the maxima and of the centers of gravity of the N *K*α and B *K*α bands as well as their half-widths remain constant within experimental errors for the both substances under study. The present XPS core-level measurements reveal that the charge state of the nitrogen and boron atoms do not change significantly when synthesizing the TK-4 ceramics from the ultra-fine TiN and TiB₂ powder mixture.

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