

# *In situ* Synthesis, Phase Composition and Microstructure of TiB<sub>2</sub> Layers under Irradiation by Power Electron Beam

N.N. Smirnyagina, Z.M. Khaltarov, A.C. Khazagarov, and A.S. Milonov

Department of Physical Problems at the Presidium of Buryat Scientific Center SB RAS,  
8, Sakhyanovoy str., Ulan-Ude, 670047, Russia  
E-mail- ionbeam@pres.bsnet.ru

**Abstract** – The thermodynamic investigation of equilibrium in Ti–B–C–O system and borides TiB<sub>2</sub> synthesis in vacuum in result of the interaction of appropriate oxides with carbon and various boriding components (B<sub>4</sub>C, B, B<sub>2</sub>O<sub>3</sub>) is carried out. Borides layers TiB<sub>2</sub> on carbon steel St45 or copper alloy M1 surface.

## 1. Introduction

Formation of refractory metals borides in surface layer allows obtaining coating with special properties as stability in melts of non-ferrous metals (TiB<sub>2</sub>). The electron beam boriding technology of such layers formation includes the following: saturating daub containing oxide TiO<sub>2</sub>, boron component and carbon was deposited on samples surface, and the treatment by an electron beam is fabricated.

Powder borides have been synthesized various methods [1]. One of which is the metal oxide reduction by boron and carbon mixture at temperatures 1773–2273 K in vacuum. However the given temperature interval did not approach for boride layers synthesis as being strengthened carbon steel melted at lower temperatures. Therefore, for formation in surface layers of refractory metals borides under electron beam action it was necessary to improve and to determined optimal conditions of boriding.

For the optimization of borides synthesis process it was necessary to deal with individual compounds properties at high temperatures in vacuum (10<sup>-2</sup>–10<sup>-3</sup> Pa), and to know phases composition and equilibrium transformations characteristic etc. At the availability of thermodynamic information on initial components, it is possible to receive the necessary data about the heterogeneous system, and to determine the phase equilibrium composition and components partial pressure in conditions inaccessible to realization of direct experiments. Originally the boriding component choice and the determination of optimum conditions for the boriding on high temperature and power expenditure are main purposes of thermodynamic consideration.

In this study, we have presented results of the thermodynamic calculations simulating the interaction between titan oxide TiO<sub>2</sub> with carbon and various boron compounds in the equilibrium conditions. We report on a new process to make TiB<sub>2</sub> layers by electron beam boriding.

## 2. Experimental methods

*Method of thermodynamic calculations.* The computations were performed with the ASTRA.4/pc package, which incorporates the thermodynamic data for various titanium borides, carbides, and oxides [2, 3]. The temperature was varied in wide interval 673–1813 K [ $T_{\text{melting}}(\text{Fe}) = 1812 \text{ K}$ ]. The pressure was varied from 10<sup>5</sup> to 10<sup>-4</sup> Pa. In some instances, the temperature was raised to 3000 K. The formation of solid solutions was left out of consideration. The condensed phases considered in the Ti–B–C–O system were C, B, B<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, Ti, TiO, TiO<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>4</sub>O<sub>7</sub>, TiB, TiB<sub>2</sub>, TiC. The gas phase include in consideration were O<sub>2</sub>, C, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, CO, CO<sub>2</sub>, B, BO, BO<sub>2</sub>, B<sub>2</sub>O<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C, Ti, TiO, TiB.

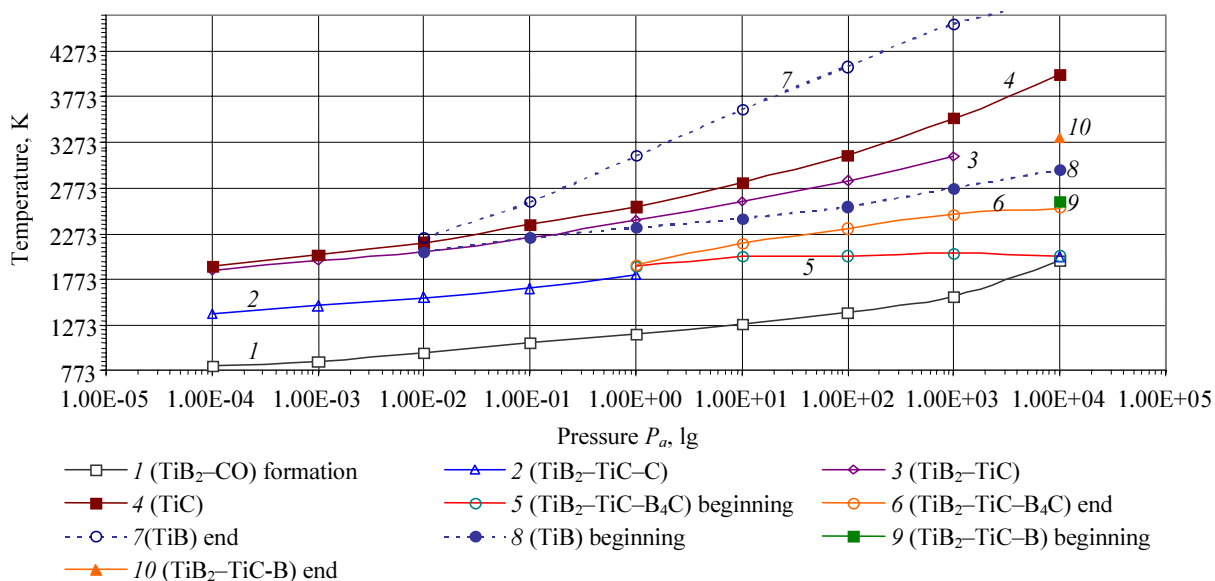
The boride layers were analyzed by x-ray diffraction. An X-ray powder diffract meter Advance D8 Bruker using Cu K $\alpha$ -radiation was employed for phase analysis and the determination of lattice parameters. The samples microstructure was observed using a metallographic microscopy METAM RV-22 and scan electron microscopy LEO 1430 VP. Microhardness was measured by using PMT-3 microhardness tester at a loading 0.5 and 1 H.

## 3. Results and discussion

### 3.1. Thermal behavior TiB<sub>2</sub>

We have been tried to simulate thermal behavior TiB<sub>2</sub>. Figure 1 shows the character of thermal behavior TiB<sub>2</sub>. The interaction TiO<sub>2</sub> with various boronizing agents (B<sub>2</sub>O<sub>3</sub>, B<sub>4</sub>C,) begins at temperatures 1900–2100 K (10<sup>5</sup> Pa), and at pressure 10<sup>-2</sup>–10<sup>-4</sup> Pa the temperature of the formation beginning decreases up to 773–900 K (Fig. 1, *a* curve 1, equilibrium of “TiB<sub>2</sub>-CO formation”). At lower temperatures in the products is present only TiC.

It is established, that TiB<sub>2</sub> it is thermally steady. Character of decomposition TiB<sub>2</sub> depends on total pressure in system. At pressure from 10<sup>-4</sup> up to 1 Pa TiB<sub>2</sub> consistently decays with forming TiC and C (curve 2, equilibrium of “TiB<sub>2</sub>-TiC-C”), then – TiB<sub>2</sub>-TiC (curve 3, equilibrium of “TiB<sub>2</sub>-TiC”), and TiC (curve 4, equilibrium of “TiC”). At the first stage, the maintenance of impurity (TiC and C) is insignificant, does not exceed 0.01–0.1 mol %. Calculations have shown, that the titanium carbide [ $T_{\text{melting}}(\text{TiC}) = 3530 \text{ K}$ ] is more thermally steady in comparison with the titanium boride [ $T_{\text{melting}}(\text{TiB}_2) = 3063 \text{ K}$ ].

Fig. 1. Thermal behavior of boride  $\text{TiB}_2$ 

Increase of pressure from 1 up to  $10^4$  Pa changes decomposition character  $\text{TiB}_2$  at presence CO, thus, as impurity it is possible to find out alongside with TiC also  $\text{B}_4\text{C}$  or a boron. Carbide  $\text{B}_4\text{C}$  is present at a temperature interval which range increases with increase of pressure (curves 5 and 6, equilibrium of “balance” “ $\text{TiB}_2$ - $\text{TiC}$ - $\text{B}_4\text{C}$ ”, the “beginning” and the “end”). After decomposition  $\text{B}_4\text{C}$  in equilibrium  $\text{TiB}_2$  and TiC are participated, and further at more heat steady remains TiC.

At pressure  $10^4$  Pa and above, the steady still have a boron, rather than  $\text{B}_4\text{C}$ , therefore it is possible to observe the following phase equilibrium “ $\text{TiB}_2$ ” (curve 1), “ $\text{TiB}_2$ - $\text{TiC}$ -B” the “beginning” (curve 9), “ $\text{TiB}_2$ - $\text{TiC}$ -B” the “end” (curve 10).

The Ti-B system is known to contain two borides. TiB decomposes at 2606 K with out melting, and  $\text{TiB}_2$  melts congruently at 3063 K. According to [4], thermodynamic calculations were shown that boride TiB cannot be obtained in the pressure range  $10^{-3}$  to  $10^5$  Pa at of up to 3000 K.

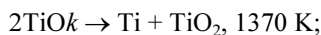
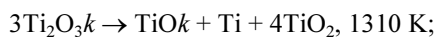
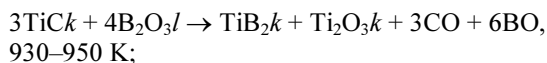
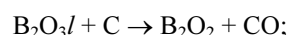
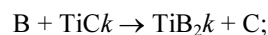
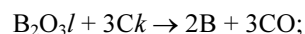
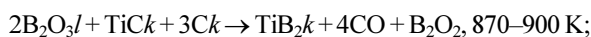
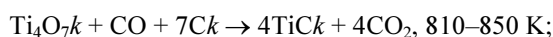
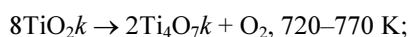
TiB is formed only in the temperature range 2850–2950 K at a pressure of  $10^4$  Pa, 2450–2650 at  $10^3$  Pa, and 1900–2150 K at  $10^{-1}$  Pa. At lower pressures, TiB does not exist.

Figure 1 (curves 8 and 7) shows the conditions of boride TiB vapor formation and existence.

### 3.2. System $\text{TiO}_2$ - $\text{B}_2\text{O}_3$ -C

When an oxide  $\text{B}_2\text{O}_3$  is used as boronizing agent, the interaction began with the dissociation of  $\text{TiO}_2$  forming  $\text{Ti}_4\text{O}_7$  at 720–770 K. TiC will be formed in result of  $\text{Ti}_4\text{O}_7$  and carbon interaction at 810–850 K and further reacts with oxide  $\text{B}_2\text{O}_3$  formed  $\text{TiB}_2$ . The highest partial pressure was for CO in a gas phase. The thermal effect  $\Delta H$  of chemical transformation  $\text{TiC} \rightarrow \text{TiB}_2$  is  $-199$  kJ/mol.

The chemical reaction in stoichiometrical mixture  $\text{TiO}_2$ : $\text{B}_2\text{O}_3$ :5 C at pressure  $10^{-3}$  Pa was



where  $k$  is the condensed phase;  $l$  is the liquid phase.

For revealing fields of coexisting phase's crystallization have been simulated phase balance in ternary system  $\text{TiO}_2$ - $\text{B}_2\text{O}_3$ -C in all concentration area through 1–5 mol %. Isothermal/isobaric cuts in a temperatures interval from 573 up to 1473 K and a range of pressure  $10^{-2}$ – $10^{-4}$  Pa have been constructed. The choice of a range is caused by a level pressure in the vacuum chamber.

The analysis of the constructed isothermal cuts has allowed revealing optimum conditions of reception single-phase boride, to track the phase transformations preceding at boride synthesis with participation various boronizing components (B,  $\text{B}_4\text{C}$ ,  $\text{B}_2\text{O}_3$ ) and to recommend temperature modes for formation of boride layers on carbon steel and copper alloys.

Calculations have shown that system  $\text{TiO}_2$ - $\text{B}_2\text{O}_3$ -C is not ternary, as two parties of concentration triangle ( $\text{TiO}_2$ -C,  $\text{B}_2\text{O}_3$ -C) not binary systems. Feature of  $\text{B}_2\text{O}_3$ -C system is dependence of phase composition from a pressure. It is the reason of dependence of the  $\text{TiB}_2$  existence area from a pressure. The isothermal sections at 873–1473 K in pressure  $10^{-2}$ – $10^{-4}$  Pa are plotted. The fields of a crystallization of all possible phases are allocated (Fig. 2).

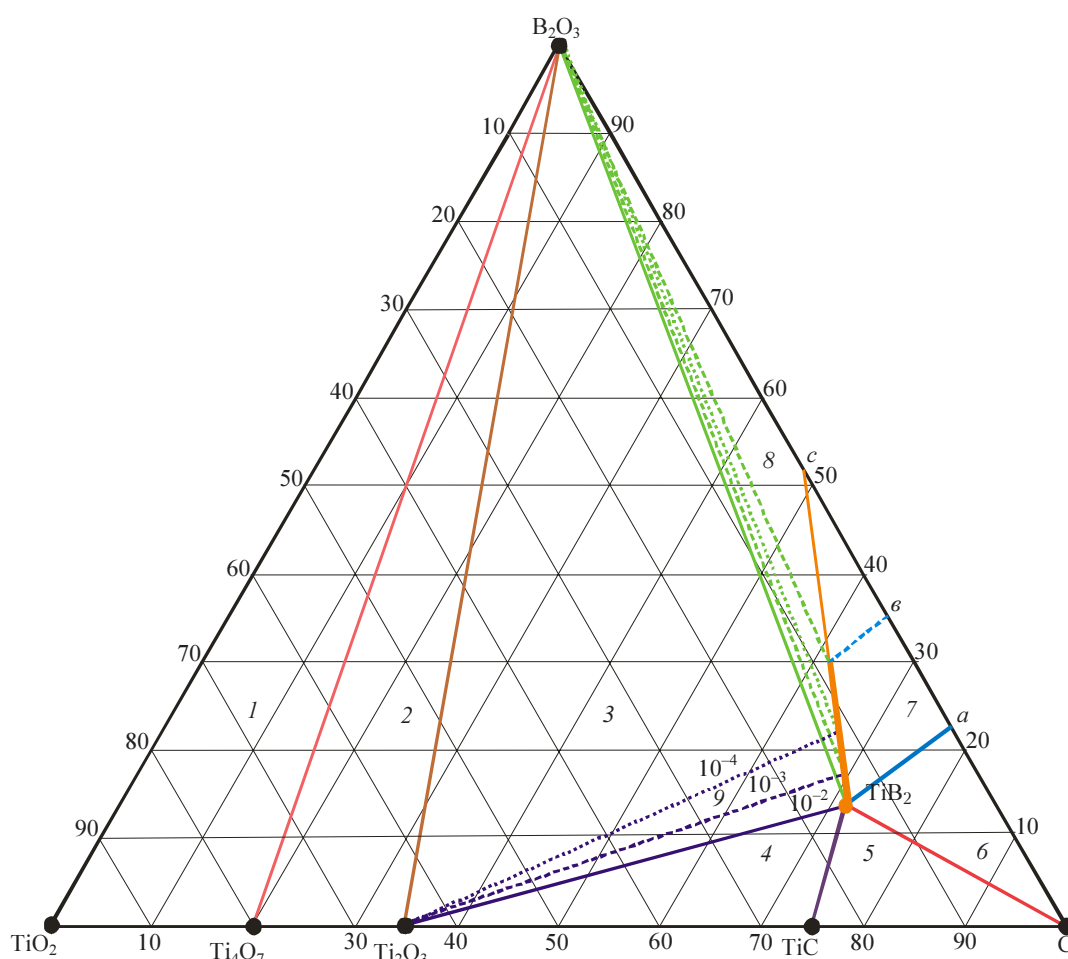


Fig. 2. The isothermal section of system  $\text{TiO}_2\text{-B}_2\text{O}_3\text{-C}$  at 1073 K: 1 –  $\text{TiO}_2\text{-Ti}_4\text{O}_7\text{-B}_2\text{O}_3$ ; 2 –  $\text{Ti}_4\text{O}_7\text{-Ti}_2\text{O}_3\text{-B}_2\text{O}_3$ ; 3 –  $\text{Ti}_2\text{O}_3\text{-B}_2\text{O}_3\text{-TiB}_2$ ; 4 –  $\text{Ti}_2\text{O}_3\text{-TiB}_2\text{-TiC}$ ; 5 –  $\text{TiB}_2\text{-TiC-C}$ ; 6 –  $\text{TiB}_2\text{-B}_4\text{C-C}$ ; 7 –  $\text{TiB}_2\text{-B}_4\text{C}$ ; 8 –  $\text{B}_2\text{O}_3\text{-TiB}_2$ ; 9 –  $\text{TiB}_2\text{-Ti}_2\text{O}_3$

In Fig. 2, the isothermal section system  $\text{TiO}_2\text{-B}_2\text{O}_3\text{-C}$  is presented at 1073 K. It is established, that interaction begins with oxide  $\text{TiO}_2$  dissociation with formation  $\text{Ti}_4\text{O}_7$  in an interval of temperatures 720–800 K. Carbide  $\text{TiC}$  is formed at interaction between oxide  $\text{Ti}_4\text{O}_7$  and carbon at temperatures 830–850 K, and further it reacts with boron oxide  $\text{B}_2\text{O}_3$  forming boride  $\text{TiB}_2$ .

Phase equilibria in system  $\text{TiO}_2\text{-B}_2\text{O}_3\text{-C}$  are complex. It is connected with  $\text{Ti}_4\text{O}_7$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{TiO}$  oxides are exists. These oxides as intermediate products are formed at the interaction between  $\text{TiO}_2$  oxide and C carbon. The phase formation feature is shown available two phase areas 7 (Fig. 2) where  $\text{TiB}_2$  and  $\text{B}_4\text{C}$  are present. The areas sizes were depend on a pressure. It can be or  $\text{TiB}_2\text{-B}_4\text{C}$  section ( $10^{-2}$  Pa), or some  $\text{B}_4\text{C}$  area which has various extent on a concentration triangle range:  $a\text{-b}$  –  $\text{B}_4\text{C}$  ( $10^{-3}$  Pa),  $a\text{-c}$  –  $\text{B}_4\text{C}$  ( $10^{-4}$  Pa).

The cuts:  $\text{B}_2\text{O}_3\text{-Ti}_4\text{O}_7$ ,  $\text{B}_2\text{O}_3\text{-Ti}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3\text{-TiB}_2$ .  $\text{TiC-TiB}_2$ ,  $\text{TiB}_2\text{-C}$ ,  $\text{TiB}_2\text{-B}_4\text{C}$  are presented. At pressure reduce with  $10^{-2}$  up to  $10^{-4}$  Pa there is the two phase area 7 containing  $\text{TiB}_2$  and  $\text{B}_4\text{C}$ . It is connected with carbide  $\text{B}_4\text{C}$  behavior which is shown by pieces

$\text{B}_4\text{C-b}$  and  $\text{B}_4\text{C-c}$ , in system  $\text{B}_2\text{O}_3\text{-C}$  being the party of a concentration triangle. Composition points are  $b$  (36 mol %  $\text{B}_2\text{O}_3$ ) and  $c$  (50 mol %  $\text{B}_2\text{O}_3$ ). Thus, boride  $\text{TiB}_2$  single-phase it is possible to observe in a point of stoichiometrical composition and on a piece  $\text{TiB}_2\text{-c}$ .

Especially it is necessary to note cut  $\text{Ti}_2\text{O}_3\text{-TiB}_2$  which changes position at pressure change from  $10^{-2}$  up to  $10^{-4}$  Pa as there is two phase area 9. At pressure  $10^{-3}$  Pa single-phase  $\text{TiB}_2$  it is reflected lines  $\text{TiB}_2\text{-b}_2\text{-b}_1$ .

Cut  $\text{Ti}_2\text{O}_3\text{-TiB}_2$  is displaced along line  $\text{TiB}_2\text{-b}_2\text{-b}_1$  up to a point  $b_2$ .

Cut  $\text{B}_2\text{O}_3\text{-TiB}_2$  is similarly displaced, and there is the two phase area  $\text{B}_2\text{O}_3\text{-b}_1\text{-b}_2$  containing  $\text{B}_2\text{O}_3$  and  $\text{TiB}_2$ .

The further pressure decrease up to  $10^{-4}$  Pa leads to displacement of cut  $\text{Ti}_2\text{O}_3\text{-TiB}_2$  in a point  $c_1$ , thus two phase area  $\text{B}_2\text{O}_3\text{-c}_1\text{-c}$  consists of  $\text{B}_2\text{O}_3$  and  $\text{TiB}_2$ . Coordinates of points are  $b_1$  (8 mol %  $\text{TiO}_2$ , 30 mol %  $\text{B}_2\text{O}_3$ , 62 mol % C),  $b_2$  (12 mol %  $\text{TiO}_2$ , 18 mol %  $\text{B}_2\text{O}_3$ , 70 mol % C),  $c_1$  (11 mol %  $\text{TiO}_2$ , 21 mol %  $\text{B}_2\text{O}_3$ , 68 mol % C).

The area 8 is observed at pressure  $10^{-2}$  and  $10^{-3}$  Pa and contains  $\text{B}_2\text{O}_3$ ,  $\text{TiB}_2$  and  $\text{B}_4\text{C}$ .

### 3.3. Boride layers TiB<sub>2</sub>

A new process was shown to make borides layers using electron beam. The electron beam boriding technology of such layers formation includes the following: saturating daub containing oxide TiO<sub>2</sub>, boron component and carbon was deposited on samples surface, and the treatment by an electron beam in vacuum is fabricated.

It is established, that phase formation in a layer at its formation on carbon steel or copper alloy depends on crystal structure initial oxide TiO<sub>2</sub>. So, if used TiO<sub>2</sub> rutile structure the products of electron beam treatment (on a metal surface and in powder rests of daub) have been identified the B-doped the rutile type (PDF 01-087-0921, sp. gr. *P42/mmm*,  $a = 0.4609$  and  $c = 0.2967$  nm). If it is to apply the TiO<sub>2</sub> anatase struc-

ture type (PDF 01-089-4203, sp. gr. *P42/mmm*,  $a = 0,3785$  and  $c = 0.9514$  nm), the TiB<sub>2</sub> boride (sp. gr. *P6/mmm*,  $a = 0.3030$  and  $c = 0.3230$  nm,) were received. Presence of titan carbide TiC as impurity is found out. Feature of interaction is formation of intermediate phases – high-temperature polymorphous form metal titan  $\beta$ -Ti. In case of borides layers the phases Fe<sub>2</sub>Ti (PDF 03-065-0602, sp. gr. *P63/mmc*,  $a = 0.4796$ ,  $c = 0.7833$  nm) are formed.

Layers TiB<sub>2</sub> are not homogeneous (Fig. 3, *a*). It is possible to observe light inclusions (microhardness values 28350 HV); under them the second light inclusions (with 13750 HV) and dark inclusions (850 HV). The eutectic has microhardness 600 HV, but a metal basis has values 290 HV. Gray inclusions settle down in a layer not chaotically, and have some ordering.

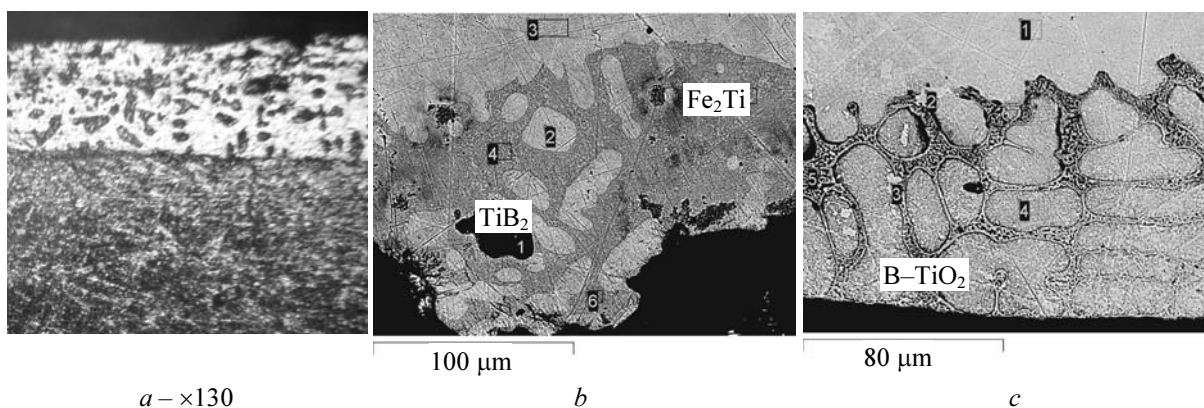


Fig. 3. Microstructure of layers TiB<sub>2</sub> on steel 45

The chemical analysis has shown that grey inclusions represent ferrite. These inclusions are formed on border metal-layer in some transitive zone which sizes do not exceed 5–10 microns. It is necessary to note, that solubility of the titan in ferrite is not found out.

The boride TiB<sub>2</sub> presence in layers proves to be true chemical analysis. Boride TiB<sub>2</sub> it is presented by black inclusions (point 1, Fig. 3, *b*). The maintenance of the titan in black inclusions is close to those in boride TiB<sub>2</sub>, instead of carbide TiC or oxide TiO<sub>2</sub>. The dark grey inclusions corresponds intermetallic compound Fe<sub>2</sub>Ti.

In the present work attempt of boride TiB<sub>2</sub> layers formation on a copper alloy M1 surface is undertaken. It became possible, as thermodynamic calculations have shown, that the titan boride is formed at  $\approx 900$  K at pressure  $P < 10^{-2}$ – $10^{-3}$  Pa. Layers TiB<sub>2</sub> by thickness 20–50 microns are received.

Thus, a new process was shown to make borides layers using electron beam. The electron beam boriding technology of such layers formation includes the following: saturating daub containing oxide TiO<sub>2</sub>, boron component and carbon was deposited on samples surface, and the treatment by an electron beam in vacuum is fabricated.

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