Synthesis, Phase Composition and Microstructure of TiB_2 and ZrB_2 Layers Formed in Vacuum Under Irradiation by Power Electron Beam

B.B. Tsyrynzhapov, N.N. Smirnyagina, A.P. Semenov

Department of Physical Problems at the Presidium of Buryat Scientific Center SD RAS,
Sakhyanovoy St., 8, 670047, Ulan-Ude Russia, E-mail- ionbeam@ofpsrv.bsc.buryatia.ru

Abstract – The thermodynamic investigation of equilibrium in Ti-B-C-O, Zr-B-C-O systems and refractory metal borides synthesis (TiB_2, ZrB_2) in vacuum in result of the interaction of appropriate oxides with carbon and various boriding components (B4C, B, B_2O_3) is carried out. Borides layers TiB_2, ZrB_2 on surface of steel 45 are received and studied.

1. Introduction

Formation of refractory metals borides in surface layer allows to obtain coating with special properties as stability in melts of non-ferrous metals (TiB_2, ZrB_2). The electron beam boriding technology of such layers formation includes the following's: saturating daub containing oxides (TiO_2, ZrO_2), boron component and carbon was deposited on samples surface, and the treatment by an electron beam is fabricated.

Powder borides have been synthesized by 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^{-2}–10^{-3} Pa), and to know phases composition and equilibrium transformations characteristic and 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 refractory metal oxides with carbon and various boron compounds in the equilibrium conditions. We report on a new process to make TiB_2, ZrB_2 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_m(Fe)=1812 K)). The pressure was varied from 10^5 to 10^{-4} 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_2O_3, B_4C, Ti, TiO, TiO_2, Ti_2O_3, Ti_3O_5, Ti_4O_7, TiB, TiB_2, TiC. The gas phase include in consideration were O_2, C, C_2, C_3, C_4, C_5, CO, CO_2, B, BO, BO_2, B_2O_2, B_2O_3, B_4C, Ti, TiO, TiB. In the Zr-B-C-O system we considered the phases C, B, B_2O_3, B_4C, Zr, ZrO_2, ZrB_2, and ZrC and the gas phase species O_2, C, CO, CO_2, B, BO, BO_2, B_2O_2, B_2O_3, B_4C, Zr, ZrO_2.

The boride layers were studied by X-ray diffraction and metallographic. An X-ray powder diffract meter D8 Advance Bruker using Cu K – radiation was employed for phase analysis and the determination of lattice parameters. Microhardness and microstructure of samples was measured by PMT-3 hardness tester at a loading 0,5 and 1 H and with digital camera C4000zoom.

3. Results and Discussion

Thermal behavior MeB_2

We have been tried to simulate thermal behavior MeB_2. It is established, that TiB_2 it is thermally constant. Fig. 1 shows the character of thermal behavior TiB_2. The interaction TiO_2 with various boronizing agents (B_2O_3, B_4C) begins at temperatures 1900–2100 K (10^5 Pa), and at pressure 10^{-2}–10^{-4} Pa the temperature of the formation beginning decreases up to 773–900 K (fig. 4, a curve 1, equilibrium of

"TiB$_2$-CO formation"). At lower temperatures in the products is present only TiC. It is established, that TiB$_2$ it is thermally steady (fig. 4). At presence of a gas phase (CO) in the decomposition products can be TiC and B$_4$C, and also C or B.

Character of decomposition TiB$_2$ depends on total pressure in system. At pressure from 10^{-4} up to 1 Pa TiB$_2$ consistently decays with formation TiC and C (a curve 2, equilibrium of "TiB$_2$-TiC-C"), then – TiB$_2$ – TiC (a curve 3, equilibrium of "TiB$_2$–TiC"), and TiC (a 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_m TiC=3530 K) is more thermally steady in comparison with the titanium boride (T_m TiB$_2$=3063 K).

Increase of pressure from 1 up to 10^4 Pa changes decomposition character TiB$_2$ at presence CO, thus, as impurity it is possible to find out alongside with TiC also B$_4$C or a boron. B$_4$C is present at a temperature interval which range increases with increase of pressure (curves 5 and 6, equilibrium of "balance "TiB$_2$-TiC-B$_4$C", the "beginning" and the "end"). After decomposition B$_4$C in equilibrium 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 B$_4$C, therefore it is possible to observe the following phase equilibrium "TiB$_2$" (a curve 1), "TiB$_2$-TiC-B" the "beginning" (a curve 9), "TiB$_2$-TiC-B" the "end" (a curve 10).

The Ti-B system is known to contain two borides. TiB decomposes at 2606 K with out melting, and TiB$_2$ melts congruently at 3063 K. According to [4], ther-modynamic calculations were shown that TiB boride 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) are shown the conditions of TiB boride vapor formation and existence.

Character of thermal ZrB$_2$ boride decomposition is similar, but has some difference. ZrB$_2$ boride single phase it is fixed only in pressure less 10 Pa. ZrO$_2$ oxide and carbon as an impurity is found in more high pressure.

Thus, presence of carbides and carbon as products of thermal decomposition of borides refractory metals can testify to lack of boron or its compounds.

System TiO$_2$-B$_2$O$_3$-C

When an oxide B$_2$O$_3$ is used as boronizing agent, the interaction began with the dissociation of TiO$_2$ forming Ti$_4$O$_7$ at 720–770 K (Fig. 2, *a*). TiC will be formed in result of Ti$_4$O$_7$ and carbon interaction at 810–850 K and further reacts with oxide B$_2$O$_3$ formed TiB$_2$. The highest partial pressure was for CO in a gas phase (Fig. 2, *b*). At 700–900 K the CO contents decreased. It is found that CO and carbon interact with Ti$_4$O$_7$ forming TiC. The behavior of various boron oxides is interesting at temperature increase in system. The B$_2$O$_3$ occurred at 873 K, the contents it in the beginning of grows, but then began to decrease with at 923 K. The B$_2$O$_2$ was found at 893 K, and the BO at 993 K. At higher then 1253 K in a gas phase there were TiO, TiO$_2$ and titanium vapor Ti. The thermal effect ΔH of chemical transformation TiC→TiB$_2$ is 199 кJ/mol.

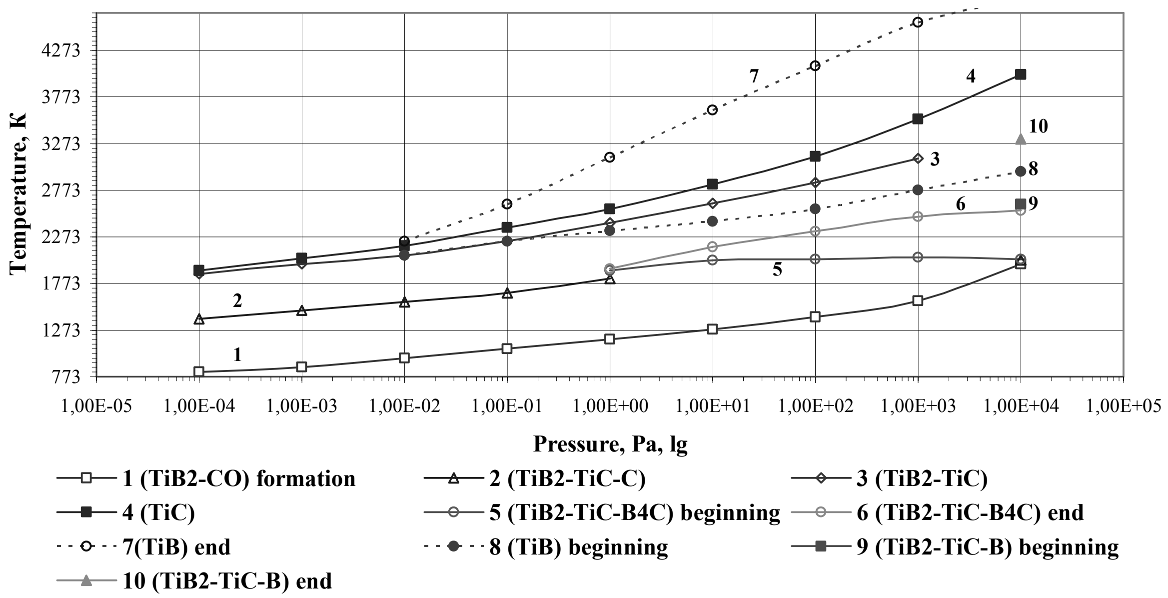

Fig. 1. Thermal behavior TiB$_2$

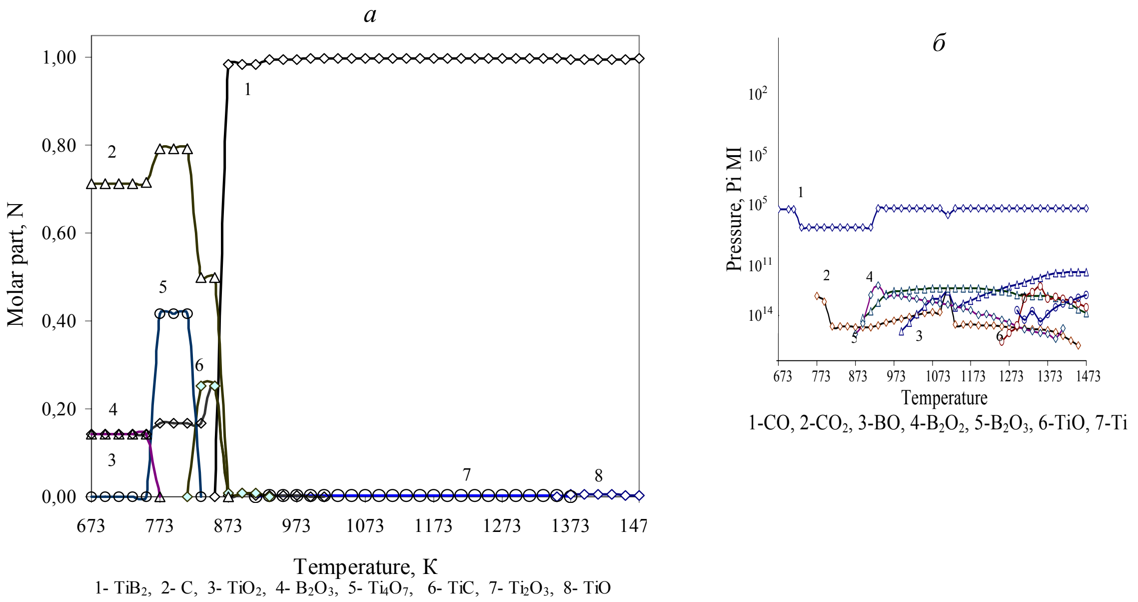

Fig. 2. Interaction in the mixture TiO_2:B_2O_3:C=1:1:5: (a) — condensed phases, (b) — gas phase

The chemical reaction in stoichiometrical mixture TiO_2:B_2O_3:C=1:1:5 at pressure 10^{-3} Pa were

$8TiO_2k \to 2Ti_4O_7k+O2$ 720–770 K
$Ti_4O_7k+CO+7\ Ck \to 4\ TiCk+4CO_2$ 810–850 K
$2B_2O_3l+TiCk+3Ck \to TiB_2k+4CO+B_2O_2$ 870–900 K
$B_2O_3l+3Ck \to 2B+3CO$
$B+TiCk \to TiB_2k+C$
$B_2O_3l+C \to B_2O_2+CO$
$3TiCk+4B_2O_3l \to TiB_2k+Ti_2O_3k+3CO+6BO$ 930–950K
$3Ti_2O_3k \to TiOk+Ti+4TiO_2$ 1310 K
$2TiOk \to Ti+TiO_2$ 1370 K

k — condensed phase, l — liquid phase.

The TiB_2 synthesis from oxide TiO_2 with various boronizing agent proceeded with minimum energy with participation of boron, then B_4C and B_2O_3. Greatest energy were observed for compositions with participation of boron oxide B_2O_3, then boron carbide B_4C. The difference is 550–600 kJ/kg (B_2O_3) and 2–3 kJ/kg (B_4C).

Calculations have shown that system TiO_2-B_2O_3-C is not ternary, as two parties of concentration triangle (TiO_2-C, B_2O_3-C) not binary systems. Feature of B_2O_3-C system is dependence of phase composition from a pressure. It is the reason of dependence of the TiB_2 existence area from a pressure. The isothermal sections at 873–1473 K in pressure10^{-2}–10^{-4} Pa are plotted. The fields of a crystallization of all possible phases are allocated (fig. 3).

Phase equilibriums in system TiO_2-B_2O_3-C are more complex, than in ZrB_2-B_2O_3-C. It is connected with Ti_4O_7, Ti_2O_3, TiO oxides are exists. These oxides as intermediate products are formed at the interaction between TiO_2 oxide and C carbon. The phase formation feature is shown available two phase areas 7 (fig. 3) where TiB_2 and B_4C are present. The areas sizes were depend on a pressure. It can be or TiB_2-B_4C section (10^{-2} Pa), or some B4C area which has various extent on a concentration triangle range: a-b - B4C (10^{-3} Pa), a-c-B4C (10^{-4} Pa).

TiB_2 and ZrB_2 borides formation have been depending on structure initial MeO_2 oxides. So, if used TiO_2 rutile structure type the products of electron beam treatment (on a metal surface and in powder rests of daub) habe been identified the B-doped the rutile (ASTM 01-087-0921, sp. gr. P42/mmm, a=0,4609 and c=0,2967 nm, z=2). If it is to apply the TiO_2 anatase structure type (ASTM 01-089-4203, sp.gr. P42/mmm, a=0,3785 and c=0,9514 nm, z=2), the TiB2 boride (sp. gr. P6/mmm, a=0,3030 and c=0,3230 nm,) were received. Presence of TiC and ZrC as impurity is found out. Feature of interaction is formation of intermediate phases — high-temperature polymorphous form β-Ti and β-Zr. In case of borides layers the phases Fe_2Ti (ASTM 03-065-0602, sp. gr. P63/mmc, a=0,4796, c= 0,7833 nm, z=4) and Fe_3Zr (ASTM 00-017-0360, sp. gr. Fd3m, a=1,169 nm, z=28) are formed.

The thickness of the TiB_2 and ZrB_2 layers attains f 80–100 and 150–180 μm, respectively. Layers TiB_2 are not homogeneous. It is possible to observe light inclusions (microhardness values 2835 HV); under them the second light inclusions (with 1375 HV) and dark inclusions (850 HV). The eutectic has microhardness 600 HV, but a metal basis has values 290 HV. Dark inclusions settle down in a layer not chaotically, and have some ordering.

The chemical analysis (with a prefix) (scanning electron microscope (SEM) LEO 1430VP with ener-

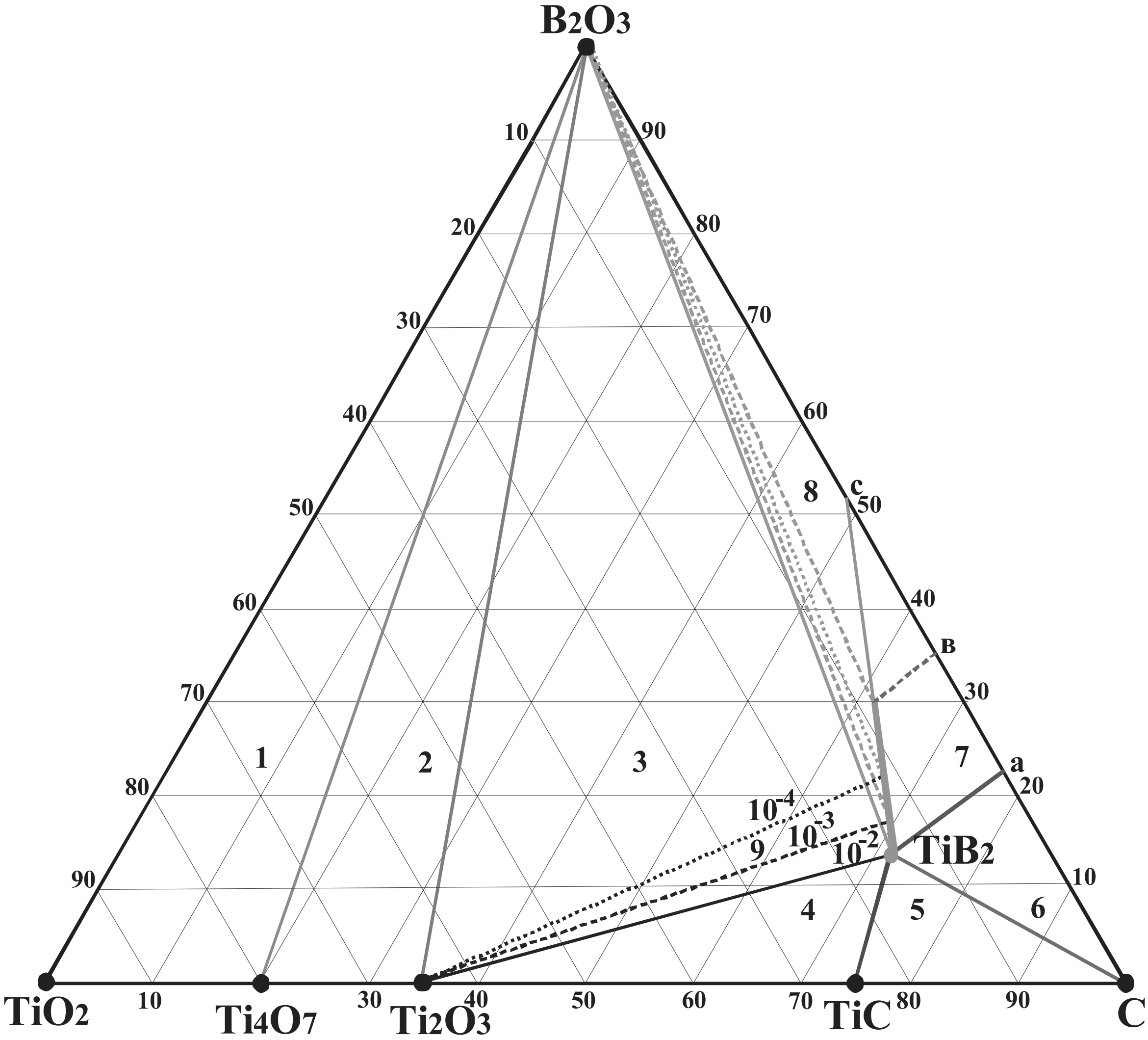

Fig. 3. The isothermal section of system TiO_2-B_2O_3-C- at 1073 K: 1 – TiO_2-Ti_4O_7-B_2O_3, 2 – Ti_4O_7-Ti_2O_3-B_2O_3, 3 – Ti_2O_3-B_2O_3-TiB_2, 4 – Ti_2O_3-TiB_2-TiC, 5 – TiB_2-TiC-C, 6 – TiB_2-B_4C-C, 7 – TiB_2-B4C, 8 – B_2O_3-TiB_2, 9 – TiB_2-Ti_2O_3

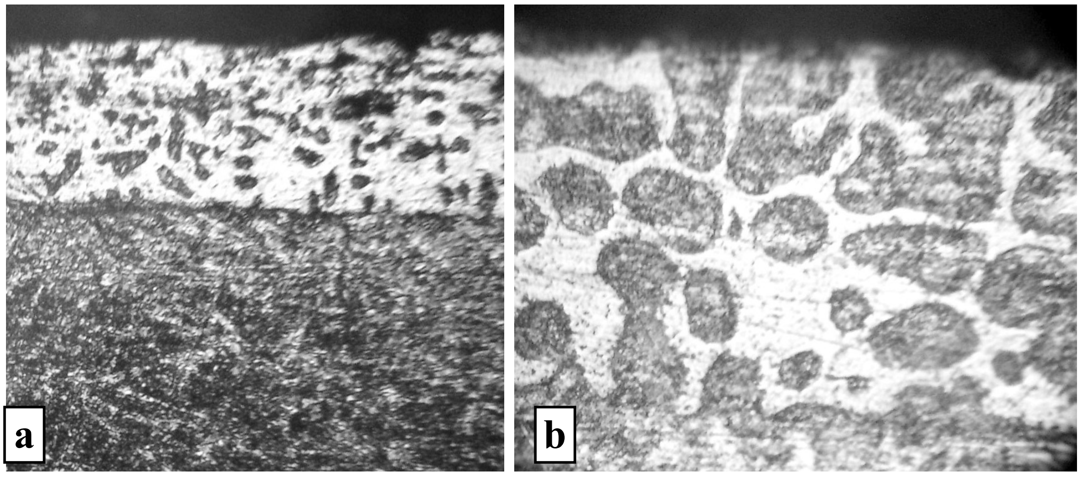

Fig. 4. Microstructure of layers TiB_2 on steel 45: a) ×130, b) ×500

gy dispersive analyzer INCA Energy 300 Oxford Instruments) has shown, that dark inclusions represent ferrite. These inclusions are formed on border metallayer in some transitive zone which sizes do not exceed 5–10 microns. It is necessary to note, that solubility of the titan and zirconium in ferrite is not found out.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's: saturating daub containing oxide TiO_2, boron component and carbon was deposited on samples surface, and the treatment by an electron beam in vacuum is fabricated.

Reference

[1] Matkovich V.I. *Boron and refractory borides.* Berlin: Springer Verlag, 1977.

[2] Vatolin N.A., Moiseyev G.K., Trusov B.G. *Thermodynamic modeling in high temperature inorganic systems.* Moskow, Metallurgy, 1994. 352 p.

[3] Sinyarev G.B., Vatolin N.A., Trusov B.G. Moiseyev G.K., *Application of the COMPUTER for thermodynamic calculations of metallurgical processes,* M.: Science, 1982, 264 p.

[4] Smirnyagina N.N., Sizov I.G., Semenov A.P., Inoganic materials, 38, 48–54 (2002) (in Russia).