Thermodynamic Modeling of Phase Equilibrium in Me-B-C-O (Me-Ti, Zr, V) System in Vacuum

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Abstract – Thermodynamic modeling (ASTRA-4/pc) is executed and the influence of total pressure (10^{-2}–10^{-4} Pa) and temperatures (range 773–1473 K), composition of a boronizing agent and B_2O_3 oxide role on phase equilibriums in Me-B-C-O (Me=Ti, Zr, V) systems is discussed. The isothermal/isobaric sections of MeO_2-B_2O_3-C (Me=Ti, Zr) systems are plotted. Borides MeB_2 layers on carbon steel samples St20 and 45 are obtained by electron beam processing in vacuum, the chemical and phase compositions are analyzed, and the microstructure is investigated.

1. Introduction

In [1–3] thermodynamic analysis of the TiO_2-B (B_4C, B_2O_3)-C and V_2O_3-B (B_4C, B_2O_3)-C systems was carried out with the purpose of search of optimal conditions of the MeB_2 boride synthesis and layers formation by electron beam processing in vacuum. It is established, that at pressure 10^{-2}–10^{-3} Pa interaction between TiO_2 and V_2O_3 oxides with different the boronizing components (B, B_4C, B_2O_3) and carbon is probably at 872–973 K. The sequence of the chemical transformations is shown at the MeB_2 synthesis is. A role of B_2O_3 oxide is established. As is known [4,5], there are also other B-O compounds vapors at heating, for example, B_2O_2, presence which plays a main role during restoration of transitive metals oxides by boron at the carbon presence at vacuum (10^{-1}–10^{-2} torr, or accordingly 10 – 1 Pa). In spite of the fact that this method is widely applied in the industry to reception of borides powders never the less phase equilibrium in the ternary MeO_2-B(B_4C, B_2O_3)-C systems are not complex studied.

We present the results of the thermodynamic modeling of the thermal behavior B_2O_3 at presence of carbon at pressure range 10^{-2}–10^{-4} Pa. The isothermal/isobaric sections of MeO_2-B_2O_3-C (Me=Ti, Zr) ternary systems are plotted. The influence of B_2O_3 oxide evaporation at the MeB_2 borides layers formation of is shown.

2. Experimental methods

Method of thermodynamic calculations. The thermodynamic calculations are executed with ASTRA.4/pc package [6,7]. The calculations were carried out in temperature range 673–1813 K and in pressure range from 10^5 to 10^{-4} Pa. The formation of solid solutions was left out of consideration.

We used a database of thermodynamic properties of all phases (metal or elements, oxides, borides, carbides) in systems. In Ti-B-C-O system it 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; in Zr-B-C-O system – C, B, B_2O_3, B_4C, Zr, ZrO_2, ZrB_2, ZrC; and in V-B-C-O system – C, B, B_2O_3, B_4C, V, VO, V_2O_3, VO_2, V_2O_5, VB, V_3B_4, VB_2.

Phase equilibriums in the ternary systems are investigated in all concentration area and composition are varied from 1–5 mol%. Isothermal/isobaric sections at 773 – 1473 K in pressure from 10^{-2} to 10^{-4} Pa have been plotted.

3. Results and Discussion

MeB_2 (Me=Ti, Zr, V) boride formation

Thermodynamic calculations have shown that for borides synthesis it is preferable to use the boron or B_4C boron carbide. The greatest energy Q necessary to obtain MeB_2 are observed for the mixture with B_2O_3 oxide, the least for B_4C, and then for a boron. The difference in Q is 550–600 kJ/kg and 2–3 kJ/kg (Ti-B-C-O system), both 950 kJ/kg and 2–3 kJ/kg (V-B-C-O system).

Feature of the phase formation in the mixture with B_4C or B is occurrence B_2O_3 oxide and corresponding carbide at low temperatures. Then they are react at more heats with the borides formation.

Thermal behavior B_2O_3.

We have made the attempt to thermodynamic consider the thermal behavior B_2O_3 oxide as it defines phase formation in the ternary systems. In the condensed phase we considered B, B_2O_3, and in a gas phase included O, O_2, B, and all known oxygen components of boron BO, BO_2, B_2O_2, B_2O_3, B_2O. It is established, that the B_2O_3 oxide at pressure 10^5 Pa evaporates at 2335 K, thus the B_2O_2 oxide appears in vapor at 2113 K, and the B_2O_3 oxide at more temperature (> 2273 K). Alongside with evaporation B_2O_3 (2335 K), in the gas environment it is possible to observe the dissociation of B_2O_2 oxide with BO_2 oxide formation, and also atomic and molecular oxygen (Fig. 1). At 2773 K the atomic boron is in vapor.

Pressure decrease in system leads to change of character dissociation диссоциации. Since pressure from 1 Pa, the B_2O_3 oxide dissociates forming оксиды BO_2, B_2O_2 and BO. Last is most thermally stability. Occurrence of atomic and molecular oxygen is observed at more temperatures.

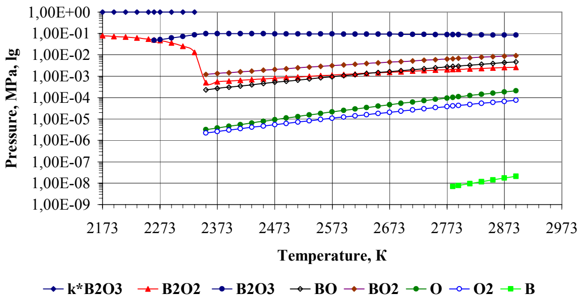

Fig. 1. Composition of gas phase at evaporation of B_2O_3 oxide in total pressure 10^5 Pa

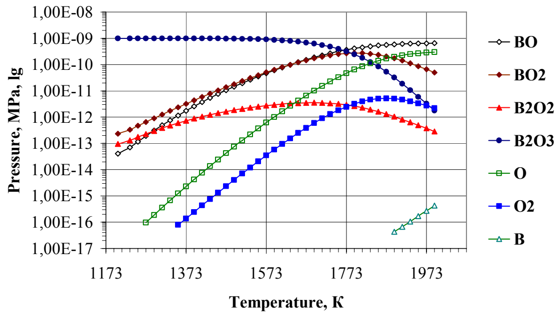

Fig. 2. Composition of gas phase at evaporation of B_2O_3 oxide in total pressure 10^{-3} Pa

Pressure decrease up to 10^{-3} Pa leads to the atomic oxygen formation at 1273 K, and molecular oxygen O_2 at 1373 K, thus the temperature of evaporation and thermal decomposition B_2O_3 is 1170–1200 K (Fig. 2).

It is necessary to stop in detail on the interaction in B_2O_3-C system. B_2O_3-C system represents nonquasibinary cut in ternary B-C-O_2 system.

Figure 3 demonstrates the phase equilibriums in the ternary B-C-O_2 system at pressure 10^{-3} Pa. It is established, that in a temperature range from 973 K up to 1473 K cuts B_4C-CO, B_2O_3-CO, B_2O_3-CO_2 are quasi binary. Interaction B_2O_3 and C leads to boron carbide B_4C or boron formation (a point *a* and *d*). The B_4C boron carbide *(a)* it is formed at temperature 973 K.

The temperature rise up to 1173 K leads to occurrence of two phase area *5* (B_4Cк and CO). On cut B_2O_3-C the pieces *ab* and *ac* are put. At 1273 K B_2O_3 oxide evaporates and dissociates with formation of B_2O_2, BO oxides in gas phase.

There is an area *3* in which are gaseous B_2O_2, CO and B_2O_3 (a piece *c-B_2O_3*). At this temperature the boron *(d)* is formed. Areas *6* and *7* are three-phase: Bк, B_2O_2 and CO, a piece *cd*) and (Bк, B_4Cк, CO, a (piece *ad*). Thus, it is established, that interaction between B_2O_3 and carbon defines the phase formation in the ternary systems MeO_2-B (B_4C, B_2O_3)-C.

<u>Phase formation in ZrO_2-B_2O_3-C system</u>

We have tried to simulate the phase balance in MeO_2-B_2O_3-C systems. It is necessary to note, that the investigated systems are not ternary, as two parties of a concentration triangle (MeO_2-C, and B_2O_3-C) not binary system.

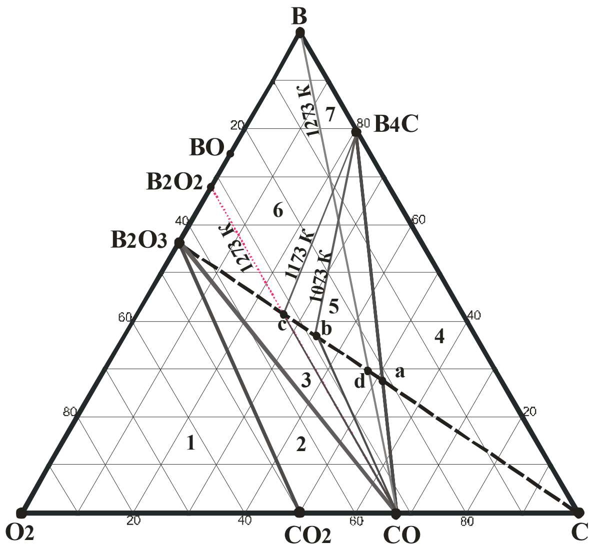

Fig. 3. The phase equilibriums in ternary B-C-O_2 system in pressure 10^{-3} Pa: *1* – O_2,B_2O_3,CO_2; *2* – CO_2,B_2O_3, CO; *3* – B_2O_3,B_2O_2,CO; *4* – CO,B_4C,C; *5* – B_4C,CO, *6* – B_4C,BO,B_2O_2, *7* – B_4C,B,CO

Figure 4 represents the phase equilibriums in ZrO_2-B_2O_3-C system at pressure 10^{-3} Pa (the isobaric section). We shall note that this system is characterized by the most simple phase equilibriums. At 913 K ZrB_2 boride is formed, but at 973 K in ZrO_2-C cut of the party of a concentration triangle, it is fixed ZrC carbide. In system ZrO_2-B_2O_3-C in a temperature range from 973 up to 1473 K it is possible to reveal cuts ZrO_2-ZrB_2, ZrB_2-ZrC, ZrB_2-C and ZrB_2-B_4C.

The temperature rise up to 1173 K leads to occurrence of the two phase area *4* containing ZrB_2 and B_4C. As B_4C in these conditions changes on a piece *ab* (1073 K), *ac* (1173 K) (Fig. 3) the area *4* increases from B_4C *(a)* up to 50 mol % B_2O_3 on party B_2O_3-C of a concentration triangle.

Cut ZrB_2-B_2O_3 exists in temperature ranges from 973 K up to 1073 K, and thus the area *5* containing ZrB_2, B_2O_3 and B_4C is formed. It is revealed, that areas *4* and *5* change the sizes because of feature of thermal behavior B_4C. Further, at 1173 to and 1273 K because of evaporation and dissociation B_2O_3 in system B_2O_3-C there is an area 51–66 mol % B_2O_3 in which only gaseous components – B_2O_3 B_2O_2 and CO (area *3,* Fig. 3) are fixed. It leads to occurrence of area *7* at which is present only ZrO_2 as cut ZrO_2-ZrB_2 is transformed to piece *ZrO_2-c*. It leads to that single-phase ZrB_2 boride is found out not in a point of stoichiometrical mixture, but on piece *ZrB_2-c*. The area *8* is two phase, at it are present ZrO_2 and liquid B_2O_3.

The further rise in temperature leads to occurrence ZrO_2 in areas *7* and *8*.

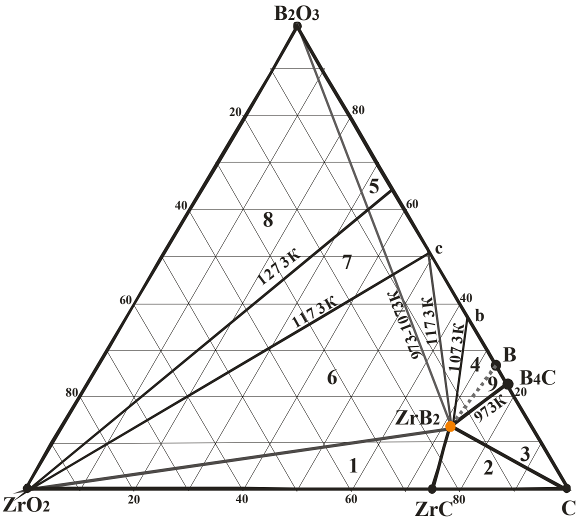

Fig. 4. The isobaric section at 10^{-3} Pa in ZrO_2-B_2O_3-C system: *1* – ZrO_2-ZrC-ZrB_2, *2* – ZrC-ZrB_2-C, *3* – B_4C-ZrB_2-C, *4* – B_4C-ZrB_2, *5* – ZrB_2-B_2O_3-B_4C, *6* – ZrO_2-ZrB_2-B_2O_3, *7* – ZrO_2-ZrB_2, *8* – ZrO_2-B_2O_3, *9* – ZrB_2-B-B_4C

Thus, thermodynamic study of phase formation in ZrO_2-B_2O_3-C system has allowed defining the thermal properties ZrB_2. It is established, that ZrB_2 it is fixed only at pressure <10 Pa in a temperature ranges from 873 up to 1473 K. Temperature increase leads to interaction ZrB_2 with the gas environment (CO) and to formation of an impurity – ZrC. At more high pressure in stoichiometrical mixtures presence of impurity – ZrO_2 and carbon is found out.

Phase formation in TiO_2-B_2O_3-C system

It is established, that TiB_2 also it is thermally steady. In products of their decomposition can be TiC, and also C, B_4C or B. Character of its thermal decomposition depends on pressure in system. At pressure range from 10^{-4} up to 1 Pa at presence of a gas phase (CO) TiB_2 consistently decays with formation TiC and C, and then – TiC, however the maintenance of these impurity slightly, does not exceed 0,01 – 0,1 mol %. Increase of pressure from 1 up to 10^5 Pa changes character of decomposition and as impurity it is possible to find out B_4C or boron. These phases exist at temperatures which interval increases with increase of pressure.

In Ti-B-C-O_2 system it is possible as well the TiB boride formation. According to [5–6], TiB decays in a solid phase at pressure 10^5 Pa. As have shown thermodynamic calculations, TiB it is formed only in a gas phase at pressure above 10^{-1} Pa.

Figure 5 presented the isothermal section at 1073 K in TiO_2-B_2O_3-C system. It is established, that interaction begins with dissociation of TiO_2 oxide with formation of Ti_4O_7 oxide in temperature ranges 720–800 K. TiC is formed at interaction between Ti_4O_7 and carbon at 830–850 K, and further it reacts with B_2O_3 forming TiB_2. The thermal effect ΔH chemical transformation $TiC+B_2O_3 \rightarrow TiB_2$ is 175–177 кJ/mol.

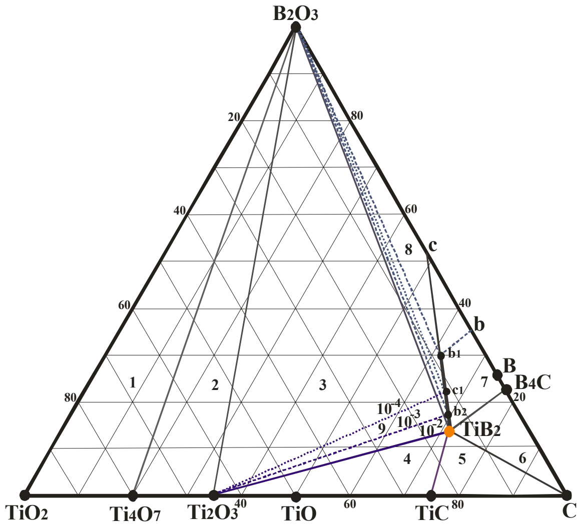

Fig. 5. The isothermal section in TiO_2-B_2O_3-C system at 1073 K: *1* – TiO_2-Ti_4O_7-B_2O_3, *2* – Ti_4O_7-Ti_2O_3-B_2O_3, *3* – Ti_2O_3-B_2O_3-TiB_2, *4* – Ti_2O_3-TiB_2-TiC, *5* – TiB_2-TiC-C, *6* – TiB_2-B_4C-C, *7* – TiB_2-B_4C, *8* – B_2O_3-TiB_2-B_4C, *9* – TiB_2-Ti_2O_3

In this system at 1073 K cuts are presented B_2O_3-Ti_4O_7, B_2O_3-Ti_2O_3, B_2O_3-TiB_2. TiC-TiB_2, TiB_2-C, TiB_2-B_4C. At pressure decline with 10^{-2} up to 10^{-4} Pa there is the two phase area *7* containing TiB_2 and B_4C. It is connected with behavior B_4C which is shown by presence of pieces B_4C-*b* and B_4C-*c* in system B_2O_3-C, the party of a concentration triangle. Composition of point's *b* and *c* are 36 and 50 mol % B_2O_3, respective. Single phase TiB_2 it is possible to observe in a point stoichiometrical mixture, and also on a piece *TiB_2-C*.

It is necessary to note cut Ti_2O_3-TiB_2 which change position at change of pressure from 10^{-2} up to 10^{-4} Pa, thus there is a two phase area *9*. At 10^{-3} Pa single phase TiB_2 it is reflected lines TiB_2-b_2-b_1. Cut Ti_2O_3-TiB_2 is displaced along line TiB_2-b_2-b_1 up to a point *b2*. Thus cut B_2O_3-TiB_2 is similarly displaced, and there is two phase area B_2O_3-b_1-b_2 containing B_2O_3 и TiB_2. The further pressure decline up to 10^{-4} Pa leads to displacement of cut Ti_2O_3-TiB_2 in a point *c1*, thus two phase area B_2O_3-c_1-*c* consists from B_2O_3 and TiB_2. Coordinates of points are *b1* (8 mol % TiO_2, 30 mol % B_2O_3, 62 mol % C), *b2* (12 mol % TiO_2, 18 mol % B_2O_3, 70 mol % C), c_1 (11 mol % TiO_2, 21 mol % B_2O_3, 68 mol % C). The area *8* is observed at pressure 10^{-2} and 10^{-3} Pa and contains B_2O_3, TiB_2 and B_4C.

Thus, MeB_2 (Me=Ti, Zr, V) it is possible to receive in the mixtures containing 12÷14 mol % MeO_2 – 14÷20 mol % B_2O_3 – 67÷71 mol % C at 973–1473 K at pressure range from 10^{-2} up to 10^{-4} Pa.

Synthesis and properties of MeB_2 layers

Preliminary results of electron beam boriding of carbon steels are presented. The thickness of TiB_2 layer was of the order of 80–100 μm, ZrB_2 – 100–150 μm, VB_2 – 50 μm.

Figure 6 demonstrates the microstructure of ZrB_2 layers. We used the scanning electronic microscope (SEM) LEO 1430VP with energy dispersive analyzer INCA Energy 300 Oxford Instruments. The chemical composition of the cross-section is simultaneously certain. It is necessary to note, that simultaneous analysis of Zr and B is impossible in view of overlapping analytical lines Kα of a series of these atoms. Determination of boron in all investigated samples was accompanied by a high error that led only to the qualitative analysis. Layers in a cross-section cut are non-uniform in distribution of phases on a layer thickness. It is possible to observe light inclusions (Fig. 6.) which great bulk is chaotically concentrated nearby or near to a layer surface, and contains atoms Zr and C.

In all investigated samples observed precise border has undressed "layer-metal". However in a layer are found out grey oval inclusions which chemical compound is similar to steel 45 (Fig. 6.). In a layer black impregnations which composition includes atoms Zr and Fe are fixed.

According to x-ray diffraction (XRD) date, the heat-treatment products (layers and powder remains of the paste) consisted of borides in conformity with phase diagram data. We used diffractometer D8 ADVANCE Bruker with Cu K_{α}-radiation. The XRD patterns of the boride layers showed peaks of α-Fe, ZrB_2, ZrC, ZrO_2, Fe_3Zr phases.

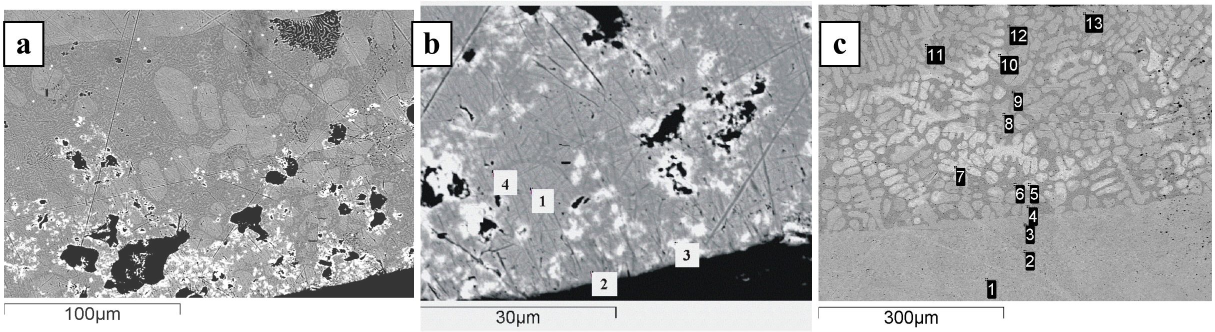

Fig. 6. SEM image of ZrB_2 layers on surface of steel 45

Fe_3Zr phase is formed as at interaction between ZrO_2 and boron the intermediate zirconium is formed. In powder remains of the paste XRD study the presence of the high-temperature form β-Zr is fixed. At layer formation the β- Zr and α-Fe phases are formed the intermetallic phase Fe_3Zr with fcc cubic cell. In [8] Fe_3Zr phase was obtained from crystallization of amorphous alloys $Fe_{90}Zr_7B_3$ or $Fe_{87}Zr_7B_6$. It is not revealed formations of a solid solution of zirconium in ferrite.

Presence of initial ZrO_2 oxide and ZrC carbide can testify that at electron beam processing in vacuum there is an evaporation intermediate B_2O_3 that leads to a deviation from stoichiometrical composition. To reduce this influence up to a minimum, we have tried to form layers under a blanket amorphous B_2O_3. The application of a blanket amorphous B_2O_3 (1 volume reactionary paste = 1 volume paste with B_2O_3) leads to formation of more uniform boride layers (Fig. 6.c).

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