Thermodynamic Modeling of the Vacuum Synthesis of Transition Metal Borides for Electron Beam Borating

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Abstract – Thermodynamic analysis of the Ti-B-C-O and Zr-B-C-O systems was carried out with the aim of establishing the conditions of TiB_2, TiB, ZrB_2 formation at temperature from 273 to 1813 K and total pressures from 10^5 to 10^{-3} Pa. Preliminary results of electron-beam boronizing demonstrate the feasibility of producing refractory-metal borides coating on the surface of carbon steels in a vacuum of 10^{-2}–10^{-3} Pa.

1. Introduction

As were known [1], powders of refractory borides can be prepared by a variety of methods, including the reduction of metal oxide by a mixture of boron carbide and carbon at temperatures ranging from 1500 to 1800 °C in a vacuum of about 1 Pa for 1 h in graphite-rod or metallic-heater furnaces. However, the temperature range 1500–1800 °C is unsuitable for boride coatings, because steels melt at lower temperatures. To optimize the synthesis of borides, it is necessary to take into account the behavior of the starting materials and reaction intermediates at high temperatures and low pressures (10^{-2}–10^{-3} Pa), to know the phase composition of the reaction products and the characteristics of the equilibrium transformations involved, etc. From the thermodynamic properties of the starting reagents, one can derive the necessary information data about the heterogeneous system, and to determine the equilibrium composition of the phases present and the partial pressure of vapor species under conditions unattainable in direct experiments.

In this report, we presented thermodynamic calculations modeling the interaction of refractory-metal oxides with carbon and different boron compounds under equilibrium conditions. We also report our experimental results on the preparation of coatings based on titanium and zirconium borides by electron-beam boronizing.

2. Thermodynamic Calculations

Thermodynamic modeling was carried out with the aim of optimizing the synthesis conditions of refractory-metal borides on the surface carbon steels. In computations, we varied the temperature, total pressure in the system, and composition of the boronizing agent.

The thermodynamic calculations were performed with the ASTRA.4/ps package, which incorporates the thermodynamic data for various titanium and zirconium borides, carbides, and oxides [2, 3]. The temperature was varied in the range 673–1813 K (melting temperature of iron Fe 1812 K) and the pressure was varied from range 10^5 to 10^{-3} Pa. The starting mixtures were chosen so as to obtain TiB_2 (composition 1 – $2TiO_2$:B_4C:3C, TiO_2:2B:2C or TiO_2:B_2O_3:5C) and TiB (composition 2 – $4TiO_2$:B_4C:7C, TiO_2:B:2C or $2TiO_2$:B_2O_3:7C). In some instances, the temperature was raised to 3000 K.

The formation of solid solutions was left out of consideration. According with [2], the condensed phases in 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 vapor species included in consideration were O_2, C, CO, CO_2, B, BO, BO_2, B_2O_2, B_2O_3, B_4C, Ti, TiO, TiB.

Thermodynamic calculations were used to determine the temperature-dependent composition of the phases in system; partial pressures of the vapor species present; and thermodynamic properties of the system, including the total enthalpy H, entropy S, and equilibrium heat capacity C_P. The analysis of $H(T)$ data in certain temperature range allows one to reveal sharp changes attributable to equilibrium chemical or phase transformations yielding new or intermediate compounds. The change in total enthalpy H at transformation endpoint per mole of condensed substance at the temperature where H begins to rise sharply is close to the thermal effect of the equilibrium transformation. In addition, H data can be to determine the specific energy necessary to heat the system from 298 K up to the desired temperature T [4].

3. Results and Discussion

The Ti-B system is known to contain two borides. TiB decomposes at 2606 K with out melting and TiB_2 melts at 3063 K [5]. The Ti-B-C system contains no ternary phases (titanium carboborides). All these results refer to atmospheric pressure.

The main results of our thermodynamic calculations are illustrated by an example starting mixture 1 which yield TiB_2 will be formed at pressure 10^{-2}–10^{-3} Pa. First temperature of TiB_2 formation depends on total pressure in the system. So, the reaction of TiO_2 with various boron agents (B_2O_3, B_4C, B) begins between 1900–2100 K at 10^5 Pa and between 850 and 900 K at 10^{-2} to 10^{-3} Pa.

System TiO$_2$-B$_4$C-C or TiO$_2$-B-C

The possible condensed phases are C, B$_2$O$_3$, TiO$_2$, Ti$_2$O$_3$, TiO and TiC. The condensed state can be submitted both fluidic and solid phases. Condensed phases were notched s by ymbols "s" (solid) or "l" (liquid) and "g" (gas phase) in the text.

The formation of TiB$_2$ begins at 873 K (Fig. 1, a). The reaction in the mixture containing B$_4$C or B first yield B$_2$O$_3$, then TiC, and finally TiB$_2$.
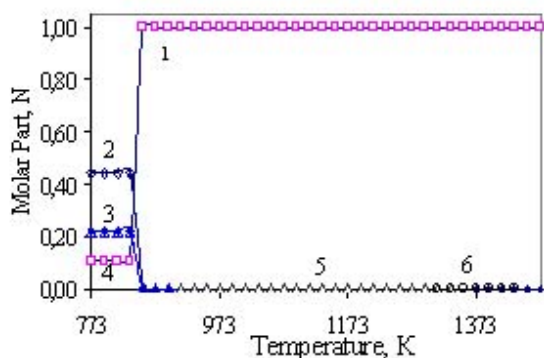
1- TiB$_2$, 2- C, 3- B$_2$O$_3$, 4- TiC, 5- Ti$_2$O$_3$, 6- TiO
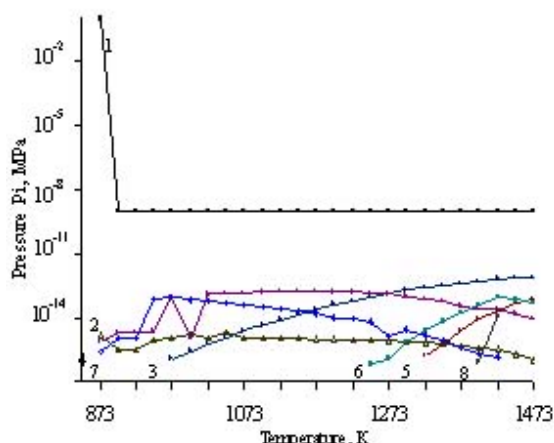
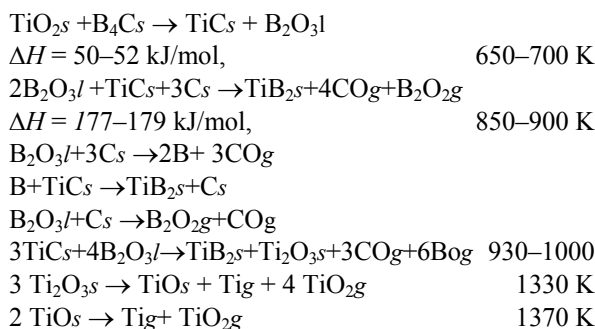1- CO, 2- CO$_2$, 3- BO, 4-B$_2$O$_3$, 5-Ti, 6- TiO, 7- B$_2$O$_2$, 8-TiO$_2$

Fig. 1. Interaction of mixture 2TiO$_2$: B$_4$C : 3C: (a) – condensed phases, (b) – gas phases

In the gas phase, highest partial pressure the in temperature interval of 873–1813 K is that of CO (Fig. 1, b). The gas phase also contains CO$_2$, whose partial pressure remains almost constant over the entire temperature range examined. The behavior of various boron oxides at increased temperature in the system is interesting. The BO partial pressure rises starting at 923 K, and the B$_2$O$_2$ pressure decreases above this temperature. Above 1223 K, the gas phase contains TiO, TiO$_2$, and titanium Ti vapor.

he formation of TiB$_2$ is preceded by the formation of TiC. To evaluate the thermal effects of equilibrium chemical transformation, we used the change in total enthalpy at the transformation endpoint per mole of the condensed substance at the temperature where H begins to rise sharply. Thermodynamic calculation

shows that the transformation width is as small as 5 to 10 K. In this way, we attempted to asses the thermal effects of different interactions with participation of condensed phases.

The chemical reactions in stoichiometric mixture (TiO$_2$:2B:2C and 2TiO$_2$:B$_4$C:3C) at 10^{-2}–10^{-3} Pa are:

TiO$_2$s +B$_4$Cs → TiCs + B$_2$O$_3$l
ΔH = 50–52 kJ/mol,   650–700 K
2B$_2$O$_3$l +TiCs+3Cs →TiB$_2$s+4COg+B$_2$O$_2$g
ΔH = 177–179 kJ/mol,   850–900 K
B$_2$O$_3$l+3Cs →2B+ 3COg
B+TiCs →TiB$_2$s+Cs
B$_2$O$_3$l+Cs →B$_2$O$_2$g+COg
3TiCs+4B$_2$O$_3$l→TiB$_2$s+Ti$_2$O$_3$s+3COg+6Bog 930–1000
3 Ti$_2$O$_3$s → TiOs + Tig + 4 TiO$_2$g   1330 K
2 TiOs → Tig+ TiO$_2$g   1370 K

The formation of TiB$_2$ is preceded by the formation of TiC. The stoichiometric mixtures contain a slight excess of Ti$_2$O$_3$ (mole fraction no higher than 0,0005), which dissociates at higher temperatures (above 1330 K) to form TiOs and Ti and TiO$_2$ vapor. These conclusions were drawn from an analysis of the equilibrium compositions of the condensed and gas phases. The associated thermal effects could not be estimated because of the small amounts of reactants.

Calculations show that mixtures 1 are carbon-deficient. The excess TiC and B$_2$O$_3$ react at 930–1000 K to form Ti$_2$O$_3$s and BO vapor. To prevent this process, an excess of carbon should be added.
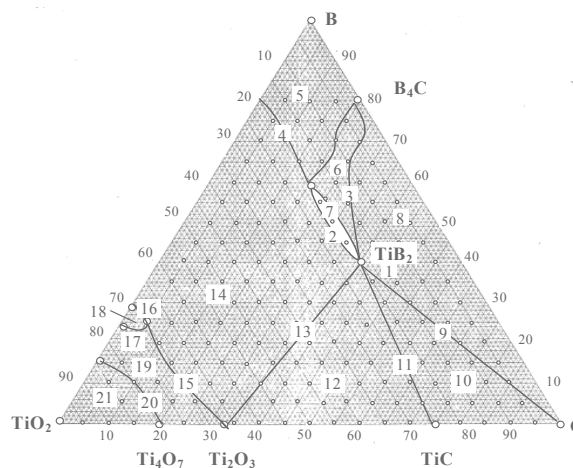

Fig. 2. The isothermal section of the system TiO2-B-C- at 1073 K and 10^{-3} Pa: 1 – TiB$_2$; 2 – B$_2$O$_3$-TiB$_2$; 3 – B$_4$C-TiB$_2$; 4 – B$_2$O$_3$-TiB$_2$; 5 – B$_2$O$_3$-B$_4$C-TiB$_2$; 6 – B$_4$C-TiB$_2$; 7 – TiB$_2$; 8 – TiB$_2$-B$_4$C-C; 9 – TiB$_2$-C; 10 – TiC-TiB$_2$-C; 11 – TiC-TiB$_2$; 12 – Ti$_2$O3-TiC-TiB$_2$; 13 – Ti$_2$O$_3$-TiB$_2$; 14 – B$_2$O$_3$-Ti$_2$O$_3$-TiB$_2$; 15, 16, 17 – Ti$_2$O$_3$-B$_2$O$_3$; 18 – B$_2$O$_3$-Ti$_2$O$_3$; 19 – B$_2$O$_3$-Ti$_4$O$_7$-Ti$_2$O$_3$; 20 – B$_2$O$_3$-Ti$_4$O$_7$; 21 – B$_2$O$_3$-TiO2-Ti$_4$O$_7$

We tried to simulate phase equilibriums in system TiO$_2$-B-C at pressure 10^{-3} Pa. In Fig. 2 are submitted an isothermal slit at temperature 1073 K. The fields of a crystallization of all possible phases are allocated. It
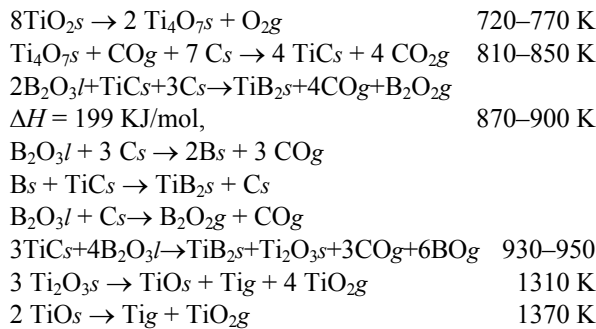
is shown that TiB₂, as a single-phase substance, can be obtained in mixes of composition 18÷22 mol% TiO_2-40÷60 mol% B –20÷40 mol% C.

System TiO_2-B_2O_3-C

When an oxide B_2O_3 is used for synthesis TiB₂, the interaction begins with dissociation of TiO_2 forming Ti_4O_7 at 720–770 K (Fig. 3, *a*). TiC is formed in result of reaction between Ti_4O_7 and C at 810–850 K and then reacts with B_2O_3 to form TiB₂.

In the gas phase (Fig. 3, *b*) the highest partial pressure was that of CO. At temperature 700 to 900 K, the content of CO is decreased. It is bound that CO and C react with Ti_4O_7 to form TiC. Except for CO, the presence CO_2 at 770 to 1473 K is decreased. The behavior of various boron oxides is interesting at pinch of temperature in system. B_2O_3 occurred at 873 K, in the beginning its content grew, but then began to decrease at 923 K. B_2O_2 was found at 893 K, and BO at 993 K. Above 1253 K, the gas phase contains TiO, TiO_2 and vapor of Ti.

The chemical reactions in stoichiometric mixture TiO_2:B_2O_3:5C at 10^{-2}–10^{-3} Pa are:

$8TiO_2s \rightarrow 2\ Ti_4O_7s + O_2g$	720–770 K
$Ti_4O_7s + COg + 7\ Cs \rightarrow 4\ TiCs + 4\ CO_2g$	810–850 K
$2B_2O_3l + TiCs + 3Cs \rightarrow TiB_2s + 4COg + B_2O_2g$	
ΔH = 199 KJ/mol,	870–900 K
$B_2O_3l + 3\ Cs \rightarrow 2Bs + 3\ COg$	
$Bs + TiCs \rightarrow TiB_2s + Cs$	
$B_2O_3l + Cs \rightarrow B_2O_2g + COg$	
$3TiCs + 4B_2O_3l \rightarrow TiB_2s + Ti_2O_3s + 3COg + 6BOg$	930–950
$3\ Ti_2O_3s \rightarrow TiOs + Tig + 4\ TiO_2g$	1310 K
$2\ TiOs \rightarrow Tig + TiO_2g$	1370 K

The energy Q necessary to obtain TiB₂ by reacting TiO_2 and various boron components rises in the sequence B < B_4C < B_2O_3 (Fig. 4). The difference in Q is 550–600 (B_2O_3) and 2–3 kJ/kg (B_4C).

Thermodynamic calculations showed that the carbon deficiency is observed in stoichiometrical mixture 1. The exuberant quantities of TiC and B_2O_3 reacted at 930–1000 K to form Ti_2O_3s, thus, the BO was taken out in a gas phase. For prevention of this process, it is necessary to enter into system some carbon surplus. The calculations showed that the excess from stoichiometrical mixture is up to 0.5–1.0 mol % CO. The introduction of such amount of carbon resulted in shaping single-phase titanium boride. This result has major value for electron beam boronizing . The carbon can be present as uncontrollable impurity getting in boride coating from boron daub. The free carbon occurs in system as a result of a thermal decomposition organic binding, which composition includes polymer or resin.

Thermodynamic calculations showed that TiB (mixture 2) cannot be obtained in the pressure range 10^{-3} to 10^5 Pa at temperatures of up to 3000 K. Independent of the boron agent , the reactions in mixture 2 yield TiB₂ and TiC. At higher temperatures, the forming compounds dissociate and all condensed phases vaporize. The TiB is only present in a gas phase at pressure 10^4 Pa in temperature interval of 2850–2950 K. Temperature range of formation TiB decreased up to 2450–2650 K at pressure 10^3 Pa and 1900–2150 K at pressure 10^{-1} Pa. The further decrease of pressure in system did not result in boride TiB formation.

The results of the thermodynamic calculations were used to optimize the synthesis conditions of refractory-metal borides coating.. The boron carbide B_4C was chosen as borionizining agent. Some carbon deficiency into stoichiometrical mixture was compensated by introduction organic binding, which will
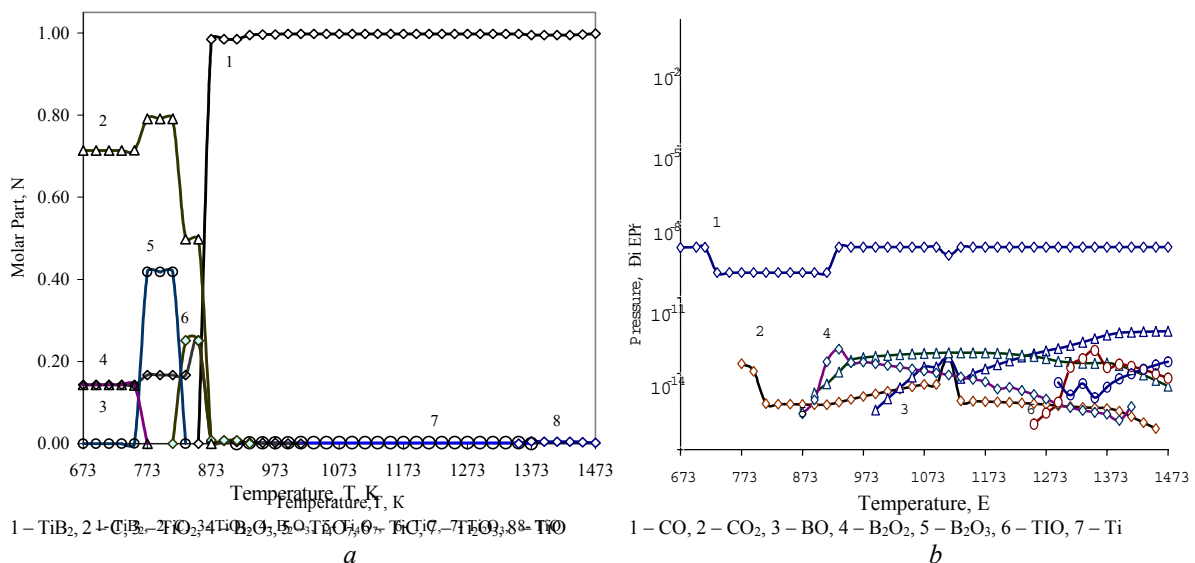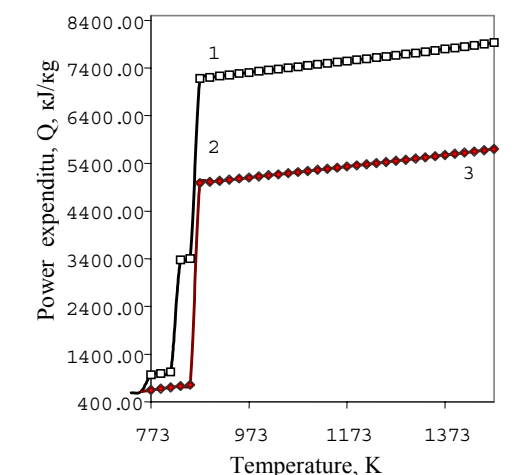
1 – TiB₂, 2 – TiO₂, 3 – Ti₄O₇, 4 – B₂O₃, 5 – TiC, 6 – Ti₂O₃, 7 – TiO₃, 8 – TiO
a

1 – CO, 2 – CO_2, 3 – BO, 4 – B_2O_2, 5 – B_2O_3, 6 – TIO, 7 – Ti
b

Fig. 3. Interaction TiO_2:B_2O_3:5C: (*a*) – condensed phases, (*b*) – gas phase

usually be utilized in boriding daubs for giving of fabricability at drawing last on a handled surface.

1 – $TiO_2 + B_2O_3 + C$, 2 – $TiO_2 + B_4C + C$, 3 – $TiO_2 + B + C$

Fig. 4. Power expenditures in mixture 1

Microstructure of Boride Coating

According to X-ray diffraction (XRD) data, the heat-treatment products (coating and powder remains of the paste) consisted of borides in conformity with their phase diagrams data. The X-ray diffraction patterns of the boride coating showed peaks from α-Fe, Fe_3C and TiB_2, CrB_2 and W_2B_5.

Based on X-ray diffraction study into powder daub rests after electron beam boriding, the main phases are TiB_2, CrB_2 and W_2B_5. We have been determined the hexagonal lattice parameters: for TiB_2 a = 0.3027 (4) c = 0.3220 (5) nm and for CrB_2 a = 0.2948 (4) c = = 0.3082 (5) nm (space group 6 P/mmm) and for W_2B_5 a = 0.2975 (7) c = 1.387(2) nm (space group 6P3/mmc).

Figure 5 displays the microstructures of TiB_2, CrB_2 and W_2B_5 based coating prepared from oxides. Depending on electron heating parameters, 2 mechanisms of layers formation are possible: diffusive (Fig. 4, *a* the layer is formed from liquid phase) and melt surface (Fig. 4, *b*). The layers formed from a liquid phase had heterogeneous structure. The formation of these borides in the presence of boron carbide is a complex physicochemical process. The phase composition of the coatings agrees with phase-diagram data.

The formation of surface layers by the first mechanism allowed receiving layers of much greater thickness, thus the quality of a surface is sharply worsened. The thickness of TiB_2 layer was of the order of 80–100 μm, CrB_2 – 600 μm and W_2B_5 – 15–20 μm.
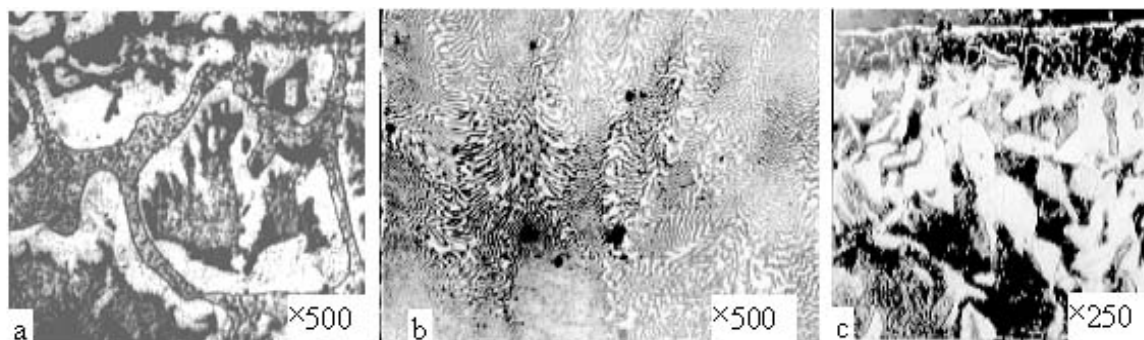

Fig. 5. Boride coating microstructure on steel 45: (a) TiB_2, (b) CrB_2, (c) W_2B_5

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