Synthesis of Borides Vanadium Layers Under Power Electron Beam in Vacuum

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Abstract – Thermodynamic modeling with the purpose of revealing of the mechanism and sequence of the phase transformations proceeding at synthesis of boride vanadium layers on surface of carbon steel alloys is executed. Influence of pressure and temperatures, boronizing agent on phase formation in the V-B-C-O_2 system is discussed. The isothermal sections of ternary V_2O_3-B-C, V_2O_3-B_4C-C systems are plotted. VB_2, V_3B_4, VB borides layers are received, and the microstructure and microhardness are studied.

1. Introduction

The boronizing of metals and alloys enhances their surface hardness, wear resistance, etc. In [1, 2] the preparation of hard coating based on refractory-metal borides (TiB_2, CrB_2, VB_2 and W_2B_5) on the surface of carbon steels by vacuum electron beam processing of a boron-containing paste painted on the base materials were described. As a rule the multicomponent coasting containing the refractory metal borides have been formed by methods of thermochemical treatment as a result of interaction of the boron component with refractory metal, or due to saturation by boron of a refractory metal impurity or an alloy.

As is known [3], powers of refractory, alkali, and rare-earth borides can be prepared by a variety of methods, including the reaction of metal oxides by a mixture of boron carbide and carbon at temperatures range 1500–1800 °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 producing boride coating, because steels melt at lower temperature. Thermodynamic analysis of the V-B-C-O system was carried out with the aim of established the condition of V-B borides formation at temperatures from 673 to 1813 K and total pressure in system from 10^5 to 10^{-3} Pa.

These calculations are executed only for mixtures of stoichiometrical composition. However that the boron is born in a gas phase, in these compositions the presence of carbides is observed.

In this work, we report results of the thermodynamic calculations modeling the interaction of vanadium oxide with carbon and various boron components under equilibrium conditions are resulted. The isothermal sections of ternary V_2O_3-B-C, V_2O_3-B_4C-C systems are presented. We also present our experimental results on the preparation of coating based on vanadium borides by electron beam boronizing.

2. Thermodynamic calculations

Thermodynamic calculations were carried out with the ASTRA 4/pc package, which incorporates the thermodynamic data for various vanadium oxides, borides and carbides [4,5]. The temperature was varied in range 273–1473 K, and the pressure was varied from 10^5 to 10^{-4} Pa. The research was carried out in all concentration range (triangle) through 5 mol.%. The formation of solid solutions was left out of consideration.

The condensed phases considered in the V-B-C-O system were C, B, B_2O_3, B_4C, V, VO, V_2O_3, V_2O_4, V_2O_5, V_3B_4, VB, VB_2, VC. The gas phase included in consideration were O_2, C, CO, CO_2, B, BO, BO_2, B_2O_2, B_2O_3, B4C, V, VO, VO_2.

3. Results and Discussion

Thermodynamic calculations have shown that formation of VB_2 boride should pass through stages of formation of VC vanadium carbide and the lowest a V_3B_4. It is established, that the beginning temperature of boride formation depends on total pressure in the system. Figure 1 demonstrates the temperatures of VB_2, V_3B_4, VC formation in stoichiometrical mixtures at different pressure.

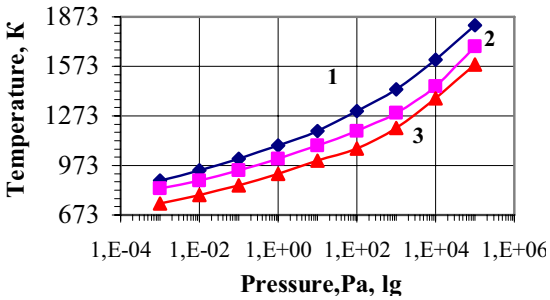

Fig. 1. The temperatures formation of VB_2 (1), V_3B_4 (2), VC (3) in the mixture with V:B:C:O=2:4:3:3

The reaction of V_2O_3 with boronizing agent (B_2O_3, B_4C, B) begin between 2400–2450 K at a pressure of 10^5 Pa, and at range 850–900 K at 10^{-2}–10^{-3} Pa. The reaction first yield VC, then V_3B_4, and finally VB_2. V_3B_4 is formed in the range 1600–1620 K at 10^5 Pa and in the range 830–850 at 10^{-3} Pa. The reactions in the mixture containing B_4C or B first yield B_2O_3, then VC, V_3B_4, and finally VB_2. The thermal effect of the reaction (ΔH) $VC(c^*)+B_2O_3(l^{**})\rightarrow VB_2(c)$ is 167 kJ/mol.

The chemical reactions in stoichiometrical mixture V_2O_3:B:C =1:1:3 and V_2O_3:B_4C:C =1:1:2 at pressure 10^{-2} and 10^{-3} Pa are:

$V_2O_3c + B_4Cc \rightarrow VC + B_2O_3c$ 273–298 K

$V_2O_3c + Bc \rightarrow V + B_2O_3l$

$2B_2O_3c + 3VC + 3Cc \rightarrow V_3B_4c + 6CO$ 410–450 K

$V_3B_4c + 2B_2O_3c + 4C \rightarrow 3VB_2c + 4CO + B_2O_2$ 880–930 K

$2B_2O_3c + Cc \rightarrow B_4Cc + CO$ 930–950 K

$4VB_2c \rightarrow V_3B_4c + V$ 1570–1600 K

*– condensed phase, * *– liquid phase

The synthesis of VB_2 from V_2O_3 and B_2O_3 proceeds in an analogous manner, but this system is carbon deficient, and the excess B_2O_3 vaporizes. Above 1513 K VB_2 dissociates to form V_3B_4(c) and B and V vapors.

V_3B_4 is formed at 833 K, following the formation of VC. The H of the reaction VC V_3B_4 is 157 kJ/mol.

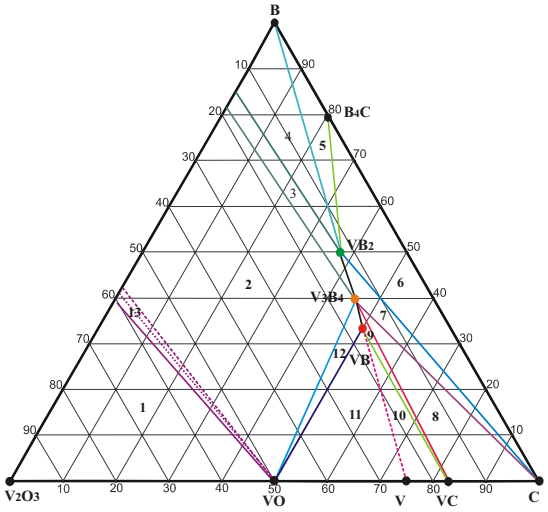

Fig. 2. The isothermal section of the V_2O_3-B-C system at 1273 K (pressure 10^{-3} Pa): 1 – V_2O_3,VO; 2 – VO,V_3B_4; 3 – V_3B_4,VB_2; 4 – VB_2,B; 5 – VB_2,B_4C,B; 6 – VB_2,B_4C,C; 7 – V_3B_4,VB_2,C; 8 – VC,V_3B_4,C; 9 – VB,VC,V_3B_4; 10 – V,VB,VC; 11 – VO,VB,V; 12 – VO,V_3B_4,VB; 13 – VO

VB is formed at 1113 K via the reacting between V_3B_4 and VC. The thermal effect H of the reaction $VC+V_3B_4$ VB is 68 kJ/mol. VB is stable up to 1593 K. At higher temperatures, it reacts with the gas phase to form V_3B_4.

The energy necessary to synthesize VB_2 by reacting V_2O_3 and boronizing agents rises in the sequence $B<B_4C<B_2O_3$. The difference in energy consumption is 950 and 2–5 kJ/kg, respectively.

Figure 2 demonstrates the isothermal section of the V_2O_3-B-C system at 1273 K. It is established that two V_2O_3-B and V_2O_3-C systems is no binary. These systems are the boundaries of concentration triangle. They represent cuts of ternary V-B-O_2 and V-C-O_2 systems, which are the planes of a concentration tetrahedron. It is necessary to note, that investigated V_2O_3-B-C system is not ternary.

The analysis of phase equilibriums has shown, that at pressure 10^{-3} Pa in the ternary V_2O_3-B-C system at 873–973 K the V_3B_4 and VB_2 borides are formed. The quasi binary cuts will be: VB_2-C, VB_2-B_4C, and also V_3B_4-V_2O_3, V_3B_4-VO, V_3B_4-VC, and V_3B_4-C. It is possible to allocate area 3 where are phases V_3B_4, VB_2 and B_2O_3. This area appears owing to not binarities of the double V_2O_3-B system.

The VB boride is formed in the ternary V_2O_3-B-C system at 1073 K. It is appears the additional areas containing of the phase: V_3B_4, VC, VB (8); VB, VO, VC (9) and V_3B_4, VO, VB (10), accordingly.

The rise of temperature up to 1173 K leads to change the phase equilibrium with participation of V_2O_3 oxide by VO oxide in the ternary V-B-O_2 and V-C-O_2 systems, being sides of a concentration tetrahedron. As the V_2O_3-B and V_2O_3-C systems are not binary in them the steady VO oxide appears. The area of VO oxide existence increases in process of rise in temperature from 1173 up to 1473 K.

Besides with the temperature raise at 1173 K the complication of phase structure due to occurrence of the condensed vanadium in the system is observed.

Feature of system V_2O_3-B-C is presence of area of single-phase VO oxide (a field 13, fig. 2). Reduction of pressure with 10^{-2} up to 10^{-4} Па leads increase in area (60÷55 mol % V_2O_3). The temperature decrease leads to the phase transformation, the disappearance of VO oxide, and the occurrence of V_2O_3 and V_3B_4.

The results of the thermodynamic calculations were used to optimize the synthesis condition of vanadium borides. VB_2, V_3B_4 and VB coating were produced by electron beam processing of a boron containing paste painted on the surface of carbon steel 45. The paste consisted of the starting mixture (V_2O_3 oxide, boron B_4C carbide, and carbon) and an organic binder (1:10 solution of the BF-6 adhesive in acetone) in a volume ratio of 1:1. The processing time was 2–5 min, and the electron beam power was 150–300 W. The pressure in vacuum chamber was no higher than $2\cdot10^{-3}$ Pa. The starting materials used were technical-grade B_4C, charcoals (birch), and special pure-grade V_2O_3.

The process was run in a vacuum system incorporating an EPA-60-04.2 electron gun and electron beam control unit.

According to x-ray diffraction (XRD) date, the heat-treatment products (coating and powder rema-

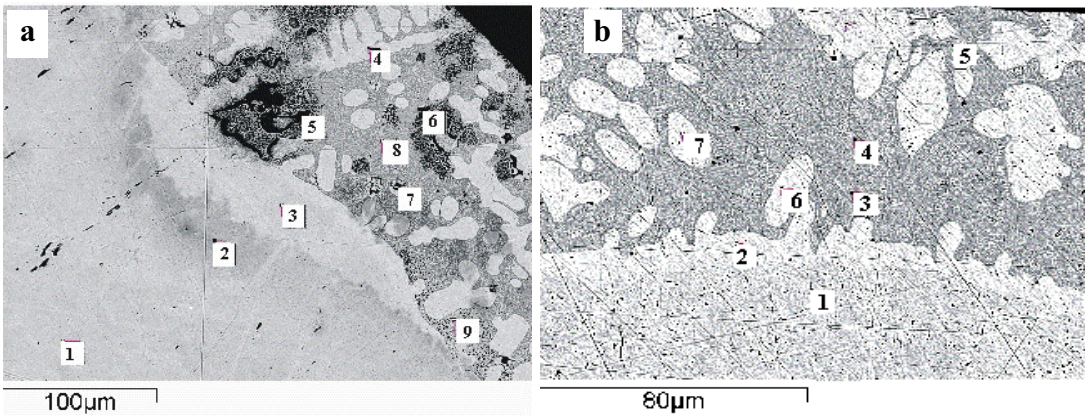

Fig 3. SEM image of VB_2 layers on surface of steel 45: a – VB_2; b – VB_2+B_2O_3

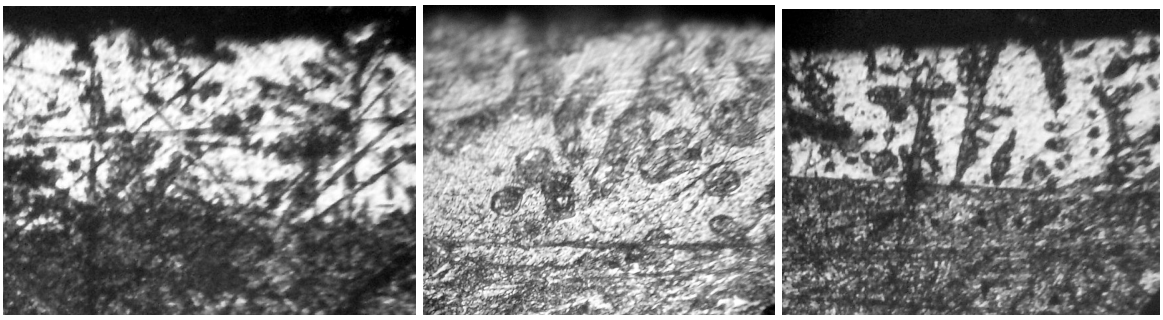

Fig.4. Microstructure of VB2, V3B4, VB layers on the surface of steel 45, 500

ins 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 coasting showed peaks from α-Fe, Fe_3C. Semi quantitative analysis (scan electron microscope LEO 1430VP with energy dispersive analyzer INCA Energy 300 Oxford Instruments of the polished cross-sections was performed and check of the coasting composition. The boride layers there were the reflexes of different intensity belonging vanadium solution into ferrite (composition of Fe_9V, sp.gr. Im3m with cubic lattice a=0,2878 nm), vanadium carbide (VC, sp.gr. Fm3m with cubic lattice a=0,4165 nm, NaCl structure type).

The gray including (point 3, 4 on fig. 3, *a*, and 2, 5, 7 on fig. 3, *b*) is the ferrite (Fe_9V).

Figure 4 displays the microstructure of VB_2, V_3B_4, and VB boride. The thickness of the VB_2, V_3B_4, VB layers attains 100–230, 150–200, 100–150 μm, respectively.

Research of a microstructure has shown that layers of vanadium borides are formed with participation of a liquid phase. The mechanism of their formation is complex physical and chemical process. In a layer it is possible to observe light inclusions (borides), dark inclusions (vanadium ferrite), eutectic, and also very fine black inclusions, which itself intermetallic compounds FeV. Microhardness of borides are 2300 HV, and eutectic are 650–700 HV.

We report on a new process to make V-B layers by electron beam boronizing.

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