Self-Heating Synthesis of Borides Layers under Power Electron Beam in Vacuum

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Abstract – Borides layers ZrB_2, VB_2, V_3B_4, VB on surface of steel 3, 20, 45 under the electron beam heat treating are received and studied. The possible mechanism of layers formation of refractory metals borides on a surface carbonaceous steel is considered.

1. Introduction

The surface layers saturation of metals and alloys by boron will carry out with the purpose of increase of their surface hardness, abrasion resistance etc. Multicomponent layers, containing borides of refractory metals, as a rule, form by methods of chemical-thermal treatment in result of the boriding component interaction with refractory, or at the expense of boron saturation a refractory impurity of metal or alloy.

In work [1] was informed about hardening coating formation on basis refractory metal borides (TiB_2, CrB_2, VB_2, W_2B_5) on carbon steels under influence of an electron beam in vacuum. As the boride layers formation came true on steel surface, at a choice of conditions of refractory metal borides synthesis it was necessary to take into account peculiarities metal basis melting.

Powder borides have been synthesized various methods, for example, self-heating synthesis (SHS) [2]. 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. Work [3] has presented results of the thermodynamic calculations simulating the interaction between refractory metal oxides with carbon and various boron compounds in the equilibrium conditions.

In this study, we report a new process to make MeB_2 (Me = Zr, V) layers by electron beam heat treating.

2. Experimental methods

Synthesis of borides ZrB_2, VB_2, V_3B_4, VB carried out on a surface samples made from carbon steels (St3, 20, 45). Samples prepared by daub drawing on a previously prepared surface of steel. Boride layers were received from reactive daub containing oxides (V_2O_3, ZrO_2), boron carbide B_4C and carbon C (birch charcoal). The daub composition entered 1:1 on volume of reactive mixture and organic binding – solution 1:10 glue BPH-6 in acetone.

The electron beam treatment has been carried out in an electro-vacuum installation with a powerful industrial axial electron gun [4]. The pressure in chamber did not exceed $2 \cdot 10^{-3}$ Pa.

The boride layers were analyzed by X-ray diffraction. An X-ray powder diffract meter Advance D8 Bruker using Cu Kα-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

Self-heating synthesis of refractory borides begin as a result of electron beam penetration with energy 20 keV on depth 2.8–3.5 microns in the reactionary stoicheometrical mixture containing MeO_2, B_4C, C (Table). SHS proceeds with greater speeds (2–5 microns/s) and is accompanied by a bright luminescence of reaction front behind which interaction products are formed. As thermal effect of reaction of boride formation, it is not enough for the fusion of SHS products it turns out powder mixture which can or be used directly, or in its further electron beam heat treating to coating receive.

Table. Electron beam heat treating parameters at boride refractory metal layers formation at $U = 20$ kV

	ZrB_2	VB_2	V_3B_4	VB
Reactionary daub thickness, μm	67	44.8	68.4	78.6
Depth of a electron penetration beam, μm	2.83	3.50	3.27	3.24
Layer thickness, μm	120	100	150	100
Boride thickness, μm	33.0	13.1	24.0	33.5
SHS time, s	33.5	22.4	34.2	39.3

The crystals formed at hardening, can get the various form depending on conditions of their growth. They can be polyhedrons, dendrite, needle, lamellar, etc. Crystallization begins from a surface. In a direction of heat removal, i.e., it is perpendicular to a surface
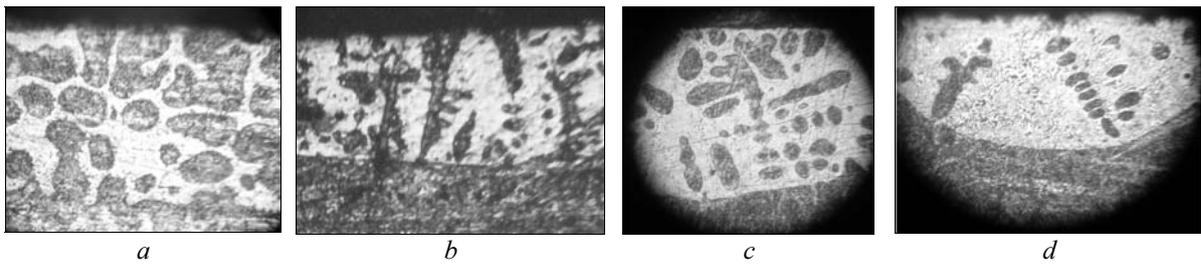
Fig. 1. Microstructure of layers ZrB_2 (a –×300); VB (b –×130); V_3B_4 (c –×300); VB_2 (d –×300) on steel 20

a crystal grows more quickly, than in other directions. For dendrite or the branched out treelike crystal orientation for all branches is characteristic crystal identical. It is more quickly cooled a liquid, the there is a branching that is accompanied by occurrence of a plenty of superficial defects is more often. Branched out dendrite formation at crystallization raises its speed, but thermodynamically they are less steady. Dendrite structure can be revealed only by etching, as well as borders between dendrite. Especially well comes to light a dendrite structure in the metal containing impurity, as spaces and borders dendrite dressing by impurity.

Dendrites in all borides layers represent the ferrite inclusions of metal base (Fig. 1)

As is known, solubility of transitive metals (Zr, V) in liquid and solid iron is defined by a parity of metal radiuses [5]. Zirconium is not dissolved iron, and vanadium forms solid solutions in α-Fe. In this connection the dendrite inclusions contain in boride layers of % V. Ability to give solid solutions increases at rise in temperature a little, but their allocation (hardening) is carried out by quenching.

In Figure 2 the layer ZrB_2 structure is presented from which it is visible, that layers on thickness of a polish cross section are non-uniform in distribution of various phases.
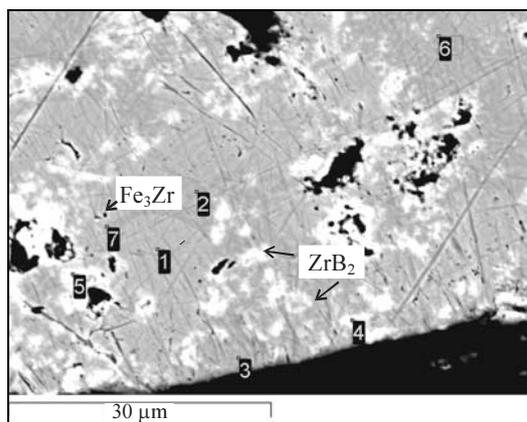

Fig. 2. SEM image of layers ZrB_2 on steel 45

It is possible to observe light inclusions which great bulk is chaotically concentrated near to a layer surface, and contains atoms Zr and B. In all investigated samples, observed precise border has undressed "layer-metal". In a layer are found out light grey oval

inclusions, a chemical composition which it is similar to initial steel 45. In them, it is possible to fix presence of chrome, manganese, silicon, a range of concentration which corresponds to those in volume of a metal matrix. Appreciable solubility of zirconium in iron it is not revealed. In layer black inclusions which chemical analysis is close to structure compound Fe_3Zr is found.

Boride ZrB_2 it is formed, if used oxide ZrO_2 with monoclinic structure and an elementary cell $a = 0.5313$, $b = 0.52125$, $c = 0.51471$ nm and $\beta = 99.218^o$. At layers and the daub rests is present carbide ZrC.

Interaction feature is formation of intermediate phase's metals which presence is shown on x-ray patterns of the reactionary mixture rests the presence of high-temperature polymorphic form β-Zr. On diffractogramm of borides layers the reflexes of reflections belonging intermediate phase's metals, for example Fe_3Z_r (a cubic face cell with parameters $a = 1.169$ nm) are observed.

In this connection it is necessary to note, that formation Fe_3Z_r testifies about participation of a surface in a layer formation. In SHS products, there is a metal zirconium which reacts with iron surface forming Fe_3Zr. According to [6], atoms Zr and B cause the iron amorphous. At cooling amorphous alloys $Fe_{93-x}Zr_7B_x$ ($x = 3.6$ at % B) with a speed 20 K/min there is a primary crystallization and allocation nanostructure particle α-Fe wish the size from 14 (from temperature 875 K) up to 12 nm (893 K). Formation of compound Fe_3Zr with a face cubic cell is observed at secondary crystallization with participation α-Fe and a residual amorphous phase. The increase in the maintenance of boron > 12 at % B leads to crystallization under other scheme: at primary crystallization are allocated metastable crystallite with the size up to 35 nm with structure cubic "$Fe_{12}Si_2ZrB$" (Sp. gr. $I3m\bar{4}$) which at rise temperature to 1003 K crystallize with participation of an amorphous phase and form α-Fe and Fe_3Zr, and further – α-Fe and ZrB_2.

According to X-ray analysis on a borides layers surface there are following phases: ZrB_2, ZrC, ZrO_2, Fe_3Zr, α-Fe. Presence of initial oxide ZrO_2 (monoclinic phases) and carbide ZrC can testify, that at electron beam processing in vacuum there is an evaporation of intermediate oxide B_2O_3 which leads to a deviation from stoicheometrical composition in an initial mixture. As much as possible to lower this influence, uses of a protecting amorphous oxide B_2O_3 have tried to

generate layers with. The layers which are not containing carbide ZrC have been as a result received.

Layers ZrB_2 also are non-uniform on thickness of a layer, in them separate inclusions with the maximal microhardness 28000 MPa are observed.

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 cell with $a = 0.2878$ nm), vanadium carbide (VC, Sp. gr. *Fm3m* with cubic lattice cell $a = 0.4165$ nm, NaCl structure type).

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 very fine black inclusions FeV. Microhardness of borides are 2300 HV, and eutectic are 650–700 HV.

In Figures 3 and 4 the layers VB, V_3B_4, VB_2 structure, investigated on a scanning electronic microscope is presented. Microscopic research with simultaneous characterization of a chemical composition has confirmed non-uniform distribution of structural components on a layer thickness. At all investigated samples

there were inclusions in the dendrite form which represent vanadium ferrite, solubility of vanadium in ferrite reaches from 0.9 up to 1.45 mass % V.

In Figure 3, *a* in the field of a point 5 it is shown, how there is a dendrite formation. It confirms formation on a metal basis surface of the melted off narrow zone. Thickness of a zone reaches 5–7 microns, is uniform on all area of a surface of samples.

In all borides layers are available eutectic with the maintenance of 2.2–2.5 and 3.13–3.30 mass % V in which, possibly, inclusions borides or carbides vanadium having very small sizes (for example, as in Fig. 3, *b*) settle down. Carbide phases of vanadium have the sizes from 5–7 microns (point 3, Fig. 3, *b*). According to phase diagram of system Fe–V–C [7] vanadium is good carbide forming element. Besides it, in a layer presence compound FeV (point 4, Fig. 3, *b*) is found out.

It is possible to allocate light grey oval inclusions (point 3, 4, Fig. 3 and point 2, 6, 7, Fig. 4) and a light strip on border has undressed "layer-metal" which contain up to 0.9–1.15 mass % V; black inclusions (point 5 and 6, Fig. 3), belonging carbide/boride vanadium with the maintenance up to 84–88 mass % V; and also eutectic with 3.01–3.65 mass % V. Borides V_3B_4 and VB are found out in the form of separate inclusions having the size up to 5 microns.
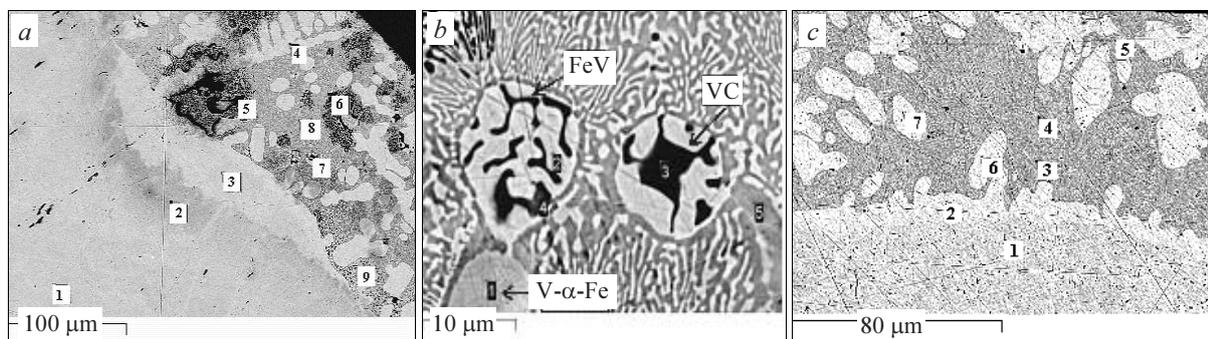

Fig. 3. SEM image of VB_2 layers on surface of steel 45: *a*, *b* – VB_2; *c* – $VB_2+B_2O_3$
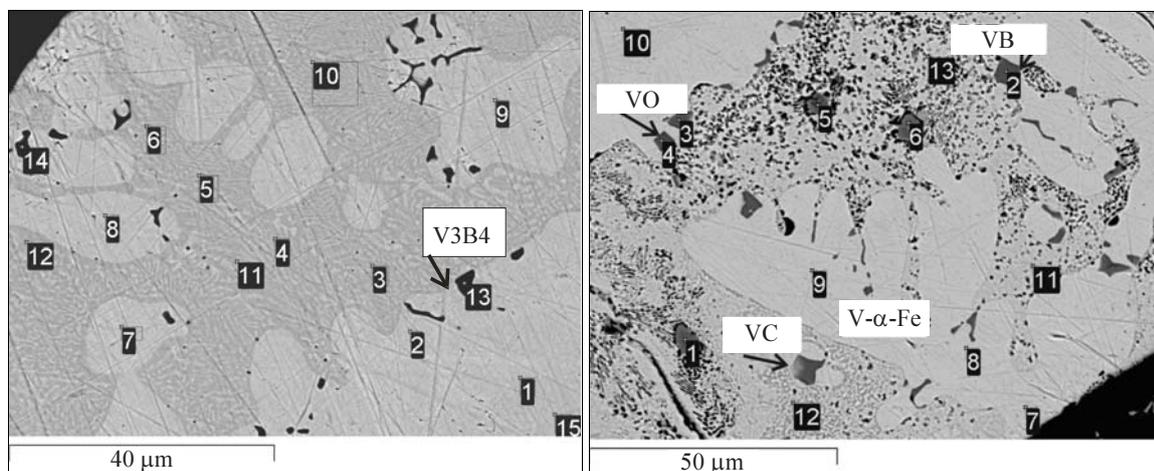

Fig. 4. SEM image of V_3B_4 and VB on steel 45

Measurement of microhardness also has shown its non-uniform distribution on thickness in a cross-section. Separate very rare inclusions have 24000 HV and settle down in layers surface. It is necessary to note, that in layers VB the lowest values of micro-hardness are observed. Layers are characterized by the most complex disorder structure. Possibly, it is possible to try to explain it to that it boride undergoes the most complex phase transformations at the formation.

Thus, as a result of electron beam heat treating in vacuum it was possible to synthesize and form the layers of borides ZrB_2, VB, V_3B_4 VB_2.

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

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