FEATURES FORMATION OF THE BORIDES TRANSITION METALS LAYERS BY AN ELECTRON-BEAM SURFACING OF SHS PRODUCTS IN VACUUM

ОСОБЕННОСТИ ФОРМИРОВАНИЯ СЛОЕВ БОРИДОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ ПРИ ЭЛЕКТРОННО-ЛУЧЕВОЙ НАПЛАВКЕ ПРОДУКТОВ СВС В ВАКУУМЕ

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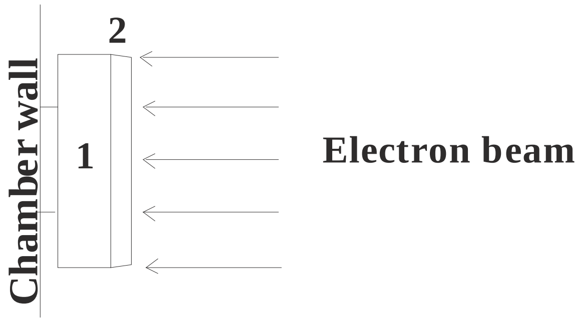
Absract: *The formation features of transition metals borides at high temperatures and low pressures were investigated and discussed the conditions of formation, structure and wear properties of boride layers on the surface, formed in electron beam processing in a vacuum.*
KEYWORDS: Electron beam, borides, alloys, microhardness, X-ray diffraction, structure, the self-propagating high-temperature synthesis (SHS), heating.

1. Introduction.

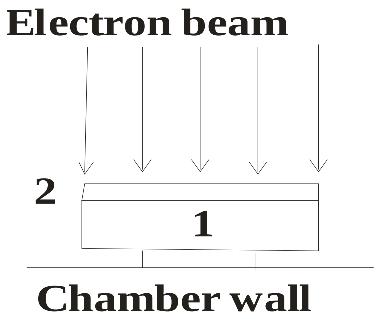
Today in the conditions of ever-evolving technology the requirements to the strength of machine, tool and instrument materials, and especially to their high-temperature strength and heat-resistant, are increasing. Borides of transitive metals have high melting temperature (over 2000^{o}C) and the values of hardness, quite resistant to oxidation, are therefore of particular interest to form a coating on them. Boride layers have high physical and mechanical properties. Microhardness of the layers up to 2000 MPa, and these values can be stored up to ~600÷700^{o}C, that allows to use borating to increase wear resistance of produce operating at high temperatures [1-3].
In the paper, layers were obtained by electron beam borating (EBB) [4]. On pre-prepared samples surface daub thickness of 0,5÷1 mm were applied. The saturating daub consists of boron carbide B_4C and an organic binder. Electronic heating was carried out during 2-5 minutes at a power density of 2÷2,5 W/cm^2. The residual pressure in the vacuum chamber was less than 2×10^{-3} Pa.

2. The experimental part.

On figure 1 schemes of pulse and continuous electron beam processing are presented. Feature of installation with a pulse electron beam of microsecond duration is vertical accommodation of process able samples at horizontal input of an electron beam and heat removal (Figure1.a). In experimental installation of continuous action samples are placed horizontally (Figure 1.b), and the electron beam is entered and warmly removed vertically.
Various accommodations of samples in relation to input character of an electron beam, in our opinion, should lead to different conditions of formation boride coatings. Vertical accommodation of samples not should to lead to precise boundary of a layer-metal. At continuous heat removal the alloy should "flow down" on a surface of the process able metal sample. As a result of pulse electron beam processing it should be formed the indistinct (not sharp) boundary of a layer-metal. Horizontal accommodation of the sample does not influence on formation coating process and boundary character of a layer-metal.



a) pulse



b) continuous action

Figure 1. *Scheme of electron beam processing: 1- metal sample; 2- daub*

Heating of samples carried out an electron beam in three pulse modes with parameters: an accelerating pressure {voltage} - U=12-45 кВ; a beam current - I_r=30-145 A; duration of one impulse - t=50-75 μc; quantity of impulses - N=от 3 up to 2600; frequency of impulses following of a beam current - *f=0.3* Hz; and energy density up to W=1-18 J/cm^2 (Table 1).
Electron heating in a stationary mode was performed using a specially designed electric-power plants, containing a powerful electron gun melting EPA-60-04.2 with a control unit and a high-voltage rectifier Buell V-TPE-2-30k-2U HL4. Vacuum unit is extremely compact in design. The pressure in chamber did not exceed 2×10^{-3} Pa.

Table 1
Parameters of pulse electron beam processing at TiB_2 layers formation

Type	Ir, A	U, V	*f*, Hz	t, μs	N, pulse numbers	W, J/cm^2
1	30	12	0,3	75	1600	1-2
2	40	15	0,3	75	2600	2-3
3	40	15	0,3	75	2600	2-3
	145	25	0,3	50	3	18

Studies carried out on samples of 15 mm diameter and a height of 7 mm, made of carbon steel and St20 U8A. Used saturating or reaction daub. Saturating daub contained boron component (amorphous boron or boron carbide), and an organic binder. The composition of the reaction mixture plasters were stoichiometric oxide TiO_2/ZrO_2, the boron / boron carbide and carbon, and an organic binder. Moreover, use of protective coating on the basis of boron oxide B_2O_3. The starting materials used titanium oxide synthesized with the structure of anatase, oxide ZrO_2 synthesized from zirconil nitrate, amorphous boron "technical" and boron carbide, "h", birch charcoal. The compositions of daubs were boron ingredients and organic binders in the ratio of 1:1 by volume. As the organic binder solution is applied 1:10 glue BPH-6 in acetone.

X-ray diffraction (XRD) was carried out on a diffractometer D-8 Advance company Bruker for Cu K_λ - radiation that comes with the Bank of International Center of powder diffraction patterns ICDD PDF-2 Data Base Card for identification of different phases.
The microhardness was measured on PMT-3 microhardness. The load on the diamond pyramid was 5 and 10 g.
The microstructure of the cross-sections of samples was investigated by microscope METAM PB-21 equipped and software system ImageExpert Pro 3.3 for quantitative metallographic analysis.

3. *Results and discussion*

3.1. Initial metal samples.

The x-ray analysis of samples has shown that in them independently of a mode of electron beam processing there is a surface strengthening which leads to partial formation martensite on a surface, depth up to 50-100 µm.

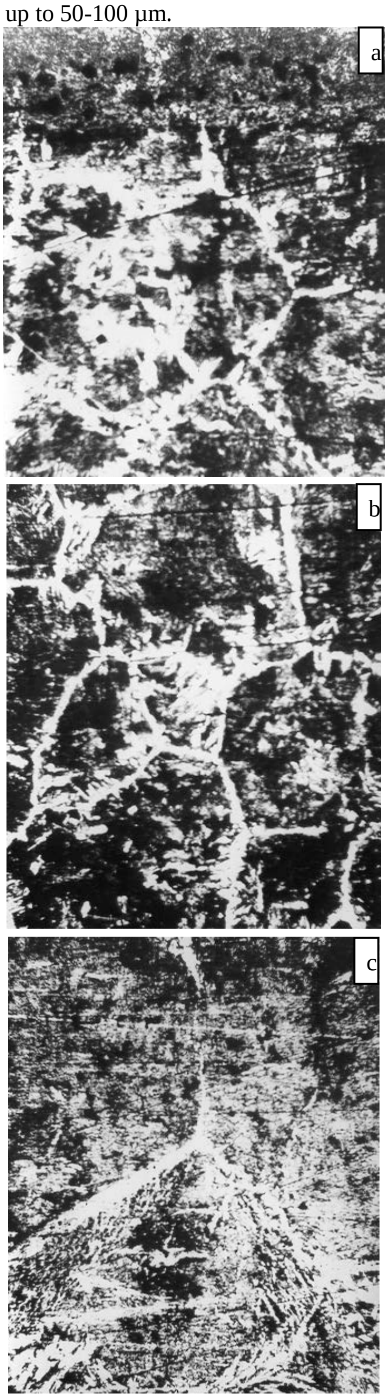


Figure 2. *Microstructure of samples from steel 20 (W=480, ×350): (a) τ=180 c; (b) τ= 90 c; (c) τ=150 c*

On x-ray pattern of all samples there were reflexes of reflections (200) and (002), having intensity from 5 up to 10 %. Parameters of a tetragonal cell depend on a type of electron heating, in particular, from processing duration. Observed change of cell parameters from *a=0.2867* nanometer and *c=0,2924* nm (a degree of tetragonal distortion from *c*/*a*=1,02) to *a*=2,868 nanometer and *c*=2,981 nm (*c*/*a*=1,04) at increase of electron beam processing duration from 90 up to 180 c, for example, at continuous electron beam processing.
On figure 2 microstructures of samples of steel 20 processed by an electron beam with surface alloying are presented. Under the thin melted off layer (5-70 µm) observed poorly etching (in 4 %-th solution HNO_3 in ethyl spirit) a transitive layer (Figure 2.a), which microhardness a little above microhardness of the basic metal: 175±5 and 160±5 *HV*, accordingly.
The temperature of heating samples was not below 1100-1200 °C, which was reflected in processes of a microstructure formation. On figure 2.b and 2.c it is possible to observe perlite and ferrite components, and ferrite has the form of focused Vidmashtett plates originating from compact ferrite allocation. The increase in electron beam processing duration led to increase in the sizes of grains and lengths ferrite plates. Vidmashtett structure is characterized by presence lamellar extra ferrite allocations.
Samples of steel 20 after electron beam processing in vacuum are no equilibrium, in them phase transformations are not finished. It is necessary to notice, that martensite plates could be observed in a cross-section cut of the samples processed by pulse electron beam. Especially it was characteristic for the samples processed in the conditions of third type (Table 1).

3.2 Electron beam alloying products of self-extending high-temperature synthesis.

As a pulse electron beam processing in proceeds at pressure 10^{-3}-10^{-3} Pa the interaction reaction oxide TiO_2/ZrO_2 with boron compound (B_4C/B) and carbon should proceed at lower temperatures, than at pressure P=10^{-2}-10^{-3} Pa, i.e. in the conditions of continuous electron beam processing [5]. In a range of pressure from 10^{-4} to 10^{-5} Pa the temperature of thermal decomposition and dissociation of intermediate boron oxide B_2O_3 which plays an essential role in the chemical transformations proceeding at synthesis MeB_2 boride decreases. Moreover, in the presence of a protective layer B_2O_3 which is specially entered at synthesis and layer MeB_2 formation, thermodynamically formation of boron is possible. The boron as the uncontrollable impurity can participate in formation of boride coating and is present at boride iron Fe_2B or FeB.
Figure 3 shows plots of weight change layer based on ZrB_2, TiB_2 and carbon steels 20 and 45 of the reaction plasters containing oxides of transition metals, boron and amorphous carbon.

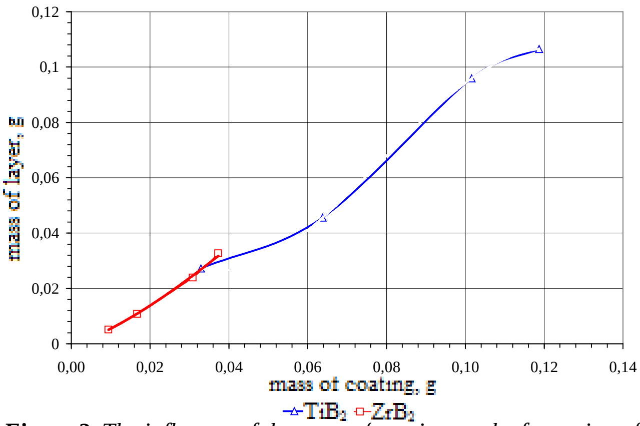


Figure 3. *The influence of the mass of coating on the formation of layers of borides of titanium and zirconium*

We have assumed the electron-beam surfacing nature of the coatings formation of TiB_2 and ZrB_2 borides.
Layers repeat relief's of an initial metal, but by detailed considerations have a complex structure, eutectic type, with

dendrite inclusion and separate parts in the size to 10 μm. Dendrites are most strictly organized near to a surface.

Table 2

Physico-chemical parameters of the electron beam surface in the formation of l transition metals borides layers at U = 20 keV

Parametr	TiO_2	ZrB_2
The thickness of the reaction daub, μm	235	67
The penetration depth of e-beam, h_o μm	3,3	2,83
The layer thickness, μm	300	120
The thickness of boride, h_b, μm	121,4	33,0
Time of SHS process, s	117,5	33,5

In coating formation and its crystallization the big role is played by heat removal. Electron beam processing is characterized by high speeds of a heat-conducting path in the basic volume of a material $\approx 10^4$-10^9 K/s.

Microhardness measurements have shown its non-uniform distribution on a layer thickness. The values of separate structural components in a layer are from 10 to 30 μm. Microhardness has the maximum values near to a surface 2000 -2300 *HV* and a metal basis 100-150 *HV*.

Thus, the presented data testify to a main role of a relative positioning of an electron beam concerning a surface of the processed sample at formation of boride TiB_2 coating. The electron beam, irrespective of a way of its formation (a pulse or continuous mode) is used as a source of heating and initiator of self-extending high-temperature synthesis of TiB_2. The TiB_2 layers have a complex structure of eutectic type with dendrite inclusions which in the conditions of the directed crystallization is focused from the main axis of linear dendrites in a heat removal direction.

4. Conclusions

As a result of penetration of the electron beam with energy of 20 KeV to a depth of 2.8-3.5 μm in reaction mixtures containing MeO_2, B, C, begins the process of self-propagating high-temperature synthesis of refractory boride. SHS process takes place at high speeds (microns/c), accompanied by a luminous efficacy of the reaction front, in which the reaction products formed. Since the heat of formation reaction boride enough to reflow SHS products, the powder mixture is obtained, which can either be used directly, or in the future it is heated to obtain coating. During deposition SHS products observed partial melting surface within a narrow zone (5-7 μm) with a small amount of melt (5-10 mm^3) at which crystallization occurs forming boride layers. Crystallization melted zone begins immediately after the termination of an electron beam exposure takes place in a small volume of the melt and leads to the formation dendrite-like structure.

Dendrites of boride layers are the initial inclusion ferrite metal matrix.

5. Acknowledgments

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6. Literature

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