Structure and Properties of Boride Layers Produced by Electron Beam in Vacuum

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Abstract – Conditions of formation, structure and properties of boride layers on carbonaceous steel 45 at electron beam borating are investigated. New process to make borides layers (Fe_2B, FeB, CrB_2, W_2B_5) using electron beam are reported. The microstructure and microhardness of boride layers are investigated and are compared to layer properties obtained at solid phase borating. Formed layers were heterogeneous structure combining solid and weak components and resulting in to fragility reduction of boride layer.

1. Introduction

Durability and reliability of machines details and mechanisms in many respects are defined by properties of surface layer, such as the staining and wear, and formation of endurance cracks begins with a surface. Recently in a surface engineering the technologies of surfacing by the concentrated streams of energy created by laser radiation, high-temperature plasma, electron and ion beams will utilize ever more. This treatment enables capability purposeful to change a surface layer condition of machine details and tool etc., as a consequence to refine them.

We presented results of boride layers formation on carbon steels under a powerful electron beam. The microstructure and microhardness and phase composition of boride layers on steel 45 are investigated.

2. Experimental methods

The electron beam boriding. Boride layers were received by different methods, namely, with use sating daub from an amorphous boron or boron carbide B_4C or from reactive daub containing an oxides (Fe_2O_3, Cr_2O_3, WO_3), boron carbide and carbon C (birch charcoal) [1]. The daub was piled up a previously preformed surface of samples with thickness of 0.5–1 mm. Borating components and the organic binding (the solution 1:10 glue BF-6 in acetone) was entered into the daub composition.

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

The solid phase borating was carried out at temperature 950 °C and duration 4 h in a powder mixture containing 97% B_4C and 3% KBF_4 in the container with fusible mechanism [3].

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

3.1. Boride Fe_2B, FeB layers

Figure 1 shows the microstructure of boride layers. It is established, that at electron beam boriding on a metal surface brightly expressed layers of the thickness about 350–360 microns (the daub from amorphous boron) and depths up 100–110 micron (the daub from B_4C) will be formed. In both cases, the precise border between the layer and metal basic is founded. In comparison with the metal basic, the layers have lower speed of the etching that testifies to them of considerably high corrosion stability.

The structures of surface layers after solid phase borating and electron beam boriding are distinct. The layer after solid phase borating showed a needle-like structure and the transition zone settles down under it's (Fig. 1, *a*). The transition zone after electron beam boriding was not observed and the legible boundary between a layer and base metal was observable (Fig. 1, *b* and *c*). The layer consists of rounded crystals, which are settling down on a surface and a eutectic.

The X-ray diffraction analysis is established that layers contain the iron borides Fe_2B and FeB. The relative maintenance of these borides has veiled from composition of daub. In case of amorphous boron, it is boride FeB, and carbide boron it is boride Fe_2B. Besides, on x-ray diffraction patterns there are the lines of different intensity belonging to the cementite Fe_3C and ferrite α-Fe. The boride layer formed from daub B_4C (Fig. 1, *c*) consists from round off engagements, which locating on the layer surfaces and eutectic. The microhardness values 820–840 and 510–530 HV for the layer surfaces and eutectic were obtained.

Fig. 1. Layers boride microstructure formed on steel 45 surface: solid phase borating (*a*) and electron beam boriding – daub from amorphous boron (*b*) and B_4C (*c*) (*a* – × 250; *b*, *c* – × 500)

The rounds off engagements are primary crystals of borides that answers entropic criterion of stability of the crystals limited form at the crystallization in conditions, approached to equilibrium. In turn, the boride round form determine the form of eutectic crystals.

The boride layer formed from daub with amorphous boron has other structure (Fig. 1, *b*). It consists of particles of the various forms: rhombic, prismatic, dendritically. On layer surface the continuous light film with needles, directed deep into of a sample is placed. Microhardness of film makes up 1200–1250 HV. Inside this film the rare (1–2) large inclusions with microhardness 1750–1820 HV is meet. Under the film, there are the primary crystals and eutectic with microhardness 840–880 and 500–540 HV, accordingly.

According to [4], the boride iron Fe_2B has tetragonal crystal lattice (Space group I4/mcm with parameters of an elementary cell $a = 0.51087$, $c = 0.42497$ nm). At layer formation from daub with amorphous boron, the iron boride crystals have been inherited the form of an elementary cell. Therefore, the primary crystals of borides have the form of rhombuses, parallelograms etc., caused by different corner inclination of the crystal lattice (prism) to plane of polished specimen. It is necessary to note, that the similar forms of borides crystals are observed and at laser boriding [5].

According to data X-ray diffraction analysis, the layer after solid phase borating consists from iron boride FeB and boron cementite $Fe_3(C, B)$. The microstructure of boride layers is showed on Fig. 1, *a*. In mild steels the boride layer has a needle structure, at which the needles of borides growing together in the basis, will form a continuous layer. The plume allocations of carboborides phase are joined directly to the boride needles. Microhardness of borides needles makes up 1300–1350 HV, plume allocations – 300–330 HV. Thickness of borides layers are 70–90 microns.

We have made attempt of Fe_2B, FeB, CrB_2, and W_2B_5 layers formation during their synthesis from mixtures with participation $Fe_2O_3/Cr_2O_3/WO_3$, B_4C, and C on a surface of steel 45. For this purpose a mixture of $4Fe_2O_3$:B_4C:11C (Fe_2B), $2Fe_2O_3$:B_4C:5C (FeB), Cr_2O_3:B_4C:2C (CrB_2), and $8WO_3$:$5B_4C$:19C (W_2B_5) took and carefully frayed in an agate mortar, mixed with organic binding. Electron beam treatment was carried out in vacuum not above $2 \cdot 10^{-3}$ Pa at capacity of electron beam 250–450 W during 1–3 min.

Electron beam boriding from sating daub, possibly, occurs on diffusion mechanism. Application of an electron beam promotes increase in diffusion of boron in volume of metal, interaction and formation iron borides (Fig. 2).

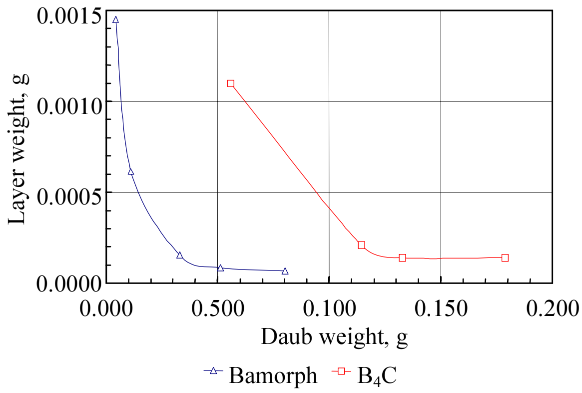


Fig. 2. Influence of daub weight on boride layer weight (270 W, treatment 5 min)

At use reactionary daub on the basis of transitive metals oxides, it is possible to observe the facing mechanism of boride layers formation (Fig. 3).

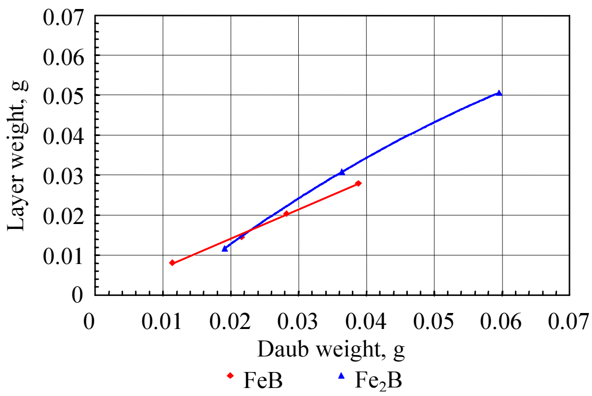


Fig. 3. Influence of daub weight on boride layer weight (300 W, treatment 5 min)

The layers thickness made 200–280 microns (Fe_2B), 50–80 microns (FeB) and 600 microns (CrB_2). The microstructure of a Fe_2B layer is presented on Fig. 4, *a*. The structure is complex, includes primary crystals of boride, dendrite inclusions, and eutectic. In Fig. 4, *b* the microstructure of a FeB layers is resulted. According X-ray analysis, the dendrite inclusions are the B-doped ferrite (boron solid solution into α-Fe).

During formation of a layer by electron beam boriding the evaporation of boron oxides is observed. Therefore, to prevention of a deviation of a reactionary mixture from the stoichiometrical composition we applied a blanket of amorphous powder of boron oxide.

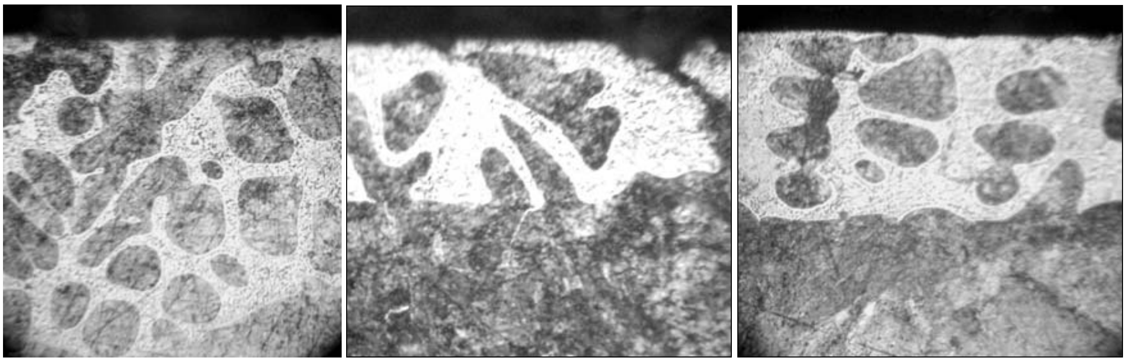
Application of a blanket by amorphous powder of the boron oxide promoted reception of the equilibrium borides coating. In all layers we observed eutectic having microhardness 650–700 HV. The round and extended inclusions had the ordered arrangement in a layer, their microhardness was 1080 and 1150 HV (FeB layers), and 1250, 1150 HV (FeB + B_2O_3 layers), accordingly. The round inclusions were only in Fe_2B layers (1200 HV) and Fe_2B + B_2O_3 (1150 HV).

According to X-ray analysis, the layers are mainly consisted from borides Fe_2B or FeB.

3.2. Boride CrB_2 layers

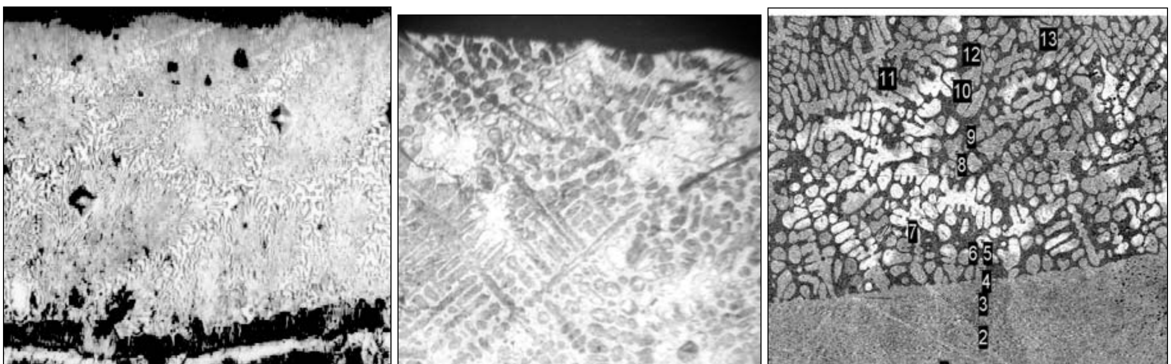
The structure of boride layers CrB_2 (Fig. 5) is the most interesting. Layers are homogeneous, without greater areas of inclusions as for a case with or without protection of boron oxide B_2O_3. There are small oval grey inclusions of dendrite type which settle down in the certain order and the maintenance of chrome in them does not exceed 0.19% Cr (Fig. 5, *a*). Besides, it is possible to observe eutectic, and separate black impregnations at which there are atoms Cr and C (B).

Research of a microstructure and a chemical composition characterization of layer CrB_2 with protection from boron oxide B_2O_3 have revealed its complex structure (Fig. 5, *c*). Features of a structure of layer CrB_2 + B_2O_3 are shown in the ordered arrangement of light, light grey oval inclusions in dark grey eutectic field of a layer. Inclusions are non-uniform on all volume and contain different quantities of chrome. A metal basis (Fig. 5, points 1, 2, 3) and boride layer are separated from each other by a transitive thin zone in which there are atoms Fe and Cr (point 4). In light (points 7, 10) and light grey inclusions (points 5, 8, 11, 13) presence 2.3–2.7 mass % Cr. In light inclusions, presence of atoms Mn is not fixed.



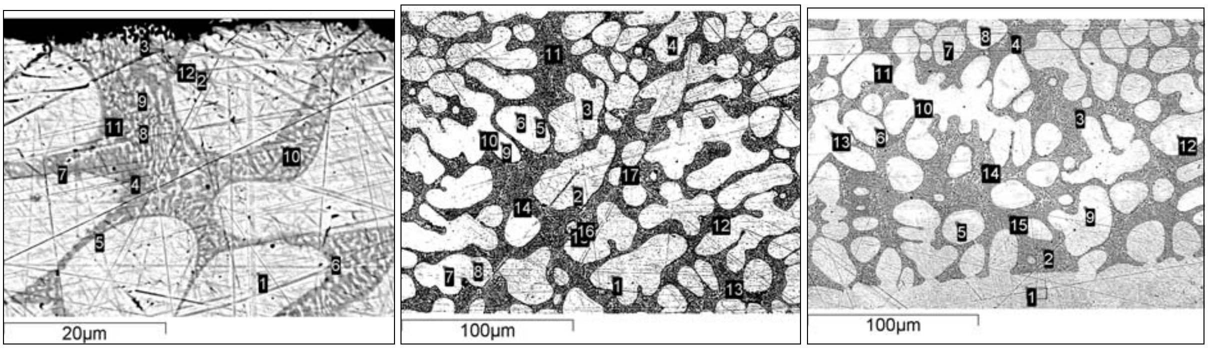
a *b* *c*

Fig. 4. Microstructure of boride layers Fe_2B (*a*), FeB (*b*) and FeB + B_2O_3 (*c*): × – 400



a *b* *c*

Fig. 5. Microstructure of layers CrB_2 (×250) (*a*), CrB_2 + B_2O_3 (×300) (*b*)



a *b* *c*

Fig. 6. Structure of layers $CrB_2 + B_2O_3$

In Fig. 6, layer structure on thickness is presented. Special interest represents dark grey eutectic in which atoms B are found out, and interface area (Fig. 6, *a*).

In interface layer zone an inclusions contain different quantities of chrome atoms from 3.05–3.35, up to 4.35–4.60 and 5.35–5.45 mass %. Besides, it is possible to observe separate black impregnations at which there are atoms Cr and C (B). Boride CrB_2 there is in reflowing areas of a layer, as him density below, than a density of liquid Fe–Cr–C/B.

Measurement of microhardness also confirms non-uniform distribution on structural components and a role of a metal sample reflowing zone the in formation of layers.

Phase composition of boride chrome layers to define difficultly. Presence of following phases is identified: chrome ferrite $Cr_{0.03}Fe_{0.97}$ (PDF 03-065-4607, Sp. gr. *Im3m*, with the cubic cell $a = 0.286920$ nm), CrFeB (PDF 00-051-1410, Sp. gr. *Fddd*, with a rhombic cell $a = 1.45349$, $b = 0.7303$, $c = 0.42149$ nm).

3.3. Boride W_2B_5 layers

Formation of layers is carried out with the daubs on the basis boride W_2B_5 or reactionary daubs containing oxide WO_3, boron carbide B_4C and carbon.

In all products of electron beam heat treating of daub (on a metal surface and in powder rests) borides according to their phase diagrams is formed.

X-ray patterns are the lines of different intensity belonging ferrite (α-Fe), cementite (Fe_3C). Using of boride tungsten W_2B_5 in daub composition allows receiving superficial layers (Fig. 7).

The layer also contains and boride W_2FeB_2.

In Figure 8 the layers microstructure received with reactivity daub without reflowing is presented. Thickness of layer W_2B_5 is 15–20 microns.

Parameters of elementary cells are certain for W_2B_5: $a = 2.975(7)$ $c = 13.87(2)$ (sp. gr. $6P_3/mmc$).

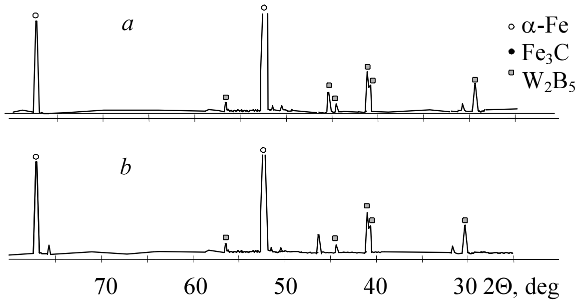


Fig. 7. X-ray pattern of boride layers on steel St45: *a* – W_2B_5; *b* – WO_3:B_4C:C

Fig. 8. Microstructure of layers W_2B_5, ×500

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