

Boriding of carbon steels by the electron beam treatment in vacuum

D E Dasheev, N N Smirnyagina, V M Khaltanova and A P Semenov
Institute of Physical Materials Science SB RAS, 670047, Ulan-Ude, Russia

E-mail: fokter@mail.ru

Abstract: Conditions of formation, structure and properties of boride iron layers on carbonaceous steels 3 and 45 at electron beam borating are investigated. New process to make layers of iron borides (Fe_2B , FeB) using electron beam is 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 to fragility reduction of boride layer.

Keywords: electron beam, borides, micro hardness, structure, phases composition

1. Introduction

Surface modification of metals and alloys can increase the service life and reliability of the various machine parts and tools. Recently, along with the traditional in modern engineering methods for producing coatings that increase the hardness and wear parts, such as carburizing, nitriding, carbonitriding, borating, chromium etc., are increasingly using beam technologies, such as the processing of the laser beam and electron beam. The use of electronic heating with high ($>10^9 \text{ W/cm}^2$) power density in a vacuum has the advantage due to the rapid inertia less achieve extremely high temperatures and ease of heating controls in a wide temperature range.

In this paper, the conditions for the formation, structure and properties of the layers based on iron borides on carbon steels 3 and 45 under the influence of the electron beam in a vacuum were investigated.

2. Experiment methods

The solid phase borating was carried out in a powder mixture in a container with a fusible mechanism on a following mode: powder composition – 97 wt. % B_4C and 3 wt. % KBF_4 , temperature – 950°C , duration – 4 hours [1].

As a result on a surface it was formed a boride layer by thickness 70-100 μ . The subsequent electron beam processing carried out at following modes: an electron beam current 10 mA, an accelerating voltage 22 kV, time of treatment 10, 15 and 50 s.

Electron beam boriding. Samples were prepared by daub drawing on a previously prepared surface of steel. The daub composition was consisted of 1:1 the boriding compounds (boron carbide B_4C or amorphous boron) and the organic binding. The solution 1:10 glue BF-6 in acetone has been used in quality the binding. After drawing daubs by thickness 1 mm samples dried before complete removal acetone [2].



Self-propagating high-temperature synthesis (SHS) of boride layers. Layers Fe_2B and FeB were synthesized from reaction daub containing mixtures of boron carbide B_4C , oxide Fe_2O_3 , carbon C (birch charcoal) and the organic binding. The electron beam treatment has been carried out in an electro-vacuum installation with a powerful industrial axial electron gun [3]. The pressure in chamber did not exceed 2×10^{-3} Pa.

The boride layers were analyzed by X-ray diffraction. An X-ray powder diffractometer Advance D8 Bruker using $\text{Cu K}\alpha$ - radiation was employed for phase analysis and the determination of lattice parameters. Microhardness of prepared layers was measured by using PMT-3 hardness tester at a loading 0.5 and 1 H. Microstructure of the layers formed was determined by metallographic microscope "Neophot-21" or "Metam-21RB".

3. Results and Discussion

Figure 1 shows the microstructure of boride layers. 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 (Figure 1.a). Microhardness of boride needles come up to 1300-1350 MPa, cirrus selections is 300-330 MPa. Thickness – 70-90 μ .

Boride layers after electron beam boriding. It is established, that at electron beam boriding on a metal surface brightly expressed layers of the thickness about 350-360 μ (the daub from amorphous boron) and depths up 100-110 μ (the daub from B_4C) will be formed. In both cases, the fixed boundary 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 transition zone after electron beam boriding was not observed and the legible boundary between a layer and base metal was observable (Figure 1. b, 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 depended from daub composition. In case of an amorphous boron forest it FeB , and B_4C – Fe_2B . Besides, on X-ray diffraction patterns there are the lines of different intensity belonging to the cementite Fe_3C and ferrite $\alpha\text{-Fe}$.



Figure 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 - $\times 250$, b, c - $\times 500$

The boride layer formed from daub B_4C (figure 1.c) consists from round off engagements, which locating on the layer surfaces and eutectic. The microhardness values 820-840 and 510-530 MPa for the layer surfaces and eutectic were obtained. 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 close to equilibrium. According to this criterion, if the value of the entropy of fusion (ΔS) is less than 2 kcal/mol \times K to the crystals are rounded [4]. Obtained in work [5], the values of the entropy of melting for iron boride Fe_2B is $\Delta S=1.5$ kcal/mol \times K. In turn, the rounded forms borides determine the shape of the eutectic crystals.

The boride layer formed from daub with amorphous boron has other structure (figure 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 MPa. Inside this film the rare (1-2) large inclusions with microhardness 1750-1820 MPa is meet. Under the film there are the primary crystals and eutectic with microhardness 840-880 MPa and 500-540 MPa, respectively.

According to [6], 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 [7].

Method of electron beam boriding [2], its mechanism is likely to be a modification of the method of solid-phase saturating boriding daub for thermochemical treatment. Its novelty is the impact of the electron beam on the boron containing daub in vacuum. The use of a highly concentrated source of energy allows you to quickly transfer the energy of the electron beam in its collision with the surface of the treated metal or alloy, heat the contact area to a very high temperature. This increases the diffusion of boron from saturating daub on the surface and its penetration into the bulk metal, the interaction and the formation of iron borides (figure 2). Boride layer thickness depends on the composition of boriding component. 300-360 μ thick layers obtained with boron, and thickness of 100-150 μ – boron carbide. Application of an electronic beam promotes increase in diffusion of boron in volume of metal, interaction and formation iron borides.

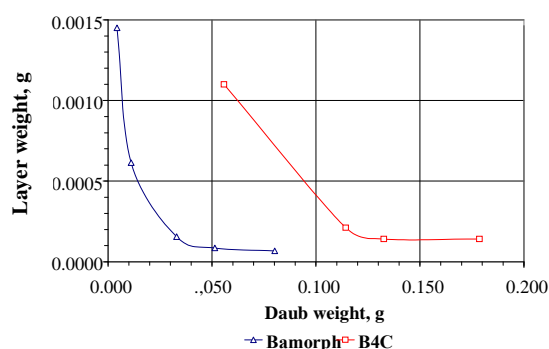


Figure 2. Dependence of mass boride layer on the number of layers boriding component (steel St3, W = 270 W, exposure time 5 min)

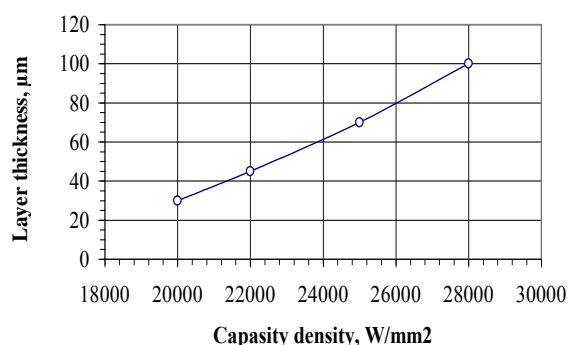


Figure 3. The influence of electron beam power to the thickness of boride layer (steel St3, coating based B amorphous, exposure time 1 min)

Figure 2 shows the dependence of the mass-forming layer of the total weight of the saturating coating. The total number of adhesive layers is ranged from 1 to 5 (amorphous boron) and 1 – 4 (B_4C). As follows from figure 2, for the formation of boride layer with the highest weight (thickness) is enough to put one boriding adhesive component, as in the case of boron, and the application of boron carbide. Initial samples steel 45 were pre-normalized at 930°C for 7 min, cooled in air.

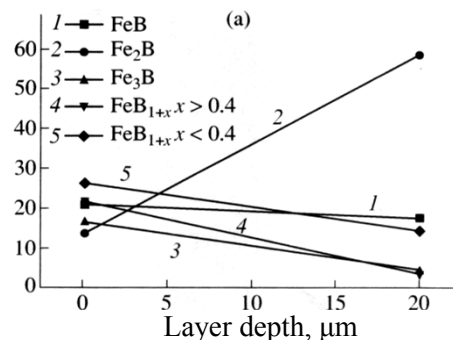
Boride layer thickness depends on the power of the electron beam (figure 3). This relationship has the big practical importance, as allows control technological indicators (specific capacity and an electron beam current and accelerating voltage) depending on size of a preferred thickness of a boride layer.

Boride layers structure after the subsequent electron beam treatment. The boride layers microstructure is resulted on figure 1. Besides, in this figure the boride layers structure after the further electron beam processing is presented. It is known [1] that boride layers on low carbon steels have a

needle structure at which borides, growing together in the bases, form a continuous layer. Directly borides needles adjoin allocation plumose carbo-boride phases. Microhardness of boride needles makes 1300-1350 MPa, plumose allocation 300-330 MPa. A layer thickness was 70-90 μ .

The mechanism of proceeding structural changes is studied by a method selective on depth Mossbauer spectroscopy [8].

Quantity of phases



Quantity of phases

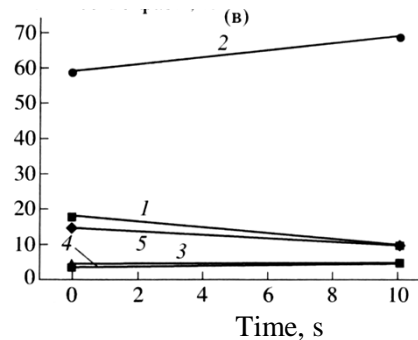


Figure 4. Change of phase composition of boride layer on depth: a)- the initial sample; b)- after electron beam processing (20 μ)

Microhardness measurement have shown, that on a surface of the sample it makes 2000 - 2050 MPa, and on depth 20-30 μ make 1600-1650 MPa, that will be corresponding with literary data of microhardness of iron borides FeB and Fe₂B.

For presentation the phase analysis of boride sample, received from Mossbauer spectra, is resulted on figure 4. Apparently from this figure, the surface layer of the sample on 70 % consists from enriched by boron of borides phases, while on depth 20 μ dominating (60 %) a crystal phase are Fe₂B. The quantity of phases rich with boron essentially decreases with depth. It is established, that after 19 seconds of electron beam processing the sharpest changes of phase composition occur in thin surface layer: very sharply increases (by 50 %) relative quantity of phase Fe₂B. With depth increase of surface layer to 20 μ of change in phase composition after an irradiation keep the same tendency, but changes become weaker: the maintenance of phase Fe₂B increases by 10 % and maintenance FeB decreases for 8 %. At comparison with metallographic analysis of these samples, it is visible, that this process speaks increase in density of needle layer Fe₂B and, thereby, reduction of the zone filled with phases rich with boron.

Because of a warming up surface boride layers under the influence of an electron beam (~ 1323-1373 K) dot defects begin diffused to borders of grains, forming a new defective zone that leads to essential increase in speed of diffusion of boron atoms in depth of the sample on cracks and between grains boundary owing to a gradient of temperatures. Besides, in parallel to it there is a sputtering of boron atoms from a layer under the influence of an electron beam [9].

Sputtering process, in our opinion, also leads to sharp reduction of quantity of the most sated disorder phase FeB_{1+x} located on a boron surface pine with concentration of boron 0.4. Thus in adjoining surface layer occur segregation and hashing of atoms. Because of all these processes, there is an impoverishment of boron phases in surface areas. Occurring destruction of disorder phases and boron diffusion in depth of the sample leads recrystallization of phases in favor of steadier at existing in surface layer to temperature ~ 1373 K phase Fe₂B. And speed of these transformations in thin surface layer depth ~ 0.3 μ above, than in thicker layer depth to 20 μ that is caused by a temperatures gradient and the limited layer process of sputtering of boron.

Electron beam fusing of SHS products. In this paper, we attempt to form the layers based on borides Fe₂B and FeB in the synthesis of their stoichiometric mixtures with Fe₂O₃, B and C on the surface of steel 45. To do this, take a mixture of the initial components in a ratio of Fe₂O₃: 3B: 3C

(Fe₂B) and Fe₂O₃: 2B: 3C (FeB), thoroughly ground in an agate mortar, mixed with an organic binder and the reaction surface of the sample steel 45. Electron beam processing was carried out in a vacuum at most 2×10^{-3} Pa at power electron beam $W = 250-450$ W for 1-3 min.



Figure 5. Microstructure of boride layer Fe₂B (a), FeB (b) on the surface of St45: $\times 400$.

According to the X-ray phase analysis, boride layer is mainly composed of boride Fe₂B. Layer of the sample with a stoichiometric mixture of Fe₂O₃: 2B: 3C incorporates boride FeB.

The thickness of boride layers was 200-280 μ (Fe₂B) and 50-80 μ (FeB). Microstructure layer based Fe₂B presented at figure 5.a.

The structure of the complex includes primary boride crystals, including dendrites and eutectic. In figure 5.b shows the microstructure layer based boride FeB.

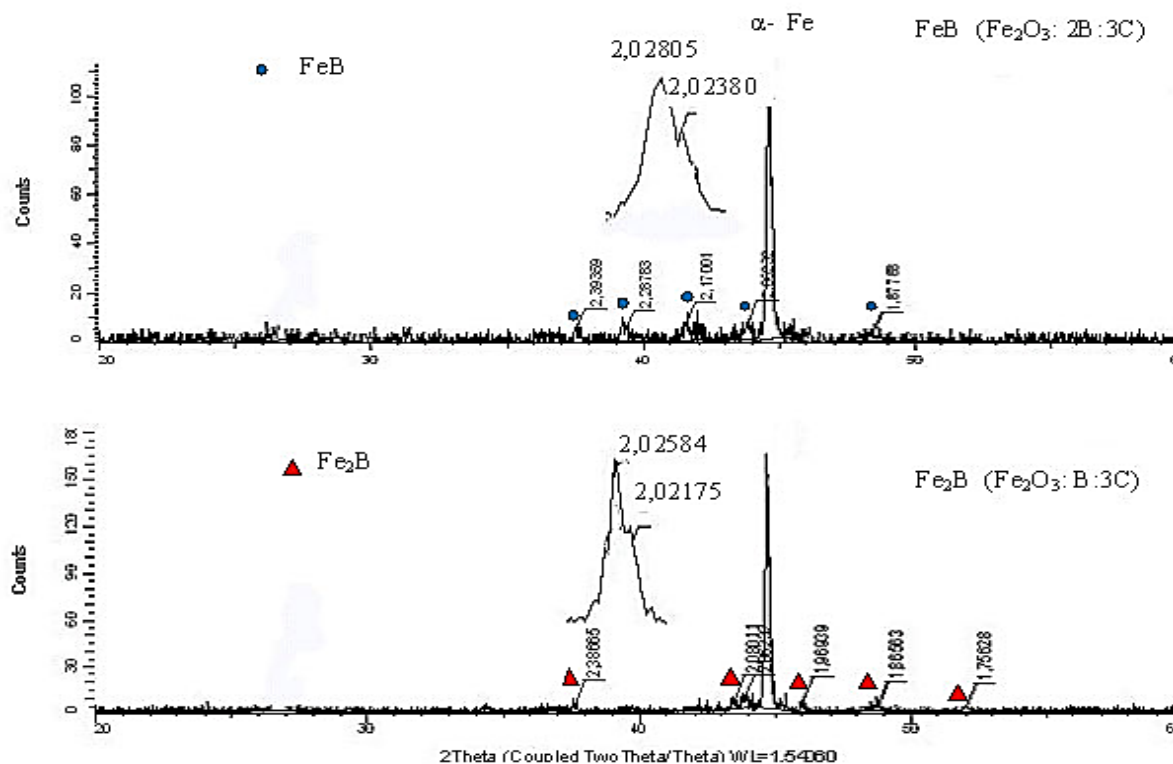


Figure 6. X-ray phase analysis of produced boride layers.

Figure 6 shows the X-ray phase analysis of produced boride layers. Dendrites are ferritic inclusions with parameters cells, $a = 0.2821$ nm). In the original steel 45 ferrite has a cubic volume-centered cell with $a = 0.2869$ nm. The use of high-resolution diffractometer D8 enabled to detect the x-ray lines

reflexes plane (110) ferrite owned metal base. Also, found reflection from 20 % intensity, which, in our opinion, is the ferrite, which is formed during crystallization narrow melted near-surface zone.

Application of the protective layer of amorphous boron oxide contributes towards equilibrium boride layer (figure 7). Rounded and elongated inclusions were ordered arrangement in the layer in the layers of their microhardness were $\text{Fe}_2\text{B} + \text{B}_2\text{O}_3$ (1650 and 1850 MPa), $\text{FeB} + \text{B}_2\text{O}_3$ (1800 and 2350 MPa), respectively.

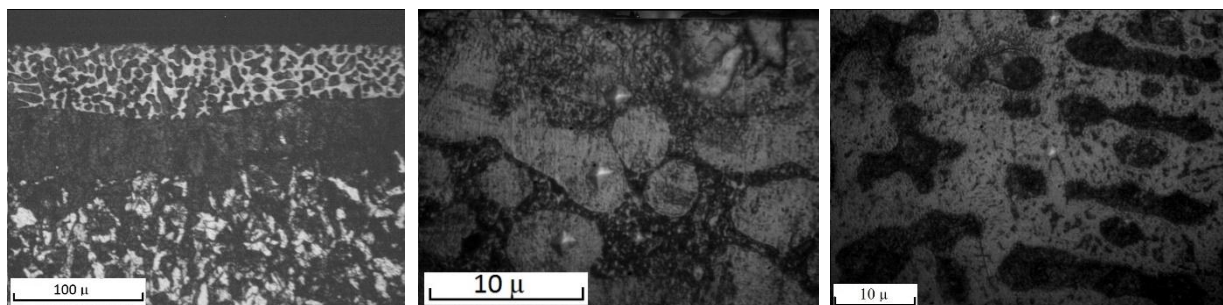


Figure 7. Layer structure $\text{Fe}_2\text{B} + \text{B}_2\text{O}_3$ at St45

For FeB: by reflex [110] cubic unit cell parameters: α -Fe (metal matrix) $a=0.2868$ nm, α -Fe (dendritic crystal), $a=0.2821$ nm. For Fe_2B : by reflex [110] cubic unit cell parameters: α -Fe (metal matrix) $a=0.2865$ nm, α -Fe (dendritic crystal), $a=0.2859$ nm.

4. Conclusions

Conditions of formation, structure and properties of boride iron layers on carbonaceous steels 3 and 45 at electron beam borating are investigated.

New process to make layers of iron borides (Fe_2B , FeB) using electron beam are reported. Carrying out boriding with participation of intensive electron beam has essentially changed layer structure, morphology of allocated phases, character and distribution formed in a pressure face zone of compounds. There was a basic possibility of a composite boride layer formation with heterogeneous disperse, instead of column (needle or tooth similar) morphology of boride crystals arrangement. Designing of the various composite layers combining another way "firm" and "soft" phases can give the chance to receive on a steels surface the boride layers possessing various plasticity.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research, projects no. 14-14-08-31412_mol_a and 15-48-04217r_sibir_a.

References

- [1] Directory ed. Liakhovich L S 1981 *Chemical and heat treatment of metals and alloys* (Moscow: Metallurgy)
- [2] Semenov A P, Sizov I G, Smirnyagina N N etc. *Patent RU 2186872*, 2002. BI number 22.
- [3] Semenov A P, Smirnyagina N N, Sizov I G 2001 *Metal technology* **4** 32-34
- [4] Taran, V I 1978 *The structure of eutectic alloys* (Moscow: Metallurgy) p. 312
- [5] Tavadze F N, Goribashvili V I, Nakaidze S H 1983 *Metallurgy and heat treatment of metals* **1** 2-3
- [6] Kubaschewski O 1985 *Diagrams of binary systems based on iron* (Moscow: Metallurgy) p. 25-28
- [7] Safonov A N 1998 *Metallurgy and heat treatment of metals* **1** 5-9

- [8] Novakova A A, Kuzmin R N 1989 *Mössbauer conversion spectroscopy and their using* (Moscow: Lomonosov Moscow State University) p. 72
- [9] Berish R 1986 *Sputtering of solid body by ion bombardment* (Moscow: Mir) p.448