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# Modeling of the electron-beam boriding in the system Fe-B-C-$O_2$

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**Abstract**. This paper reviews the conditions of iron borides formation and simulation of surface layers saturation depending on the stoichiometry of original components. Temperature fields have been investigated as well, which form certain phases in accordance with the pressure in the chamber and the power of the electron beam. A thermodynamic study of phase equilibria in Fe-B-C-O systems has been performed. This was done in order to optimize conditions for forming functional layers on the surface of iron-carbon alloys as a result of electron beam boriding in vacuum. Furthermore, strength characteristics of iron boride layers have been determined. Then these layers obtained by different methods and using various source components have been thoroughly compared with each other during the analysis.

## 1. Introduction

There are many methods and techniques that exist for improving the qualitative properties of surface layers, such as strength, wear resistance, hardness, ductility, corrosion resistance etc. Modification of metals' and alloys' surface allows increasing the service life and reliability of various parts of machines and tools. Along with traditional and modern machine building methods of obtaining protective coatings, which increase the hardiness and wear resistance of tools, such as carbonization, nitriding, carbonitriding, boriding, chroming etc., the beam technology, for example laser and electron beam processing, increasingly prevails in recent years [1]. Thus, obtaining products with optimized functional properties and structure for specified conditions is some kind of challenge for our present-day industries. Therefore, such method as treatment with concentrated energy flux which generates locally and globally heterogeneous body structure can be referred to one of the most promising ways in this field. Using the electron beam as a heat source can significantly enhance the ability of surface modification of metals and alloys [2].

This article describes thermodynamic study of Fe-B-C-O phase equilibrium in a high vacuum. Thermal processes at electron beam treatment of different power have been analyzed and simulated. The article also deals with the gradual construction of mathematical model of thermal fields arising due to sample exposure by the electron beam.

## 2. Experimental part

### *2.1. Modeling phase equilibrium and revealing of fields of crystallization borides and carbides in systems Fe-B-C-$O_2$*

In the present study used interface of a program complex TERRA [3]. Calculations were carried out in the range from 300 to 2073 K at a variation of the general pressure in system in a range from $10^5$ to $10^-$

[3] Pa. In calculations considered following phases: oxides FeO, $Fe_2O_3$, $Fe_3O_4$, $B_2O_3$; carbides $B_4C$, $Fe_3C$; borides FeB, $Fe_2B$.

### *2.2. Experimental technique*

During the experiment we used the electron beam installation of special design which is equipped with a powerful electron beam projector (gun) on thermal cathodes [4]. During this experiment we used metal samples (St 3, 45) in the form of cylinders of 15 mm diameter and 7 mm in height. The surface of a sample was coated by various stoichiometric compositions such as $Fe_2O_3$:3B:3C, $Fe_2O_3$:2B:3C. Then this coated surface was exposed to highly concentrated steams of energy (20 keV) which initiated the SHS process accompanied by the high heat release. Electron beam treatment was carried out in vacuum not higher than $2\times10^{-3}$ Pa with electron beam power of 250-450 W for 1-3 minutes. Finally, we obtain solid combustion products, particularly iron borides.

X-ray phase analysis was carried out on the Phaser 2D Bruker (Cu $K\alpha_1$ – radiation). The microstructure of layers was investigated by METAM PB-22 microscope with the program NEXSYS Image Expert. The Vikers (HV) microhardness measurements are made by pressing a diamond indenter, of a specified shape, into the surface with a known force.

## 3. Results and their discussion

### *3.1. The analysis of thermal fields and phase equilibria*

The thermodynamics of phase equilibria in Fe-B-C-O systems has been studied in order to optimize conditions for forming functional layers on the surface of titanium and iron-carbon alloys as a result of electron-beam boriding in vacuum.

Thermal properties and the character of $Fe_2B$ and FeB boride dissociation have been simulated depending on the total pressure in the system. Thus, the temperature and pressure influence on its behavior was determined. For example, an interaction of $Fe_2O_3$ with various boronizing components ($B_2O_3$, $B_4C$, B) at pressure of $10^5$ Pa begins at temperature of 1300-1600 K, as well as at pressure of $10^{-2}$-$10^{-3}$ Pa the temperature falls down to 850-900 K. It is found that in mixtures with $B_4C$ and B the phase transformation should originally occur in condensed state with $B_2O_3$ liquid phase formation. The layers have a clear boundary between the base and the layer itself. The thickness of layers is 200-350 μm and microhardness comes to 3500 MPa.

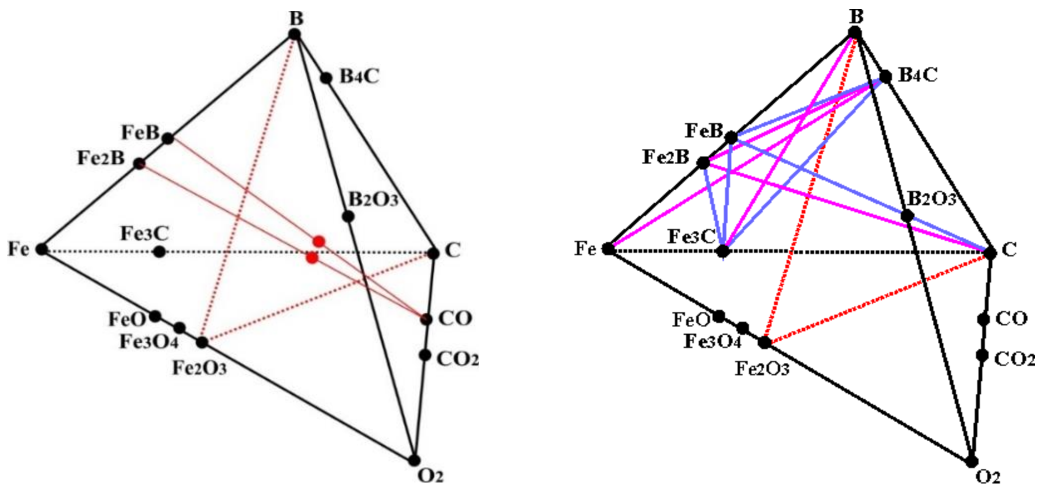


**Figure 1.** Concentration tetrahedron system Fe-B-C-$O_2$: a - general view, b - view of the Fe-B-C plane.

Fig. 1a shows the concentrated tetrahedron of $Fe$-$B$-$C$-$O_2$ system and Fig. 1b displays all possible cuts in Fe-B-C ternary system. This ternary system was the subject of a detailed study because the electron beam boriding uses amorphous boron B and boron carbide $B_4C$ as boronizing components. The phase equilibria in Fe-B-C have been studied. The crystallization fields of all possible phases have been defined, as well as temperature and pressure influence on its behavior has been determined. (fig. 2). It shows that Fe-$B_4C$ cut is not quasi-binary.

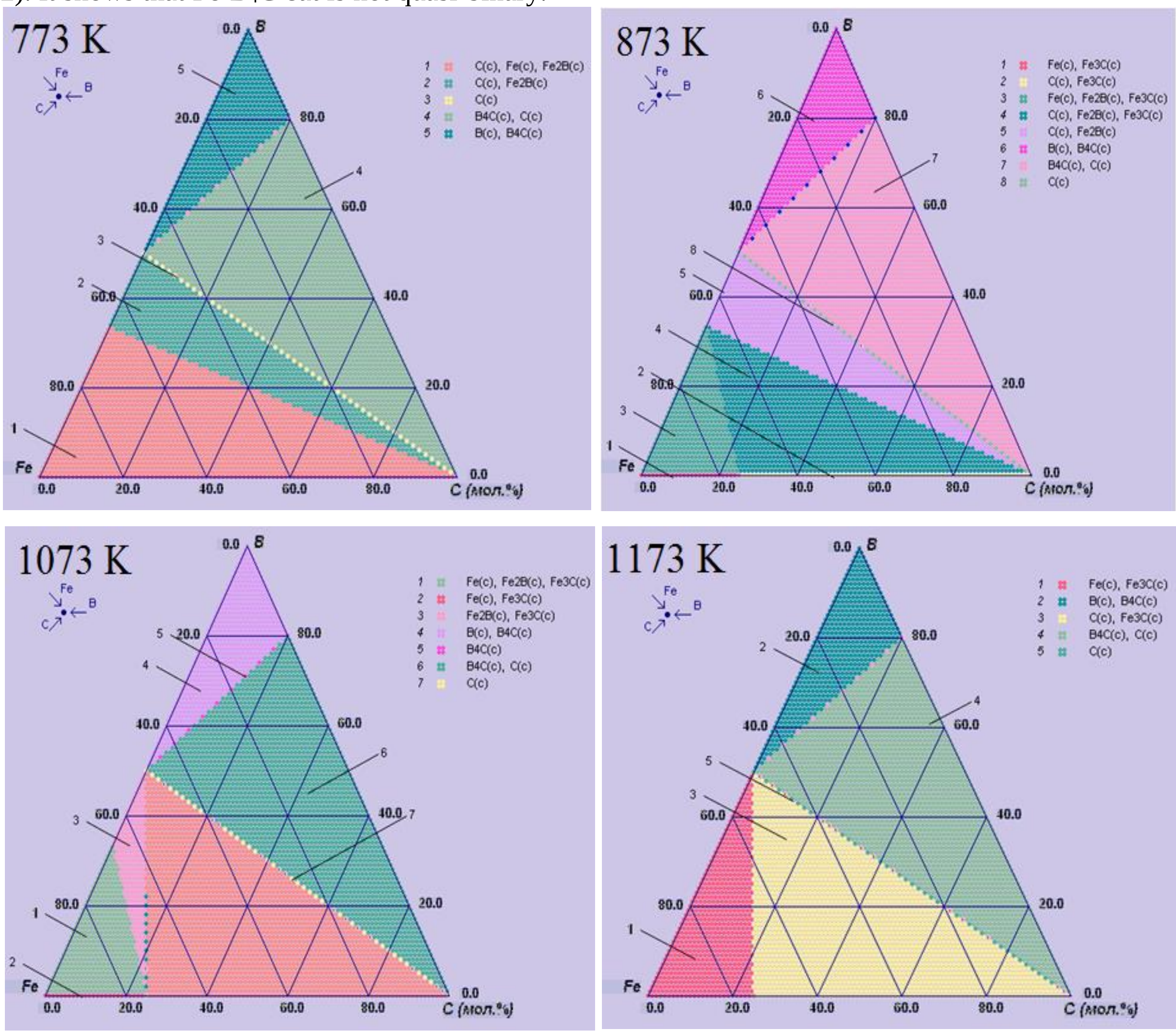


**Figure 2.** Phase equilibria in the Fe-B-C in the temperature range from 773 to 1173 K under a pressure of $10^{-3}$ Pa.

Fig. 3 shows the isotherms in Fe-B-C systems at pressure of $10^{-3}$ Pa which indicate significant release of the energy, that initiates SHS interaction process of Fe with $B_4C$ resulting in the formation of iron carbide as a secondary phase with respect to the metal base. This may occur in the structure of the boride layer obtained by electron beam boriding. Hence, such studies of the boride layer structure support this assumption.

### *3.2. 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 microns (the daub from amorphous boron) and depths up 100÷110 microns (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.

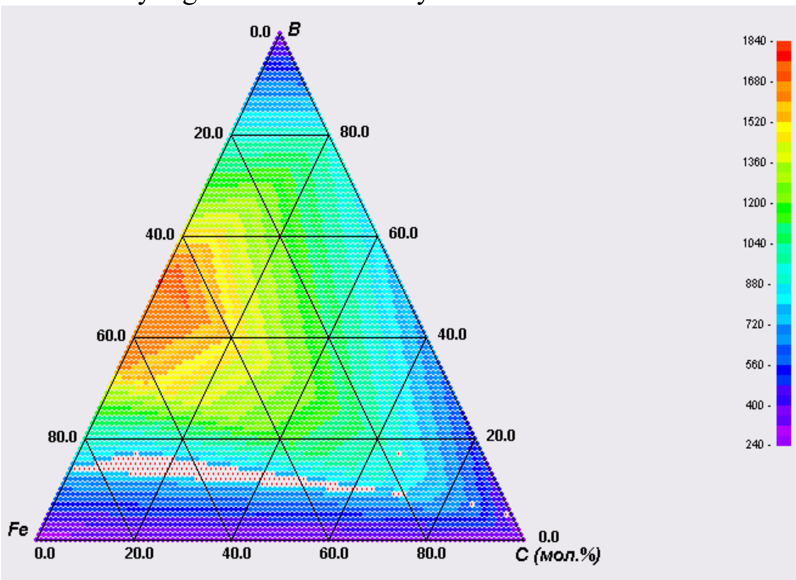


**Figure 3.** The isotherms in the system Fe-B-C at a pressure of $10^{-3}$ Pa.

The transition zone after electron beam boriding was not observed and the legible boundary between a layer and base metal was observable (Fig. 4.a, b). The layer consists of rounded crystals are settling down on a surface and a eutectic.

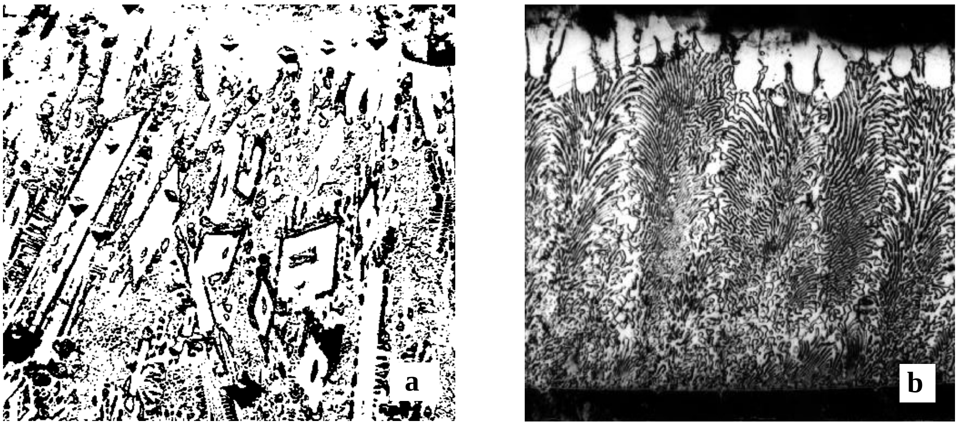


**Figure 4.** Layers boride microstructure formed on steel 45 surface (× 500):
a – electron beam boriding-daub from amorphous boron; b – from $B_4C$.

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 α-Fe.

The boride layer formed from daub $B_4C$ (Fig. 4.b) consists from round off engagements, which locating on the layer surfaces and eutectic. The micro hardness values 820÷840 and 510÷530 MPa for the layer surfaces and eutectic were obtained. The rounds of 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 ($\Delta S$) is less than 2 kcal/mol × K to the crystals are rounded. Obtained in work, the values of the entropy of melting for iron boride $Fe_2B$ is $\Delta S$ = 1,5 kcal/mol × 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 (Fig. 4.a). 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 micro hardness 1750÷1820 MPa is meet. Under the film there are the primary crystals and eutectic with micro hardness 840÷880 MPa and 500÷540 MPa, accordingly.

### *3.3. Self-propagating high-temperature synthesis (SHS) of iron borides*

Among the electron-beam technologies is worth allocating a vacuum electron-beam welding, in which are implemented at the same time the processes of powder metallurgy and classical metallurgy in the electron beam directly on the sample. For this technology, typically use of thermoreacting powder mixtures, in which can be implemented a SHS and process liquid phase sintering with using products of synthesis. Thermoreacting powder mixture contains different components that reduce the temperature of interaction. By lowering the pressure in the chamber is also reduced the temperature of formation of borides. FeB and $Fe_2B$ layers were synthesized from a reaction mixture containing the boron carbide $B_4C$, oxide $Fe_2O_3$ , carbon C and the organic binder. Electron beam technologies give credit for a vacuum electron-beam surfacing where we can observe simultaneous processes of powder metallurgy and classical micrometallurgy in the electronic beam directly on the parts. This method is characterized by using heat-sensitive powder mixtures with possible self-propagating high-temperature synthesis (SHS) and liquid-phase sintering by using chemicals. Heat-sensitive powder mixtures contain different components that allow reducing the interaction temperatures. The temperature of boride formation is also reduced due to pressure drop down in the chamber. $Fe_2B$ and FeB layers have been synthesized from a reaction mixture containing boron carbide $B_4C$, $Fe_2O_3$ oxide, C carbon and the organic binder.

As mentioned above the decrease of the total pressure in the chamber accompanied by temperature reduction allows forming iron borides. When the pressure is $10^{-3}$ Pa, the temperature for generating iron borides is~900 K which allows to form the layer without melting the steel surface but during the beam exposure accompanied by a large amount of energy due to SHS, the thin melt layer (5-7 μm) appears on a metal surface. This melted layer is embedded by boride particles which are evenly distributed throughout the whole surface. After the beam exposure the crystallization process results in the formation of a dendroid layer. Dendrites grow along the heat transfer perpendicular to thermal fields. (Figure 5).

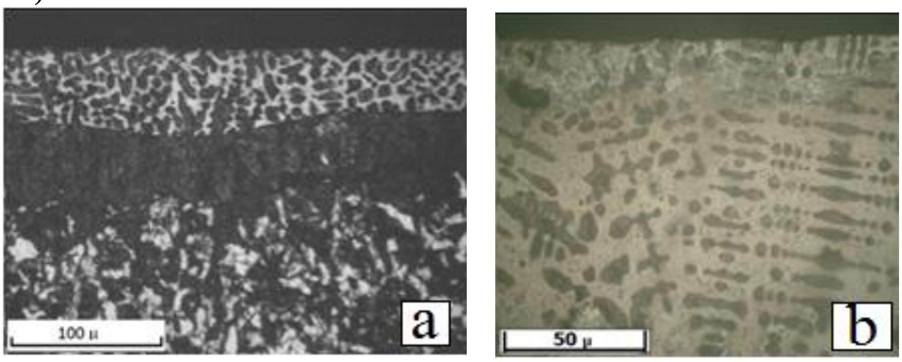


**Figure 5.** The structure of the boride layer $Fe_2B + B_2O_3$.

The study of layers' microhardness obtained by this technique proves that the hardest borides are FeB of 1200-1500 MPa. Microhardness of $Fe_2B$ borides – 1100-1300 MPa. Separate particles located on the surface of a layer are the hardest with its microhardness of 3000-3500 MPa (Figure 6). The thickness of this microlayer is about 10 μm. Microhardness was measured using PMT-3 microhardness tester according to Vickers method.

The analysis showed that in the layer there are a phase of iron borides FeB and $Fe_2B$.X-ray diffraction is shown in figure 7. 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.

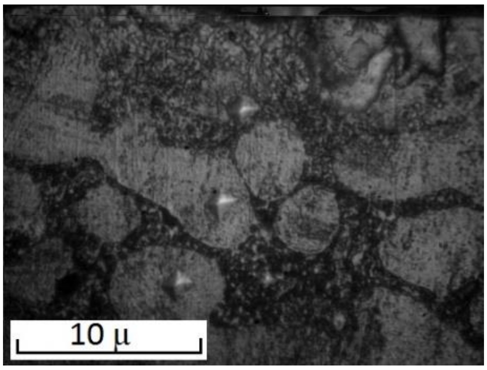


**Figure 6.** Microhardness of boride layers $Fe_2B$.

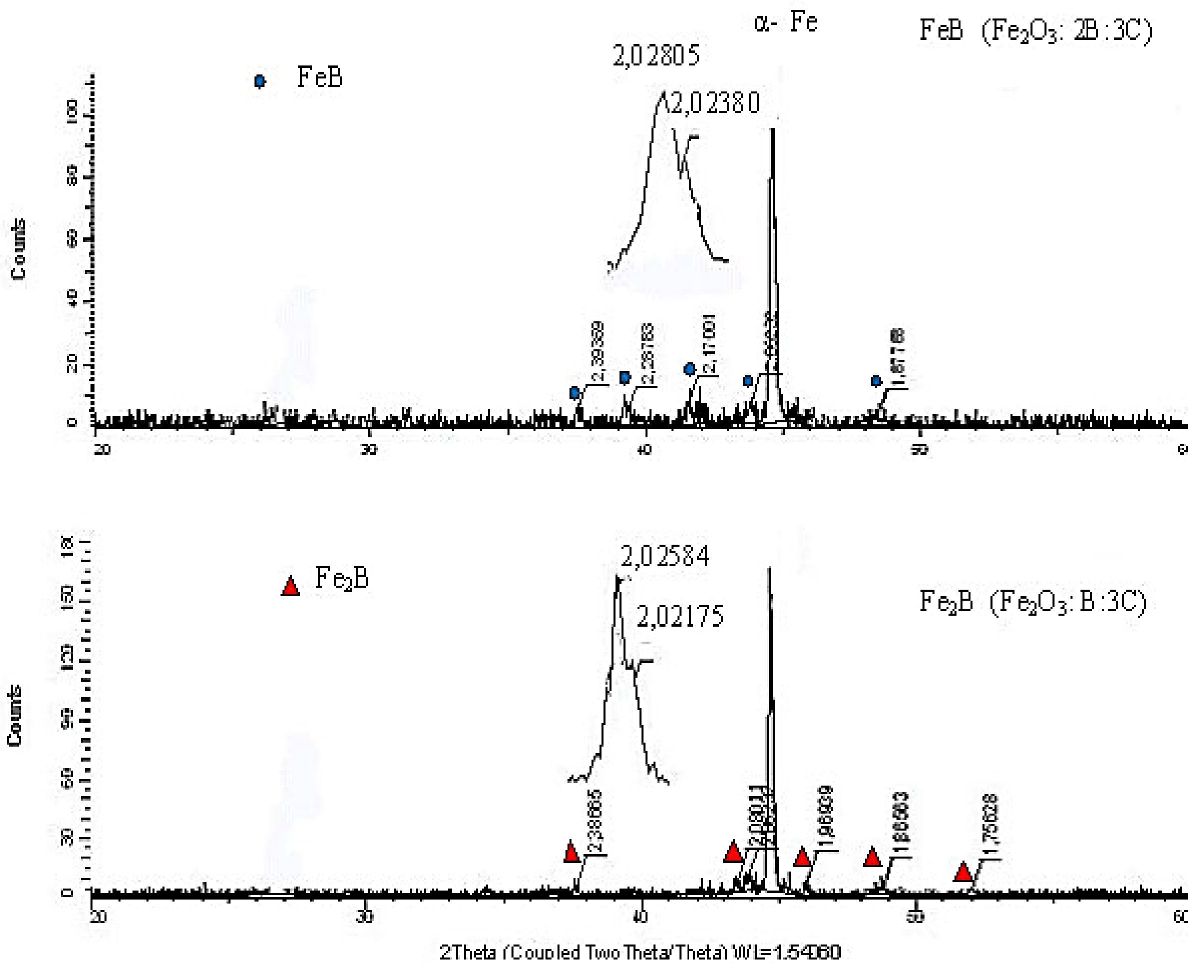


**Figure 7.** X-ray phase analysis of produced boride layers.

The study of layers structure confirmed this method of coating on the base of iron borides. Microstructure shows the principles of crystallization of the boride layer. Photos made by METAM PB-22 microscope with NEXSYS Image Expert provide a clear image of the visible boundary between the layer and the base as well as the zone of thermal exposure by the electron beam. The thickness of the whole layer runs up to 250 μm.

## 4. Conclusion

This paper presents the thermodynamic model of iron boride formation with the completed analysis of thermal processes and phase equilibria of given structures. It also provides investigations of strength properties of obtained iron boride layers, that prove the significant increase of microhardness and wear resistance of studied materials.

## References

[1] Dasheev D E, Smirnyagina N N 2012 *Izvestia vuz. Fizika* **55(12-2)** 51
[2] Polukonova A E, Smirnyagina N N, Dasheev D E 2015 *Modelling of heat process in processing of low-carbon steel by focused electron beam. Innovative technologies in science and education* (Proceedings of the 4th international scientific-practical conference) p. 118.
[3] Trusov B G 2002 TERRA software package for calculation of plasma chemical processes (*Materials of III Intern. Symp. on Theoretical and Applied Plasma Chemistry*. Ples.) pp. 217-218.
[4] Dasheev D E, et al. 2015 *Journal of Physics: Conference Series* **652** 012002

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