WEAR RESISTANT COATINGS ON BASED BORIDE PHASES FORMED IN THE MAGNETIC FIELD ON ALLOYS

ИЗНОСОСТОЙКИЕ ПОКРЫТИЯ НА ОСНОВЕ БОРИДНЫХ ФАЗ СФОРМИРОВАННЫХ В МАГНИТНОМ ПОЛЕ НА СПЛАВАХ

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Abstract
In this paper we study the structure, phase composition, microhardness, wear resistance boride coatings obtained on metals and alloys at complex saturation with boron and copper in various physical and chemical conditions, namely carrying satiation without application of an external magnetic field (EMF) and in its simultaneous imposition . Studies have shown that the use of EMF when applying boride coatings allows in 1.5 - 2 times reduce the duration of saturation detail and get coatings with high hardness and wear resistance.
Established that the application EMF on carbon steels formed a continuous, homogeneous boride layer, thickness is 2 times higher than the boriding without EMF. On the diffraction patterns of the surface layers of boride coatings obtained after boriding at application EMF fixed presence phases FeB and Fe_2B, the redistribution of the proportion of boride phases, the change of the crystal lattices and the decrease in the volume of the unit lattice phase FeB. When the complex is saturated steel 45 with boron and copper diffusion layer is composed of the phases FeB, Fe_2B and Cu. Chemical heat treatment with the simultaneous action of EMF leads to the formation of phases in the diffusion zone FeB and Cu, crack resistance layers obtained after saturation with boron and copper increases to 2.23 MPa · $m^{0,5}$ compared to 1.12 MPa · $m^{0,5}$ for boride coatings obtained without action EMF .
Formation diffuse boride layers under the action EMF improves tribological characteristics and leads to an increase in wear resistance of 2.2 – 2.6 times.
KEYWORDS: BORIDING, BORIDE LAYER, MAGNETIC FIELD, COPPER, DIFFUSION, MICROSTRUCTURE, MICRO HARDNESS, WEAR RESISTANCE, CRACK RESISTANCE, STRESS SPALLING

1. Introduction

Analysis of work, aimed at increasing productivity processes chemical and heat treatment, indicates that, along with traditional research in this field is the search in the direction of intensification of diffusion processes [1].

It is known that the resulting diffusion methods boride layers on steel with high hardness and wear resistance in various conditions wear as in couple of friction in dry friction-slip, and at hydroabrasive action. The main disadvantages of forming boride layers is a low growth rate boride needles and predisposition to cracking while increasing layer thickness. High operational characteristics obtained only when a layer of borides sufficiently solid foundation.

Boriding in an external magnetic field (EMF) – one of the new trends in physical materials. The external magnetic field is used to intensify the diffusion saturation working surfaces of metal products chemical elements (boron, carbon, silicon, etc.). At boriding in EMF significantly intensified diffusion processes, which in turn leads to a decrease the time necessary for saturation. Because considerable interest is the study of the effect of external magnetic field on the processes boriding.

The aim of this work was to study the structure and characteristics of complex diffuse boride coatings on iron-carbon steels obtained in powder boriding mixtures with the addition of copper containing compounds Cu_2O or Cu_3P in various physical and chemical conditions, as well as the establishment impact of the saturating powder environment on the characteristics of the coating thickness, micro-hardness, crack resistance, stress spalling, wear resistance.

2. Materials and methods research

Complex boriding powder method performed in a special container under reduced pressure at a temperature of 975 °C for 4 hours using fusible shutters. The research was conducted on samples of carbon steel (steel 20 45, U8).

Saturation alloys boron and copper performed in mixtures containing technical boron carbide B_4C and powders Cu_2O, Cu_3P. As the activator used ftoroplast.

Heating the crucible and the subsequent isothermal holding was carried out in a laboratory oven type HSOL - 1.6,3 / 11. Electric furnace at a temperature of saturation placed in the solenoid, which served as the source of the magnetic field.

After the isothermal exposure container with details removed from the furnace and cooled to room temperature in air, disclose and took out details with clean surfaces that do not require further purification.

This method has the following advantages: simplicity of the process, allows the processing of products of different configurations can be obtained diffusion layers of different thickness.

Polishing was performed on samples of diamond polishing circles paste grit from 28 to 1 micron, that provided to obtain high surface quality research. As a reagent for chemical etching using 3...5% – solution was nitric acid in ethanol; exposure – 30 - 90 sec.

Also, carried out the thermal etching by heating the polished microsection in a box furnace to a temperature of 400 °C and held at this temperature during 30 minutes and cooling on air. Thermal etching, which is known, is based on the chemical activity of the phases depending on their composition, allowing the cells to determine the place of appearance of the phases and their distribution in the structure. It should be noted that the sensitivity of cells to thermal etching phase nucleation is significantly higher than that of ordinary chemical etching. This is due to the advent of color painting phases.

Visual study, measuring the thickness of diffusion layers and microstructure coatings investigate performed on metallographic microscope Axio Observer A1m, Zeiss, in the range the increase 100...1000.

Microhardness measurements were carried out on the instrument PMT – 3 no less than 15 – 20 fields of view at a load of 0.49 – 0.98 N. Measuring accuracy microhardness was – 500 MPa.

The phase composition, quantitative analysis phase, the crystal lattice period, the volume of the elementary gratings phase, region of coherent scattering of boride coatings were analyzed on X-rays diffractometer Ultima-IV, of Rigaku, Japan, in copper $K\alpha_1$, $K\alpha_2$ monochromatic radiation and chemical composition was determined by scanning electron microscope SEM – 106I.

For measurement fracture toughness monocrystals of solid crystalline material used method Evans – Charles. In this case K_{1c} determined by the length of the radial cracks that formed around imprint of Vickers indenter, with semi-empirical relationship:

$K_{1c}=0,015\cdot(E/H)^{1/2}\cdot P/C^{3/2}$ (1)

or graphical dependence between (K_{1c}-F/H) - (H/E-F) and c/a, where F – the constant Marsha; H – Vickers hardness; a – semi diagonal imprint; c – the length of the radial cracks; E – Young's modulus [2 – 4].

Test coatings for wear resistance was carried out on the friction machine M-22M as described in [5] and GOST 26614-85 (the method of determining the tribological properties). The method consists in determining the dependence of the frictional force and wear of the mating surfaces of the sample material and the counterface (45 steel after quenching and low temperature tempering of 180 °C with a hardness 50 HRC) sliding velocity, power and computation load intensity and the coefficient of friction. To test used samples of steel 45 with boride coatings.

3. Results and discussion

The mechanism of diffusion boriding powder technical boron carbide is described in [6]. According to this operation, boron carbide at the saturation temperature recovers to the lower boride anhydride boron oxide B_2O_2 by reaction:

$B_4C + B_2O_3 \rightarrow B_2O_2 + B_mC_n$ (2)

Vapor formed B_2O_2 carried transport of boron to the surface that is saturated. In this way, boron transporter is oxygen. Vapor B_2O_2 disproportionate on the surface that is saturated with formation of atomic boron and B_2O_3 by the reaction:

$3B_2O_2 \rightarrow 2B + 2B_2O_3$ (3)

Atomic boron formed diffuses into the material to form the corresponding metal borides.

The surface that is saturated, covered with a film B_2O_3 in the molten state. The role of boron carbide is also that the point of contact with the surface of the particles is saturated, there is a restoration B_2O_3, thanks to the surface is cleaned by melting film. At this formed additional portions of B_2O_2 and is facilitated access to a vapor of B_2O_2 to the metal.

Steels St3 boriding in technical powder of boron carbide (2.13% B_2O_3) powder and boron carbide, boron anhydride purified by the same conditions (T = 1000 °C, and τ = 2 h). The thickness of the boride layer in the first case was 160 – 180 microns. At boriding in powder of boron carbide, of purified from anhydride, it fixed extremely low rate of saturation [7]. The results of this experiment show boride anhydride participate in the formation of active boron atoms.

On the basis of the data obtained, we can conclude that the carrier is B_2O_3 with boron carbide, formed suboxides boron and carbon

$5B_2O_3 + B_4C \rightarrow 7B_2O_2 + CO$ [4]

Since the temperature boriding high enough, evaporation takes place of boron oxide B_2O_3 and B_2O_3. Condensing on the products, the evaporation of oxides of boron formed melt system B_2O_3 – B_2O_3, containing ions of bivalent and trivalent boron.

A necessary requirement diffusion layer formation is the presence of near surface saturable active atomic boron addition, temperature and duration of exposure should ensure the flow of atomic diffusion of boron in steel.

In the system Fe – B mass transfer elements is carried out mainly by diffusion of boron through the boride layer to the main reaction front, located at interfaces iron – Fe_2B borides and boride Fe_2B – borides FeB [8]. In forming a diffusion layer on the metal surface reaches saturation limit of the solid solution boron (γ) the germ arises first, and then the needle borides tetragonal Fe_2B (*a* = 5,109 Å, *c* = 4,249 Å and *c**a* = 0,832), containing 8,84 % B, a density of 7.336 g\cm^3. These needles grow gradually becoming isolated in continuous layer of borides Fe_2B. Then, on the surface of boride layer having individual needle and then the second layer formed rhombic borides FeB, which has a density of 6.706 g\cm^3 (*a* = 5,506Å, *b* = 4,061Å and *c* = 2,952Å), containing 16.25% B. Application of a magnetic field leads to an intensification of the diffusive penetration of the atoms in the crystalline lattice of γ-Fe.

To establish a relationship between the phase and structure, diffusion layers obtained after saturation with boron and copper, samples were subjected to X-ray analysis. Characteristic areas diffraction pattern shown on Fig. 1 – Fig. 4.

Diffraction patterns taken from the surface of boride coatings on steel 45 after boriding without EMF showed that in the surface layer up to 15 – 20 microns formed phase FeB (Fig.1), and at the complex saturated with boron and copper without action EMF – phase FeB, Fe_2B, Fe and Cu (Fig .2).

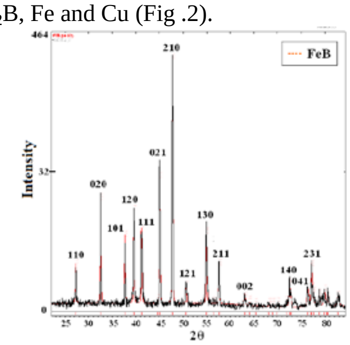


Fig. 1. *Diffraction pattern taken from the surface steel 45 with boride coatings obtained after boriding*

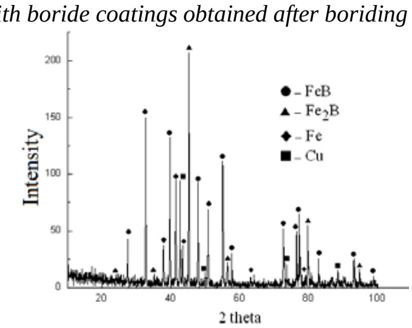


Fig. 2. *Diffraction pattern taken from the surface steel 20 with boride coatings obtained after boriding with adding powder Cu_2O, diffraction peaks of copper lines (111) (200) (220)*

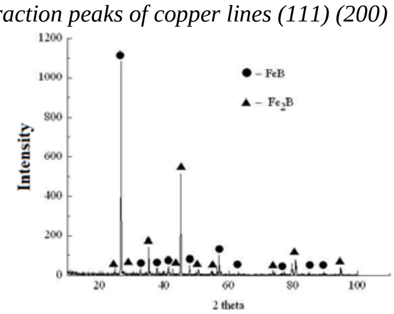


Fig. 3. *Diffraction pattern taken from the surface steel 45 with boride coatings obtained after boriding at using EMF*

In the application of an external magnetic field observed redistribution boride phase. At using EMF in boride layers observed decrease volume phase FeB and on the diffraction patterns surface layers of boride coatings fixed presence phases FeB and Fe_2B (Fig. 3), and after the complex saturation boron and copper under conditions of external magnetic fields fixed phases FeB and Cu (Fig. 4).

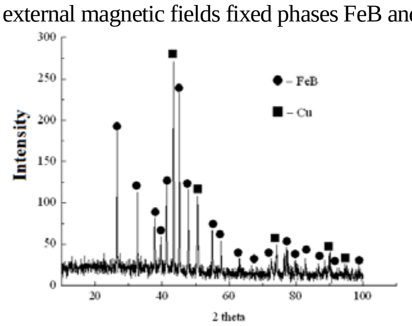


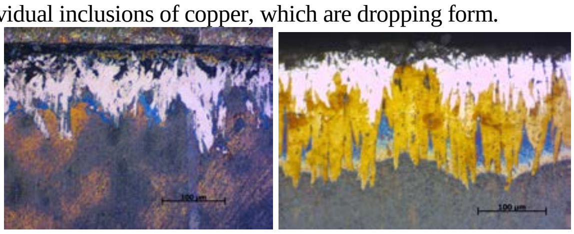
Fig. 4. *Diffraction pattern taken from the surface steel 45 with boride coatings obtained after boriding at using EMF and introduction to the saturating environment copper-containing powder Cu_2O, diffraction peaks of copper lines (111) (200) (220)*

When applying EMF in boride layers observed the redistribution of the proportion of boride phases, changes in the crystal lattice period and a decrease volume of the unit lattice phase FeB (Table. 1). When the complex saturated with boron and copper steel 45 diffusion layer composed of the phases FeB, Fe_2B, Fe and Cu. Chemical heat treatment (CHT) with the simultaneous action of EMF leads to the formation of the diffusion zone phases FeB and Cu. When the complex saturated with boron and copper volume ratio of copper in the surface layer, the results of X-ray diffraction, volume was 4%, and at the CHT with the simultaneous action of EMF quantity of copper component in the surface phase FeB increased to 18.9% (Table. 2). Areas of coherent scattering in phase FeB, obtained by complex saturation with boron and copper with the simultaneous action of EMF, decreased to 38.3 nm as compared to 66.1 nm in the phase FeB, obtained without action EMF.

Table 1. *Parameters crystal lattice phase after boriding and complex saturation with boron and copper in different physical - chemical conditions*

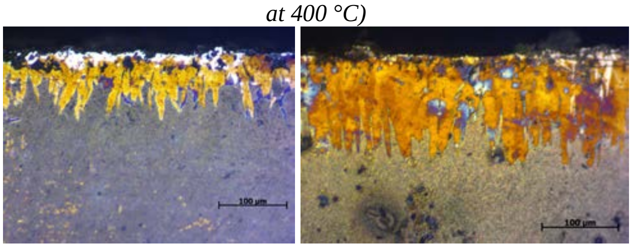
The process of saturation	Name of the phase	Parameters of crystal lattice, Å			Volume (A^3)
		a	b	c	
Boriding without EMF	FeB	4,056248	5,497254	2,944663	65,66
Boriding + EMF	FeB	4,048051	5,497390	2,943259	64,50
	Fe_2B	5,104722	5,104722	4,242536	110,55
Complex saturation with boron and copper without EMF	FeB	4,052739	5,494320	2,942284	65,52
	Fe_2B	5,095910	5,095910	4,247051	110,29
	Fe	2,948823	2,948823	2,948823	25,64
	Cu	3,669155	3,669155	3,669155	49,40
Complex saturation with boron and copper + EMF	FeB	4,054046	5,492628	2,942097	65,51
	Cu	3,606553	3,606553	3,606553	46,91

Metallographic analysis established that obtained the powder technology coating after saturation with boron and copper have a structure with a clear boundary between the coating – base (Fig. 5 and Fig. 6). Diffusion layers are needle of iron borides, which are oriented perpendicularly to the sample surface and are wedged in the ferritic grains. In the near-surface zone boride phase FeB concentrate individual inclusions of copper, which are dropping form.



a ***b***

Fig. 5. *Microstructures complex boride coatings on steel 45 obtained in different physical – chemical conditions: a – boriding, duration saturation – 4 hours, x200; b – boriding + EMF, saturation duration – 2 hours, x200 (color high temperature etching at 400 °C)*



a ***b***

Fig. 6. *Microstructures coatings on steel 45 obtained after complex saturation with boron and copper in different physical – chemical conditions: a – complex saturation with boron and copper without EMF, duration saturation – 4 hours, x200; b – complex saturation with boron and copper + EMF, saturation duration – 2 hours, x200 (color high temperature etching at 400 °C)*

Table 2. *Quantitative phase analysis of boride layers and layers obtained after complex saturation with boron and copper in different physical - chemical conditions*

The process of saturation	Name of the phase	Contents (%)
Boriding without EMF	FeB	100
Boriding + EMF	FeB	15,8
	Fe_2B	84,2
Complex saturation with boron and copper without EMF	FeB	62
	Fe_2B	30,5
	Fe	3,5
	Cu	4
Complex saturation with boron and copper + EMF	FeB	81,1
	Cu	18,9

Obtaining boron coating at simultaneous applying allows in 1.5 – 2 times to reduce the period saturation detail and get coatings with high hardness, wear resistance, crack resistance. At applying the EMF changing morphology boron layers, needles grains decreases sharply, disappear individually disappear sprouted grain borides in the matrix. Needles boron phases closely adjoin to each other and formed a continuous, homogeneous boron layer thickness is in 1.5 times higher than the boriding without EMF.

Investigation of the kinetics of growth of boride layers in a variety of physical - chemical conditions. It was established that after the diffusion saturation in boriding mixture for 4 hours without EMF obtain coating thickness of 125 – 150 microns, whereas when applied EMF formed coating thickness of 160 – 195 microns in 2 hours; at complex saturation with boron and copper at 4 hours without EMF formed coating thickness of 160 – 185 microns, whereas at after saturation with boron and copper the conditions in action EMF at 2 hours diffusion saturation obtained boride phase thickness to 200 – 230 microns.

Conducted research showed that microhardness boride phase after boriding was respectively – phase FeB – 19 – 20 GPa, and phase Fe_2B – 16,5 – 17,5 GPa (Fig. 7). In the complex saturation with boron and copper using EMF get boride layers of microhardness – for phase (Fe, Cu)B – 17 – 18 GPa, and for phase $(Fe, Cu)_2B$ – 15 – 16 GPa. Thus, the complex saturation with boron and copper, observe a decrease of microhardness boride layers and increasing plasticity (Fig. 8).

The calculated data crack resistance and stress spalling, which may occur in the boride phases, depending on physical - chemical conditions on the steel 45 is presented in Table 3.

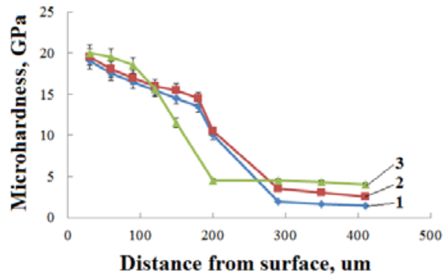


Fig. 7. Microhardness boride phase after boriding at using EMF, on the steels: 1 – steel 20; 2 – steel 45, 3 – U10

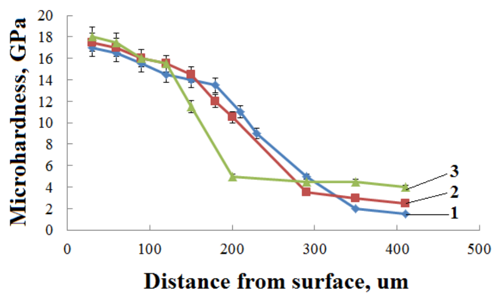


Fig. 8. *Microhardness boride phases obtained after complex saturation with boron and copper at using EMF, on the steels: 1 – steel 20; 2 – steel 45, 3 – U10*

The highest level of of crack resistance is achieved in the boride phases produced in powdered environments with copper powder when applying EMF, and accordingly is 2.23 MPa · $m^{0,5}$, wherein the spalling stress is 420 MPa. Then as at boriding without action EMF crack resistance – 1.12 MPa · $m^{0,5}$ and stress spalling – 160 MPa. Increase the value of spalling stress in layers obtained after complex saturation with boron and copper is caused the formation of higher viscosity phase, for which crack resistance K_{1C} 1.2 – 1.5 times higher than the output phase boride (FeB, Fe_2B).

Table 3. *Crack resistance and spalling stress coating obtained in different physical – chemical conditions (phase Fe_2B)*

Physical-chemical conditions of saturation	K_{1c}, MPa · $m^{0,5}$	$\sigma_{spalling}$, MPa
Boriding without EMF	1,12	160
After complex saturation with boron and copper without EMF	1,52	225
Boriding at applying EMF	1,79	345
After complex saturation with boron and copper at applying EMF	2,23	420

A study wear resistance of coatings of boride obtained in different physical - chemical conditions (Table 4). As counterbody used steel 45 after hardening and low tempering with hardness 50 HRC. It was established that the diffusion boride coating obtained by application of external magnetic fields have a higher tribological characteristics. Thus, the average linear wear boride coatings obtained in EMF is reduced by 2.4 times, and the friction coefficient is 0.63 compared to 0.66.

Table 4. *Tribotechnical characteristics boride coatings obtained in different physical – chemical conditions: 1 – boriding without EMF; 2 – after complex saturation with boron and copper without EMF; 3 – boriding at applying EMF; 4 – after complex saturation with boron and copper at applying EMF*

Coating	Coef. of friction	Linear wear of the friction pair, I, um, The road friction (km)			Mass wear, I (mg/km)		Average linear wear of the friction pair, $I_{average}$, um/km (3 km traversed)	Spot of contact area on the sample, S (cm^2)
		1	2	3	sample	counter-body		
1	0,66	7	19,5	26	0,94	1,6	8,7	0,26
2	0,65	6,4	14,7	17,7	0,51	1,2	5,9	0,23
3	0,63	6,0	8,4	16,4	0,45	0,95	5,5	0,22
4	0,6	5,2	7,2	10,1	0,25	0,45	3,4	0,18

Complex saturation of carbon steels, boron and copper at using EMF improves the wear resistance of boride layers in 2.2 – 2.6 times compared with 1.4 – 1.5 times without the use of EMF, this is due to the formation of more perfect structure with a smaller quantity pores and higher crack resistance and spalling stress which grow up to 420 MPa as compared with 160 MPa for diffusion boride layers.

4. Conclusion

Application EMF with simultaneous deposition boride coating allows 1.5 – 2 times to decrease the duration of the saturation detail, and obtain a coating of high hardness, wear resistance.

When applying EMF in boride layers observed the redistribution of the proportion of boride phases, changes in the crystal lattice period and a decrease volume of the unit lattice phase FeB and change the morphology of boride layers. Observed a decrease needle-like grains, disappear individually disappear sprouted grain borides in the matrix. Needles boron phases closely adjoin to each other and formed a continuous, homogeneous boron layer thickness is in 1.5 times higher than the boriding without EMF.

Investigation of the kinetics of growth of boride layers in a variety of physical - chemical conditions. It was established that after the diffusion saturation in boriding mixture of carbon steels at simultaneous action EMF coating thickness increases, and the duration of the saturation decreases to 1.5 – 2 times.

Established that ehe highest level of of crack resistance is achieved in the boride phases produced in powdered environments with copper powder when applying EMF, and accordingly is 2.23 MPa · $m^{0,5}$, wherein the spalling stress is 420 MPa. Then as at boriding without action EMF crack resistance – 1.12 MPa · $m^{0,5}$ and stress spalling – 160 MPa. Increase the value of spalling stress in layers obtained after complex saturation with boron and copper is caused the formation of higher viscosity phase, for which crack resistance K_{1C} 1.2 – 1.5 times higher than the output phase boride (FeB, Fe_2B).

Formation diffuse boride layers under the action EMF improves tribological characteristics and leads to an increase in wear resistance of 2.2 – 2.6 times.

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