STRUCTURE AND PROPERTIES OF SURFACE LAYERS METALS ON THE BASIS OF HIGH SOLID BORIDE OBTAINED IN CONDITIONS OF AN EXTERNAL MAGNETIC FIELD

СТРУКТУРА И СВОЙСТВА ПОВЕРХНОСТНЫХ СЛОЕВ МЕТАЛЛОВ НА ОСНОВЕ ВЫСОКОТВЕРДЫХ БОРИДОВ ПОЛУЧЕННЫХ В УСЛОВИЯХ ДЕЙСТВИЯ ВНЕШНЕГО МАГНИТНОГО ПОЛЯ

Prof. dr. Chernega S.[1], Poliakov I.[1], Krasovskiy M.[2]
[1]National Technical University of Ukraine "Kiev Polytechnic Institute", Kiev, Ukraine
e-mail: smchernega@mail.ru; polykov_igor@mail.ru
[2]The Frantsevich Institute for Problems of Materials Science of NAS of Ukraine, Kiev, Ukraine

Abstract: *In this paper we study the structure, phase composition, microhardness, crack resistance, wear resistance boride coatings obtained at complex saturation with boron and copper in the application of an external magnetic field (EMF). Investigations have shown that this method allows the application of boride coatings in 1.5 - 2 times decrease the duration saturation detail, and receive coating with high hardness, wear resistance, crack resistance.*
It is established that the application EMF formed a continuous, homogeneous boride layer with thickness coatings in 2 times higher than boride coatings without EMF for the equal duration of the process. When imposing EMF in boride layers observed the redistribution quantitative relation boride phases, namely: decrease of volume phase FeB, and on diffractograms surface layers boride coatings obtained after boriding fixed presence phases FeB and Fe_2B. After complex saturation boron and copper in the application of external magnetic fields fixed phases FeB and Cu.
The researches have shown that the highest spalling stress value is reached in boride phases, obtained in powder environments with copper powder at the application of EMF, and respectively is 420 compared with 225 MPa for coating obtained without EMF. Increased shear stress values in complex layers obtained after saturation with boron and copper caused by the formation of phases more viscosity, for which crack K_{1c} in 1.4 - 2.0 times higher than the initial boride phases FeB and Fe_2B.
Application of EMF at boriding improves tribological characteristics of coatings: decreases coefficient of friction and increase in 1.5 - 2.5 times wear resistance.
***KEYWORDS**: MAGNETIC FIELD, BORIDING, COMPLEX SATURATION WITH BORON AND COPPER, BORIDE LAYER, DIFFUSION, FRICTION, MICROSTRUCTURE, MICROHARDNESS, WEAR RESISTANCE, CRACK RESISTANCE*

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.

2. Materials and Experiment

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 steel 20 45, U10.

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 [2].

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 sec.

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.

Phase composition of coatings 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.

Test coatings for wear resistance was carried out on the friction machine M-22M as described in [3] 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 50HRC) 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 [4]. According to this operation, boron carbide at the saturation temperature recovers to the lower boride anhydride boron oxide B_2O_2 by reaction:

$$B_4C + B_2O_3 \rightarrow B_2O_2 + B_mC_n$$

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:

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

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 boronized 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. 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

$$5B_2O_3 + B_4C \rightarrow 7B_2O_2 + CO$$

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.

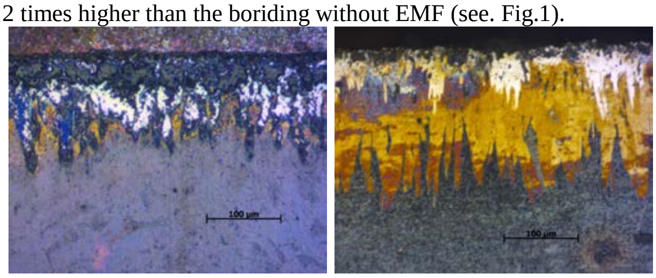
A necessary requirement diffusion layer formation is the presence of near surface saturable active atomic boron addition, temperature and duration of exposure should ensure the flow of atomic diffusion of boron in steel.

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 [5]. 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 Å), 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 the transport direction of boron ions in the liquid phase of the melt system of $B_2O_2 – B_2O_3$ to the boundary with the crystal lattice of Fe-γ and quickly penetration into the pores of an atom in the crystal lattice of Fe-γ.

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.1). 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.

This method obtaining boron coating 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 2 times higher than the boriding without EMF (see. Fig.1).



a *b*

Fig.1. *Microstructures complex boride coatings on steel 20 obtained in different physical – chemical conditions: a – boriding, duration saturation – 4 hours, x200; b – boriding, in EMF, saturation duration – 2 hours, x200*

Investigation of the kinetics of growth of boride layers in a variety of physical - chemical conditions. It was found that after the diffusion saturation in boriding mixture for 4 hours without EMF obtain coating thickness of 150 microns, whereas when applied EMF formed coating thickness of 200 microns in 2 hours; at 4 hours without saturation with boron and copper for EMF formed coating thickness of 175 microns, whereas at after saturation with boron and copper the conditions in action saturation with boron and copper in FMF diffusion saturation at 2 hours boride phase grow coating thickness to 230 microns (Fig.2 and Fig.3).

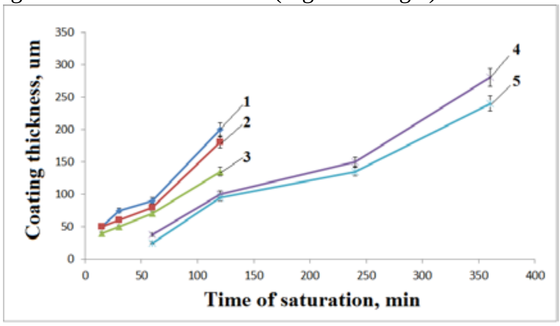


Fig.2. *Kinetic curves of growth boride coatings obtained after boriding: where 1 – boriding with using an external magnetic field, on the steel 20; 2 – boriding with using an external magnetic field, on the steel 45; 3 – boriding with using an external magnetic field, U10; 4 – boriding without magnetic field, on the steel 20; 5 – boriding without magnetic field, U10*

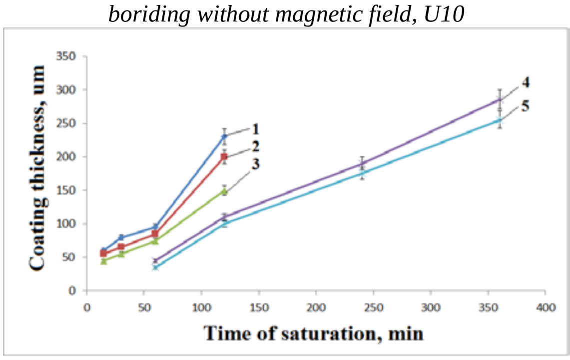


Fig.3. *Kinetic curves of growth boride coatings obtained after complex saturation with boron and copper, where 1 – complex saturation with boron and copper at using EMF, on steel 20; 2 – complex saturation with boron and copper at using EMF, on steel 45; 3 – complex saturation with boron and copper at using EMF, U10; 4 – complex saturation with boron and copper without EMF, on the steel 20; 5 – complex saturation with boron and copper without EMF, U10*

Conducted research showed that microhardness boride phase after boriding was respectively – phase FeB – 18 GPa, and phase Fe_2B – 15,5 GPa (Fig.4). In the complex saturation with boron and copper using EMF get boride layers of microhardness – for phase (Fe, Cu)B – 16,5 GPa, and for phase $(Fe, Cu)_2B$ – 14,5 GPa. Thus, the complex saturation with boron and copper, observe a decrease of microhardness boride layers and increasing plasticity (Fig.5).

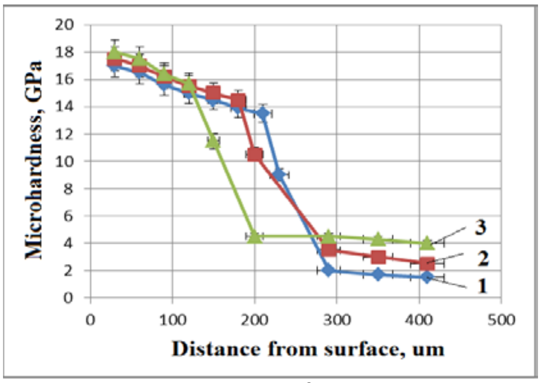


Fig.4. *Microhardness boride phase after boriding at using EMF, on the steels: 1 – steel 20; 2 – steel 45, 3 – U10*

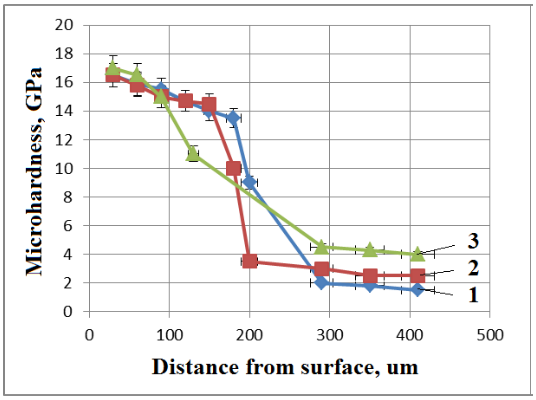


Fig.5. *Microhardness boride phases obtained after complex saturation with boron and copper at using EMF*

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 in Fig.7 and Fig.9.

Diffraction patterns taken from the surface boride coatings on steel 20 after boriding without EMF showed, that in the surface layer up to 15 um formed phase FeB (Fig.6), while after complex saturation with boron and copper – phase FeB and Cu (Fig.7). 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.8), and after complex saturation with boron and copper – phase FeB and Cu (Fig.9).

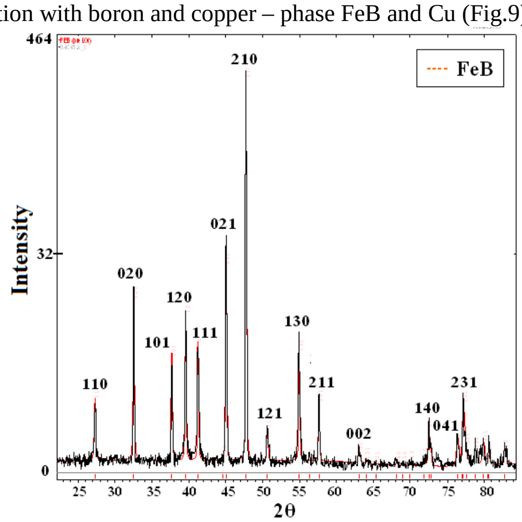


Fig.6. *Diffraction pattern taken from the surface steel 20 with boride coatings obtained after boriding*

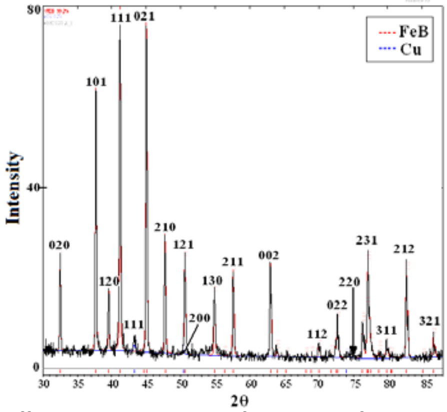


Fig.7. *Diffraction pattern taken from the surface steel 20 with boride coatings obtained after boriding with adding powder Cu_2O, diffraction peaks of copper lines (111) (200) (220)*

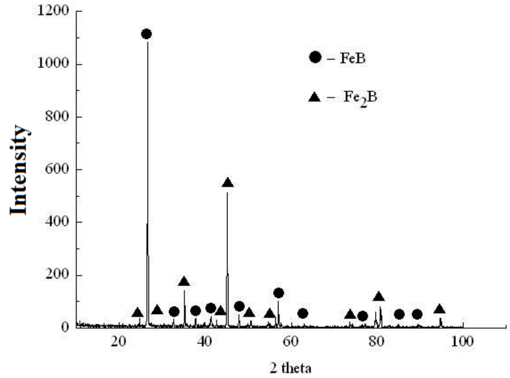


Fig.8. *Diffraction pattern taken from the surface steel 20 with boride coatings obtained after boriding at using EMF*

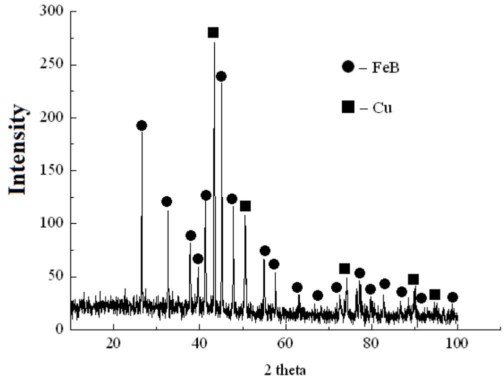


Fig.9. *Diffraction pattern taken from the surface steel 20 with boride coatings obtained after boriding at using EMF and introduction to the saturating environment copper-containing powder Cu_2O, diffraction peaks of copper lines (111) (200) (220)*

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:

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

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.

Calculated data spalling stresses that may occur in boride phases depending on the physical and chemical conditions of the steel to 45 are presented in Table 1.

The highest level of spalling stress is achieved in boride phases obtained in powder environments with participation copper powder at overlay EMF, and respectively is 420 compared with 225 MPa for coating obtained without EMF. Increased shear stress values in complex layers obtained after saturation with boron and copper caused by the formation of phases more viscosity, for which crack K_{1c} in 1.4 – 2.0 times higher than the initial boride phases FeB and Fe_2B.

Table 1. *Calculated data spalling stress boride coatings (phase FeB)*

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

Research wear resistance boride coatings obtained in different physical - chemical conditions (Table 2). Established that diffusion coating obtained with an external magnetic field have higher tribotechnical characteristics.

Table 2. *Tribotechnical characteristics boride coatings*

Coating	Coef. of friction	Linear wear of the friction pair of $I_{average}$, um (3 km)	Mass wear, I (mg/km)		Linear wear of the friction pair of $I_{average}$, um/km (3 km)	Spot of contact area on the sample, S (cm^2)
			sample	counter-body		
Boriding without EMF	0,66	17,3	0,94	1,6	8,6	0,26
After complex saturation with boron and copper without EMF	0,65	12,5	0,41	1,5	5,9	0,23
Boriding at applying EMF	0,63	8,4	0,25	0,95	3,6	0,22
After complex saturation with boron and copper at applying EMF	0,6	7,9	0,25	0,45	3,3	0,18

4. Conclusions

Investigations have shown that this method saturation (Boriding and complex saturation with boron and copper at applying EMF) allows the application of boride coatings in 1.5 – 2 times decrease the duration saturation detail, and receive coating with high hardness, wear resistance, crack resistance.

At applying the EMF changed the morphology of boride layers, needle-shaped grains decreases sharply, disappear separately sprouted into the matrix grain borides. Needle grain boride phases in close contact with each other and formed a solid, homogeneous boride layer thickness is in 2 times higher than the boriding without EMF.

The investigation of the kinetics growth boride layers on carbon steel in different physical and chemical conditions. It was established that after the diffusion saturation of carbon steels in boride mixtures at using EMF, increases coating thickness and the duration of the saturation decreases in 2 – 3 times.

At the application of an external magnetic field observed redistribution boride phases. At overlay EMF in boride layers observed decrease volume phase FeB and on diffraction pattern surface layers boride coatings obtained after boriding presence phases FeB and Fe_2B. After complex saturation with boron and copper in conditions of action an external magnetic fields recorded phases FeB and Cu.

The highest spalling stress value is reached in boride phases, obtained in powder environments with copper powder at the application of EMF, and respectively is 420 MPa at crack resistance 2.23 MPa · m^{0,5} compared to 225 MPa at crack resistance 1.52 MPa · m^{0,5} for coating obtained without EMF. Increased spalling stress values in complex layers obtained after saturation with boron and copper caused by the formation of phases more viscosity, for which crack K_{1c} in 1.4 – 2.0 times higher than the initial boride phases FeB and Fe_2B.

At application of EMF at boriding improves tribological characteristics of coatings: decreases coefficient of friction and increase in 1.5 – 2.5 times wear resistance.

5. References

[1] L.D. Demchenko Effect of preliminary plastic deformation on the structure and properties of nitrided layers in Fe / L.D. Demchenko, V.M. Nadutov, Y.S. Cherepova // OTTOM-4. – K. – 2003. – P. 205 – 209.

[2] S.M. Chernega Improving the wear resistance of the surface layers of metals and alloys with boride coatings of copper / Chernega S.M., Poliakov I.A. // News of the National Technical University of Ukraine «Kyiv Polytechnic Institute». – Series of Mechanical Engineering. – 2011. – 2, № 61. – P. 104 – 110.

[3] A.A. Adamovskiy Method of research tribological characteristics of superhard materials based on dense modifications of boron nitride / A.A. Adamovskiy, V.M. Yemtsov, V.T. Varchenko // Adhesion melts and soldering materials. – Kiev. – The Frantsevich Institute for Problems of Materials Science of NAS of Ukraine Institute of Problems of Materials Frantsevich NAS. – 2009. – Vol. 42 – P. 77 – 84.

[4] Y.N. Podrezov Features hardening alloys commercially pure titanium under uniaxial tension and rolling / Y.N. Podrezov, N.V. Minakov // Electron microscopy and strength of materials. – Kiev. The Frantsevich Institute for Problems of Materials Science of NAS of Ukraine Institute of Problems of Materials Frantsevich NAS. – 1998. – P. 34 – 42.

[5] Boronization steel. Voroshnin L.G., Lyakhovich L.S., "Metallurgy". – 1978. – 240 p.