STRUCTURE FORMATION AND CHARACTERISTICS OF COMPLEX BORIDE COATINGS ON STEEL, OBTAINED IN CONDITIONS OF ACTION MAGNETIC FIELD

СТРУКТУРООБРАЗОВАНИЕ И ХАРАКТЕРИСТИКИ КОМПЛЕКСНЫХ БОРИДНЫХ ПОКРЫТИЙ НА СТАЛЯХ СФОРМИРОВАННЫХ В УСЛОВИЯХ ДЕЙСТВИЯ МАГНИТНОГО ПОЛЯ

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Abstract: *In this paper was investigated the formation of complex diffusion boride layers on metastable austenite Cr-Mn-N steel powder method. Calculate the value of the diffusion coefficient in different physical – chemical conditions and the thermodynamic potential chemical reactions. Defined phase composition layers obtained on the metastable austenite Cr-Mn-N steel. It is established that the application of an external magnetic field (EMF) leads to a redistribution of the proportion boride phases in the surface layers, changes the period of crystal lattice and increasing the diffusion coefficient.*
KEYWORDS: *BORIDING, BORON LAYER, STRUCTURE, DIFFUSION, FRICTION, MICROSTRUCTURE, MICROHARDNESS, WEAR RESISTANCE, MAGNETIC FIELD.*

1. Introduction

Austenite Cr-Mn-N steel refers to wear resistant steel in which metastable austenite during operation undergoes a phase change to create ε - martensite [1]. However, in the demanding conditions of intense loading at hydroabrasive wear in different corrosive environments, such as hydraulic gate fittings parts with Cr-Mn-N steel, a problem improvement operational characteristics [1]. An effective method is the use of chemical heat treatment (CHT) using boron and other saturation elements. CHT allows creating on the surface of the material structure, which is composed of highly rigid boride phases [2]. However, diffusive multicomponent boriding quite energy consuming process, therefore to reduce energy consumption necessary to use methods for intensification the process saturation. One of these methods is the application of an external magnetic field (EMF), the so-called magnetic thermo chemical treatment [3,4].

To solve this problem, we used a complex diffusive saturation of the surface layer of Cr-Mn-N steel boron or boron and copper at simultaneous action of EMF.

The aim of this work was to study diffusive boride coatings and coatings obtained after saturation with boron and copper on Cr-Mn-N steel, obtained in different physical - chemical conditions, namely: conducting saturation without the use of an external magnetic field (TMF), and at simultaneous application.

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2. Materials and Experiment

Processes borating and complex saturation with boron and copper performed powder method in a special at a temperature of 975 °C during 2, 4, 5 and 6 hours using fusible valves. Saturation steels boron or boron and copper performed in powder mixtures on the basis of technical boron carbide B_4C with the addition of powders Cu_2O, as a source of copper and fluoroplast as activating additions.

To create a magnetic field coil (solenoid) used, which consisted of 635 windings tires aluminum alloy, the size of 10x20 mm; the current strength – 60 A; the magnetic induction – 35 mT. For magnetic thermo chemical treatment in coil placed high temperature furnace with crucible and packed in them saturated mixture for boriding with samples of Cr-Mn-N steel.

Investigation of the structure of boride coatings on Cr-Mn-N steel performed on microsections subjected a high temperature etching at 400°C at excerpt 30 minutes in the furnace with followed by cooling to room temperature in air.

Microstructural studies coatings and measuring the thickness of diffusion layers was carried out on metallographic microscope Axio Observer A1m, Zeiss, in the range the increase 100...1000.

Microhardness measurements were carried out on the equipment PMT – 3 no less than 15 – 20 fields of view at a load of 0.49 – 0.98 N. Measuring accuracy microhardness was – ±300 MPa.

Research of the chemical composition of coatings performed microrengenospectral analysis on electronic scanning microscope – SEM 106 with increasing in 2000 time, accuracy – 0.01% by weight.

Phase composition, quantitative analysis phase, the periods of the crystal lattice, volume of elementary lattice phase, regions of coherent scattering in boride coatings were analyzed for X-ray diffractometer Ultima-IV of Rigaku (Japan), in the copper Kα monochromatic radiation.

Testing of coatings on the wear resistance performed on friction machine [5].

3. Results and discussion

X-ray analysis metastable austenite Cr-Mn-N steel with diffusion coating established that at boriding without using EMF in the surface layer of 10 - 15 microns formed phase FeB, (Fe,Cr)B and CrB (Fig. 1, a). Diffusion layers analysis boride coatings obtained without action EMF shown next phase composition, after removal of 15 microns detected phase

FeB, (Fe,Cr)B, CrB and Fe_2B (Fig. 1, b); after removal of 20 microns - (Fe, Cr) B, CrB and Fe_2B (Fig. 1, c).

At the study coatings obtained by complex saturation with boron and copper without action EMF was established following phase composition: in the surface layer of 10 - 15 microns - FeB, (Fe,Cr)B and Cu (Fig. 2, a); after removal of 15 microns - FeB, (Fe,Cr)B and CrB (Fig. 2, b); after removal of 15 microns - FeB, (Fe,Cr)B, CrB and Fe_2B (Fig. 2, c).

In the result layered analysis it was found the next phase composition coating obtained by complex saturation with boron and copper from the surface: FeB, Cu → (Fe,Cr)B → CrB → Fe_2B.

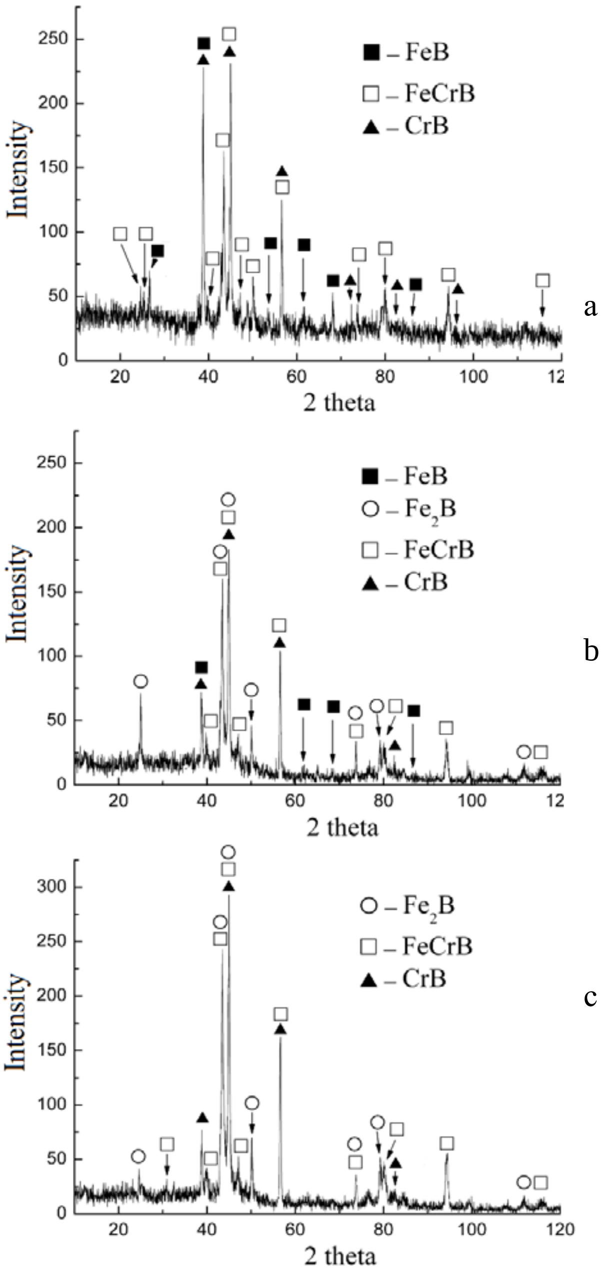

Fig.1: *Diffraction pattern taken from the surface of metastable austenite Cr-Mn-N steel with boride coatings obtained after boriding without using EMF, duration saturation 5 h: a – initial state coatings (after saturation);b – after removal of 15 micron coating; c – after removal of 20 micron coating*

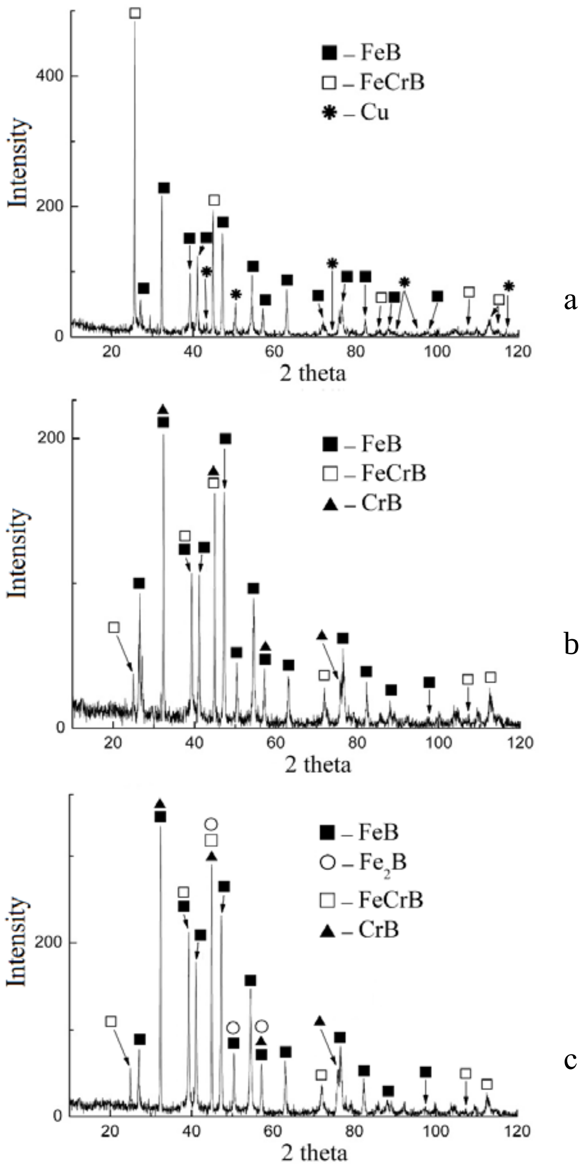

Fig.2: *Diffraction pattern taken from the surface of metastable austenite Cr-Mn-N steel with boride coatings obtained after complex saturation with boron and copper without action EMF, duration saturation 5 h: a – initial state coatings (after saturation);b – after removal of 15 micron coating; c – after removal of 15 micron coating. Diffraction peaks Cu correspond crystallographic planes: (111) (200) (220) (311)*

At overlay EMF observed an increase thickness of boride coating and particular phase FeB. In the result on diffraction pattern of the surface layers boride coatings obtained after boriding in conditions activity EMF fixed availability phase FeB, (Fe,Cr)B and CrB (Fig. 3, a). After removing 12 micron coating was found next phase composition: FeB, (Fe,Cr)B, CrB and Fe_2B (Fig. 3, b). Removing yet 15 microns showed no change in the phase composition (FeB, (Fe,Cr)B, CrB and Fe_2B) (Fig. 3, c).

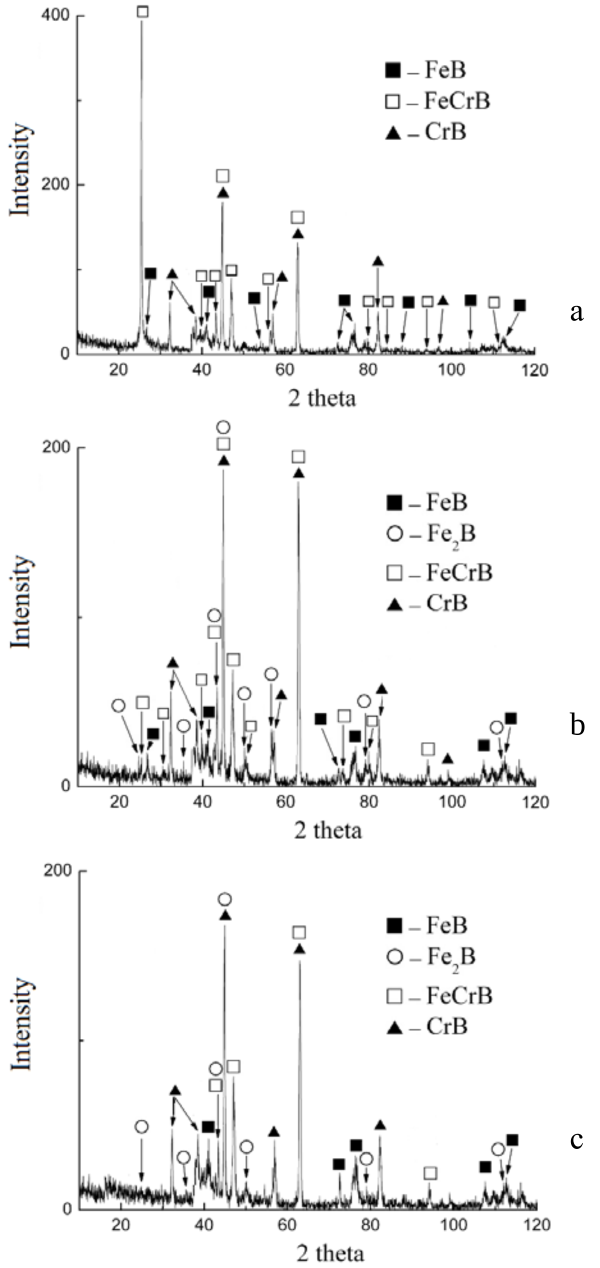

Fig.3: *Diffraction pattern taken from the surface of metastable austenite Cr-Mn-N steel with boride coatings obtained after boriding in conditions of action EMF, duration saturation 2 h: a – initial state coatings (after saturation); b – after removal of 12 micron coating; c – after removal of 15 micron coating*

After complex saturation boron and copper in conditions of action EMF, since formed coating greater thickness than at boriding, then on the diffraction pattern fixed phases FeB and Cu (Fig. 4, a). After removing 10 micron coating was found next phase composition: FeB, (Fe,Cr)B and Cu (Fig. 4, b), and after the removal yet 15 microns fixed phases FeB, (Fe,Cr)B, CrB and Cu (Fig. 4, c).

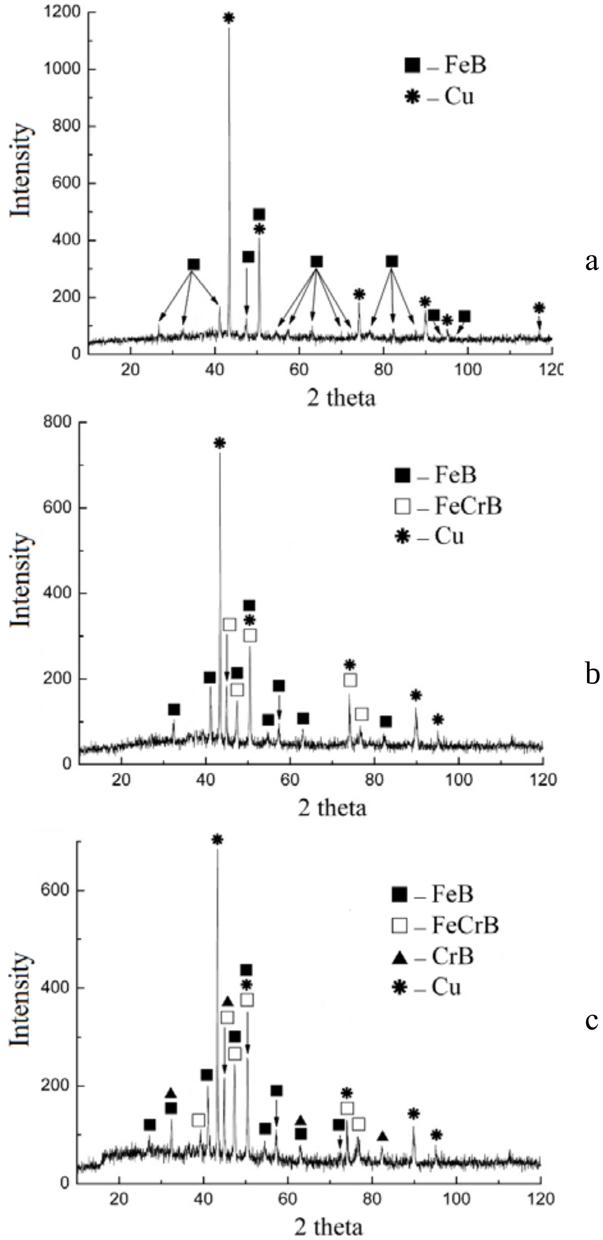

Fig.4: *Diffraction pattern taken from the surface of metastable austenite Cr-Mn-N steel with boride coatings obtained after complex saturation with boron and copper in conditions of action EMF, duration saturation 2 h: a – initial state coatings (after saturation);b – after removal of 10 micron coating; c – after removal of 15 micron coating. Diffraction peaks Cu correspond crystallographic planes: (111), (200), (220), (311), (222)*

Overlay ZMP leads to an increase of separate layers boride phases and redistribution of quantitative correlation of phases in the surface layers and changes of crystal lattice periods (Table.). At complex saturation with boron and copper volume fraction of copper in the surface layer based on the results X-ray diffraction studies amounted to 2%, while chemical - heat treatment with this overlay ZMP amount of copper in the surface phase component FeB increased to 5%.

Boride phases which are formed in the magnetic field have a lower volumes elementary crystal lattice (see Table.) and crystallites (coherent scattering region).

Table. *Parameters of the crystal lattice phase, coherent scattering region and quantitative phase analysis surface of metastable austenite Cr-Mn-N steel after boriding and complex saturation boron and copper in different physical – chemical conditions*

Process saturation	Phases	Parameters crystal lattice, Å			The volume of elementary crystal lattice ($Å^3$)	Contents phase (%)	Coherent scattering region, Å
		a	b	c			
Boriding without action EMF	FeB	4,176	5,554	3,007	70	19	1214 ±27
	FeCrB	14,619	7,287	4,213	449	11	122 ± 10
	CrB	2,994	7,820	2,895	68	69	174 ± 35
Boriding in conditions of action EMF	FeB	4,106	5,558	2,947	67	24	554 ± 14
	FeCrB	14,537	7,316	4,211	448	20	37,3 ± 8
	CrB	2,959	7,664	2,951	67	56	113,5 ± 8
Complex saturation with boron and copper without action EMF	FeB	4,105	5,540	2,950	67	76	1251 ± 41
	FeCrB	14,520	7,370	4,142	443	22	255 ± 9
	Cu	3,615	3,615	3,615	47	2	-
Complex saturation with boron and copper in conditions of action EMF	FeB	4,086	5,504	2,950	66	46	197 ± 15
	Cu	3,614	3,614	3,614	47	5	572 ± 81

In the process of forming boride coatings and coatings obtained after saturation with boron and copper occurs mass transfer between the surface material and an active gas environment, which is formed in the reaction space in during chemical reactions. These reactions can take place simultaneously or sequentially, not only in the volume of active gas phase, but at the interface of processed material, as well as within the latter. These reactions significantly affect the progress of the formation of coatings.

Of experimental studies preceded the definition of basic chemical reactions that take place in a closed reaction environment by means of thermodynamic analysis. As the initial components used boron carbide powder, copper oxide and teflon, and heat exposure which, in a closed reaction space leads to the passage of a large number of chemical reactions.

It was calculated more than 100 oxidation - restoration reactions that take place in the complex saturation steel boron or boron and copper. To determine the thermodynamic possibility of chemical reactions, calculated change in the thermodynamic potential chemical reactions at different values of temperature using HSC 5.1 CHEMISTRY.

In the result of research were singled groups reactions exchange type, in which the thermodynamic probability formation of interaction products is much higher than from other reactions (Fig. 6)

1. $14Fe + B_2O_3 + 3B_4C = 14FeB + 3CO(g)$
2. $28Fe + B_2O_3 + 3B_4C = 14Fe_2B + 3CO(g)$
3. $42Fe + 2B_2O_3 + 6B_4C = 14Fe_2B + 14FeB + 6CO(g)$

4. $7Cr + B_2O_3 + 3B_4C = 7CrB_2 + 3CO(g)$
5. $14Cr + B_2O_3 + 3B_4C = 14CrB + 3CO(g)$
6. $70Cr + 3B_2O_3 + 9B_4C = 14Cr_5B_3 + 9CO(g)$
7. $91Cr + 5B_2O_3 + 15B_4C = 14Cr_5B_3 + 14CrB + 7CrB_2 + 15CO(g)$

8. $7Mn + B_2O_3 + 3B_4C = 7MnB_2 + 3CO(g)$
9. $14Mn + B_2O_3 + 3B_4C = 14MnB + 3CO(g)$
10. $28Mn + B_2O_3 + 3B_4C = 14Mn_2B + 3CO(g)$
11. $49Mn + 3B_2O_3 + 9B_4C = 14Mn_2B + 14MnB + 7MnB_2 + 9CO(g)$

12. $3Cu_2O + 2Fe = 6Cu + Fe_2O_3$
13. $3Cu_2O + 2Cr = 6Cu + Cr_2O_3$
14. $2Cu_2O + Mn = 4Cu + MnO_2$
15. $7Cu_2O + B_4C = 14Cu + 2B_2O_3 + CO(g)$

16. $13{,}86Fe + B_2O_3 + 3B_4C + 14Cr = 12{,}6Fe_{1,1}Cr_{0,9}B_{0,9} + 3CO(g)$
17. $14Fe + B_2O_3 + 3B_4C + 14Cr = 14FeCrB + 3CO(g)$

As shown in Fig. 5 and Fig. 6, the thermodynamic probability formation boride phase FeB, Fe_2B, CrB, FeCrB increases with increasing temperature as evidenced by the decrease Gibbs free energy.

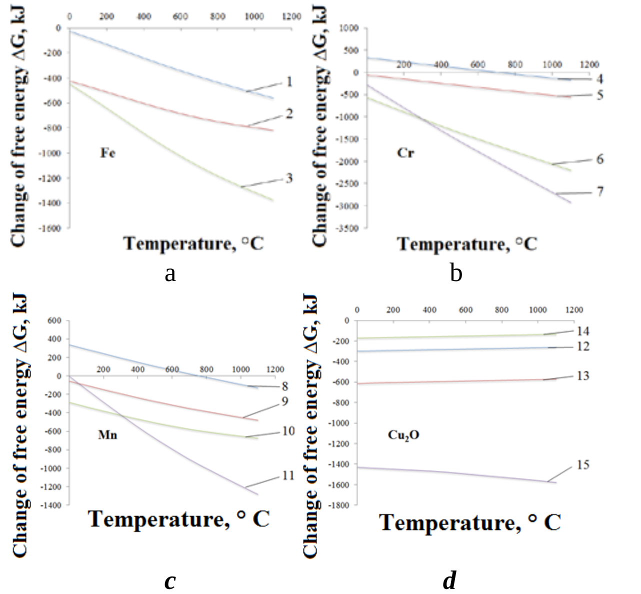

Fig.5: *The dependence change of the free energy of formation boride phases from temperature:a - Fe, b - Cr, c - Mn, d - Cu_2O Cu_2O (1 - 15 - number of thermochemical reactions).*

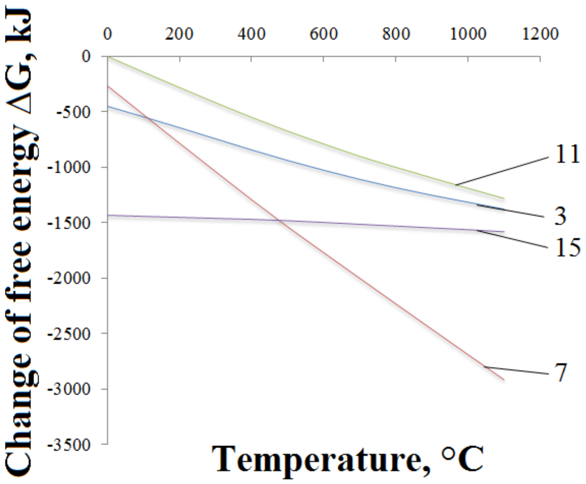

Fig.6: *The dependence change of the free energy of formation boride phase temperature Cu_2O (3, 7, 11, 15 - the number of thermochemical reactions)*

Using original function Crump obtained from Fick diffusion equation for one-dimensional task, was calculated diffusion coefficients B and Cu at during boriding and complex saturation boron and copper without using EMF and with its simultaneous action [5].

Established that the diffusion boriding without action EMF boron diffusion coefficient varies from $2{,}4 \cdot 10^{-7}$ cm^2/s in the surface layers (5 - 15 micrometers) to $1{,}1 \cdot 10^{-8}$ cm^2/s in layers, on the border with matrix (50 microns). Overlay magnetic field leads to an increase in the diffusion coefficient and boriding of simultaneous action EMF it varies from $1{,}3 \cdot 10^{-6}$ cm^2/s to $2{,}2 \cdot 10^{-7}$ cm^2/s.

Also calculated diffusion coefficient of copper at complex saturation boron and copper without action EMF and it simultaneous action. Established that the diffusion coefficient of copper at complex saturation boron and copper without action EMF varies from $7{,}8 \cdot 10^{-11}$ cm^2/s to $8{,}8 \cdot 10^{-12}$ cm^2/s, while the imposition of a magnetic field leads to an increase diffusion coefficient of copper in the surface layer of material, while diffusion coefficient varies from $4{,}1 \cdot 10^{-10}$ cm^2/s to $2{,}8 \cdot 10^{-11}$ cm^2/s.

4. Conclusions

At simultaneously saturation metastable austenite Cr-Mn-N steel boron or boron and copper on the surface is formed coating, which is composed with borides FeB, FeCrB, CrB and Fe_2B, and at complex saturation with boron and copper also is probable presence in the diffusion layer copper accumulations. According to Fig. 5 (d) Cu_2O can react with Fe, Cr, Mn, B_4C with form atomic Cu, and which diffuses into the surface layers of diffusion boride coating.

Layers X-ray analysis found the phase composition boride coatings and coatings obtained at complex saturation with boron and copper on metastable austenite Cr-Mn-N steel without and in conditions of action EMF. Found a correlation between the phase composition boride phases and thermodynamic calculations course of chemical reactions at diffusion boriding and complex saturation with boron and copper steels. Applying an external magnetic field leads to an increase layers boride phases in the coating. Observed the increase quantitative content phase FeB and on the diffraction pattern surface layers boride coatings obtained after boriding in conditions of action EMF fixed phase FeB, (Fe,Cr)B and CrB, and after complex saturation with boron and copper in conditions of action ZMF - FeB and Cu. It is established that the use of EMF leads to an increase diffusion coefficients of boron and copper in order..

5. References

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