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THE INFLUENCE OF THE pH VALUE AND THE CATION COMPOSITION OF DISPERSION MEDIUM ON THE FORMATION OF IRON-OXYGEN STRUCTURES ON STEEL SURFACE

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The peculiarities of the formation of iron-oxygen structures on steel surface due to its contact with aqueous dispersion medium within a wide range of pH values and in presence of cobalt and silver have been studied by X-ray diffraction in situ. It has been shown that well crystallized cobalt- and iron-containing spinel ferrites are formed at neutral pH value of aqueous medium. The contact of steel surface with alkaline medium results in formation of weakly crystallized iron oxyhydroxides. The structure of lepidocrocite is formed on steel surface due to its contact with acid dispersion medium in absence of metal ions such as cobalt and silver.

INTRODUCTION

The problem of nowadays which is formulated for scientists who are studying the systems with nanosized objects is the directional obtaining of the individual particles with particular physicochemical, colloid-chemical and mineralogical properties [1]. When introducing an insignificant addition of such particles into macrosystems and composite materials of different nature they acquire new physicochemical properties [2]. The nanosized particles with para- and ferrimagnetic properties are the most required for medical and biological aims, for example as magnetic carriers for direct delivery of medical preparations in a magnetic field [3], target therapy [4], diagnostics of a range of diseases [5].

Numerous methods of formation of the iron-oxygen particles of different crystallographic modifications include the electrochemical synthesis on the surface of iron (steel) [6] and inert (gold, silver, platinum) [7] electrodes. The advantages of such systems lie in limiting the admixture quantity in iron oxide and controlling the process of phase formation. Addition of different compounds such as metal salts into the system gives a possibility to get the particles of spinel ferrites [8] or 'core-shell' composites [9] that have wider variety of use than simple iron oxides and hydroxides. A study on the initial stage of formation of the iron-oxygen structures on steel surface should allow us to expand the spectrum of iron oxides, oxyhydroxides, and spinel ferrites and to define the most important parameters of synthesis controlling this process.

The present work is an extension of the investigation of the processes of phase formation on steel surface by its contact with air oxygen and aqueous dispersion medium. In our previous article [10] a process was shown of the formation of surface iron-oxygen particles caused by the contact of steel with ferric and ferrous aqueous solutions. The results showed the formation of the Fe(II)-Fe(III) layered double hydroxides at the initial stage of the phase formation that were transformed into structures of magnetite, goethite or lepidocrocite depending on the presence of oxidant and ferrous or ferric irons in dispersion medium. The aim of this work is to study the process of the formation of the surface iron-oxide structures due to the contact of steel surface with aqueous solution within a wide pH range and in the presence of cobalt chloride and silver nitrate in aqueous solution.

EXPERIMENTAL

The process of the formation of different iron-oxygen structures on steel surface have been carried out by procedure described in [10]. For the experiment the carbon steel was used containing %: C – 0.14-0.22; Si – 0.05-0.15; Mn – 0.4-0.65; Cr – 0.3; Ni – 0.3; P – 0.04; S – 0.05; N – 0.01. The main method of investigation was X-ray diffraction *in situ*. An additional method was scanning electron microscopy. The dispersion media were aqueous solutions within wide range of pH values (from 1.5 to 11.0) prepared by addition of definite quantities of hydrochloric acid or sodium hydroxide solutions into dispersion medium. For the preparation of the cobalt-containing solutions, cobalt chloride was used with cobalt concentration of 100 mg/dm^3. And for silver-containing solution, silver nitrate was chosen with silver concentration of 1 mg/dm^3. The range of pH values with added cations was from 2.5 to 11.0.

The process of formation of the iron-oxygen structures was carried out to the stationary state of the system that meant the constant phase composition and mass of the surface structures as well as the chemical composition of the dispersion medium. For the chemical analysis of the dispersion medium, the standard procedure was used [11].

RESULTS AND DISCUSSION

The influence of the pH value on the formation of iron-oxygen structures on steel surface. The study on the process of formation of the iron-oxygen structures on steel surface within a wide range of pH value was carried out considering the state of ferrous and ferric iron in dispersion medium. Our investigation [12] shows five characteristic ranges of pH values defining the processes of arising and developing iron-oxygen structures of different crystallographic modifications which run due to various mechanisms. At the same time, on the basis of experimental data [13] and the analysis of the thermodynamic functions of the reaction of the phase formation [8] a supposition was made about the behavior of the system Fe^0 (Steel) – H_2O –O_2 capable to change the pH values of the initial solution in the wide range of pH to neutral value. Direct testing of this factor using specified indicators (nitrasin yellow and phenolic red) shows the pH value in the range from 7.0 to 9.0 on steel surface. So, the XRD-investigation of the process of phase formation on steel surface *in situ* should allow us defining the degree of the influence of the pH value in the bulk of dispersion medium on the surface composition of iron-oxygen structures and their phase transformations.

Analysis of XRD-data shows the formation mainly of the phases of Green Rust, lepidocrocite and magnetite on steel surface. An additional phase is goethite.

At the pH value of 1.5 in aqueous dispersion medium both ferric and ferrous iron as well as mainly mononuclear ferric hydroxocomplexes – $Fe(OH)_2^+$ and $Fe(OH)^{2+}$ can be present. XRD-data show that under such condition as the initial phase after 2 hours of carrying out the process lepidocrocite (020) and (120) is formed. The intensity and quantity of the X-ray reflexes gradually increase. Lepidocrocite remains as the only phase up to the stationary state of the system (72 h). By the increasing the initial pH value to 4.0 in dispersion medium, ferric iron forms the separate phase of amorphous ferric hydroxide and ferrous iron is still in the form of hydrated cations. After one hour of the contact of steel with dispersion medium on its surface, the phase of lepidocrocite is formed. Magnetite is reflected on XRD-pattern after 5 hours and its intensity increases more than three times to the stationary state of the system (48 h). At the pH value of 6.5 in the system, the hydrolysis starts of the ferrous iron with the formation of the $FeOH^+$ complex. After 2 hours, lepidocrocite appears, and after 5 ones, magnetite appears on the surface. The accumulation of magnetite on steel surface under such a condition is faster than the accumulation of lepidocrocite. The system is stabilized after 48 hours of contact. At the pH = 11.0, ferric and ferrous hydroxides form the precipitate in the system. As XRD-data show, the surface structures are weakly crystallized and diffraction patterns show only some reflexes of Green Rust I and low intensity peaks of lepidocrocite. After 24 hours of the phase formation on steel surface, two peaks appear of magnetite (311) and (220) which intensity insignificantly grows. Figure 1 shows the kinetic regularities of changing of the % mass of lepidocrocite (Fig. 1*a*) and magnetite (Fig. 1b) depending on the value of initial pH of dispersion medium.

On the base of the data obtained, the optimum condition for direct formation of the iron oxyhydroxide – lepidocrocite is acid dispersion medium and for magnetite formation is neutral dispersion medium.

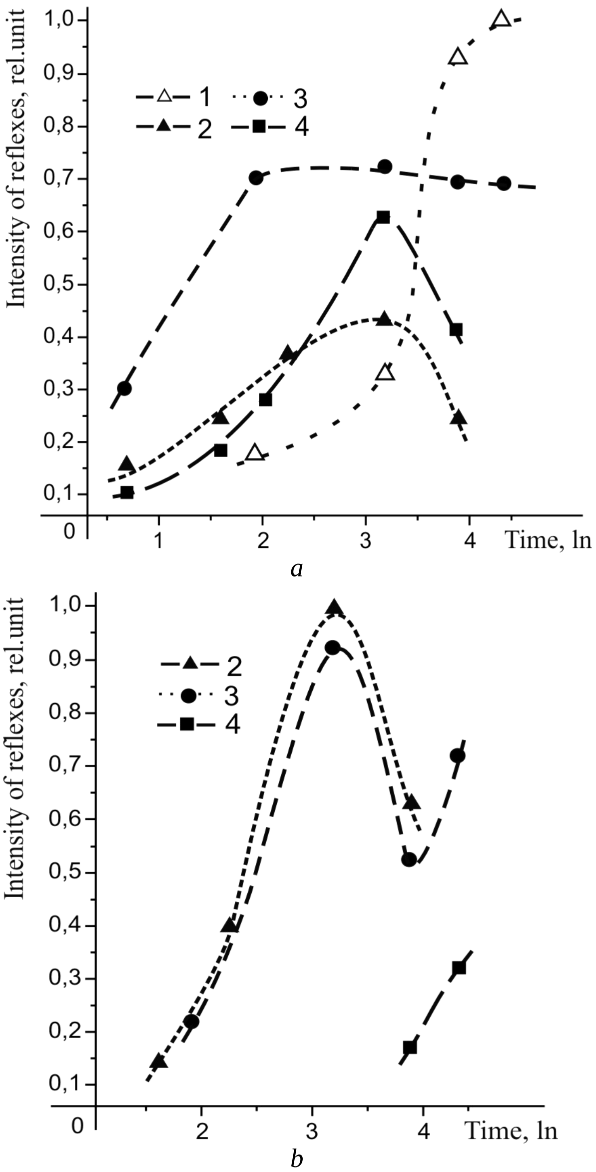


Fig. 1. Intensity of X-ray reflexes: *a* – lepidocrocite, *b* – magnetite formed on steel surface due to its contact with dispersion medium at initial pH values: *1* – 1.5; *2* – 4.0; *3* – 6.5; *4* – 11.0

The possible reactions can occur in such conditions are: for oxyhydroxides

$$2Fe(OH)_2 + 0{,}5O_2 \rightarrow 2FeOOH + H_2O \qquad (1)$$

$$Fe(OH)^{2+} + OH^- \rightarrow Fe(OH)_2^+ \rightarrow$$
$$\rightarrow FeOOH + H^+ \qquad (2)$$

$$Fe(OH)_2^+ + 2Fe(OH)_2 + 0{,}5O_2 \rightarrow$$
$$\rightarrow 3FeOOH + H_2O + H^+ \qquad (3)$$

and for magnetite (or spinel ferrite):

$$2Fe(OH)_2 + Me^{2+} + 1/2O_2 \rightarrow$$
$$\rightarrow MeFe_2O_4 + H_2O + 2H^+ \qquad (4)$$

$$2Fe(OH)^+ + Me(OH)_2 + 1/2O_2 \rightarrow$$
$$\rightarrow MeFe_2O_4 + H_2O + 2H^+ \qquad (5)$$

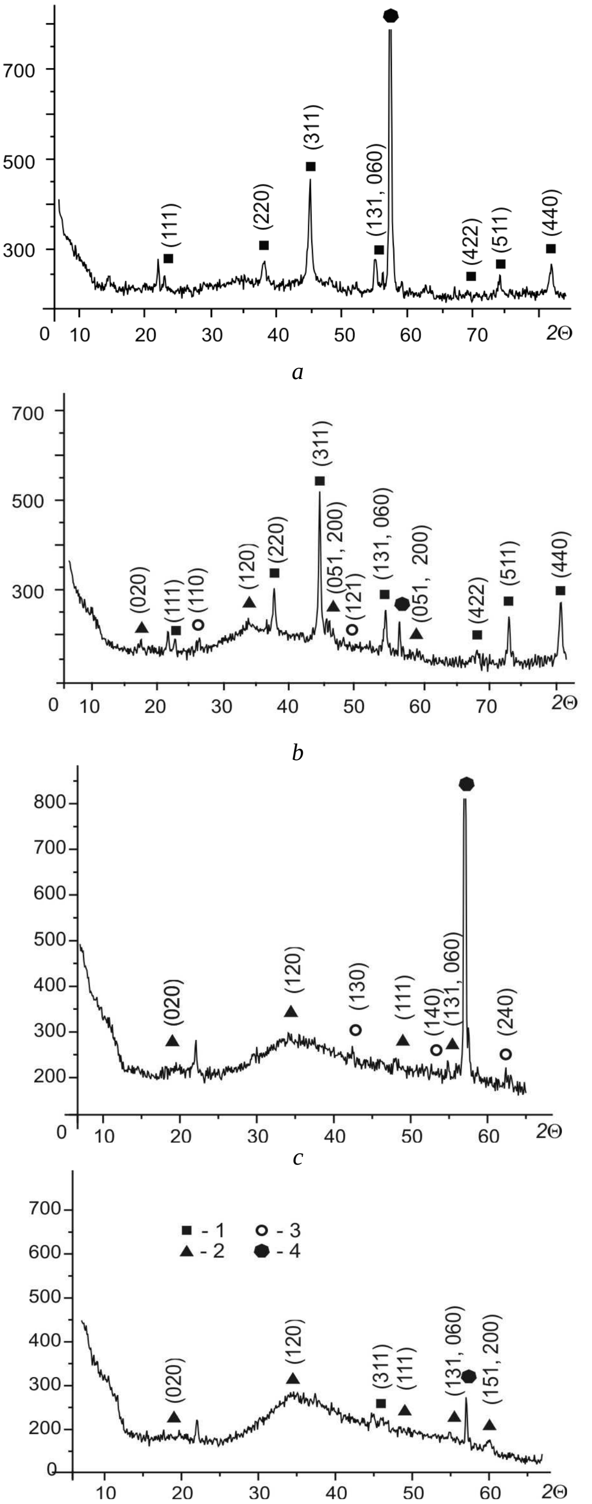
$$2Fe(OH)_2 + Me(OH)_2 + 1/2O_2 \rightarrow$$
$$\rightarrow MeFe_2O_4 + 3H_2O \qquad (6)$$

where Me(II) = Fe(II), Co(II).

The absence of the vivid reflexes on the XRD-patterns of Green Rust can indicate that this structure is not accumulated on steel surface and undergoes the phase transformation immediately after formation of lepidocrocite or magnetite phases. The development of the lepidocrocite or magnetite can run either independently from each other (at pH = 6.5) or they are the chain links of the phase transformation: lepidocrocite–magnetite (at pH=4.0).

The formation of the iron-oxygen structures on steel surface due to its contact with the cobalt chloride aqueous solution. The addition of cobalt ions into the dispersion medium influences the phase composition of ultra disperse iron-oxygen particles and leads to the formation the iron-cobalt spinel ferrite as an additional phase [14]. This process to a considerable degree depends on the pH value of the dispersion medium contacting with steel surface and does not significantly depends on the quantity of cobalt ions in the solution. Cobalt ions undergo to hydrolysis within the range of pH 6.6–9.2 (by $C_{Co(II)} = 1$ mol/dm^3) and at the range of pH 9.2–14.1 cobalt remains as hydroxide in the system [15].The investigation of the phase composition of the surface structures was carried out depending on the speciation of cobalt in the dispersion medium.

As XRD-data show (Fig. 2*a*), in the presence of cobalt ions on steel surface, spinel ferrite (311) is formed during one hour and its intensity picks increase during 24 hours. The lepidocrocite phase appears only after 24 hours from the beginning of the process of phase formation (Fig. 2*b*). During next 24 hours the intensity of spinel ferrite reflexes slowly decreases and that of lepidicrocite reflexes increases. The possible mechanism of this process is the destruction of spinel ferrite, for example by oxidizing ferrous iron in the lattice. When the dispersion medium contains cobalt hydroxide, the formation of surface structures is connected with that of weakly crystallized iron oxyhydroxides – lepidocrocite and goethite (Fig. 3*c*). The phase of spinel ferrite is identified only after 24 hours of phase formation (Fig. 2*d*).



a

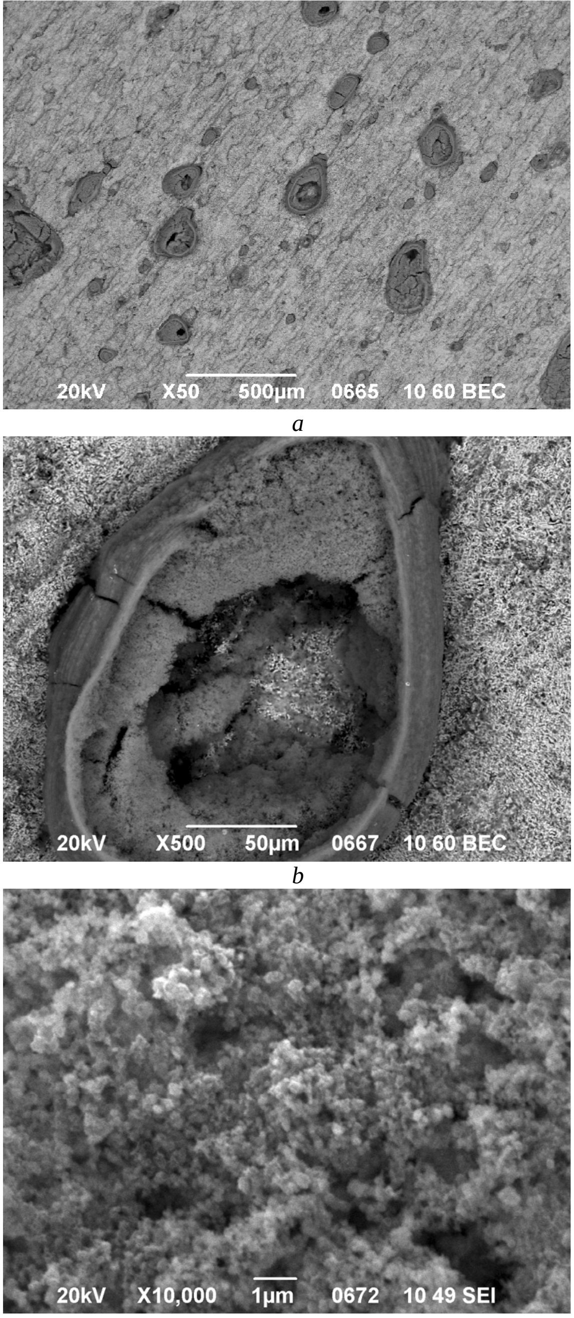
b

c

d

Fig. 2. XRD-data of surface structures formed on steel surface due to its contact with cobalt-containing dispersion medium: *a* – pH=6.5 after 4 h of contact of steel with solutions; *b* – pH=6.5 after 24 h; *c* – pH=11.0 after 1 h; *d* – pH=11.0 after 24 h. Numbers correspond to the phases: *1* – cobalt ferrous spinel ferrite, *2* – lepidocrocite γ-FeOOH; *3* – goethite α-FeOOH, *4* – iron Fe^0

Figure 3 shows the SEM-images of steel surface. There are the areas of the iron-oxygen structures appearing on the defects of surface (Fig. 3*a*, *b*) and the initial iron-oxygen structure (Fig. 3*c*). The absence of the Green Rust reflexes on the X-ray patterns can be explained by its location on the defects of steel surface (in the pittings) and its relatively low concentration (lower than the limit of sensitivity of X-ray diffraction).



a

b

c

Fig. 3 The localization of the centers of formation the initial iron-oxygen structures on steel surface due to its contact with cobalt hydroxide (*a*, *b*) and initial iron-oxygen structure (*c*)

It should be noted that under experimental conditions the structure of spinel ferrite can contain ferrous iron as well as cobalt cations. But the identity (similarity) of interplanar spacing of magnetite and cobalt spinel ferrite makes it impossible to use X-ray diffraction to divide these structures. Therefore to define the ratio Fe:Co in the structure of spinel ferrite the X-ray fluorescence analysis was used which allowed us to estimate the iron and cobalt content in the phase. The influence of the cobalt concentration in dispersion medium on the chemical composition of spinel ferrite was studied within a wide range of $C_{Co(II)}$ (from 1 to 1000 mg/dm^3). The results show that in all the samples the cobalt to iron ratio is of 7–13% to 93–87%, respectively. So, by varying cobalt concentration in neutral dispersion medium, it is impossible to form nanosized spinel ferrite particles containing different amounts of ferrous iron and cobalt. The formation mechanism of spinel ferrites under experimental conditions is described by the reactions (4)–(6) related to the formation of magnetite on steel surface contacting with aqueous solution within pH range of 4.0-6.5 (in the bulk) or by addition of ferrous iron into the system at neutral dispersion medium [10].

The formation of the iron-oxygen structures on steel surface due to its contact with aqueous solution of silver nitrate. Salt adding into dispersion medium contacting with steel leads to the formation of iron-oxygen phases on its surface and can also lead to reducing silver on the surface of iron oxides [16]. The formation of surface iron-oxygen structures in presence of $AgNO_3$ in dispersion medium depends on hydrolysis of silver characterized by formation of silver oxide Ag_2O and occurs at pH values of 6.2 (C_{Ag+}=1 mol/dm^3) and 8.2–11.2 (C_{Ag+}=0.01 mol/dm^3) [15]. The partial solubility of silver oxide in aqueous results in existence of other forms of silver: Ag^+, AgOH and $Ag(OH)_2^-$ [17]. An investigation of the formation of the surface structures in presence of silver was carried out for its cationic and hydroxide forms. As XRD-data show, in the presence of silver ions in dispersion medium the phases of lepidocrocite and magnetite are formed on steel surface after 1 hour of contact (Fig. 4*a*). The intensity of the magnetite reflexes grows faster than that of lepidocrocite but at the stationary state of the system it gets down (Fig. 4*b*).

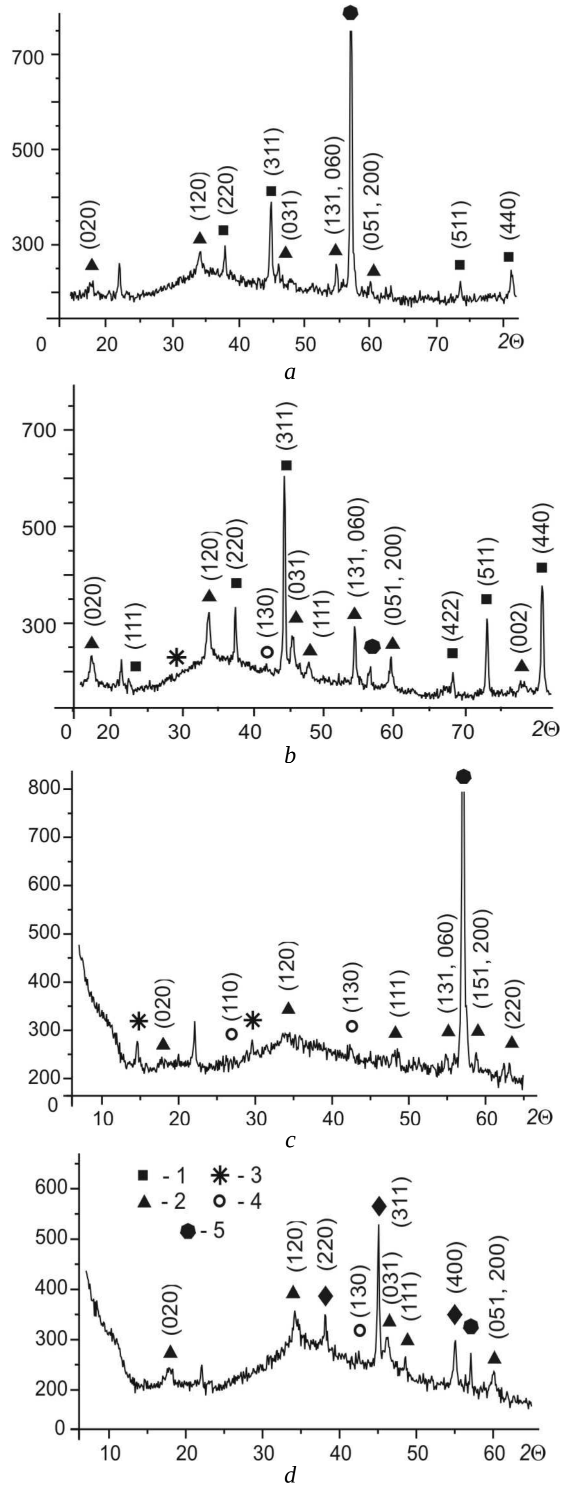
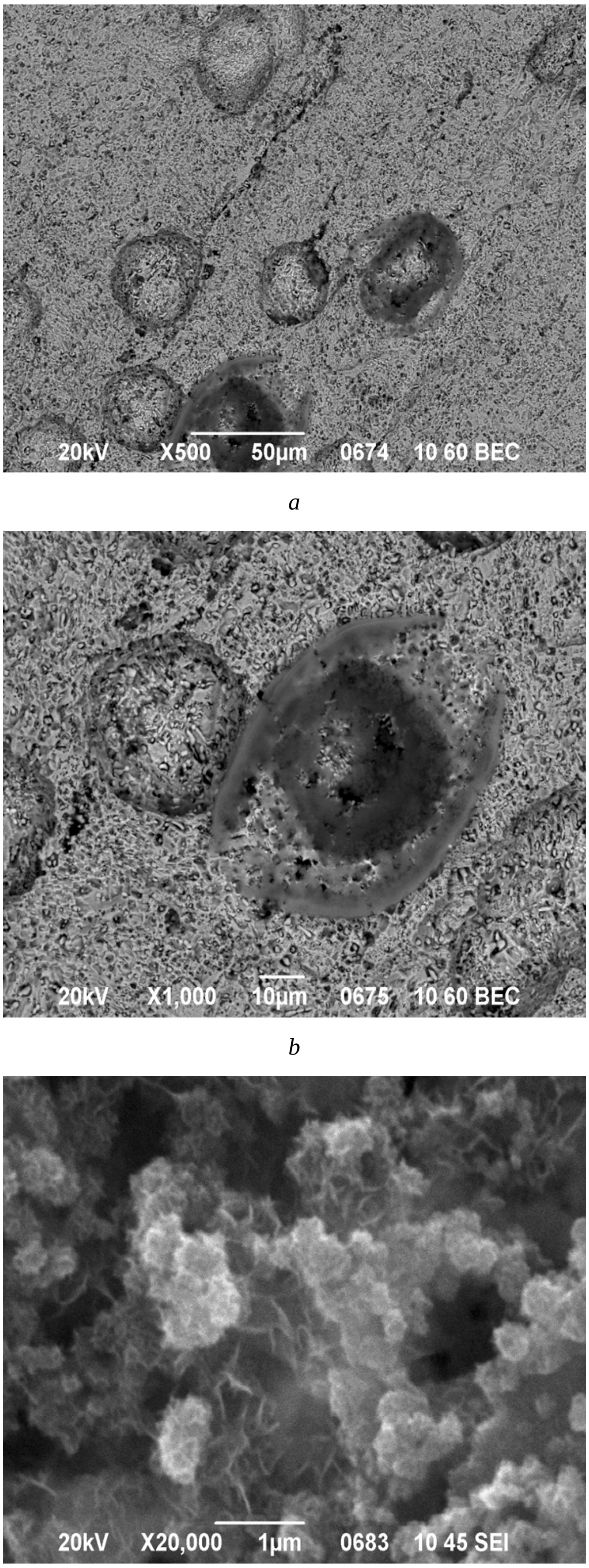


Fig. 4. XRD-data of surface structures formed on steel surface due to its contact with silver-containing dispersion medium: *a* – pH=6.5 after 5 h of contact of steel with solutions; *b* – pH=6,5 after 48 h; *c* – pH= 11.0 after 1 h; *d* – pH=11.0 after 70 h. Numbers correspond to the phases: *1* – magnetite $FeFe_2O_4$, *2* – lepidocrocite γ-FeOOH; *3* – Green Rust I; *4* – goethite α-FeOOH; *5* – iron Fe^0



a

b

c

Fig 5. The localization of the process of formation of iron-oxygen structures on the surface defects (*a*), steel surface (*b*), the structure of Green Rust I (*c*)

Due to the interaction of the aqueous solution of silver hydroxide with steel surface, XRD-pattern shows the reflexes of lepidocrocite, goethite, and Green Rust I (Fig. 4*c*). Interplanar spacing of Green Rust I allows us to identify the structure obtained as hydroxycarbonate GR (CO_3^{2-}) [18]. After 24 hours of conducting the process on steel surface, the phase of magnetite is identified with intensity reaching a maximum at stationary state of the system (70 hours). Figure 5 shows SEM-images of the steel surface with areas where the iron-oxygen structures appear.

The mechanism of formation of iron-oxygen structures on steel surface, probably, consists in the formation of ferrous hydroxide and its transformation to the Fe(II)–Fe(III) layered double hydroxides and then to phase of lepidocrocite and magnetite:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2;$$

$$6Fe(OH)_2 + 0{,}5O_2 + CO_2 + 2H_2O \rightarrow \rightarrow Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3\cdot 2H_2O;$$

$$4Fe^{2+} + 2Fe^{3+} + 12OH^- + CO_3^{2-} + 2H_2O \rightarrow \rightarrow Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3\cdot 2H_2O;$$

$$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3\cdot 2H_2O + O_2 \rightarrow \rightarrow 6\gamma\text{-}FeOOH + H_2CO_3 + 4H_2O;$$

$$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3\cdot 2H_2O + 0{,}5O_2 \rightarrow \rightarrow 2FeFe_2O_4 + H_2CO_3 + 7H_2O;$$

$$2\gamma FeOOH + Fe(OH)_2 \leftrightarrow FeFe_2O_4 + 2H_2O;$$

So, the optimum condition for the formation of magnetite particles on steel surface in presence of silver ions is the neutral dispersion medium and relatively low concentration of silver (0.1–1 mg/dm^3). Evidently the process of the formation of lepidocrocite and magnetite is connected with phase transformation of the Fe(II)–Fe(III) LDH formed on steel surface as initial structures.

CONCLUSIONS

The investigation of the formation of iron-oxygen structures on steel surface due to its contact with aqueous dispersion medium within the pH range of 1.5 to 11.0 shows a dependence of the phase composition on the conditions of carrying out the process. So, in acid dispersion medium on steel surface well crystallized iron oxyhydroxide – lepidocrocite is formed; in weak-acid and neutral medium the main iron-oxide structure is magnetite. In alkaline dispersion medium the surface structures of oxyhydroxides are lepidocrocite and goethite characterized by weak crystallization.

An addition of cobalt cations into dispersion medium on steel surface leads mainly to the formation of the structure of cobalt spinel ferrite. The addition of cobalt hydroxide into dispersion medium does not lead to the formation of spinel ferrite. The final products of phase formation are weakly crystallized iron oxyhydroxides.

The contact of steel surface with aqueous solution of silver nitrate leads to the formation of magnetite and in the presence of silver hydroxide, the typical surface structures are weakly crystallized iron oxyhydroxides.

The results of the research allows us to detect the optimum conditions for the formation of the structure of lepidocrocite on steel surface in acid dispersion medium and that of magnetite in neutral dispersion medium in the absence of cations in both cases. The cobalt spinel ferrite is formed in the presence of cobalt ions in neutral dispersion medium. All the structures formed in alkaline dispersion medium are weakly crystallized iron oxyhydroxides.

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Вплив величини pH і катіонного складу дисперсійного середовища на утворення залізо-кисневих структур на поверхні сталі

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Методом рентгенофазового аналізу in situ досліджено особливості формування залізо-кисневих структур на поверхні сталі при її контакті з водним дисперсійним середовищем у широкому діапазоні значень pH та в присутності кобальту і срібла. Показано, що добре окристалізовані структури феришпінелі – магнетиту і фериту кобальту утворюються при нейтральних значеннях pH середовища. При контакті сталі з лужним дисперсійним середовищем на поверхні у всіх випадках утворюються слабко окристалізовані оксигідроксиди заліза. Структура лепідокрокіту утворюється на поверхні сталі при її контакті з кислим дисперсійним середовищем за відсутності катіонів.

Влияние величины pH и катионного состава дисперсионной среды на формирование железо-кислородных структур на поверхности стали

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Методом рентгенофазового анализа in situ исследованы особенности формирования железо-кислородных структур на поверхности стали при ее контакте с водной дисперсионной средой в широком диапазоне значений pH и в присутствии кобальта и серебра. Показано, что хорошо окристаллизованные структуры ферришпинели – магнетита и феррита кобальта формируются при нейтральных значениях pH среды. При контакте стали со щелочной дисперсионной средой на поверхности во всех случаях образуются слабо окристаллизованные оксигидроксиды железа. Структура лепидокрокита образуется на поверхности стали при ее контакте с кислой дисперсионной средой в отсутствие катионов.