EFFECT OF TEMPERATURE ON KINETIC REGULARITIES OF FORMING NANOSIZED PARTICLES ON STEEL SURFACE CONTACTING WITH AQUEOUS DISPERSION MEDIUM

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The specific character of forming nanosized structures on steel surface contacting with air and aqueous dispersion medium in the range of temperatures from 3 to 70 °C has been studied. The development of iron-oxygen structures leads to morphological γ-row. As the initial structure the hydroxycarbonate Green Rust under the most conditions has been found. Two branches of phase transformation scheme under full and limited oxidation have been suggested. The optimum condition for forming lepidocrocite is low temperatures (25–35 °C) and for forming magnetite is middle ones (50 °C). The kinetic regularities of the XRD-pick amounts of lepidocrocite and magnetite from temperatures were calculated.

INTRODUCTION

The interest in nanosized ferromagnetic materials leads to the search of new methods of their synthesis. Our investigations [1] are directed to getting nanosized iron-oxygen structures of different crystallographic modifications in the system of a rotating steel electrode which alternately contacts with aqueous dispersion medium and air oxygen. The most important parameters of the phase formation processing in such a system are chemical composition and pH value of dispersion medium, presence of oxidant and temperature. The influence of temperature on the process of forming nuclear particles of protolepidocrocites (Green Rusts) and ferrihydrite in the St3–H_2O–O_2 system was presented in our previous work [2]. The understanding of the role of steel surface attracts our attention to this area of nucleation and growth of iron-oxygen structures. The surface processes on steel surface when it contacts with aqueous solution containing ferric and ferrous iron were studied in [3]. The results showed the presence of hydroxysulphate Green Rust on steel surface as the initial phase which further developed in the range of γ-row iron-oxygen structures. Addition of cobalt and silver cations into dispersion medium does not change the phase composition of nanosized precipitates on steel surface. Spinel ferrite structures are mainly the products of the reaction in neutral medium, but increasing the pH value

leads to forming weakly crystallized iron oxyhydroxides, such as lepidocrocite γ-FeOOH and goethite α-FeOOH [4]. So, pH rate plays a definite role in the mechanisms of the phase formation, but it is limited by the electrochemical properties of the system [5]. One of the determinate parameters of carrying out the process of the phase formation can be the temperature on steel surface, specifically due to its influence on hydrolysis and oxidation of ferrous species [6, 7].

The influence of the temperature on the phase composition of surface structures and kinetic regularities of their development on steel surface were chosen as the purpose of the present investigation.

MATERIALS AND METHODS

The method of forming iron-oxide surface structures was described in [3, 4]. We use the rotating steel disk for creating a plug-in steel electrode contacting with air oxygen and aqueous solution. The temperature conditions are provided by application of TS-1/80-SPU thermostat. The process of the phase formation is carried out at the following temperatures: 3, 10, 25, 35, 50 and 70 °C. As dispersion medium the distilled water and cobalt chloride water solution with $C_{Co(II)} = 100$ mg/dm^3 are chosen. The pH value for all systems is 6.5. The process of the phase formation leads to the stationary state of the system.

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As the main investigation methods of X-ray diffraction *in situ*, scanning electron microscopy (SEM) and math methods of data-processing operation are used.

RESULTS AND DISCUSSION

XRD-data show the structures of iron-oxygen morphological γ-row which are nucleated and grown on steel surface in the temperature range from 3 to 70 °C. Fig. 1 shows certain XRD patterns of the structures formed at different temperatures.
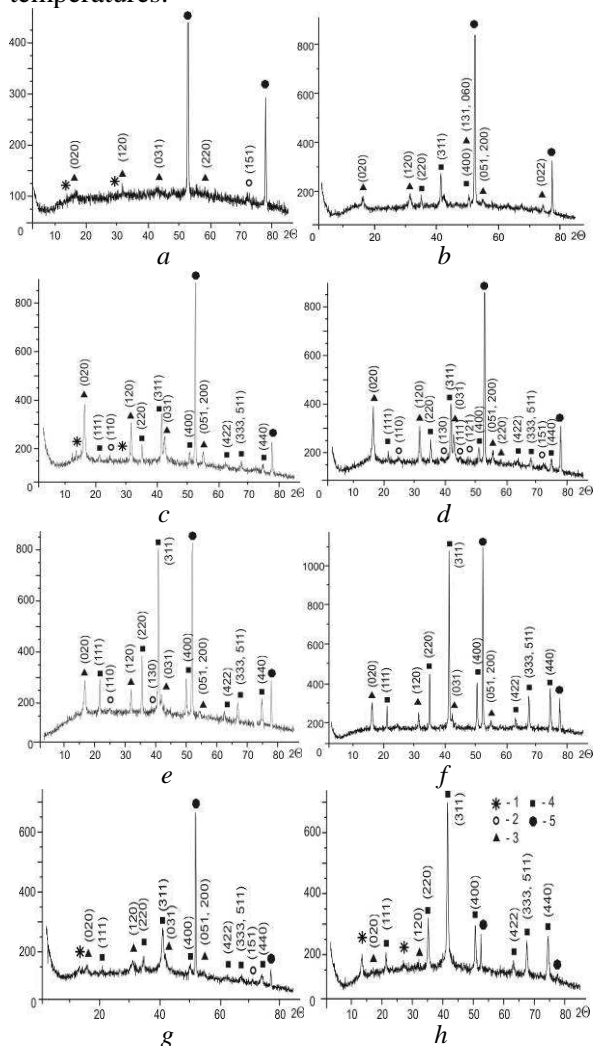

Fig. 1. XRD patterns of iron-oxygen structures which are formed on steel surface contacting with water dispersion medium in the temperature range from 3 to 70 °C are the following: *a* – 3 °C 72 h; *b* – 10 °C 72 h; *c* – 25 °C 48 h; *d* – 35 °C 10 h; *e* – 50 °C 21 h; *f* – 70 °C 18 h; in presence cobalt ions: *g* – 10 °C 75 h; *h* – 50 °C 72 h. Numbers correspond to the phases: *1* – hydroxycarbonate Green Rust; *2* – goethite α-FeOOH, *3* – lepidocrocite γ-FeOOH; *4* – spinel ferrite (magnetite $FeFe_2O_4$ or cobalt ferrous spinel

ferrite); *5* – iron Fe^0

So, at 3 °C weak reflexes of lepidocrocite γ-FeOOH as the only phase are present on steel surface during the whole experiment. The temperature increasing to 10 °C results in appearing magnetite $FeFe_2O_4$ as the second phase after 48 h of the process carrying out. At 25 °C the reflexes of lepidocrocite and magnetite are shown on XRD-pattern after 2 h of the process. During 72 h the reflex intensity of both phases increases step-by-step. At 35 °C the quantity of lepidocrocite increases during 10 h, and then it does not change. The quantity of magnetite grows during 48 h and then it decreases after 72 h of the process. Their first reflexes appear after 2 h contact of steel surface with aqueous medium. Under such conditions the phases of Green Rust I and goethite α-FeOOH are present in the composition of surface structures. At 50 °C the intensity of lepidocrocite reflexes gradually increases and the intensity of magnetite reflexes achieves its maximum after 48 h of contact and then it insignificantly decreases. At 70 °C the following three phases are formed in the system: lepidocrocite, magnetite and a small amount of goethite. The quantity of lepidocrocite and magnetite grows during 9 h and 18 h respectively; in both cases it reaches its maximum and then decreases. The biggest goethite picks are noticed on XRD pattern after 9 h of the process; its intensity decreases and then later does not change. In presence of cobalt ions, the structure of cobalt ferrous spinel ferrite is dominant. The content of lepidocrocite and Green Rust is insignificant.

The amount (in relative units) of lepidocrocite and magnetite picks after 5 and 48 h of the phase formation are shown in Fig. 2a and Fig. 2b respectively. The reflexes of lepidicrocite (120) and magnetite (311) were chosen for comparing. The points related to cobalt spinel ferrite are presented in Fig. 2b for comparing with ferrous spinel ferrite (magnetite). As a result of regularities presented the process of lepidicrocite formation does not depend on the temperature during initial five hours of experiment, but after 48 h the content of lepidocrocite sharply decreases in the temperature range from 35 to 70 °C. On the contrary, the content of magnetite depends on the temperature of the process carrying out. So, after 5h the differences in picks intensity of magnetite depending on the

temperature are not big, but after 48h this regularity grows to 50 °C and then goes down.

The analysis of the system containing cobalt ions shows some similarity in the behaviour of magnetite and ferrous cobalt spinel ferrite. So, at 50 °C during 5h and 48h the intensity of spinel ferrite pick (311) in presence of cobalt is only a little lesser (Fig. 2*b*).
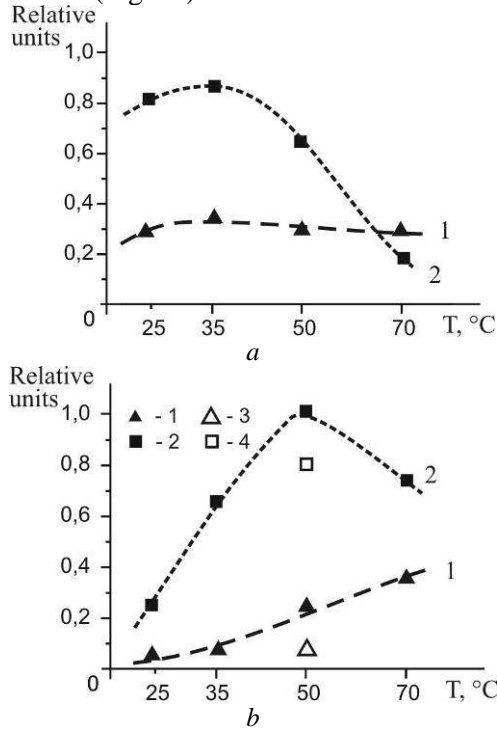

Fig. 2. The temperature regularities of the pick intensity on XRD patterns: *a* – lepidocrocite; *b* – spinel ferrites. Numbers correspond to: *1* – 5 h; *2* – 48 h, *3* – cobalt ferrous spinel ferrite, 5 h; *4* – cobalt ferrous spinel ferrite, 48 h

Fig. 3 shows the morphology, size and shape of the iron-oxides particles formed at different temperatures on steel surface. TEM images (Fig. 3*a*) show a Fe(II)-Fe(III) LDH as initial phase on steel surface. That structure belongs to the first type and presence of carbonate-ions and XRD pattern indicate it as hydroxycarbonate Green Rust $Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O$. Formation of such structure under experimental conditions is possible during saturation of the system with ferrous iron, its slow oxidizing on steel surface, the system contact with air, and as a result presence of carbonate species in it. The above mentioned conditions were described in [8].

The lepidocrocite particles are needle-shaped (Fig. 3*b*). At a higher temperature of the phase formation, the needles of lepidocrocite would be more deformed (Fig. 3*c, d*). The magnetite particles are of

spherical form and their size is ~50–80 nm (Fig. 3*e*). The cobalt ferrous spinel particles are shown in Fig. 3*f*.

a   *b*
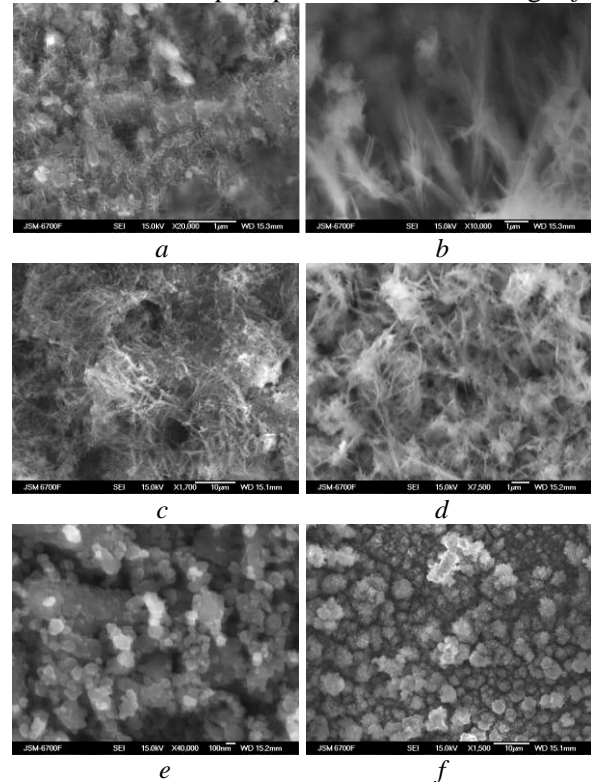
c   *d*

e   *f*

Fig. 3. The iron-oxygen structures formed on steel surface in the temperature range from 3 to 70 °C: *a* – hydroxycarbonate Green Rust (10 °C, 75 h), *b* – lepidocrocite (10 °C, 75 h); *c* – lepidocrocite (25 °C, 10 h); *d* – lepidocrocite (50 °C, 5 h); *e* – magnetite (70 °C, 5 h); *f* – cobalt ferrous spinel ferrite (25 °C, 10 h)

The analysis of the mechanisms of the phase formation on steel surface shows a few ways possible under experimental condition. The most probable way is connected with the formation of ferrous hydroxide $Fe(OH)_2$ or Fe(II)-Fe(III) LDH and their transformation to lepidocrocite or magnetite (Fig. 4).
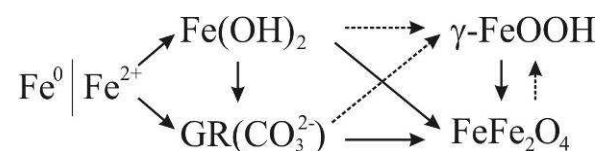

Fig. 4. A scheme of the phase transformation of surface structures possible under full and limited oxidation
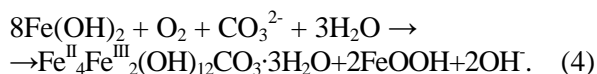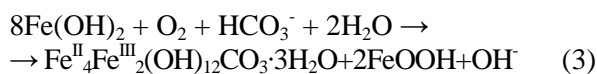
The factors which determine the initial species and chemical reactions in the system are oxidizing condition and presence of ferrous iron in dispersion medium. So, the oxidizing way is marked by a dashed line (Fig. 4). The way of the

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phase formation, when the oxidant is limited and ferrous iron is present, is marked by a firm line (Fig. 4). The reactions describing the phase formation are presented below.
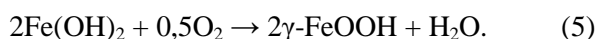
The first way. The formation of ferrous hydroxide from ferrous iron on steel surface (1) and under hydrolysis in solution (2)

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad (1)$$

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+. \qquad (2)$$
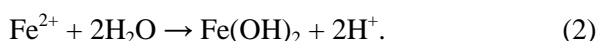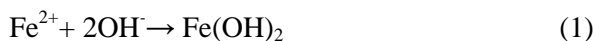
The formation of hydroxycarbonate Green Rust $Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O$ $(GR(CO_3^{2-}))$ from ferrous hydroxide

$$8Fe(OH)_2 + O_2 + HCO_3^- + 2H_2O \rightarrow$$
$$\rightarrow Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O + 2FeOOH + OH^- \qquad (3)$$

$$8Fe(OH)_2 + O_2 + CO_3^{2-} + 3H_2O \rightarrow$$
$$\rightarrow Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O + 2FeOOH + 2OH^-. \qquad (4)$$

The formation of lepidocrocite γ-FeOOH

$$2Fe(OH)_2 + 0{,}5O_2 \rightarrow 2\gamma\text{-}FeOOH + H_2O. \qquad (5)$$

The oxidation of Green Rust with the formation of lepidocrocite

$$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O + O_2 \rightarrow$$
$$\rightarrow 6\gamma\text{-}FeOOH + H_2CO_3 + 5H_2O. \qquad (6)$$
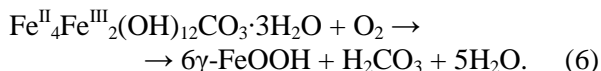
The oxidation of magnetite with the formation of lepidocrocite

$$2FeFe_2O_4 + 0{,}5O_2 + 3H_2O \rightarrow 6\gamma\text{-}FeOOH. \qquad (7)$$
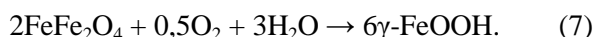
The second way. Direct transformation of Green Rust to magnetite $FeFe_2O_4$ under low oxidation condition

$$Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3 \cdot 3H_2O + 0{,}5O_2 \rightarrow$$
$$\rightarrow 2FeFe_2O_4 + H_2CO_3 + 8H_2O. \qquad (8)$$
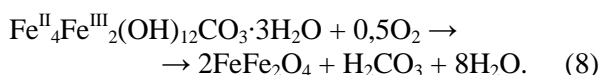
The formation of magnetite $FeFe_2O_4$ in presence of ferrous iron

$$2\gamma\text{-}FeOOH + Fe^{2+} \rightarrow FeFe_2O_4 + 2H^+. \qquad (9)$$

The presence of cobalt ions in the system and its interacting with ferrous and ferric spices leads to forming a cobalt ferrous spinel ferrite according to different reactions:

$$2Fe(OH)_2 + Co^{2+} + 0{,}5O_2 \rightarrow CoFe_2O_4 + H_2O + 2H^+, \quad (10)$$

$$2Fe(OH)_2 + CoOH^+ + 0{,}5O_2 \rightarrow CoFe_2O_4 + 2H_2O + H^+. \quad (11)$$
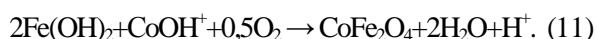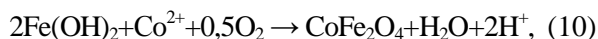
Relative concentrations of $FeFe_2O_4$ and γ-FeOOH, C/C_{max}, on the disc surface were estimated using the X-ray diffraction. The time dependences of C/C_{max} are shown in Fig. 5. C_{max} is the concentration corresponding to the

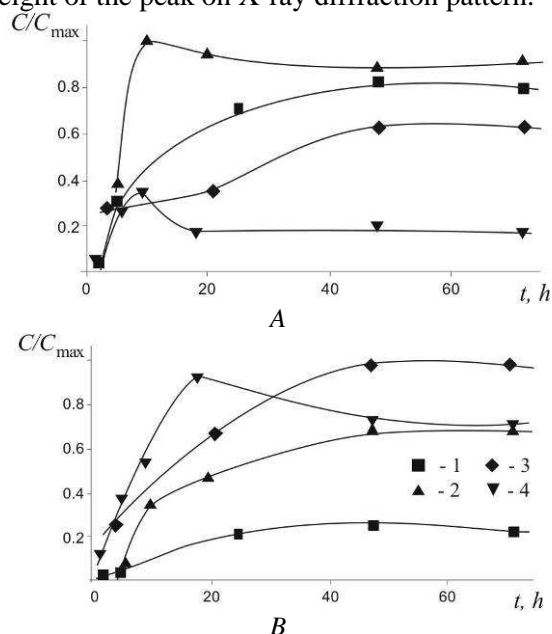the concentration corresponding to the maximum height of the peak on X-ray diffraction pattern.

Fig. 5. Dependences of relative concentrations γ-FeOOH (*a*) and $FeFe_2O_4$ (*b*), C/C_{max}, on steel surface in time *t*. Numbers correspond to temperatures: *1* – 25; *2* – 35, *3* – 50; *4* – 70 °C

An approximate estimate of concentration velocity change ($FeFe_2O_4$ and γ-FeOOH) was done taking into account the accumulation of lepidocrocite and magnetite phases on the surface, partial transformation of lepidocrocite phase into magnetite one and decreasing concentration of both phases due to the certain physicochemical processes such as destruction or diffusion into the bulk. The differential equation system was created in order to describe these processes

$$\frac{dC_1}{dt} = k_{11}C_{00} + k_{2\rightarrow1}C_2 - k_{12}C_1,$$

$$\frac{dC_2}{dt} = k_{21}C_{00} - k_{2\rightarrow1}C_2 - k_{22}C_2,$$

where C_1 – $FeFe_2O_4$ concentration, k_{11} – reaction rate constant of $FeFe_2O_4$ formation from initial substance, $k_{2\rightarrow1}$ – reaction rate constant of $FeFe_2O_4$ formation from γ-FeOOH, k_{12} – rate constant of $FeFe_2O_4$ concentration decreasing; C_2 – γ-FeOOH concentration, k_{21} – reaction rate constant of γ-FeOOH formation from initial substance, k_{22} – rate constant of γ-FeOOH concentration decreasing. One can suppose that concentration of initial substance is constant (C_{00} = const). The result of integration is as follows

$$C_2 = \frac{k_{21}}{k_{2\to1}+k_{22}} C_{00}\left(1-e^{-(k_{2\to1}+k_{22})t}\right),$$

$$C_1 = \left(\frac{k_{11}C_{00}}{k_{12}} + \frac{k_{2\to1}}{k_{12}}\frac{k_{21}}{k_{2\to1}+k_{22}} C_{00}\left(1-e^{-(k_{2\to1}+k_{22})t}\right)\right)\times$$
$$\times\left(1-e^{-k_{12}t}\right). \tag{12}$$

The coefficients k_{12} and $(k_{2\to1}+k_{22})$ at different temperatures were obtained by approximating experimental findings by the equations (12). Fig. 6 shows the dependences of k_{12} and $(k_{2\to1}+k_{22})$ on the temperature T.
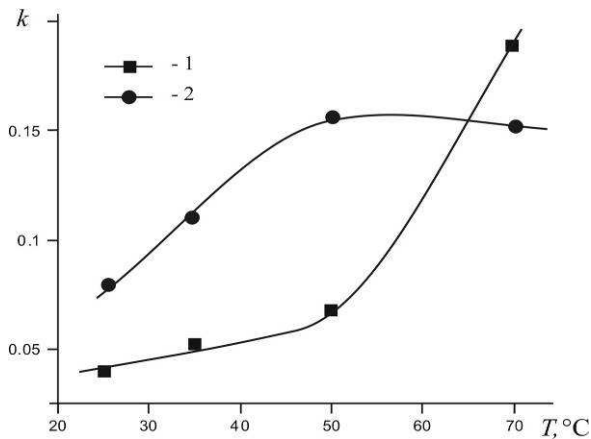

Fig. 6. Reaction constant rate: *1 – k_{12}* and *2 – ($k_{2\to1}+k_{22}$)* versus the temperature T

For most processes, the reaction constant depends on the temperature exponentially. It's expressed by the Arrhenius equation

$$k \propto e^{-\frac{E}{RT}}.$$

In the case of constant k_{12}

$$k_{12} \propto \exp\left(-\frac{E_{12}}{RT}\right).$$

In the case of constants sum one can use the equation

$$k_{2\to1} + k_{22} = A\exp\left(-\frac{E_{2\to1}}{RT}\right) + B\exp\left(-\frac{E_{22}}{RT}\right),$$

where $E_{2\to1}$ and E_{22} – activation energy, A and B – coefficients.

Approximate value of activation energies $E_{12}\sim16.2$ kJ/mol and $E_{2\to1}\sim E_{22}\sim21.5$ kJ/mol (at $T<50$ °C) was obtained by approximating experimental findings by the Arrhenius functions.

At $T>50$ °C both dependences are not compatible with Arrhenius equation. It can be explained by appearance of more complicated reactions.

CONCLUSION

The investigation of forming nanosized structures on steel surface contacting with aqueous solutions in the temperature range from 3 to 70 °C shows the phase development in the iron-oxygen morphological γ-row. As initial structures the Fe(II)-Fe(III) LDH – hydroxycarbonate Green Rust are found and their formation is connected with the specific conditions in the system such as low oxidation level, presence of ferrous iron in dispersion medium, and contact of the steel surface with air. The lepidocrocite and magnetite $FeFe_2O_4$ phases are typical of the whole temperature range and small amount of goethite appears only under limited conditions. In presence of cobalt ions the structure of cobalt ferrous spinel ferrite is formed on steel surface. The mechanisms of the phase formation depend on oxidation condition and saturation of the dispersion medium by ferrous iron. Two branches of phase transformation scheme under full and limited oxidation were suggested. The kinetic regularities were calculated for the lepidocrocite and spinel ferrite formation and for the phase transformation of lepidocrocite into spinel ferrite. The optimum condition for the forming lepidocrocite is low temperatures (25–35 °C) and for forming spinel ferrite is middle temperatures (50 °C).

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Вплив температури на кінетичні залежності утворення нанорозмірних частинок на поверхні сталі, яка контактує з водним дисперсійним середовищем

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Досліджено особливості формування нанорозмірних структур на поверхні сталі, яка контактує з повітрям і водним дисперсійним середовищем у діапазоні температур 3–70 °С. Розвиток залізо-кисневих структур відбувається у межах морфологічного γ-ряду. Вихідною структурою визначено гідроксікарбонатний Green Rust. Запропоновано схему фазових перетворень за двома гілками: повного та обмеженого окиснення. Оптимальні умови утворення лепідокроку визначені за низьких температур (25–35 °С), а магнетиту – за середніх (50 °С). Розраховано кінетичні залежності величини дифракційних піків лепідокроку та магнетиту від температури.

Влияние температуры на кинетические зависимости формирования наноразмерных частиц на поверхности стали, контактирующей с водной дисперсионной средой

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Исследованы особенности формирования наноразмерных структур на поверхности стали, контактирующей с воздухом и водной дисперсионной средой в диапазоне температур 3–70 °С. Развитие железо-кислородных структур происходит в пределах морфологического γ-ряда. В качестве исходной структуры был взят гидроксикарбонатный Green Rust. Предложена схема фазовых трансформаций по двум ветвям: при полном и при ограниченном окислении. Оптимальные условия формирования лепидокрокита определены при низких температурах (25–35 °С), а магнетита – при средних (50 °С).

Рассчитаны кинетические зависимости величины дифракционных пиков лепидокрокита и магнетита от температуры.