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KINETIC REGULARITY OF THE FORMATION OF Fe (II)–Fe (III) LDH STRUCTURES (GREEN RUST) ON THE STEEL SURFACE IN PRESENCE OF THE $FeSO_4$ AND $Fe_2(SO_4)_3$ WATER SOLUTIONS

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The kinetic regularity of origin and transformation of the Fe (II)–Fe (III) LDH structures on the steel electrodes surface contacting with $FeSO_4$ and $Fe_2(SO_4)_3$ dispersion medium at free access of the air oxygen into the system was studied. X-ray diffraction was chosen as the main method of investigation. It was shown that regardless of oxidation level of iron with its concentration 10^2–10^3 mg/dm^3 on electrode surface the GR(SO_4^{2-}) phase was formed staying single for almost 5 hours. The phase transformation of embryonic GR(SO_4^{2-}) surface structures occur with formation of morphological composites of iron-oxygen γ-row: lepidocrocite γ-FeOOH and magnetite Fe_3O_4, and α-row structure representative, goethite α-FeOOH.

INTRODUCTION

The present state of the chemistry science has created conditions for close connection with branches of knowledge which need the production of new materials, for example, on the basis of iron which can be used for the needs of biology and medicine, particularly for creating magnetic carriers for controlled transport of a medical product in the magnetic field, the developing new antioxidant protection of organism, creating antitumoral preventive and therapeutic medicine, etc. Fe (II)–Fe (III) LDH or *Green Rust* have got magnetic [1] and reducing [2] properties and they can transform to iron oxyhydroxides and oxides of different crystallographic modifications [3] or ferrites by creating favorable conditions of synthesis (oxidation conditions, chemical composition and pH meaning, addition of stabilizing components and surface modifiers). At the same time, reaction ability of such structures limits the time of their existence in standard conditions which might bring to difficulties in LDH investigations and there is the necessity of applying additional ways of their treatment and stabilization [4]. Fe (II)–Fe (III) LDH structures are composed from hydroxides layers, which are formed from octahedrons $Fe^{II-III}(OH)_6$, with interlayer water molecules and anions which compensate the charge of Fe (III) hydroxides layers and supply electroneutrality of the structure. In general, the structure of Green Rust corresponds to the chemical composition $[Fe^{II}_{(1-x)}Fe^{III}_{x}(OH)_2]^{x+} \cdot [(x/nA\cdot(m/n)H_2O)]^{x-}$ [5]. In laboratory, the Fe (II)–Fe (III) LDH structures are obtained by chemical or electrochemical techniques [6, 7].

Traditional investigation methods of Fe(II)–Fe(III) LDH are Mőssbauer and Raman spectroscopy, X-ray diffraction, scanning electron microscopy (SEM). The aim of our investigation is studying the kinetic regularity of origin and transformation of the Fe (II)–Fe (III) LDH structures on the steel electrodes surface contacting with $FeSO_4$ and $Fe_2(SO_4)_3$ dispersion medium at the condition of free access of the air oxygen into the system.

MATERIALS AND METHODS

The studying of process Fe (II)–Fe (III) LDH formation has been carried out on the surface of the disk electrode from finished steel (St3) with composition (%): 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 $Fe_2(SO_4)_3\cdot$and $FeSO_4$ solutions in pH range from 3.0 to 11.0 with Fe concentrations from 10 to $1 \cdot 10^3$ mg/dm^3 have been chosen as dispersion medium. X-ray diffraction (XRD) was chosen as the main method of investigation. Measurement was taken on computer-aided equipment (DRON 3) with filtered emission of iron anode in discrete conditions of plotting with pitch of 0.1 degree and time of piling in every point 4 s. The addition module was used for recording this process *in situ*. The rotation of the steel disk supplied the variable contact of their surface with air and dispersion medium. The scanning electron microscopy (SEM) was suggested as additional visualization technique of the derived samples.

RESULTS AND DISCUSSION

The study of formation the embryonic structures of Fe (II)–Fe (III) LDH into Fe (II) and Fe(III) sulfate solution shows the presence of hydroxysulfate Green Rust II (GR(SO_4^{2-})) with general composition $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4{\sim}8H_2O$ [8] after 10–20 min; spatial group of this structure is trigonal – $P\bar{3}m1$; parameters of elementary lattice are a=0.5524$_1$ nm, c=1.1011$_3$ nm, V=0.29097 nm^3 and Z=1/2. Fig. 1 shows a XRD-data of GR(SO_4^{2-}) structure after 40 min from the beginning of observation and additional plot shows kinetic correspondence of intensity of the most important characteristic picks 1.090 and 0.548 nm (planes (001) and (002), respectively).

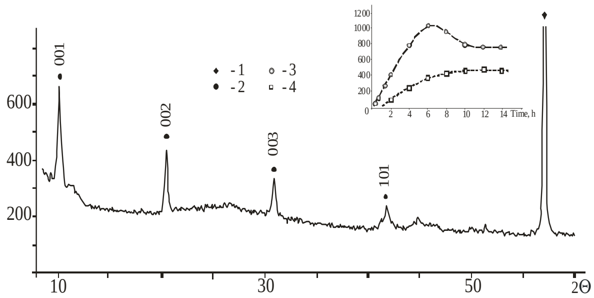
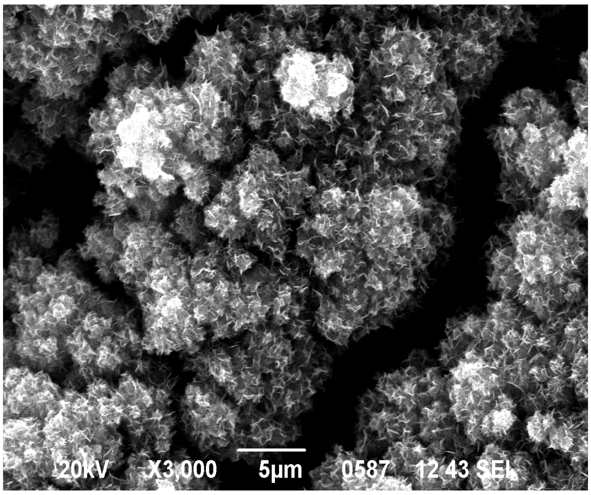


Fig. 1. XRD data of hydroxysulfate Green Rust (GR(SO_4^{2-}) sample: *1* – α-Fe^0, *2* – GR(SO_4^{2-}); the kinetic of reflection intensity the planes of GR(SO_4^{2-}): *3* – (001), *4* – (002) on the additional graph

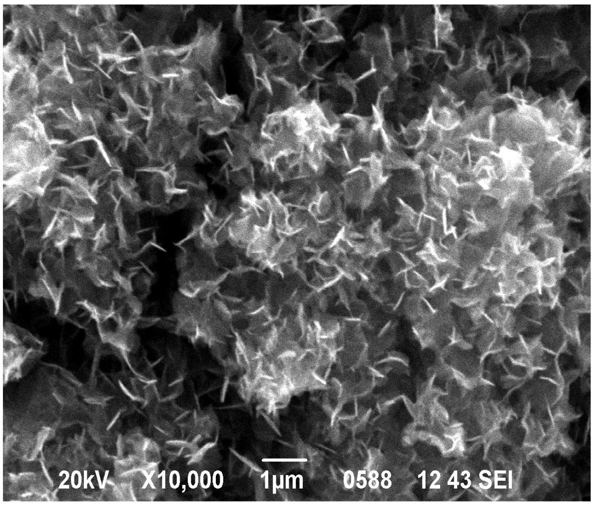
The formation of the GR(SO_4^{2-}) structure was ascertained in pH range from 3.0 to 11.0 by the experimental investigation. Derived experimental data show the growth of bulk of Green Rust on the steel surface during 3–5 hours when Fe (II) and Fe (III) salts with contents of cation about 10^2–10^3 mg/dm^3 were dissolved into distilled water. Than GR structures are transformed into Fe (III) oxyhydroxides phases. The rate of oxyhydroxides within of surface structures grows and comes up to the maximum after 72 hours. At the extreme points of pH value the formations of hydroxysulfate Green Rust II (GR(SO_4^{2-}) occurres in pittings. By lowering the initial iron concentration to 10 mg/dm^3 and variating the pH value the formation of phase GR(SO_4^{2-}) is not always identified by XRD but its presence was confirmed by SEM. In that condition of carrying out the process the phase consisting of surface structures is characterized by the decreasing the relative quantity of phase GR and increasing relative % mass the total mass phase α- and γ-iron oxyhydroxides and magnetite. With it in Fe (II) system the intensiveness of growing GR phase and speed of that process exceed twice that result as compared with Fe (III) system.

Under the contact of the electrode surface with dispersion medium the relative quantity of magnetite Fe_3O_4 phase had come up to the maximum in 24 hours and than decreased. The total mass of iron oxyhydroxides, on the contrary, increases and after 72 hours of the experiment makes up ~80% of the total mass of surfaces of iron-oxygen structures. Fig. 2 shows electronic microphotos of GR(SO_4^{2-}) structures which were obtained in neutral dispersion medium on the surfaces of a steel electrode at contacting with saturated air oxygen of dispersion medium. The particles of Fe (II)–Fe (III) LDH (size 0.5–1.0 μm) contact with one another and participate in formation of solid layer on electrode surfaces.

In accordance with the derived data an assumption was made about the mechanism of the processes of iron-oxygen structures formation on the steel electrode surface which was contacting with water dispersion medium and air oxygen. During the first hours of the processing in the thin films initial iron-oxygen structure is formed on the surface containing the Fe (II) and Fe (III) cations and according to the XRD-data corresponding to hydroxysulfate Green Rust (GR(SO_4^{2-}). According to literature source [9], the development of such a structure could occur due to formation of goethite α-FeOOH phase by oxidation Fe (II)–Fe (III) LDH with oxygen dissolved in dispersion medium. In our case this process occurs as a result of the forced oxygen delivering to electrode surface at the expense of its rotating under changeable contact with air and dispersion medium. Another typical process was phase transformation of Green Rust into lepidocrocite γ-FeOOH [10]. As in [11], in both cases the mechanism of phase transformation could be divided into two stages – partial destruction of phase Green Rust and secondary precipitated well ordered structures of iron (III) oxyhydroxides.



a



b

Fig. 2. Structures of Fe (II)–Fe (III) layered double hydroxide (GR(SO_4^{2-})) formed on the surface of steel electrode by its contact with water dispersion medium at free access of air oxygen into the system

The formation of magnetite phase at the beginning of the process of structure formation, according to [12], could occur by oxidation in lattice of Fe (II)–Fe (III) LDH~33% Fe (II): in that case phase of magnetite supplement or replace the structural elements of Green Rust. The following oxidation of iron goes by destruction of the phase magnetite Fe_3O_4 and Green Rust and formation well-crystallizing needle-shaped particles of lepidocrocite γ-FeOOH [12]. In general, the transformation of the structure GR(SO_4^{2-}) into the phases of iron (III) oxyhydroxides or magnetite could pass by the following reactions

$$2Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 + 1.5O_2 \rightarrow$$
$$\rightarrow 10FeOOH + 2FeSO_4 + 7H_2O$$

$$2FeOOH + Fe^{2+} + 2OH^- \rightarrow FeFe_2O_4 + 2H_2O$$
$$(\Delta G^0_{298} = -24.4 \text{ kcal/mol})$$

$$Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 + 0.5O_2 \rightarrow$$
$$\rightarrow 2Fe_3O_4 + H_2SO_4 + 5H_2O$$

In its turn oxidation of the magnetite at the expense of air oxygen facilitates the formation of the iron oxyhydroxide

$$2FeFe_2O_4 + 0.5O_2 + 3H_2O \rightarrow$$
$$\rightarrow 6FeOOH\ (\Delta G^0_{298} = -49.7 \text{ kcal/mol}).$$

Thus the replacement of oxidation condition and entering the system by the hydroxyl ions and Fe (II), for example by the passing electrochemical Red-Ox reaction on the steel surface, gives an opportunity to control the process of phase formation and to get separate phases GR(SO_4^{2-}), FeOOH or Fe_3O_4 on the steel surface. In the same time, as a consequence of direct interaction between the products of electrode processes near-electrode space the formation of iron (II) hydroxide and its oxidation to magnetite are possible [13]

$$6Fe(OH)_2 + O_2 \rightarrow$$
$$\rightarrow 2Fe_3O_4 + 6H_2O\ (\Delta G^0_{298} = -123.0 \text{ kcal/mol})$$

or by oxidation $Fe(OH)_2$ in presence of Fe (II) and SO_4^{2-} – to phase of GR(SO_4^{2-}). As in [14], such transformation has topotactical character, i.e. the oxidation of Fe (II) occurs by partial rearrangement of $Fe(OH)_2$ lattice without lattice destruction

$$5Fe(OH)_2 + Fe^{2+} + SO_4^{2-} + 0.5O_2 + 9H_2O \rightarrow$$
$$\rightarrow Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot 8H_2O$$
$$(\Delta G^0_{298} = -2522.1 \text{ kcal/mol}).$$

However, in our case the formation of $Fe(OH)_2$ was not seen.

CONCLUSIONS

The investigation of kinetic correspondence of formation of the embryonic Fe (II)–Fe (III) LDH structures (Green Rust) on the steel surface in presence of the $FeSO_4$ and $Fe_2(SO_4)_3$ water solutions was recorded *in situ* by X-ray diffraction. It was shown that regardless of oxidation level of iron with its concentration 10^2–10^3 mg/dm^3 on electrodes surface the phase $GR(SO_4^{2-})$was formed and stayed single for almost 5 hours. A change of the conditions of carrying out the process resulted in considerable decrease of hydroxysulfate Green Rust ($GR(SO_4^{2-})$ emergence.

The phase transformation of embryonic surfaces structures $GR(SO_4^{2-})$ occurs with formation of morphological composites of iron-oxygen γ-row: lepidocrocite γ-FeOOH and magnetite Fe_3O_4 and α-row structure representative, goethite α-FeOOH. Changing the physical-chemical condition processing of phase formation, such as quantity of oxidant which comes to electrode surface, could change the way of the process going to the side of formation of other iron-oxygen structures.

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Кінетичні закономірності формування структур Fe (II)–Fe (III) ШПГ (Green Rust) на поверхні сталі в присутності водних розчинів $FeSO_4$ та $Fe_2(SO_4)_3$

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Досліджені кінетичні закономірності зародження та перетворення структур Fe (II)–Fe (III) шаруватих подвійних гідроксидів (ШПГ) на поверхні сталевого електрода, який контактує з дисперсійним середовищем, що містить $FeSO_4$ *та* $Fe_2(SO_4)_3$*, за умови вільного надходження в систему кисню повітря. Головним методом дослідження був рентгенофазовий аналіз (РФА). Показано, що незалежно від ступеня окиснення заліза в дисперсійному середовищі при його концентрації* 10^2*–*10^3 *мг/дм*^{3} *на поверхні електроду утворюється фаза* $GR(SO_4^{2-})$*, яка залишається єдиною протягом 5 годин. Фазові трансформації зародкових поверхневих структур* $GR(SO_4^{2-})$ *проходять з утворенням залізокисневих структур γ-ряду: лепідокрокіту γ-FeOOH і магнетиту* Fe_3O_4 *та представника α-ряду, гетиту α-FeOOH.*

Кинетические закономерности формирования структур Fe (II)-Fe (III) СДГ (Green Rust) на поверхности стали в присутствии водных растворов $FeSO_4$ и $Fe_2(SO_4)_3$

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Исследованы кинетические закономерности зарождения и трансформации структур Fe (II)-Fe (III) слоевых двойных гидроксидов (СДГ) на поверхности стального электрода, который контактирует с дисперсионной средой, содержащей $FeSO_4$ *и* $Fe_2(SO_4)_3$*, при свободном доступе в систему кислорода воздуха. Основным методом исследования был рентгенофазовый анализ (РФА). Показано, что независимо от степени окисления железа в дисперсионной среде при его концентрации* 10^2*–*10^3 *мг/дм*^{3} *на поверхности электрода образуется фаза* $GR(SO_4^{2-})$*, которая остается единственной в течение 5 часов. Фазовые трансформации зародышевых поверхностных структур* $GR(SO_4^{2-})$ *проходят с образованием железо-кислородных структур γ-ряда: лепидокрокита γ-FeOOH и магнетита* Fe_3O_4 *и представителя α-ряда, гетита α-FeOOH.*