

# НАНОЧАСТИЦЫ, НАНОКЛАСТЕРЫ, НУЛЬМЕРНЫЕ ОБЪЕКТЫ

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## THE MECHANISM OF FORMATION OF THE ULTRA DISPERSE IRON OXIDE MINERALS ON STEEL SURFACE IN PRESENCE OF Cu(II), Ag(I), Au(III), Pt (IV), Pd(II)

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**Key words:** *ultradisperse iron oxide minerals, process of phase formation, precious metals*

*Process of formation of ultra disperse iron oxide minerals on steel surface by its contacts with air oxygen and dispersion medium containing ions of cuprum, argentums, aurum, platinum and palladium was studied. The formation of phase's hydroxysulphate Green Rust, magnetite and lepidocrocite on steel surface by concentrations of electropositive metals 1–10 mg/dm<sup>3</sup> was shown. Mechanism of phase formation occurs by two stages: adsorption of ions from dispersion medium on Green Rust surface with partly reduction of ions and oxidation of GR to magnetite or lepidocrocite and reduction of the rest metal ions on magnetite surface. Interacting iron oxide phases with electropositive ions add colloidal stability to composite particles.*

Novadays the ferromagnetic nanosized particles with different physical-chemical, colloidal-chemical and crystallographic properties are widely used for medical and biological aims [1, 2]. At first, the use of such structures is connected with the creation of range of medicals and new means of diagnostics of oncological diseases [3, 4]. Nanosized particles with magnetic properties have particular biological activity dependent on their nature and could be used to investigate the processes in organism [5, 6] and to create new functional materials of medico-biological purpose [7, 8]. At present the undisputed leaders which are used in medico-biological researches are most common ultra disperse iron oxides of maghemite  $\gamma\text{-Fe}_2\text{O}_3$  or magnetite  $\text{Fe}_3\text{O}_4$  because of their biocompatibility [9]. They are formed by co-precipitation of ferric and ferrous salts in alkalescent dispersion medium [10], by high-temperature synthesis [11], by mechanochemistry [12], by sol-gel synthesis [13], by red-ox potential method [14, 15], by a reverse micelle method [16] and a range of other methods including addition of stabilizing substance [17,

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18]. At the same time, a lot of publications are devoted to the use in medicine and biology of composites and composition materials that consist of maghemite or magnetite particles covered with precious metal, for example, aurum [19–22]. Such structures are used for separation of biological objects, for example, proteins or other [23, 24], immunoassay, imaging of magnetic resonance, contrast enhancement, drug delivery [25] et al. The aim of the investigation is the studying the process of nanosized iron oxide particles formation on steel surface by its contact with water solutions containing cuprum cations and ions of precious metals.

### Objects and methods

The formation of the particles was carried out on the surface of the steel electrode (St-3) that contacted by rotation alternately with air oxygen and dispersion medium [26]. As dispersion medium has been chosen the solutions of cuprum sulphate with concentrations from 1 to 100 mg/dm<sup>3</sup> at value of pH in range from 2.5 to 12.0 and solution of precious metals: argentums, aurum, platinum, palladium, with initial concentrations 1 and 10 mg/dm<sup>3</sup>. The process of phase formation was carried out until stationary condition, when in the system the content of dispersion medium (composition of ferrous, ferric, cuprum, precious metals) and value of pH was stabilized. The chemical analysis was carried out by the standard methodics [27]. Phase compositions of ultra disperse iron oxide structures was determined by X-ray diffraction (XRD), transmission electron microscopy (TEM), electronography [28].

### Results and discussion

The investigation of the process of formation of the ultra disperse iron oxides on the steel surface in the presence of cuprum ions

Studying the process of the formation of the ultra disperse iron oxides minerals on steel surface was carried out depending on value of pH of the dispersion medium and the concentration of cuprum ions in it.

The Fig. 1 represents the result of the chemical analysis, that by initial concentration of Cu(II) = 100 mg/dm<sup>3</sup>, shows the occurrence of the classical reaction of cementation, when because of the difference of standard electrode potentials cuprum ions are reduced on steel surface and iron-constituent is desolated with entering ferrous-ions in dispersion medium.

Process of phase formation depends on pH value and can continue from 2 to 3 hours at pH = 3.0 to 24 hours at pH = 6.0, when the maximum amount of cuprum-ions (~85%) is bond from dispersion medium of steel surface. It is accompanied by changing of pH value to sub acid.

For example, the final value of pH at initial pH = 3.0 grows to pH = 5.0 and at initial pH = 6.0 it went down to pH = 5.2.

The access of air oxygen in system leads to oxidation of ferrous-ions and phase formation on steel surface, as well as in dispersion medium. The residual concentration of Fe(III) does not exceed the 4.2 mg/dm<sup>3</sup>. The decrease of initial concentration of Cu(II) to 1–10 mg/dm<sup>3</sup> changes of mechanisms of the process of phase formation: cations of cuprum practically are not reduced on steel surface and they participate in formation of iron oxide phases.

At the same time, the agglomeration of ferrous-ions in dispersion medium does not occur; the final ferric concentration there is in the range 0.6–1.7 mg/dm<sup>3</sup>, and concentration of ferric-ions does not exceed 0.3 mg/dm<sup>3</sup>. The final value of pH changes less than one.

Whereas, in such conditions the binding of the cuprum-ions hardly occurs; for example, at the value pH = 6.5 and the initial concentration of Cu(II) = 1 mg/dm<sup>3</sup> the final concentration decreased of = 0.95 mg/dm<sup>3</sup>. At the initial concentration of 10 mg/dm<sup>3</sup> in the dispersion medium remains 8.25 mg/dm<sup>3</sup> of cuprum-ions.

Analysis of the ultra disperse iron oxide phases shows the formation in the system of iron oxyhydroxides – goethite  $\alpha$ -FeOOH and lepidocrocite  $\gamma$ -FeOOH with addition of spinel ferrites, admittedly magnetite Fe<sub>3</sub>O<sub>4</sub>, which (pre)dominates in the content of the sediments at the initial concentration of Cu(II) = 100 mg/dm<sup>3</sup> (Fig. 2).

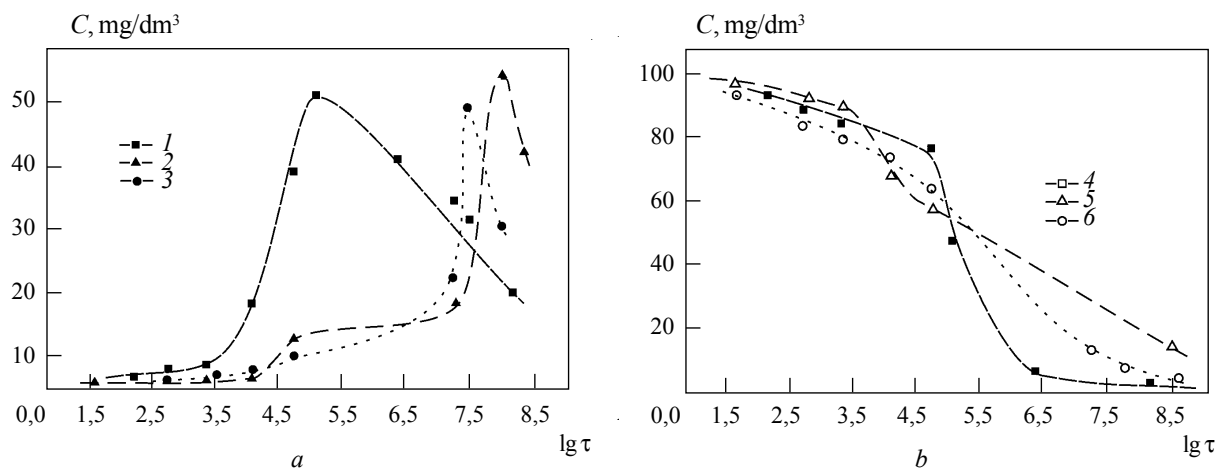


Fig. 1. Kinetic of the concentration of cations of ferrous (a) and cuprum (b) by the process of phase formation on steel surface at its contact with cuprum sulphate solution with initial concentration of Cu(II) 100 mg/dm<sup>3</sup> and at pH value: 1 and 4 at pH = 3.0; 2 and 5 at pH = 4.5; 3 and 6 at pH = 6.0

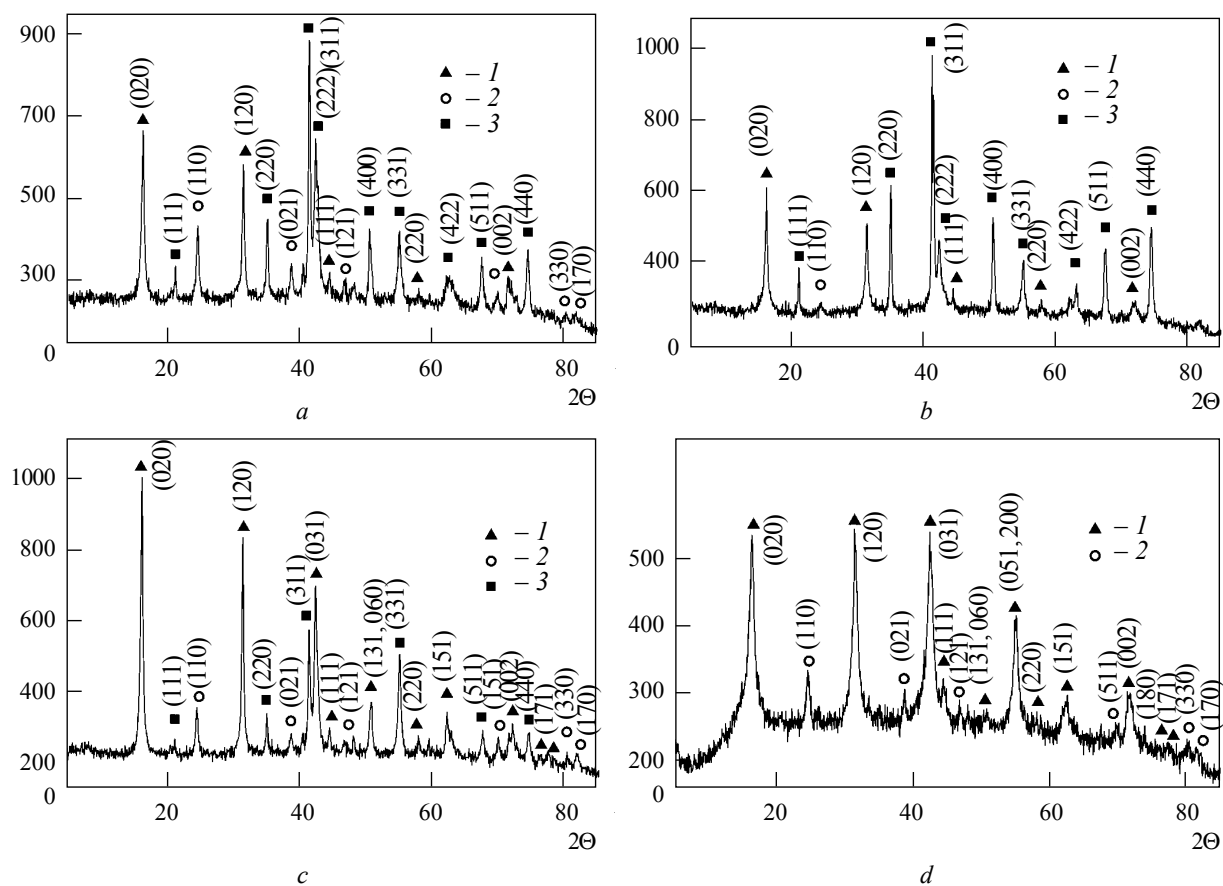


Fig. 2. XRD-data of iron oxide phases formed in the near surface layer of the steel electrode at the concentration of Cu(II) 100 mg/dm<sup>3</sup> at pH values: 1 – 3.0; 2 – 4.5; 3 – 6.0 and in dispersion medium. Numbers correspond to the phases: 1 – lepidocrocite  $\gamma$ -FeOOH, 2 – goethite  $\alpha$ -FeOOH, 3 – magnetite  $\text{Fe}_3\text{O}_4$

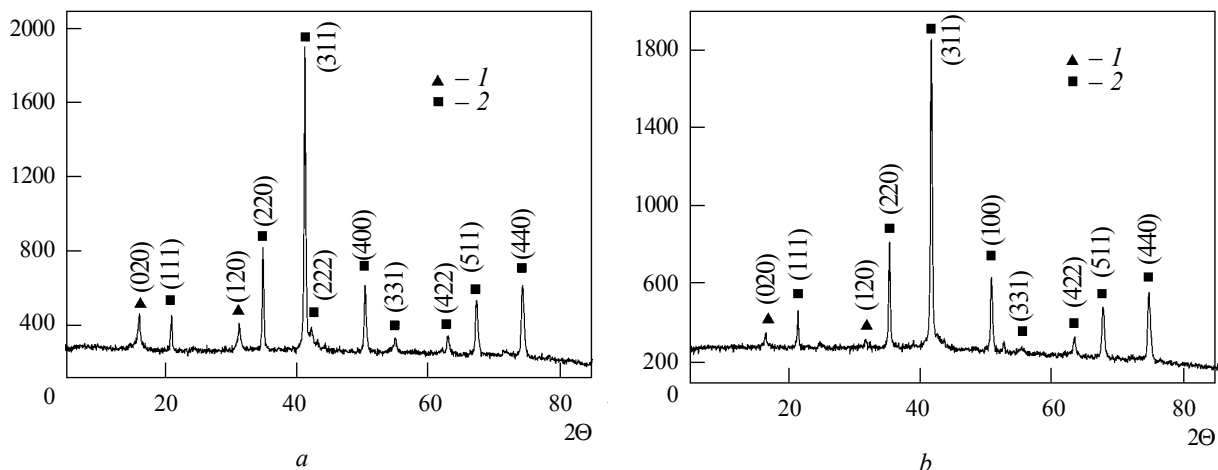


Fig. 3. XRD-data of iron oxide phases formed in the near surface layer of the steel electrode (a) and its surface layer (b) at the initial concentration of cuprum-ions  $1 \text{ mg/dm}^3$  and pH value 6.5. Numbers correspond to the phases: 1 – lepidocrocite  $\gamma\text{-FeOOH}$ , 2 – magnetite  $\text{Fe}_3\text{O}_4$

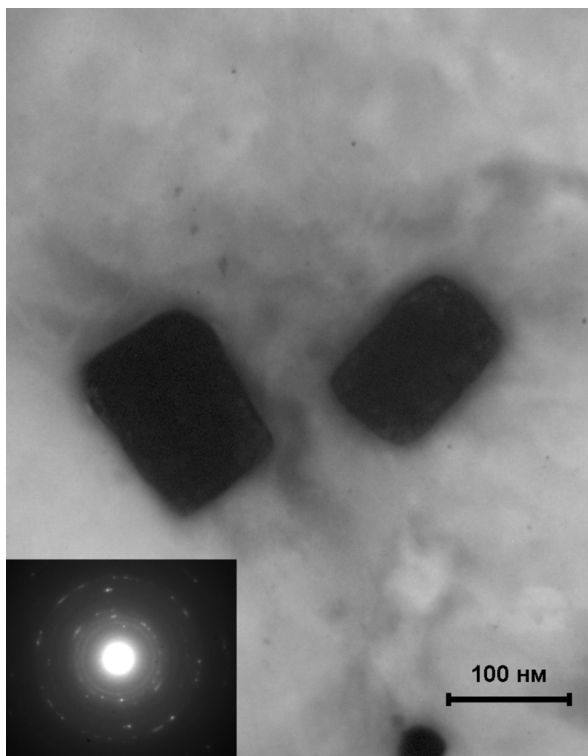


Fig. 4. Magnetite particles formed on the steel surface by its contact with solution of cuprum sulphate

At the intensity of XRD-reflexes it is possible to make an assumption that the most intensively the formation of lepidocrocite  $\gamma\text{-FeOOH}$  occurs at neutral medium and spinel ferrites – at value of  $\text{pH} = 4.5$ .

At the initial concentrations of cuprum-ions  $1\text{--}10 \text{ mg/dm}^3$  in the composition of the surface structures there dominate the phases of spinel ferrites and lepidocrocite  $\gamma\text{-FeOOH}$  (Fig. 3). As a rule, on the steel surface two layers of iron oxide phases are formed where the outer (near surface) layer (Fig. 3a) is characterized the more intensive reflexes of oxyhydroxides than phases of the inner (surface) layer (Fig. 3b).

The absence of cuprum containing phase in sediment composition, for example, cuprum ferrite, makes us think about the binding of cuprum ions by sorption on surface of iron oxyhydroxides or replacing ferric-cations in the structure of magnetite  $\text{Fe}_3\text{O}_4$ .

Fig. 4 shows TEM image of magnetite  $\text{Fe}_3\text{O}_4$  formed on steel surface by its contact with cuprum sulphate solution by concentration  $\text{Cu(II)} 1 \text{ mg/dm}^3$ .

Thus, our investigation shows that the formation of ultra disperse iron oxide minerals on the steel surface in the presence of cuprum ions in water medium is possible by two mechanisms: oxidation-reduction with reduction of cuprum-ions and oxidation of iron and oxidation of ferrous-ions with

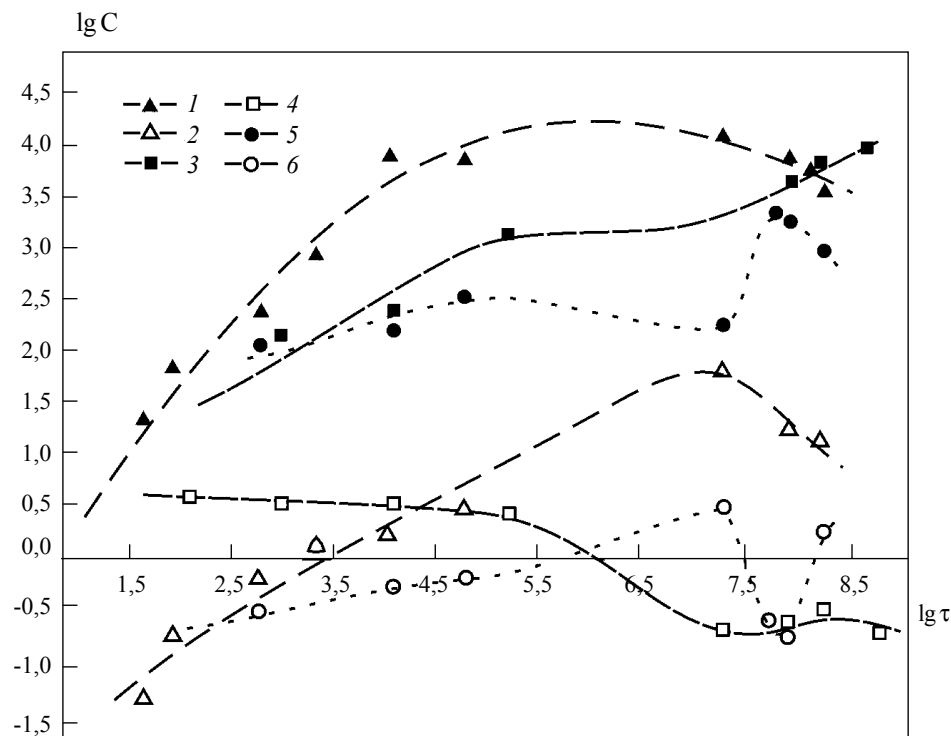


Fig. 5. Kinetic of changing the concentration of ferric and ferrous ions in the process of phase formation on steel surface in the presence of precious metals: platinum (1) – Fe total, 2 – Fe(III); palladium (3) – Fe total, 4 – Fe(III), argentums (5) – Fe total, 6 – Fe(III)

formation of iron oxyhydroxides and magnetite phases.

**The investigation of the process of formation of the ultra disperse iron oxide minerals on the steel surface in the presence of the precious metals**

The process of phase formation on the steel surface was carried out by its contact with solution containing precious metals, there were argentums, aurum and palladium with the concentration of metal ions of 1 mg/dm<sup>3</sup>; argentums and platinum with the concentration of metals 10 mg/dm<sup>3</sup>.

According to the data of chemical analysis the presence of precious metals in dispersion medium activates the anodic solution of the iron with agglomeration of ferric and ferrous ions in the dispersion medium. The final concentrations of total ferric and ferrous ions by addition of platinum were

C, mg/dm<sup>3</sup>

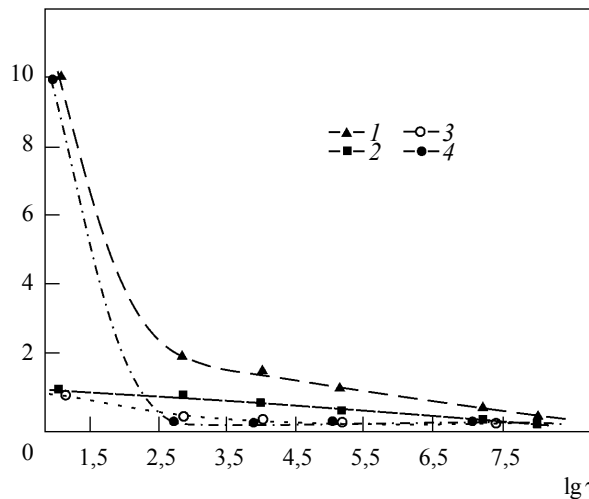
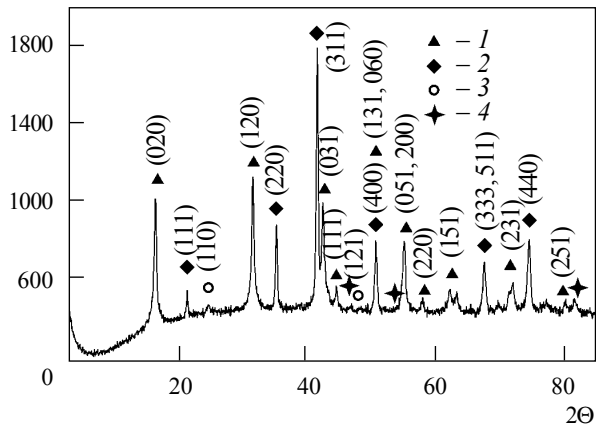
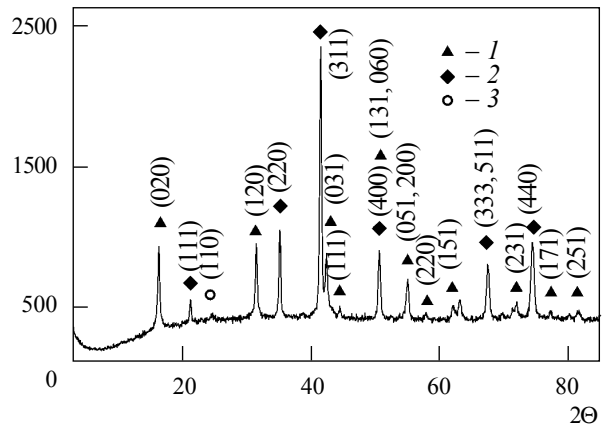


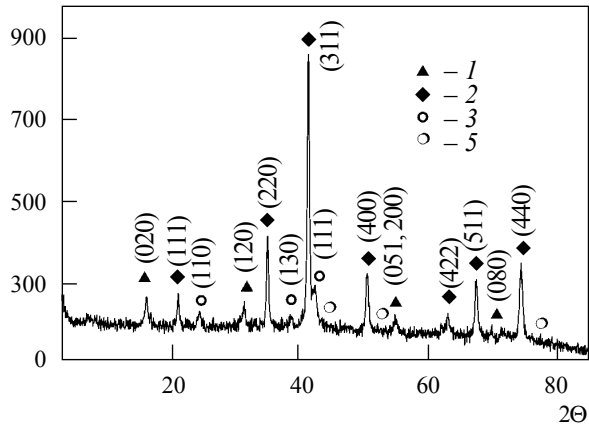
Fig. 6. Kinetic of binding of ions of precious metals: a – platinum, b – palladium, c – aurum, d – argentums



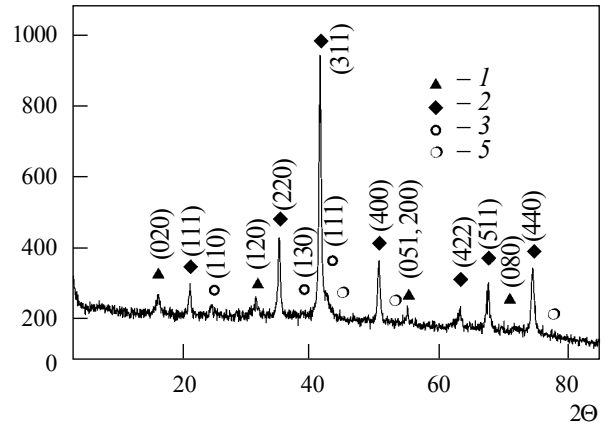
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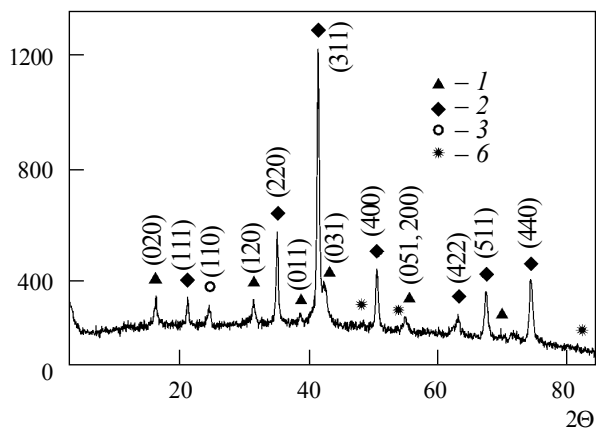
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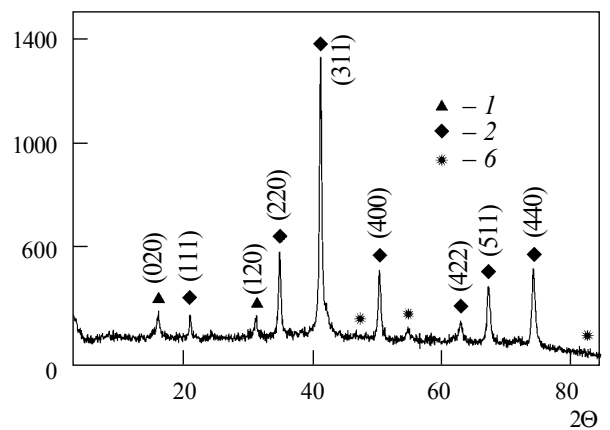
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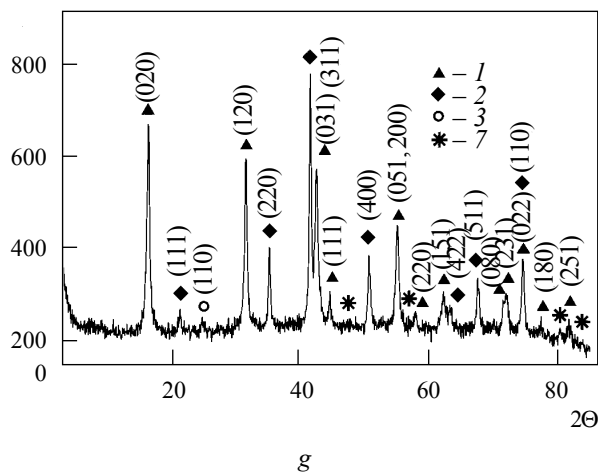


Fig. 7. XRD-data of structures formed on the steel surface by its contact with solution of: *argentums* – near surface layer (a), surface layer (b); *aurum* – near surface layer (c), – surface layer (d); *platinum* – near surface layer (e), surface layer (f); *palladium* – single layer (g). Numbers correspond to the phases: 1 – lepidocrocite  $\gamma\text{-FeOOH}$ ; 2 – magnetite  $\text{Fe}_3\text{O}_4$ , 3 – goethite  $\alpha\text{-FeOOH}$ , 4 – silver  $\text{Ag}^0$ , 5 – aurum  $\text{Au}^0$ , 6 – platinum  $\text{Pt}^0$ , 7 – palladium  $\text{Pd}^0$

40  $\text{mg}/\text{dm}^3$  and ferric ions – 1  $\text{mg}/\text{dm}^3$ ; by addition of *argentums* were 28.5 and 0.17  $\text{mg}/\text{gm}^3$ , correspondingly; by addition of *palladium* were 55.0 and 3.36  $\text{mg}/\text{gm}^3$ , correspondingly, and in the presence of *aurum* were 70.0 and 5.2  $\text{mg}/\text{gm}^3$ , correspondingly (Fig. 4). Fig. 5 shows the kinetics of concentrations of precious metals in dispersion medium on the formation of the iron oxide minerals process. The concentration of *platinum* decreases drastically from 10 to 2  $\text{mg}/\text{gm}^3$  during 15 minutes and then gradually decreasing to the final concentration  $> 0.08 \text{ mg}/\text{dm}^3$ . On the opposite the content of *palladium* (1  $\text{mg}/\text{dm}^3$ ) does not change during 24 hours and only after 70 hours decreases to 0.06  $\text{mg}/\text{dm}^3$ . The initial concentration of *aurum* (1  $\text{mg}/\text{dm}^3$ ) decrease during several hours to 0.4  $\text{mg}/\text{dm}^3$ , and then slowly decreases to 0.07  $\text{mg}/\text{dm}^3$  at the end of phase formation. The content of *argentums* decreases from 10 to 0.01  $\text{mg}/\text{dm}^3$  during 15 minutes. The initial value of  $\text{pH} = 2.5$  in systems with *platinum*, *palladium* and *aurum* by process of phase formation increases on average to  $\text{pH} = 5.3$  and in systems with *argentums* increases from 5.0 to 9.4.

As show the obtained data, the main phases of iron oxides there are lepidocrocite and magnetite. The process of phase formation in such a system goes through the stages of origin on the steel surface the phase of hydroxysulphate Green Rust, its

transformation to phase of iron oxyhydroxides and then to phase of magnetite  $\text{Fe}_3\text{O}_4$ .

Fig. 8 shows the TEM images of ultra disperse minerals formed on steel surface in the presence of the precious metals in dispersion medium.

On the basis of our own data and literature sources it is possible to make conclusions that the process of interaction of iron oxides with low concentration of metals from dispersion medium can go at any stage of formation and transformation of iron oxide phases. Articles [29, 30] show that limited oxidation in the system results in formation on steel surface derived structures of  $\text{Fe(II)-Fe(III)}$  layered double hydroxides – Green Rust. The same result was obtained in our system, where on steel surface by its contact with water dispersion medium after processing the surface by solution of sulphuric acid shows the origin of hydroxysulphate Green Rust particles is observed, which is proved by the XRD-data *in situ* [31]. Due to the presence of the ferrous iron the structure of Green Rust possesses high reducing activity with respect to the components of the dispersion medium, especially precious metals. For example, the research [32] shows that ions of *aurum*, *argentums*, *cuprum* and *mercury* by their addition in water suspension of Green Rust are reduced to metals and structure of Green Rust in its turn is oxidized to the phases of magnetite or oxyhydroxides. The distinction of the studying our

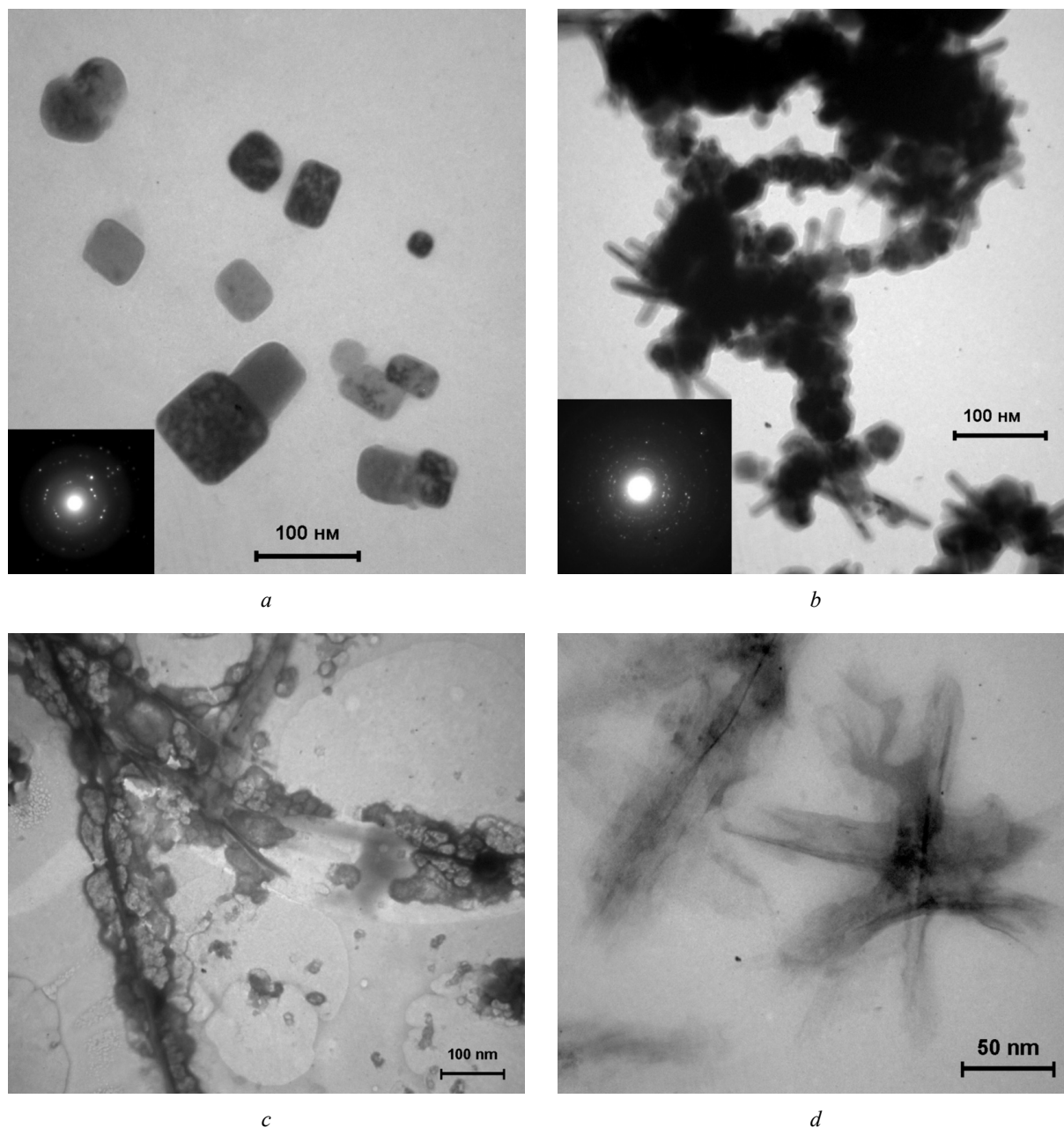


Fig. 8. The TEM images of iron oxide particles on steel surface that were formed in the presence of ions of precious metals in dispersion medium: *a* – argentum, *b* – aurum, *c* – platinum, *d* – palladium

system is that red-ox reaction goes as a single process and not as two separate as it was shown in the previous case. So, in our research there was made ferromagnetic composite compound core of maghemite and shell of argentum [33].

The initial mechanism of such interaction was sorption. At the same time, the sorption interaction of hydroxy complexes of cuprum and precious metals with iron oxide phases could go at the stage of formation of oxyhydroxides without the process



of phase transformation [34, 35] or with next phase transformation to phase of the corresponding spinel ferrite or magnetite and incorporating of cations from dispersion medium to lattice of iron oxides minerals [36].

Process of sorption could take place on iron oxide surface [37, 38]. In this case the metathesis between adsorbed cations and ferrous iron in lattice of magnetite is more likely. At that the formation of nonstoichiometric complicated oxides or solid solutions is possible.

Having analyzed kinetic of chemical composition of dispersion medium, XRD-data and TEM images it is possible to assume that in the system of steel electrode contacting with water solutions of cuprum and precious metals the process of bonding the metals-ions by iron oxides goes by two mechanisms. In the first process cuprum, aurum, argentums, platinum, palladium reduction occurs in structure of Green Rust with its transformation to phase of magnetite with including of part of ions into the structure of the iron oxide. That assumption is proved by the course of kinetic curves, there are the extremes that depend on sudden decrease of cation concentrations and contains of surface structures among which the phase of magnetite dominates. In the second process the decrease of cation concentrations slows down after the formation of magnetite. Obviously, the following redacting of remains of the metals from dispersion medium occurs on the surface of magnetite by it's partly oxidation to lepidocrocite.

That was confirmed by XRD-data. The curves simultaneously show the reflexes of oxyhydroxides and weak reflexes of reduced metals. Low intensity of peaks of aurum, platinum, palladium and argentums depends on their small (at the breaking point of sensitivity (~5%), concentrations. Decreasing initial pH value to acid medium changes of phase composition to formation of oxyhydroxides. The modification of the surface of iron oxide particles by layer of precious metal gives them of colloidal stability, which was shown in our articles [39] by the example of composites maghemite – argentums, maghemite – platinum. That opens the possibility of their practical use for investigation of biological systems.

## Conclusions

1. The result of studying the process of formation of ultra disperse iron oxide minerals on steel surface by its contact with air and dispersion medium containing of cuprum, argentums, aurum, platinum, palladium ions shows that the formation of the structures of iron-oxides occurs within  $\gamma$ -row: Green Rust – lepidocrocite – magnetite  $\text{Fe}_3\text{O}_4$ .

2. The phase composition of iron oxides depends on concentration of electropositive metals in dispersion medium. On the example of cuprum it is shown that by concentration of  $\text{Cu(II)}$   $100 \text{ mg/dm}^3$  in the system there occurs the classical reaction of cementation including the ionization of metal iron and redacting of cuprum ions on steel surface. Decreasing of concentration of cuprum to  $1\text{--}10 \text{ mg/dm}^3$  changes the mechanism of phase formation: on steel surface magnetite formed.

3. In the presence of precious metals the process of phase formation occurs by two mechanisms. At first the process of reduction of argentums, aurum, platinum and palladium take place into GR structure with its transformation to the phase of magnetite and possibly including of ions in its lattice. At second the reduction of remaining ions from dispersion medium take place on magnetite surface by its partly oxidizing to lepidocrocite.

4. By addition of precious metals in the system on stage of iron oxides particles formation their water sols obtaine the colloidal stability. Their new properties can be used by investigation of biological systems.

Исследован процесс формирования ультрадисперсных железооксидных минералов на поверхности стали при ее контакте с кислородом воздуха и дисперсионной средой, содержащей ионы меди, серебра, золота, платины и палладия. Показано, что при концентрациях электроположительных металлов  $1\text{--}10 \text{ мг/дм}^3$  на поверхности стали образуются структуры гидроксисульфатного Green Rust, магнетита и лепидокрокита. Фазаобразование проходит в две стадии: 1) адсорбция ионов дисперсионной среды на поверхности GR с восстановлением части ионов до металла и окислением GR до магнетита или лепидокрокита; 2) восстановление остаточной концентрации ионов электроположительных металлов на поверхности магнетита. Взаимодействие железооксидных фаз с электроположительными ионами придает частицам коллоидную устойчивость

**Ключевые слова:** ультрадисперсные железоксидные минералы, фазообразование, благородные металлы

Досліджено процес формування ультрадисперсних залізо-оксидних мінералів на поверхні сталі при її контакті з киснем повітря та дисперсійним середовищем, яке містить іони міді, срібла, золота, платини та паладію. Показано, що за концентрацій електропозитивних іонів 1–10 мг/дм<sup>3</sup> на поверхні сталі утворюються структури гідроксисульфатного Green Rust, магнетиту й лепідокрокіту. Фазоутворення відбувається у дві стадії: 1) адсорбція іонів дисперсійного середовища на поверхні GR з відновленням частини іонів до металу й окисненням GR до магнетиту або лепідокрокіту; 2) відновлення залишкової концентрації іонів електропозитивних металів на поверхні магнетиту. Взаємодія залізооксидних фаз із електропозитивними іонами надає частинкам колоїдної стійкості.

**Ключові слова:** ультрадисперсні залізооксидні мінерали, фазоутворення, благородні метали

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