Studies and applications of magnetic interactions in the system ”iron-copper-water”

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Abstract. The recovery of copper by iron in copper sulfate aqueous solutions was studies as a function of the external magnetic field and morphologies of iron containing steel samples. Essential retardation of the recovery by the magnetic field was found as well as decrease of iron sulfate solubility in water induced by the field. The retardation is explained by the active participation of inter-domain walls in the recovery and decreasing of their length in the magnetic field. When steel filings were used for the recovery instead of the volume samples the magnetic retardation was not notices. Applications of these results are developed for new methods of lithography of microschemes and restoration of electrical contact wires.

1. Introduction

Studies of magnetic interactions in the system ”iron-copper-water” are prospective for creation of new knowledge about processes in condensed media either on atomic-molecular scale or for volume materials. Copper is a particular chemical element due to the change of paramagnetic behavior for double ionization to diamagnetic for single charged ions [1]. So the well known process of recovery of copper by iron in water solution [2] changes essentially the ratio of diamagnetic and paramagnetic atomic components. Hence the process and the result of this reaction should be regulated effectively by external magnetic field. This is actual either for being quickly developed spintronics for transfer and treatment of information or for new technologies of microelectronics and constructions [3, 4]. Besides multi-element compositions based on copper and iron belong to the most promising materials for further understanding and development of high-temperature superconductors [5, 6]. The data presented in this paper give useful information for this field. The influence of the surface structure on the bulk properties of condensed matter is described by Dadivanyan et al. [7-13]. Theoretical studies on variational approach were carried out in the works [14, 15]. Modern types of materials investigated by Usol’tseva et al. [16-19].

2. Methods of experiments

Low carbon steel St3, technical copper and aqueous solution of copper sulfate CuSO₄ were used as model materials. Recovery of copper by iron was used as a model reaction. The magnetic field was produced by neodymium permanent magnets with diameters 40 mm and widths from 5 to 20 mm. The field at the surface of the magnets was dependent on their thicknesses and was varied from 0.05 to 0.35 Tl. The value of the magnetic field was regulated by putting several
magnets together. The process of the chemical reactions was registered by video recording of deposition of copper on the surface of the steel via the optical microscope. The solution of copper sulfate was deposited onto the steel surface by a syringe in the form of drops with diameters from 3 to 5 mm. The rate of the chemical reaction was estimated by the dynamics of deposition of copper film onto the steel surface. Samples of St3 were used in two forms; as plates and as filings. Scanning electron microscope was used for studies of the morphologies of the samples.

3. Experimental results
We found experimentally that application of the magnetic field either in normal or parallel orientations with respect to the steel surface decreases significantly the rate of the reaction of copper recovery by iron. The decrease at the maximal magnetic field of 0.35 Tl achieved 3 times.

![Figure 1](image_url)

**Figure 1.** The dynamics of the deposition of copper recovered by iron onto the steel substrate as a function of the magnetic field. The values of the field: 1 – 0 Tl, 2 – 0.05 Tl, 3 – 0.10 Tl, 4 – 0.15 Tl

Fig. 1 presents the dynamics of copper deposition as a function of time and magnetic field. These straight lines show that the amount of deposited copper grows proportionally to the time. Hence the rate of the recovery is constant during the deposition. On the other hand the relative retarding corresponding to the same increase of the magnetic field is decreased monotonically at each of the three steps. Studies of dynamics of copper deposition in the stronger magnetic field (0.35 Tl) revealed an unexpected experimental result. Creation of micro-particles of a white substance was observed at the surface of the copper sulfate drop after several minutes of the deposition (Fig. 2). Later they were concentrated at the edge of the drop as a white border. X-Ray spectral microanalysis of these particles determined the nature of these particle as water-less iron sulfate FeSO$_4$.
When a piece of copper wire with a grave was placed inside the drop of the sulfate the deposition of the copper during its recovery took place preferentially on the wire filling the grave. But the application of magnetic field during the deposition retarded this process by several times.

Influence of magnetic interactions on the phase transformations in the system iron-copper-water was found without an external magnet as well. Two drops of the copper sulfate solution with dimensions 3-5 mm were deposited onto the St3 surface at the same distance from each other. After about two minutes of the recovery the drops began to move towards each other. The mean rate of the approach was about 1 mm per minute. When the drops touched each other the bridge was formed between them and the drops stopped. The liquid flow started to move from the smaller drop to the bigger. Copper ions began to migrate in the opposite direction from the bigger drop to the smaller (Fig. 3). Regions of a transparent liquid appeared at the both sides of the bridge between the drops whereas the liquids inside the drops were opaque.

Then at the place of the smaller drop a circle from the deposited copper was formed whereas the bigger drop became of brown color and was coated with a crust. Electron microscopy of the depositions formed after drying of the drops revealed modifications of their morphologies during several days. At the beginning rectangular microcrystals and microspheres appeared (Fig. 4).

Then the rectangular crystals began transformations to tubes with square cross-section and layered structures were formed in the walls of these tubes (Fig. 5).

The microspheres were transformed to lace-like nets (Fig.4, right) and sharp layered nanocrystals were formed between them (Fig.6).

X-Ray spectral microanalysis of these depositions revealed unusual proportions of iron and sulfur concentrations (two iron atoms to one atom of sulfur).

Several additional facts were obtained in the experiments with recovery of copper by the iron filings which were put onto the polymer substrate. The first 2-3 drops of the copper sulfate deposited with the syringe onto the layer of the filings were repulsed from them. The next drop was fixed at the filings and the deposition of a copper film onto the filings was observed through the drop. When the substrate with these filings and drop were put onto the 0.35 Tl magnet the filings stood up normally to the magnet surface whereas the liquid became dense and gel-like in several seconds. When the polymer substrate with the filings was placed at the magnet before the deposition of the copper sulfate the chemical reaction was divided between two regions; at the lower parts of the filings copper was deposited onto their lateral faces whereas at their upper ends white microparticles were formed (Fig. 7).

Observations of the changes of the morphology of the copper sulfate drops deposited onto the filings without magnets revealed that the lateral surfaces of the drops are coated gradually with
Figure 3. The remnants of the two drops of the copper sulfate solution after their mutual attraction, redistribution of copper and iron and the deposition onto the steel substrate

Figure 4. Electron microscopy of the rectangular crystals (left) and the spherical forms (right) of the iron-sulfur combinations deposited onto the steel surface in the regions between the drops.

the mixture of filings and copper. Hence the filings are moving up against the force of gravity. Then the upper edge of the envelope formed around the drop created an equilateral triangle (Fig.8).

4. Discussion of the results and prospects of their practical applications
The retardation of the recovery of copper by iron is explained by three main reasons: transformations of the domain structures of steel; the magnetic resistance against transformations of paramagnetic copper to diamagnetic; repulsion of diamagnetic copper from the maxima of the magnetic field. The inter-domain boundaries inside steel accelerate the
Figure 5. The transformation of the rectangular crystals to the tubes with layered walls. The microspheres were transformed to lace-like nets (Fig. 4, right) and sharp layered nanocrystals were formed between them (Fig. 6).

Figure 6. Electron microscopy of the sharp layered crystals formed from the iron-sulfur depositions.

recovery of copper by two mechanisms. The iron ions within the boundaries are in non-profitable situation. So they are bounded weaker and are transferred to the solution faster. On the other hand, the magnetic field at the boundaries has a normal component which attracts paramagnetic copper ions and repulses the ions transformed to diamagnetic state. So the circulation of copper ions is arranged by the boundaries with corresponding acceleration of the reaction. The application of the external magnetic field of any direction increases the
Figure 7. The deposition of the copper deposition on the lower parts of the iron needles standing perpendicular to the magnet surface and of the white particles on their upper parts.

Figure 8. The forming of the copper-iron envelopes at the drops deposited onto the steel filings.

dimensions of domains with profitable orientation. Due to the growth of the domains the length of the inter-domain boundaries is decreased resulting in weakening of their accelerative influence. So local modification of the morphology of inter-domain walls can either accelerate or retard the local rates of iron etching and copper deposition. These modifications can be produced by approaching of magnetic or steel needles to the place where this regulation is needed. Hence the alternative procedure of preparation of micro-schemes in magnetic semiconductors or other magnetic materials can be developed to substitute expensive and complicated procedure of electron-beam lithography.

Creation of waterless iron sulfate in rather strong magnetic field can be explained by a necessity to reduce the magnetostatic energy by means of maximal approach of magnetic ions of iron to each other. So the molecules of water absorbed by iron sulfate without the magnetic
field are pushed away from the iron sulfate molecules and the solubility of this salt in water is reduce by the magnetic field.

Preferential deposition of recovered copper onto the copper surfaces placed inside the solution is the result of better affinity of diamagnetic copper to the copper surface in comparison with steel surface. This procedure in combination of its retardation by magnetic field can be used for local restoration of worn parts of copper contact wires just at the places of their work instead of changing the wire. The restoration device moving along the wire should fulfill two functions: the measurement of the local degree of the wear and the deposition of the necessary copper layer with the governing of the deposited amount by the magnetic field regulated automatically.

Mutual attraction of two drops of the copper sulfate solution is explained by the increase of its paramagnetic susceptibility during the substitution of copper ions by iron ions. Two mechanism provide the motions of the drops. The first one is connected with the magnetic interaction between the drops by means of oscillating magnetic moments (like the well known Van-der-Waals interactions due to oscillating electrical dipole moments of nanoparticles or molecules [20]). The second is induced by the repulsion between the paramagnetic drops and diamagnetic copper layer formed between the drop and iron substrate. Due to this repulsion the drop tries to leave the region coated with copper for a non-coated region. The motion towards the neighboring paramagnetic drop is more profitable than in other directions. When the drop touch each other the bridge between them is formed and then iron ions are attracted to the bigger drop by its magnetic field whereas diamagnetic ions are repulsed from the bigger drop to the smaller. So the first drop accumulates paramagnetic ions of iron whereas the second one accumulates diamagnetic ions of copper. The mutual repulsion between paramagnetic and diamagnetic ions prevents joining of the drops.

Double exceeding of iron concentration in comparison with sulfur concentration in the regions between the drops followed with forming of layered nanocrystals can be explained by creation of fougerite crystals where three valence iron ions are mixed with two valence ions [21]. Three valence ions can be created by additional oxidation of iron by oxygen. Then three valence ions are pushed out from the drop due to their increased electrical charge. The additional force removing these ions from the drops towards the inter-drop region results from the magnetic interactions between them and inter-drop magnetic field produced by inter-domain boundaries which have not been transformed yet by interaction with copper ions.

The magnetic interactions between iron filings and the copper sulfate solutions revealed several new features of these processes. Abrupt growth of the viscosity of the drops of the solutions just after placing the substrate with the filings and the drops onto the magnet with 0.35 Tl field can be explained by fast rearrangement of the morphology of the solution in this relatively strong field. Earlier these drops were interacting with randomly distributed weak fields of the powder-like filings. So the paramagnetic ions of iron and diamagnetic ions of copper were distributed randomly as well. Placing of the substrate onto the magnet rearranged the morphology of the filings from powder-like to needle-like with orientation of the needles normally to the magnet surface. The maximal field was concentrated in the upper region around the tops of the needles, whereas in the vicinity of the substrate the field was weaker due to opposite to the fields of the iron needles opposite to the field of the magnet. This ordering of the distribution of the field modified the morphology of the solution. The paramagnetic ions of iron were concentrated in the upper region whereas the diamagnetic ions of copper were collected at the bottom regions. In the former solution with the mixture of the ions with opposite magnetic characters the repulsive interactions between them prevail. After separation of the ions by the magnetic field the attractive interactions between paramagnetic ions of iron becomes prevailing. So the increase of the viscosity of the solution in the magnetic field can be explained by this reason at least partially.

Forming of copper depositions at the lower parts of the filing needles and the white grains
at the upper parts is the result of this separation as well. The white grains can consist from various combinations of iron, sulfur and oxygen.

The creation of combined envelopes from the filings of iron and copper depositions around the solution drops placed initially onto the layer of the filings without the external magnetic field can be attributed to combination of chemical and magnetic interactions between copper ions, copper depositions, iron ions and iron filings. At the beginning the chemical recovery of copper ions by the iron from the filings starts at the bottom of the drop. Then due to growth of the concentration of the highly paramagnetic ions of iron the long-distance attraction between the drop and the ferromagnetic micro-particles of filings is increasing as well. But these particles do not penetrate inside the drop due to the short-range repulsion due to copper deposition at the surfaces of the particles. So the magnetic microparticles of the filings are attracted to the lateral surface of the drop and gradually coat it going up against the gravitation. They do not enter inside due to the intermediate layer of copper between the particles and the solution. This layer is seen clearly at Fig 8. and providing repulsing interaction between diamagnetic copper and the paramagnetic ions of iron in the solution. Hence the envelope from the filings coated with copper is formed around the drop. We assume that the geometry of the upper boundary of this core close the ideal triangle is induced by this repulsion for minimization of the energy of non-profitable interaction of copper at the filings and paramagnetic iron in the solution.

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