

# Phase Separation of an Electrolyte during Etching and Sedimentation of Metals on a Surface of a Ferromagnetic Metal Ball in an External Magnetic Field

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**Abstract:** The influence of the Earth gravitation on the shape of the interface between the two quasi-stationary phases in an electrolyte with different magnetic susceptibilities was observed experimentally during etching and deposition of metals on a steel ball in an external magnetic field, applied parallel to the field of gravity. The shape of this interface in an electrolyte is described theoretically on the basis of the equation of the balance of osmotic, magnetic and hydrostatic pressures in the Earth's gravity.

**Key words:** Phase separation, electrolyte, etching and deposition, sedimentation, field of gravity, gradient magnetic field, magnetic susceptibility.

## 1. Introduction

Interest in the study of magnetic field effects on electrochemical systems is relating to the ability to influence on the mass transfer near an electrode surface that allows to control the properties of the surface of metals at electrode position and electro dissolution [1-4], and to control the rate of electrochemical reactions [5-10]. The effect of magneto hydrodynamic stirring of the electrolyte under the action of the Lorentz force in a magnetic field by passing an electric current through the electrolyte [11-15] is the major cause of a significant effect of a magnetic field in the course of electrochemical transformations. The most significant effects of the magnetic field are related to the electrochemical reactions at the surface the slowest stage of which is transport of reactants or reaction products. In this case mixing of the electrolyte changes the diffusion mechanism of transport into the

convective one. Therefore, the mixing of the electrolyte significantly increases the rate of electrochemical reactions, characterized by diffusion or mixed kinetics [11]. Theoretical modeling of these magneto electrolysis effects is based on the combined system of magneto hydrodynamic equations for a weakly conducting fluid and convective diffusion equation [16].

However, there are a number of experimental effects of the magnetic field on the course of cementation deposition, chemical etching and corrosion of metals [17-20], which cannot be explained by the action of the Lorentz force because current is not being passed through the electrolyte in these processes. It was revealed in Refs. [19, 20] that the spatial modulation of the electrode surface properties is mainly determined by the distribution of the inhomogeneous magneto static fields on the electrode surface. For example, it was found in Ref. [21] that the magnetic field can render the significant influence on the pitting corrosion of iron, cobalt or nickel electrodes in the form of a thin film. The

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influence of the magnetic field gradient on ferromagnetic metals corrosion was revealed due to the differences in transportation of paramagnetic oxygen around the magnetized and non-magnetized samples [22]. The effects of influence of inhomogeneous static magnetic field on the electrode position of metal layers are not explained due to the action of the Lorentz force by passing the electric current through the electrolyte and there is dependence between the properties of electrode position and between distribution of the magnetic field induction at the surface of the electrode and magnetic susceptibility of certain electrolyte components [23-25].

Until recently, there were no physical models of quantitative explanation of the effects of inhomogeneous magnetic field influence on electrochemical reactions. The problem of modeling of these processes was that the effect of inhomogeneous magnetic field influence was considered only for the ions in the electrolyte. But the magnetic energy of a single ion is in 5-6 orders of magnitude less than the energy of its thermal motion in magnetic fields of moderate strength (about 1 kOe-10 kOe). Therefore the magnetic gradient force at the electrode is less than so-called entropic force which is diffusion driving force. Consequently, the expected effects of the inhomogeneous magnetic fields influence are negligibly small for this range of magnetic fields. It was not possible in this approach, firstly, to describe the order of the magnitude of the influence of the effect of inhomogeneous magnetic field on the deposit thickness. Secondly, it was impossible to explain why there is a direct effect of the deposition of thickest metal layer in the areas of the cathode with the highest magnetic field strength under some experimental conditions while the inverse effect of deposition of the thickest metal layer in the cathode regions with minimal magnetic field strength is observed under other conditions [23-25]. Impossibility to describe the direct and inverse effects in models of influence of the inhomogeneous magnetic field on separate ions is

associated with the inability to introduce the concept of effective magnetic susceptibility [20] for a single ion because the effective magnetic susceptibility is a thermodynamic quantity.

The model of the action of the gradient magnetic forces on paramagnetic clusters or effectively paramagnetic products of electrochemical reactions is proposed in Refs. [20, 26] for a quantitative description of the influence of an inhomogeneous magnetic field on electrochemical reactions. The concept of effective magnetic susceptibility of cluster products of electrochemical transformations is proposed as well in Refs. [20, 26]. The effective magnetic susceptibility is equal to the difference between magnetic susceptibilities of nano- or microscale cluster products of electrochemical reactions and between the magnetic susceptibility of an electrolyte. The change of the sign of the effective magnetic susceptibility with changing the experimental conditions leads to the change of the direct effect into inverse in processes of electrode position, electro dissolution, cementation, corrosion and chemical etching of metals in an inhomogeneous magnetic field [19, 23-25, 27]. Moreover, the magnetic energy of clusters can be of the same order or greater than their energy of the thermal motion in the model of action of the inhomogeneous magnetic field on the cluster products of electrochemical transformations due to the sufficient size of clusters. Therefore, the inhomogeneous magnetic field will have a significant influence on the diffusion of clusters and the electrochemical reaction in this model.

It should be noted that the model that takes into account the presence of an electrolyte cluster component for the first time allowed carrying out the quantitative description of the formation of heterogeneous stationary state of the electrolyte in the electrochemical processes under the influence of an inhomogeneous magnetic field [20]. Wherein the phase separation of the electrolyte on phases with the different concentration of products of electrochemical transformations and with different magnetic

susceptibilities respectively was observed experimentally in the non-uniform magnetic field both by passing an electric current through the electrolyte and without one [7, 8, 20]. It is shown in Refs. [7, 8] that the solution areas with altered concentration of paramagnetic ions were generated by passing a current through the electrolyte near the ferromagnetic microelectrodes in an external magnetic field. The formation of such regions can be observed using chemical dyes [8]. Formation of the regions with altered concentration of corrosion products in the electrolyte is accompanied by the formation of several regions with the different rates of electrochemical reactions on the surface of the ferromagnetic metal samples including steel etching in acid solution in an external magnetic field [19, 28, 29] and cementation of metals on the surface of ferromagnetic electrodes. Formation of such areas are accompanied by a change in shape of the sample in the process of chemical etching with a clear dependence on the direction of the external magnetic field and the sign of the effective magnetic susceptibility of cluster products of electrochemical reactions [7, 8, 20, 30]. The formation of two regions on the surface of a cylindrical iron electrode was revealed in Ref. [17], the regions are characterized by different velocities of corrosion and are not related to the heterogeneity of the chemical, crystallographic and other structural properties of the electrode, but exclusively due to the inhomogeneous magnetic fields.

The ferromagnetic ball is magnetized uniformly and creates around itself a dipole type of a gradient magnetic field. The ball-shaped model object was chosen in the papers [19, 29] for this reason. Thus influence of the sample shape anisotropy on the course of electrochemical processes on its surface is excluded and the effects of inhomogeneous magnetic field influence are observed in the best way. It gives the opportunity to compare formation of the regions with different rates of etching of the ferromagnetic ball with a specific spatial distribution of magnetostatic fields

and analyze the number, shape and size of the areas formed by etching.

The shape of the interface in an electrolyte separating the regions with different magnetic susceptibilities of paramagnetic corrosion products of the magnetized steel ball was studied in Ref. [31] and the theoretical model of hydrostatic equilibrium was proposed to describe the shape and size of mentioned interface. It was theoretically shown in Ref. [31] that the phase separation of the electrolyte takes place in an inhomogeneous magnetic field if the size of clusters exceeds the critical value and it is not possible if the electrolyte contains separate paramagnetic ions in the absence of cluster components. The model of the paper [31] is applicable to the experimental conditions of negligibly small differences in densities of the electrolyte and the phase of elevated concentration of paramagnetic corrosion products because the model does not take into account the hydrostatic pressure in the Earth's gravity field.

## **2. Problem Statements**

The purpose of this paper is the investigation of the process of formation of the heterogeneous state of an electrolyte in etching and cementation of metals on the surface of the ferromagnetic metal ball in an external magnetic field parallel to the gravity force. In this paper, the model of hydrostatic equilibrium was generalized to describe a heterogeneous state of an electrolyte in an inhomogeneous magnetic field magnetized ferromagnetic ball considering the hydrostatic pressure in the Earth's gravity field. The results of theoretical modeling for the first time describe the impact of Earth's gravity to a form of the interface in the electrolyte between the phases with different magnetic susceptibilities which are formed during the electrochemical reactions on the surface of the ferromagnetic ball in an external magnetic field applied parallel to the force of gravity. The comparison of experimental data with the results of theoretical modeling was carried for the form of interface in the

electrolyte for “steel ball-electrolyte in a magnetic field” system taking on account the following physical parameters the external magnetic field strength, magnetic susceptibility of the phase enriched with the cluster products of electrochemical reactions; magnetic susceptibility of an electrolyte; density of the phase enriched with the cluster products of electrochemical reactions; density of an electrolyte; numbers of effectively paramagnetic cluster products of electrochemical reactions per unit of volume in the region of their high concentration; temperature of an electrolyte; magnetization and the radius of the ball, respectively.

### 3. Materials and Methods

#### 3.1 Experimental Research

Experimental study on the formation of a heterogeneous state of the electrolyte was carried out during the processes of etching and cementation of metals on the surface of steel ball in the external magnetic field parallel to the force of gravity. Thus the experiments were carried out on the formation and visualization of areas of high concentration of paramagnetic clusters of  $\text{Fe}^{2+}$  ions in the vicinity of the magnetized steel ball [32]. Such experiments allowed studying the processes of redistribution of the concentration of clusters of  $\text{Fe}^{2+}$  ions in the solution. In particular, the formation of such regions was investigated in the processes of etching of the magnetized steel ball in a solution of nitric acid and in the process of cementation of copper from a solution of copper sulfate on the same ball. Both the first and the second electrochemical process (etching and cementation) on the surface of the steel ball lead to formation of the surface layer of the electrolyte enriched with the clusters of the paramagnetic iron ions. At the same time the formation of the regions with high concentration of iron ions clusters was observed near the magnetic poles of the magnetized ball. The dimensions of these regions are several orders of magnitude greater than the thickness of the diffusion

layer.

The study of gravity on the form of the electrolyte regions enriched with clusters of iron ions was carried out using the installation shown in Fig. 1.

The steel ferromagnetic ball (1) was fixed on the non-conductive, non-magnetic and chemically inert holder (2) in the center of the glass cell (3). The solution of copper sulfate (4) with the concentration of copper ions  $\text{Cu}^{+2}\text{C}_{\text{Cu}} = 0.2 \text{ M}$  or the solution of nitric acid was poured into the glass cell. The two methods were used to visualize the areas with high concentration of  $\text{Fe}^{2+}$  clusters that appear in a solution of copper sulfate in cementation of copper on the steel ball or in the solution of nitric acid in etching of a steel ball. The first method supposed using chemical dyes on  $\text{Fe}^{2+}$  ions and the second method was observation without the chemical dye. The chemical dye represented  $\text{Ag}^{+}$  ions according to [32]. The concentration of  $\text{Ag}^{+}$  ions in the working solution was less than  $\text{C}_{\text{ag}} = 0.02 \text{ M}$ . The cell with a fixed specimen and the solution was placed in the center of the magnetic system (6). The external magnetic field was directed parallel to the force of gravity. Observation of the process of formation of the high concentration areas of  $\text{Fe}^{2+}$  ion clusters in a magnetic field gradient was performed using a microscope (5) (Fig. 1). During the experiment the photo and video shooting was carried out [32].

The experiments have shown that when the orientation of the magnetic field was parallel to the field

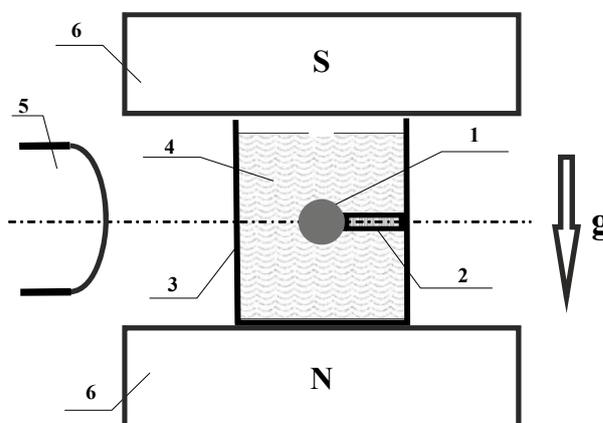
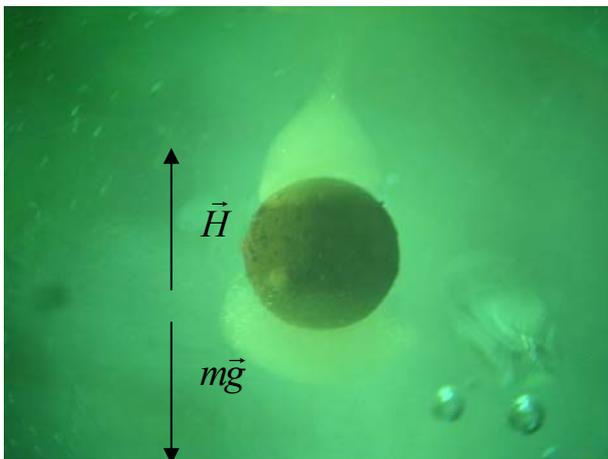


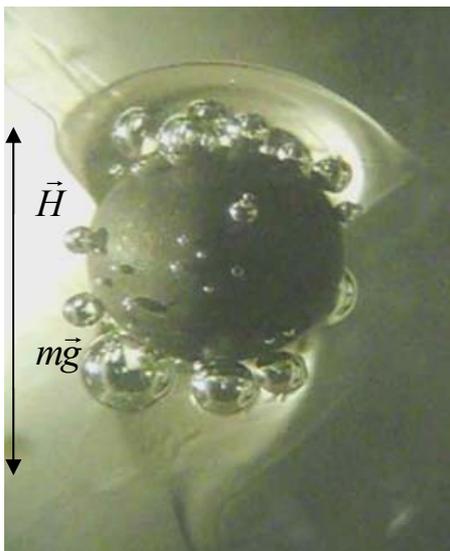
Fig. 1 The schematic image of the experimental device.

of gravity the form of regions with a high concentration of clusters of  $\text{Fe}^{2+}$  ions was not the same in the vicinity of the upper and lower magnetic poles of the ball as it is shown in Fig. 2a (image of copper cementation process with the addition of chemical dyes) and Fig. 2b (image of the steel ball etching in an aqueous solution of nitric acid without chemical dyes).

Difference of the form of the region with high concentration of the clusters of  $\text{Fe}^{2+}$  ions in the vicinity of upper and lower magnetic poles of the ball is due to the fact that the density of the solution in regions with a



**Fig. 2a** The steel ball in the solution of copper sulfate with the addition of silver nitrate solution. The ball diameter  $d = 4$  mm. The external magnetic field strength  $\vec{H} = 1,000$  Oe.



**Fig. 2b** The steel ball in the solution of nitric acid without the addition of chemical dyes. The ball diameter  $d = 4$  mm. The external magnetic field strength  $\vec{H} = 1,000$  Oe.

high concentration of the clusters of iron ions near the magnetic poles of the magnetized ball differs from the density of the solution outside these regions, i.e., in the rest of the electrolyte.

The relation between  $\rho$  and  $\rho_l$  can change depending on the experimental conditions, i.e.,  $(\rho_0 - \rho_l < 0)$  (Fig. 2a) or  $(\rho_0 - \rho_l > 0)$  (Fig. 2b) where  $\rho_0$  is a density of the region;  $\rho_l$  is a density of the electrolyte. The model of this paper assumes that the change of the sign of the difference of densities  $\rho = (\rho_0 - \rho_l)$  should result in mirror reflection of interface from the horizontal axis as it is observed in the experiment (Fig. 2a, Fig. 2b).

The process of formation of the areas with high concentration of  $\text{Fe}^{2+}$  clusters occurs in several stages. The initiation and increase of areas with high concentration of  $\text{Fe}^{2+}$  clusters is observed at the first stage (the stage of formation) (Fig. 3).

The invariance of shape and size of regions enriched with iron ions was observed at the next stage (the quasi-stationary stage) for several tens of minutes (Fig. 4). The state of these areas is quasi-stationary at this stage.

The sharp clear boundary between areas of high concentration of  $\text{Fe}^{2+}$  clusters and the rest of the electrolyte is typical for the first two stages.

The convective processes gradually lead to blurring of boundaries and deformation of the regions enriched with  $\text{Fe}^{2+}$  clusters at the third (final) stage (Fig.5 and Fig.6).



**Fig. 3** The process of formation of regions with high concentration of  $\text{Fe}^{2+}$  clusters at the initial stage. The ball diameter  $d = 4$  mm.



**Fig. 4** The process of formation of regions with high concentration of  $\text{Fe}^{2+}$  clusters at the stage of formation of the quasi-stationary state. The ball diameter  $d = 4$  mm.



**Fig. 5** The process of deformation of the regions with high concentration of  $\text{Fe}^{2+}$  clusters. The ball diameter  $d = 4$  mm.



**Fig. 6** The process of deformation of the regions with high concentration of  $\text{Fe}^{2+}$  clusters. The ball diameter  $d = 4$  mm.

These experimental observation of the processes of redistribution of the concentration of  $\text{Fe}^{2+}$  clusters in

solution in the presence of a gradient magnetic field and the field of gravity allows to trace the process of phase separation of the electrolyte, i.e. the formation of quasi-stationary heterogeneous state of the electrolyte, and to investigate the shape of the interface between phases with different magnetic susceptibilities and concentrations of electrochemical reaction products.

### 3.2 Theoretical Model

It is considered that the model of pressure equilibrium [33] for constructing theoretical models of hydrostatic equilibrium for the shape of the interface between the regions with different magnetic susceptibilities during etching of the ferromagnetic metal ball in a magnetic field applied parallel to the gravitation force.

It is also considered that the shape and size of the region are constant [20, 31] in the connection with the establishment of hydrostatic equilibrium at the interface between the two media which occurs at the quasi-stationary stage during the typical lifetime of the region with high concentration of effectively paramagnetic products of electrochemical reactions.

The equation of hydrostatic equilibrium on the interfacial surface in the electrolyte can be written neglecting the Laplace pressure on the interfacial surface similar to Eq. (2) [31]:

$$P_m + P_0 + P_g = 0 \quad (2)$$

where,  $P_m = -\frac{1}{2}\chi\bar{H}^2$  is the magnetic pressure;  $\bar{H}$  is the magnetic field strength at the interface in the electrolyte;  $\chi = \chi_0 - \chi_l$  is the effective magnetic susceptibility which is equal to the difference between the magnetic susceptibility of the region with high concentration of products of electrochemical reaction  $\chi_0$  and between the magnetic susceptibility of an electrolyte outside this region  $\chi_l$  [34];  $P_0$  is the osmotic pressure [35];  $P_g$  is the hydrostatic pressure in the Earth's gravity field.

The condition of hydrostatic equilibrium at the interface in the electrolyte has the form:

$$\frac{1}{2}\chi\bar{H}^2 + \rho gx \cos\theta = P_0 \quad (3)$$

where,  $g = 980 \text{ cm/s}^2$  is the gravitational acceleration,  $x$  is the absolute value of the radius-vector of a point at the interface,  $\theta$  is the angle between the radius-vector of a point at the interface and between the direction of the gravitation force. The center of the coordinate system is chosen at the center of the ferromagnetic ball. The hydrostatic pressure term  $P_g = \rho gx \cos\theta$  in the Earth's gravity field is introduced in the Eq. (3). The last can be written as:

$$\frac{1}{2}\chi\bar{H}^2 + \rho gR\tilde{x} \cos\theta = n_{cl}kT \quad (4)$$

where,  $\tilde{x} = x/R$   $R$  is the radius of the steel ball,  $n_{cl}$  is the number of effectively paramagnetic products of electrochemical reactions in unit volume of the region of their high concentration;  $k = 1.38 \cdot 10^{-16} \text{ erg/G}$  is the Boltzmann constant;  $T = 300 \text{ K}$  is an absolute temperature.

The schematic image of the ferromagnetic ball during cementation deposition of copper in an external magnetic field applied parallel to the force of gravity is shown in Fig.7. It shows that the two regions with high concentration of products of electrochemical reactions are formed: the upper ( $\tilde{x}_1 = +Rx \cos\theta$ ) and lower ( $\tilde{x}_2 = -Rx \cos\theta$ ) regions where the angle  $\theta$  is equal also to the angle between the direction of the external magnetic field and the radius vector of a point on the interfaces surface in the case when the external

magnetic field is applied parallel to the direction of the Earth gravitation force. These experiments show that the symmetry of the interface is observed (Fig. 7) with respect to the vertical axis at the cementation of copper from a solution of copper sulphate on the magnetized steel ball.

It is considered that the first case for the upper region where  $\tilde{x}_1 = +Rx \cos\theta$ . Then the Eq. (4) can be transformed as:

$$\frac{1}{2}\chi\bar{H}^2 + \rho gRx \cos\theta = n_{cl}kT \quad (5)$$

Then Eq. (5) is written as follows:

$$\frac{\bar{H}^2}{\bar{M}_0^2} + 2 \frac{\rho gR}{\chi M_0^2} x \cos\theta = 2 \frac{n_{cl}kT}{\chi M_0^2} \quad (6)$$

Here the substitution is used:

$$(\bar{H}^*)^2 = \frac{\bar{H}^2}{\bar{M}_0^2} \quad (7)$$

$$(\bar{H}^*)^2 = \xi^2 +$$

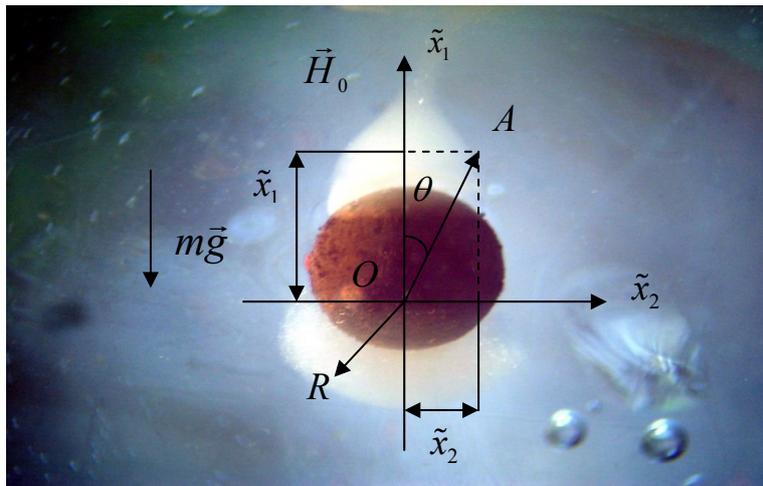
$$\frac{8\pi\xi(3\cos^2\theta - 1)}{3x^3} + \frac{16\pi^2(3\cos^2\theta + 1)}{9x^6} \quad (8)$$

where:

$$\xi = \frac{H_0}{M_0} \quad (9)$$

$$C_1 = \frac{\rho gR}{\chi M_0^2} \quad (10)$$

$$C_2 = \frac{n_{cl}kT}{\chi M_0^2} \quad (11)$$



**Fig. 7** The image of cementation of copper ions from a solution of copper sulfate on the magnetized steel ball with the addition of silver nitrate solution where  $x = OA/R$ ,  $R = 0.2 \text{ cm}$ ,  $OA = x$ ,  $\bar{H}_0$  is external magnetic field strength.

As a result the next equation is obtained (12):

$$\left(\frac{8\pi\xi}{x^3} + \frac{16\pi^2}{3x^6}\right)\cos^2\theta + 2C_1x\cos\theta + \left(\xi - \frac{4\pi}{3x^3}\right)^2 - 2C_2 = 0 \quad (12)$$

The Eq. (12) is the square one relative to  $\cos\theta$  and the two roots are obtained by solving:

$$\cos\theta_{1,2} = \frac{-C_1x \pm \sqrt{(C_1x)^2 - \left(\frac{8\pi\xi}{x^3} + \frac{16\pi^2}{3x^6}\right)\left(\left[\xi - \frac{4\pi}{3x^3}\right]^2 - 2C_2\right)}}{\frac{8\pi\xi}{x^3} + \frac{16\pi^2}{3x^6}} \quad (13)$$

There is only one physical solution with a plus sign “+” in front of arithmetic root in the solutions (13).

Similarly, the second case is considered for the lower region so that  $\tilde{x}_2 = -Rx\cos\theta$  in the Eq. (4). The next equation is obtained as a result of transformations:

$$\left(\frac{8\pi\xi}{x^3} + \frac{16\pi^2}{3x^6}\right)\cos^2\theta - 2C_1x\cos\theta + \left(\xi - \frac{4\pi}{3x^3}\right)^2 - 2C_2 = 0 \quad (14)$$

The Eq. (14) is quadratic one relative to  $\cos\theta$  and two roots are obtained by solving it:

$$\cos\theta_{1,2} = \frac{C_1x \pm \sqrt{(C_1x)^2 - \left(\frac{8\pi\xi}{x^3} + \frac{16\pi^2}{3x^6}\right)\left(\left[\xi - \frac{4\pi}{3x^3}\right]^2 - 2C_2\right)}}{\frac{8\pi\xi}{x^3} + \frac{16\pi^2}{3x^6}} \quad (15)$$

The solution with the plus sign “+” is the only physical one in Eq. (15).

#### 4. Results and Discussion

The experimental data of the formation process of regions and high concentration of electrochemical transformations products at the initial stage with the results of the theoretical modeling are compared. The values of the coefficients  $C_1$  and  $C_2$  are found

comparing the experimental data of the formation process of regions with high concentration of  $\text{Fe}^{2+}$  cluster at the initial stage with the theoretical model. The theoretical form of the interface in the electrolyte describes according to Eqs. (13) and (15) the relevant data obtained experimentally. The results obtained are shown in Fig. 8 where the points are experimental values and the solid line is the result of theoretical modeling.

Similarly, the values of the coefficients  $C_1$  and  $C_2$  are found comparing the experimental data of the process formation of regions with high concentration of clusters at quasi-stationary stage with the results of theoretical modeling. In this case the theoretical shape of the interface in the electrolyte describes according to Eqs. (13) and (15) the relevant data obtained experimentally. The results are shown in Fig. 9 where the points are the experimental values; the solid line is the result of theoretical modeling.

Similarly let's compare the results of theoretical modeling according to Eqs. (13) and (15) with the experimental data at the stage of deformation the regions with high concentration of electrochemical reaction products. The experimental values and theoretical

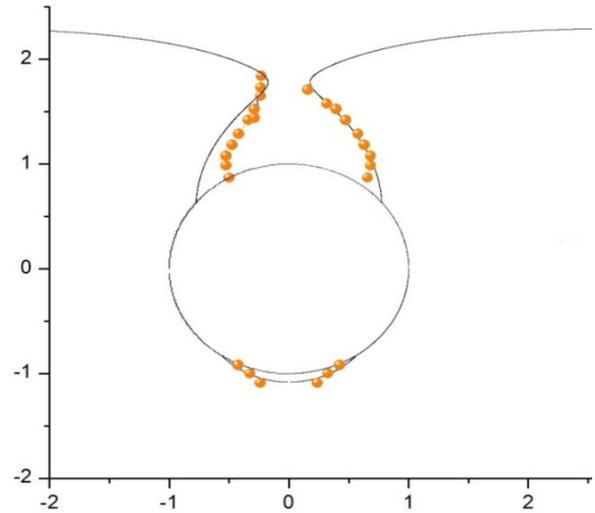


Fig. 8 The results of comparison of experimental data with the results of theoretical modeling of regions with high concentration of electrochemical reaction products at the initial formation stage. The coefficients  $C_1 = 13.5$ ,  $C_2 = 40$  for the upper region and values of the coefficients  $C_1 = 13.5$ ,  $C_2 = 40$  for the lower region. Distances at the axes are given in

units of the radius of the ball.

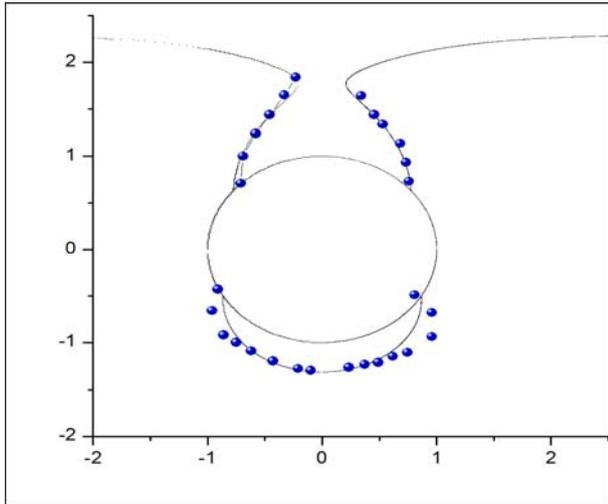


Fig. 9 The results of comparison of theoretical modeling with the experimental data for the formation process of the regions with high concentration of electrochemical reaction products at the quasi-stationary stage. The coefficients  $C_1 = 13.6$ ,  $C_2 = 40$  for the upper region; the values of the coefficient  $C_1 = 13.6$ ,  $C_2 = 13$  for the lower region. Distances at the axes are given in units of the radius of the ball.

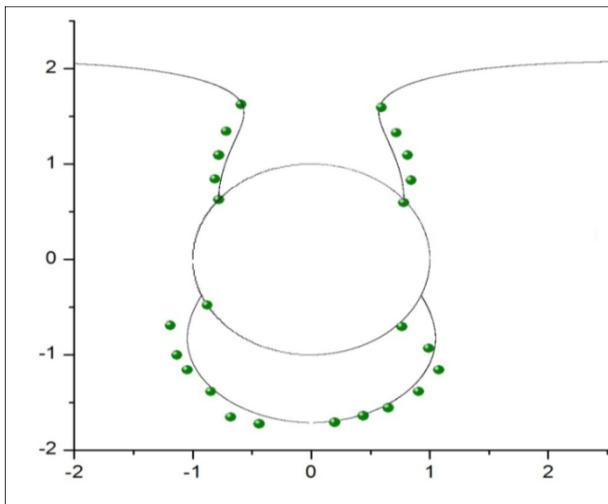


Fig.10 The results of comparison of experimental data with the results of theoretical modeling at the stage of deformation of the regions with high concentration of electrochemical reaction products. The coefficients  $C_1 = 15$ ,  $C_2 = 40$  for the upper region, the values of the coefficients  $C_1 = 4.5$ ,  $C_2 = 9.8$  for the lower region. The distances at the axes are given in units of the radius of the ball.

simulation results are shown in Fig. 10, the points are the experimental values and the solid line is the result of theoretical modeling.

Comparative analysis shows that the theoretical

model of hydrostatic equilibrium quantitatively describes the shape of the interface at etching of the steel ball in the electrolyte in the magnetic field taking into account the hydrostatic pressure in gravitation field.

The model describes the most exactly the process of formation of regions with high concentration of clusters at the initial and quasi-stationary stages because the quasi-stationary heterogeneous state of an electrolyte is observed at this stage and the equation of hydrostatic equilibrium at the interface is satisfied.

The form of the interface in the electrolyte between the regions with different magnetic susceptibilities is shown in Fig. 11 for different values of the coefficients  $C_1$  and is  $C_2$ .

Let's calculate the ratio  $(\rho/\chi)_1$  at the initial stage of formation of the regions with high concentration of electrochemical reaction products using Eq. (10) and the following values of the system parameters:  $R = 0.2$  cm,  $M_0 = 2,000$  G,  $g = 980$  cm/s<sup>2</sup>,  $C_1 = 13.5$  (Fig. 3, Fig. 8). This coefficient  $C_1 = 13.5$  is obtained by approximating

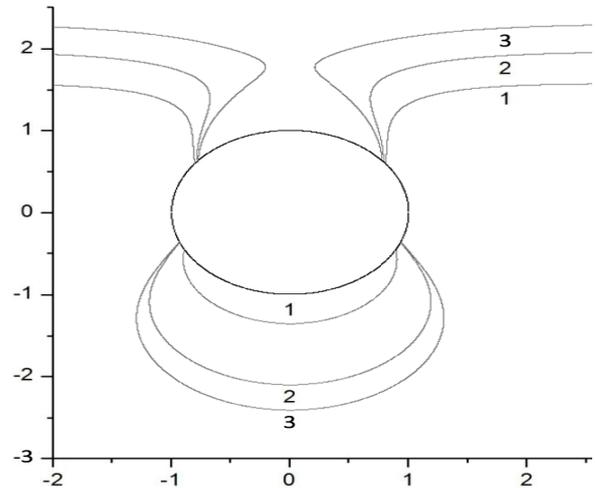


Fig. 11 The results of theoretical modeling for the various values of the coefficients  $C_1$  and  $C_2$ . The coefficient  $C_2 = 40$  for the upper region, the value of the coefficient  $C_1$  changes respectively:  $C_1 = 20$  at the initial stage (curve 1);  $C_1 = 16$  at the quasi-stationary stage (curve 2);  $C_1 = 13.6$  at the deformation stage (curve 3). The coefficient  $C_2 = 10$  for the lower region, the value of coefficient  $C_1$  changes, respectively:  $C_1 = 13.6$  at the initial stage (curve 1);  $C_1 = 1.4$  at the quasi-stationary stage (curve 2);  $C_1 = 0.6$  at the deformation stage (curve 3). The distances at the axes are given in units of

the radius of the ball.

the experimental data at the formation stage by the theoretical Eqs. (13) and (15). The result is:  $(\rho/\chi)_1 = 2.7 \times 10^5 \text{ g/cm}^3$ .

The ratio  $(\rho/\chi)_2$  is calculated at the quasi-stationary stage of formation of the regions with high concentration of electrochemical reaction products using the Eq. (10) with  $C_1 = 13.6$  (Fig.4, Fig.9). This coefficient  $C_1 = 13.6$  is obtained by approximation of the experimental data at the quasi-stationary stage. The result is the almost identical values of the density ratio to the effective magnetic susceptibility at the first and second stages:  $(\rho/\chi)_1 = (\rho/\chi)_2 \approx 2.7 \times 10^5 \text{ g/cm}^3$  because the parameters at the quasi-stationary phase are close to the parameters at the initial stage.

Similarly, the ratio  $(\rho/\chi)_3$  is calculated at the stage of deformation of regions with high concentration of electrochemical reaction products using Eq. (10). In this case, the coefficients  $C_1 = 15$  for the upper region and  $C_1 = 9.8$  for the lower areas are different from the values of these coefficients at the earlier stages (Fig. 5, Fig. 6 and Fig. 10). These values  $C_1 = 15$  and  $C_1 = 9.8$  were obtained fitting the experimental data for the upper and lower regions at the deformation stage by the Eqs. (13) and (15). As the result the ratio  $(\rho/\chi)_3 \approx 3 \times 10^5 \text{ g/cm}^3$  is obtained for the upper and  $(\rho/\chi)_3 = 9 \times 10^4 \text{ g/cm}^3$  for the lower regions.

These estimations are consistent with the estimations of the order of magnitude of the density and the magnetic susceptibility parameters:  $\rho \approx 0.1\text{-}1 \text{ g/cm}^3$ ,  $\chi \approx 10^{-6}\text{-}10^{-4}$ . Consequently,  $\rho/\chi \approx 10^3\text{-}10^6 \text{ g/cm}^3$  which is an additional argument for the adequacy of the model for the form of interface in the electrolyte between regions with different magnetic susceptibilities at the initial stage during etching and deposition of metals on the surface of the steel ball in an external magnetic field, applied parallel to the force of gravity.

As a result, the ratio of parameters  $(\rho/\chi)_1 = (\rho/\chi)_2$  is almost the same at the initial and the quasi-stationary stages for the upper and lower regions which have almost the same density and the effective magnetic susceptibility. However,  $(\rho/\chi)_3 \neq (\rho/\chi)_{1,2}$  at the deformation stage. This suggests that the destruction of

quasi-stationary state of the electrolyte during the etching of steel ball in an external magnetic field occurs after changing the value of the density and the effective magnetic susceptibility of the phase, formed due to the accumulation of cluster electrochemical reaction products in the region of their high concentration. At the same time  $\rho_3$  and  $\chi_3$  are different for the upper and lower regions. This could be due to the presence of several types of cluster products such as bubbles and micro- or nanoparticles which possess significantly different magnetic susceptibilities and densities  $\chi$  and  $\rho$ . The first tends to flow up and the second ones-down resulting in differences in the properties of the upper and lower regions.

## 5. Conclusions

The developed theoretical model of balance of osmotic, magnetic and hydrostatic pressures in the Earth's gravity field describes the shape of the interface between the regions in the electrolyte with different magnetic susceptibilities which are formed by etching the steel ball and during the deposition of copper on the surface of the steel ball in an external magnetic field parallel to force of gravity. The shape of this surface is determined by two dimensionless parameters  $C_1$  and  $C_2$  which are expressed through the physical parameters of the system "steel ball-electrolyte in a magnetic field": the magnetic susceptibility of region in the electrolyte, enriched with the clusters of electrochemical reaction products; the magnetic susceptibility of the electrolyte; the density of the electrolyte; the number of paramagnetic cluster-type electrochemical reaction products per unit volume of the region of their high concentration; temperature of the electrolyte; magnetization and the radius of the steel ball, respectively; strength of the external magnetic field.

In particular, the model describes the different forms of the interface for the upper and lower regions with increased concentration of the cluster products of electrochemical reactions, i.e. the asymmetry of the

interface with respect to the horizontal plane passing through the center of the ferromagnetic ball. This asymmetry is explained by the influence on the interface form of magnetic and hydrostatic gravitation pressures but the last is not a symmetric function of the vertical coordinate.

Thus, the form of the interface in the electrolyte between the regions with different magnetic susceptibilities during etching and deposition of metals on a steel ball in an external magnetic field, applied parallel to the field of gravity, is determined by the balance of osmotic, magnetic and hydrostatic pressures in the Earth's gravity. Namely, raising or sedimentation of the phase with magnetic susceptibility different from the rest of the electrolyte is occurring if the hydrostatic pressure of Earth gravity increases relative to the magnetic pressure depending on the relation between its density and the density of the electrolyte. The model correctly describes experimental fact of mirror reflection of the form of interface with respect to the horizontal plane (which is passing through the center of the ferromagnetic ball) if the relation of these densities  $\rho_0 > \rho_1$  changed conversely onto  $\rho_0 < \rho_1$ .

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