Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

Liquid-liquid phase separation and cluster formation at deposition of metals under inhomogeneous magnetic field

To cite this article: O Yu Gorobets *et al* 2017 *J. Phys.: Conf. Ser.* **903** 012057

View the article online for updates and enhancements.

Related content

- Determination of droplet contours in liquid-liquid flows within microchannels
  B Pulvirenti, B Rostami, G Puccetti et al.
- CFD simulation on the turbulent mixing flow performance of the liquid-liquid ejector
  W Z An, H Y Bie, C C Liu et al.
- Experimental study of liquid-liquid plug flow in a T-shaped microchannel
  A V Kovalev, A A Yagodnitsyna and A V Bilsky

IOP ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

This content was downloaded by j_w_klos from IP address 150.254.111.90 on 01/09/2018 at 17:56

Liquid-liquid phase separation and cluster formation at deposition of metals under inhomogeneous magnetic field

O Yu Gorobets[1], Yu I Gorobets[1,2], V P Rospotniuk[1], V I Grebinaha[1], A A Kyba[1]

[1] National Technical University of Ukraine "KPI", Kyiv, Ukraine
[2]Institute of Magnetism NAS of Ukraine, Kyiv, Ukraine

E-mail: rospotnyk@ukr.net

Abstract. The formation and dynamic of expansion and deformation of the liquid-liquid interface of an electrolyte at deposition of metals at the surface of the magnetized steel ball is considered in this paper. The electrochemical processes were investigated in an external magnetic field directed at an arbitrary angle to the force of gravity. These processes are accompanied by the formation of effectively paramagnetic clusters of electrochemical products – magnions. Tyndall effect was used for detection of the presence of magnions near the magnetized steel electrode in a solution. The shape of the interface separating the regions with different concentration of magnions, i.e. different magnetic susceptibilities, was described theoretically based on the equation of hydrostatic equilibrium which takes into account magnetic, hydrostatic and osmotic pressures.

1. Introduction

The effect of inhomogeneous magnetic fields (MF) on electrochemical processes is the subject of current research in the field of magnetoelectrolysis [1-8]. It was discovered experimentally [1-4] that the course of these processes depends on the gradient of MF and its distribution on the electrode surface. In particular, the formation of regions with higher concentration of electrochemical reaction products near the magnetic poles of a magnetized steel spherical sample was studied in [5-7] at the etching [5] and the deposition of metals on its surface [6, 7] under the influence of constant MF. The approach of the impact of gradient magnetic force not on single paramagnetic ions, but on the clusters of electrochemical reaction products (magnions) was proposed in [5-7]. Magnions can represent paramagnetic or effectively paramagnetic bubbles of gases, nano- and/or microparticles with their ionic environment [5-8]. Also the concept of effective magnetic susceptibility of magnions $\chi = \chi_m - \chi_s$ as the difference between magnetic susceptibilities of a magnion χ_m and a solution χ_s was introduced in this model [5-7].

The aim of this work is to study the process of the formation of a heterogeneous state of an electrolyte which is observed at the metal deposition on the surface of a spherical magnetized ferromagnetic electrode in an external MF (EMF) directed at an arbitrary angle to the direction of the force of gravity (FG) without passing of an external electric current through the solution. The theoretical model of the paper is based on the equation of hydrostatic equilibrium consisting of magnetic, osmotic and gravitational pressures and the pressure of the centrifugal force which causes the electrolyte rotation near the electrode surface with the velocity about 1 cm/s [7]. This equation allows calculating the form of the interface in liquid near the electrode surface that separates the regions with higher concentration of magnions and the bulk solution.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

2. Experimental results

Experimental observation of electrolyte phase separation at the deposition of copper ions on the surface of a steel spherical sample was carried out at angles of 90, 80, 70, 60, 50 and 40 degrees between the directions EMF to FG. The Tyndall effect was used to visualize areas with higher magnions concentrations similarly to [6]. The set of photos of liquid-liquid separation at different stages are shown in Fig. 1. Regions with higher magnion concentration are forming near the magnetic poles of the steel spherical electrode where the strength of MF (as the superposition of an uniform EMF and dipole MF of a magnetized steel spherical electrode) is the largest. In addition, the anisotropic sedimentation of copper ions near the magnetic equator of the steel spherical electrode (where the gradient MF is minimal) is observed. As it was shown in [6] the shape of interface remains almost unchanged for about 1000 seconds after its relatively fast formation. This allows considering such state of the system as the quasi-stationary one.

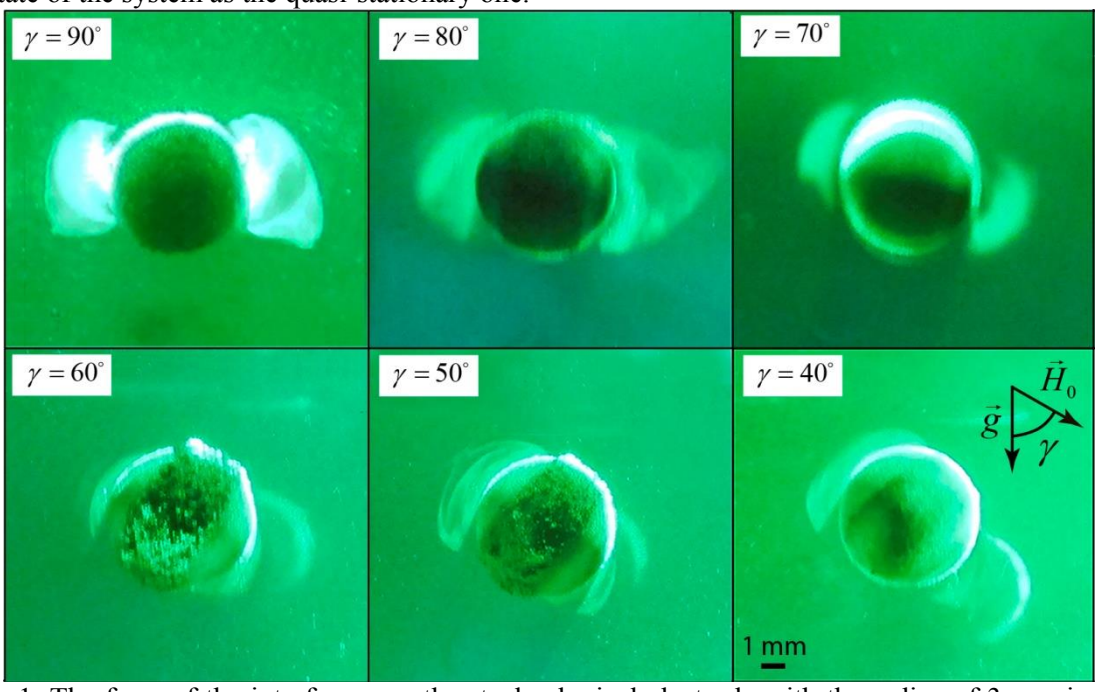

Fig. 1. The form of the interface near the steel spherical electrode with the radius of 3 mm in the $CuSO_4$ solution in an EMF H_0 = 1.8 kOe directed at different angles γ to the direction of FG.

3. Theoretical model

The hydrostatic equilibrium in an electrolyte depends on the balance of pressures at the interface between regions with different concentrations of electrochemical reaction products:

$$\Delta P_m + \Delta P_o + \Delta P_g + \Delta P_\omega = 0\,, \qquad (1)$$

where $\Delta P_o = nk_BT$ is the difference of osmotic pressures between two medium, n is magnion concentration, k_B is the Boltzmann constant, T is the absolute temperature; $\Delta P_m = -\chi \vec{H}^2/2$ is the magnetic pressure, $\vec{H} = \vec{H}_0 + \vec{H}_m$ is the MF strength which is the vector sum of EMF $\vec{H}_0$ and MF induces by a magnetized electrode $\vec{H}_m$; $\Delta P_g = \Delta\rho g r\cos(\theta - \gamma)$ is the pressure of FG, $\Delta\rho$ is the difference of densities of separated electrolyte regions, θ is the angle between $\vec{H}_0$ and radius-vector $\vec{r}$, γ is the angle between $\vec{H}_0$ and the acceleration of free fall $\vec{g}$; $\Delta P_\omega = \int \Delta\rho\vec{\omega}^2\vec{r}\sin\theta d\vec{r}$ is the pressure of centrifugal force, $\vec{\omega}$ is the angular velocity of solution rotation.

It is easy to see that the contribution of rotational effects on the shape of the interface is negligibly small. Particularly, the ratio $\Delta P_\omega/\Delta P_g \cong v^2/gR_0$ has the order of magnitude $10^{-2} \div 10^{-3}$. It was found in

the paper [6] that terms ΔP_o and ΔP_g have the same order of magnitude. This allows neglecting the last terms in the equation (1). The effect of the centrifugal force will be significant for smaller electrode sizes and higher electrolyte rotation velocities. Thus, the equation (1) in the case of a spherical ferromagntic electrode can be written as follows:

$$\cos 2\gamma \cos^2(\theta-\gamma) + \sin 2\gamma \sin(\theta-\gamma)\cos(\theta-\gamma) + B(x)\cos(\theta-\gamma) + A(x) = 0,$$

where $A(x) = \left(\frac{8\pi}{3x^3}\left[\xi\left(3\sin^2\gamma - 1\right) + \frac{2\pi}{3x^3}\left(3\sin^2\gamma + 1\right)\right] + \xi^2 - C_o \right) \Big/ \frac{8\pi}{x^3}\left(\xi + \frac{2\pi}{3x^3}\right)$, $B(x) = C_g x \Big/ \frac{8\pi}{x^3}\left(\xi + \frac{2\pi}{3x^3}\right)$,

$x = r/R_0$, R_0 is ball radius, $\xi = H_0/M_0$, $C_g = \frac{2\rho_0 g R_0}{\chi M_0^2}$, $C_o = \frac{2nk_B T}{\chi M_0^2}$.

The comparison of theoretical modeling with experimental data is shown in Fig. 2.

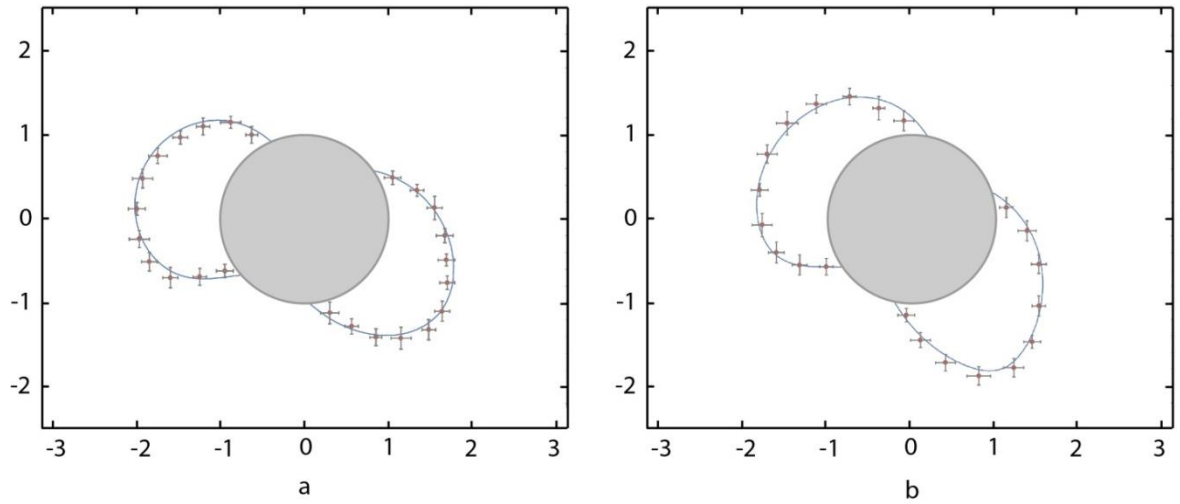

Fig. 2. The comparison of experimental data (points with errors) with theoretical modeling (solid line). The shape of the interface forming at copper deposition when EMF is directed at 70° (a) and 50° (b) to FG. a - $C_g = 6.1$, $C_o = 30$, b – $C_g = 7.4$, $C_o = 31$. Distances are given in radius of spherical ferromagnetic sample.

4. Conclusions

The formation of quasi-stationary heterogeneous state of an electrolyte and liquid-liquid phase separation were experimentally detected at the metal deposition on the surface of a magnetized ferromagnetic spherical electrode in an inhomogeneous constant MF. This state of the system exists around 10^3 sec and is characterized by the appearance of regions in the electrolyte with different magnetic susceptibilities. The change of the interface shape was investigated depending on the relative angle between the directions of EMF and FG. Metal deposition in gradient MF is accompanied by the formation of nano- and/or microclusters containing 10^4-10^5 paramagnetic ions – magnions.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 644348 (MagIC).

References

[1] Fahidy T Z 1973 *Electrochim. Acta.* **18 (8)** 607
[2] Yang X, *et. al*. 2012 *J. Phys. Chem. Lett.* **3 (23)** 3559
[3] Dunne P, Mazza L and Coey J M D 2011 *Phys. Rev. Lett.* **107** 024501
[4] Dunne P and Coey J M D 2012 *Phys. Rev. B* **85** 224411
[5] Gorobets O Yu, Gorobets Yu I, Bondar I A and Legenkiy Yu A 2013 *JMMM* **330** 76
[6] Gorobets O Yu, *et. al.* 2015 *J. Solid State Electrochem.* **19 (10)** 3001

[7] Gorobets O Yu, Gorobets Yu I and Rospotnuik V P 2014 *Condens. Matter Phys.* **17(4)** 43401
[8] Tyrrell J W G and Attard P 2001 *Phys. Rev. Lett.* **87** 176104