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On the Role of Variable Components of the Current in the Deposition of Galvanic Coatings

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Abstract: *Representation of the effect of the obtained results of the studies connected with the use of the inductance-capacitance device in the galvanic circuit on the process of the deposition and properties of the coatings owing to the change in the initial spectrum of the variable components of the current. The analysis of the works devoted to the effect of the magnetic and electric fields and applying of the alternating current on the direct current during the deposition of the coatings made it possible to support the opinion on the influence of hydrodynamic effect on the polarization of the electrode and, hence, on the properties of the coatings. In addition, the dynamic state of the electromagnetic field was found to facilitate synchronization of the stages of the electrochemical process and affect the electrolyte properties.*

Keywords: *an inductance-capacitance device, variable components of the current, properties of the coatings*

1. Introduction

Recently, the experimental works devoted to the estimation of the effect of the parameters of the inductance-capacitance device which was included in the galvanic circuit on the deposition process and coatings's properties were carried out extensively. The latter require discussion and generalization to estimate the role of the variable components of the current in deposition of the coatings.

It was shown in the published works that the use of the inductance-capacitance device (ICD) in the galvanic circuit, in which inductance (L) and capacitance (C) are connected in parallel and the device itself is connected in series, makes it possible to influence markedly the kinetics of the process (the cathode polarization, the spectrum of the current variable constituents (VC)), the current efficiency, structure, physical and mechanical properties, as well as to increase the rate of the coating deposition by enhancing the current density (i_k) [1--4]. In the case of using only L, the smoothing of pulsations of the power supply source (PS) and the current VC takes place. At Lopt the cathode potential maximally shifts towards the negative region, and in this case a decrease in the current efficiency occurs.

Joining the capacity reactivates the pulsations of the PS and current VC, whose amplitude value increases at Copt and the constituents with a higher frequency appear in the spectrum which characterises increase in the activity of the process [5]. Under these conditions of the deposition, the cathode potential shifts toward the positive region with respect to its value in the absence of the inductance-capacitance device, and its current efficiency increases. It was found that the change in the cathode potential during the deposition in the presence of the ICD was observed for ~40 min since the beginning of the plating and also within such a period after its finish, which attests to the effect of the variable constituents on the structure of the solution. In addition, at Lopt and Copt the number of crystallization centers icreases, their morphology differs substantially, the sizes of the aggregates of the sediments decrease, the microhardness increases, and the wear resistance of the coatings improves [3, 6, 7].

The aforementioned supports the fact that the changes in L, C values affect substantially the deposition process and the properties of the sediments.

2. Discussions and Generalizations

These results of the study can be explained taking into account the theoretical and experimental works that were performed to define the effect of the magnetic and electric fields, the applying of high frequency currents on the primary current during the deposition of the galvanic coatings [9-22].

In the deposited copper under the magnetic field, the changes in the surface and crystalline structure morphology can be attributed to the effect of the Lorentz force on the magnetic hydrodynamic (MHD) convection [9, 10]: fMHD = μ0Zev1xH, where μ0 is the absolute permittivity of the medium; Z is the ion charge; e is the electron charge; v1 is the ion velocity; and H is the intensity of the magnetic field.

As is seen from the above expression, fMHD depends on the charge and the ion motion velocity in the electrolyte solution, on the magnetic field intensity, as well as the location of the force lines relative to the electrode surface. The highest effect of the force lines is found to be parallel to the electrode surface.

Resulting from the MHD convection the rate of the deposition increases because of the ion mass transfer, the change in pH of the near-cathode layer, the adsorption of ions on the electrode. It is also affected by the gradient of the magnetic field (MF) and paramagnetic force, which depends on the magnetic susceptibility of ions of the metal and the MF induction.

In the case of copper deposition, due to the MHD convection, a high concentration of Cu^{2+} ions near the electrode surface is maintained, which intensifies the deposition process, enhances the rate of nucleation due to reduction in the diffusional limitations. The increase in the number of the nucleation centers occurs because of the decrease in the sizes of the diffusion zones (zones of impoverishment) due to the increase in the mass transfer rates.

A similar effect on the deposition process can be also achieved using the electric field (EF) [11]. If the EF is perpendicular to the interphase boundary, then at the intensity of $\Delta E \neq 0$ the motion of a liquid is possible due to the change in a surface tension of the liquid in the region of a higher ΔE and the induction effects induced by the electric conductivity. Such motion of liquid results from the electrodynamic force (fehd), which depends on the density of free charges in the bulk or on the surface of the liquid, the electrical constant in the liquid or in the region of the interpase boundaries, or the coefficient of the surface tension.

The analysis of the formation of a microdynamic flow of liquid in the region of a double layer and the effect of the electric field intensity E1 on the electrode surface, the macriscopic velocity Vc of the liquid was assumed to be defined by a summary effect of the impact of pulses of low molecular ions on the total mass of the liquid (at E1≠0 for a single ion of fehd = zeE1) [11]. Thus, the macrodynamic phenomena in a double layer are affected substantially by the electric field induced by the electric charge of the surface of the phase interfaces and a summary spatial charge of ions in this region.

To study the question under discussion the results that are obtained in the process of applying the pulsed low currents (up to 1 A) on the primary current are of significant interest [12--18].

The generator with an antenna fixed rigidly to the electrode was used for this purpose. It feeds the element with unipolar and rectangular current pulses with a frequency of 30--3000 kHz. The deposition process is most highly influenced by the amplitude-frequency characteristics of the current and by the mode of connection of the generator with the system. Taking into account that the variable constituents of current and the electromagnetic field can actuate mechanical oscillations (acoustic waves) in the condensed medium, the electromagnetic principle was also used for the generation of acoustic field. On the basis of the analysis of the theoretical and experimental results of the study, the rate of the processes was inferred to be defined by the driving forces, which ensure movement and create a condensed inequilibrium medium (to which electrolytes belong) of a self-maintained type, which is able to exist independently in a power generating medium also in the case of appearance of new fluctuations (the effect of kinetic memory discovered experimentally). This effect can be induced by physicochemical transformation of a structure and chemical properties of a uniform product in a limited space of a reactive medium.

All closed and open systems are influenced by the electromagnetic and acoustic noises with various intensities, which are revealed only at the level of self-maintained dissipative structures. But it is just enough to use a generator of regular noises in order to make the inequilibrium processes ordered in space and time. In this case, the kinetics of the processes becomes well-ordered as a rule, the product is uniform and a stochastic noise plays the role of an autoregulation signal. The pulses of the generator induce mechanical vibrations (acoustic) in the conductor, which agree with the frequency of the generator, and frequencies and pulses are transformed in the open inequilibrium system due to the intersection of the waves. In the active medium with an internal power supply source the non-linear processes occur, and the wave intersection leads to an amplitude growth. Most likely, the mechanism of the ultrasound effect is connected with the parametric resonance at certain frequences at which the acoustic wave induces an increase in the reactive parameters of the medium.

The character of the layers of the solution can be explained on the basis of the structures of the self-maintained type: first, self-organizing formations are developed with stable molecules, radicals and ions, which compose their own various functional properties. In turn, the latter form synchronous stable groups, which are able to respond in the form of resonance to a periodic controllable weak signal, and under its influence, a system of elements is created with anomalous kinetic properties of intensive and extensive transference into the reaction zone, which results in the increase in the rate and energy efficiency of physico-chemical processes and uniformity of the properties of the products. The reduction in the entropy production under these conditions was shown.

The increase in the rate of electrochemical processes during the applying of the high frequency field can also be explained by the effect of synergic coherency of electrochemical and electrodynamic processes inelectrolytes [18--22]. The coherency of the processes is possible as a result of the combined passage of several wave processes in time and space and is expressed in a regular constancy of connection between the phases, frequencies, polarizations, amplitudes of these waves and also the formation of steady extended objects that have a strictly ordered spatial structure. Between the field of the charged plasma of substance and the electromagnetic field there is a connection, and, therefore, the coherency between the wave modes and electromagnetic field occurs as a result of condensation of photons into the extended uniform statistical object with a topological peculiarity in a physical space. Mechanism of developing of this peculiarity of the object can be attributed to the laws of quantum motion of plasma components of the substance. Thus, these mechanisms are physico-chemical. These objects contain the electron plasma of the subjects, and the coherency of electrochemical and electrodynamical wave processes arise inside the objects as a result of action of the electromagnetic field inside the electron plasma of the electrolyte. During the condensation of a great number of quanta of electromagnetic field and in the presence of the effect of the long wave modes we can observe a strictly coherent motion of microparticles of plasma (electrons, ions, atoms, and molecules) inside the object at meso- and macromagnetic levels.

Atoms and electrons in the condensed medium can participate not only in the quantum-mechanical motion, but in the macroscopic (hydrodynamic) motion and at the same time maintaining their quantum properties at the mesolevel of multiparticles.

In the presence of volumetric macroscopic modes of a charge transfer in plasma, a macroscopic current of the charge is found to occur in which the mechanism of a resonance of the currents appears to be at certain frequencies of the electromagnetic field, since the electric system has macroscopic properties of capacity and inductance.

A substantial increase in the rate of the electrochemical processes during the applying of a high frequency field in the range of dozens and hundreds of MHz is connected not only with the change in the quantity of the current carriers of the system, but also with a structural reconstruction of the electrolyte. The presence of H and OH can lead to establishing hydrogen bonds between the characteristic radicals of the electrolyte. The effect of the RF-field will be more efficient under the conditions of a resonance-equality of the field frequency and the frequency that characterizes the hydrogen binding.

Taking into account the distinction of a cluster structure in the electrolyte and the layers adjucent to the electrode, the difficulty occurs in selecting a parametric mode considering its effect on volumetric and near-the-electrode processes. Therefore, it is next to impossible to choose a common frequency of the alternating current that affects maximally the controlled parameters of the coating. So, in this case it is necessary to use compromise values of the frequence of the applied current, which provide for the conditionally optimal characteristics of the galvanic coatings.

The use of the inductance-capacitance devices makes it possible to influence the characteristics of the initial variable components of the spectrum. Thus, in the case of the deposition of chromium coatings from a standard electrolyte using the ICD at the optimal parameters of L, C an increase in the amplitudes of the current variable components was observed in most of the spectrum components, which is characteristic for the poly-frequency resonance. These conditions markedly influenced the cathode polarization, "current efficiency", structure, microhardness and wear resistance of the coatings [3, 7].

3. Conclusions

On the basis of the aforementioned, it can be assumed that under the influence of the spectrum of the variable constituent under formation with the ICD being used, the electromagnetic field is found to be formed, which influences the degree of the hydrodynamic effect in the galvanic process. As a result, the electrode polarization changes, and, hence, the conditions of formation of the structure and properties of the coatings change as well. A dynamic state of the field most obviously facilitates synchronization of the stages of the electrochemical process that develops the resonance effect, as well as affects the electrolyte structure connected with an increase in the number of the charge carriers which accelerates the deposition rate and develops the formation of the electrolyte 'memory'.

Thus, varying inductive, capacitive parameters we can deposit coatings with different physico-mechanical properties, which in most cases cannot be developed applying the modern extensively used conditions of electrolysis.

References

[1] Gologan V.F., Bobanova Zh.I., Ivashku S.Kh. Influence of the solution of the Process of Copper Deposition while using the Inductive-Capacitive Device. Encyclopedia of Electrochemistry Research, Nova Acience publishes (USA). 2012, v. 3, p. 1013-1026.

[2] Gologan V., Bobanova Zh., Ivashku S., Mazur V., Pushkashu B. P4eculiarities of the influence of Param. an Inductance-capacitance Device parameters on Nickel Plating Process. *SurfaceEngineering and Applied Electrochemistry*. 2007, **43**(5), 307-311.

[3] Gologan V., Bobanova Zh., Ivashku S. Chromium Deposition with Application of an Induction Capacitance Device. *Surface Engineering and Applied Electrochemistry*, 2008, **44*(4), 257-263.***

[4] Gologan V., Bobanova Zh., Ivashku S., Volodina G., Mayur V., Pushkashu B. Morfology of Electrolytic Copper Coating at Application of a Power Supply with an Induction-capacitance Device. *Surface Engineering and Applied Electrochemistry*. 2008, **44**(1). 15-22.

[5] Tyagai V.A. Noises in the Electrochemic Systems. *Electrochemistry* 1975 b **10**(1), 3-24.

[6] Gologan V.F., Bobanova Zh.I., Monaiko E.V., Mazur V.A., Ivashku S.Kh., Kiriyak E. Peculiarities of the Influence of an Inductance-capacitance Device on the Initial Stage of the Crystallyzation of Electrolytic Coatings of Copper. *Surface Engineering and Applied Electrochemistry*. 2010, **46**(1), 9-15.

[7] Gologan V., Bobanova Zh., Ivashku S. Influence of an Induction-capacitance Device on the Structure and Wear Resistance of Electrolytic Chromium Coatings. *Surface Engineering and Applied Electrochemistry*. 2008, **44**(5), 353-358.

[8] Gologan V.F., Bobanova Zh.I., Bukar S.V., Ivashku S.Kh., Unguryanu V.N. The Use of Induction-capacitance Devices in Electrotechnical Processes. *Surface Engineering and Applied Electrochemistry*. 2011, **47**(3), 284-289.

[9] Matsushima H., Ispas A., Bund A., Plieth W., Fukunaka Y. Megnetic Field Effects on Microstructural Variation of Electrodeposited Cobalt Film. *J. Solide State Electrochem.* 2007, **11**, 737-743.

[10] Coey J.M.D., Phen F.M.F., Dumne P., Murry S.M. The Magnetic Concentration Gradient Force – is it Real. *J. Solide State Electrochem.* 2007, **11,** 711-717.

[11] Bondarenko N.F., Gak E.Z. *Electromagnetic Phenomena in Natural Waters.* Leningrad: Gidrometeoizdat, 1981. 151 c.

[12] Kiseleva O.L., Kolesnikov A.A, Zaremba V.E. (et al.) Rate Increase in Physico-Chemical Transformations in the Mode of Resonance Electromagnetic Acoustic Conversion. *Chim. Prom.* 2003, V. 80, no. 5, pp. 12-24.

[13] Kiseleva O.L., Kolesnikov A.A., Zarembo V.I. (et al.) Structuring of Non-Organic Materials under Radio Frequency Weak Electromagnetic Fields. *Non-Organic Materials,* 2004, V. 40, no. 1, pp. 96-102.

[14] Zarembo V.I. and Kolesnikov L.L. Background Resonance-Acoustic Control of Heterogeneous Processes. *Theor. Fundamentals Chem. Technology*, 2006, V. 40, no. 5, pp. 520-532.

[15] Zarembo V.I., Kolesnikov A.A., and Ivanov E.V. Background Electromagnetic Acoustic Control of Structural and Plastic Properties of Metal Materials. Izv. RAN, Ser. Fiz., 2006, V. 70, no. 8, pp. 1088-1091

[16] Zarembo V.I., Discharge of Copper-Magnesium Galvanic Element in a Weak Electromagnetic Field. *J. Phys. Chem.,* 2007, V. 81, no. 7, pp. 1339-1341.

[17] Kolesnikov A.A., Zarembo Ya.V., Puskov L.V., and Zarembo V.I. Electrochemical Reduction of Zinc on a Steel Cathode in a Weak Electromagnetic Field. *J. Phys. Chem.*, 2007, V. 81, no. 10, pp. 1914-1916

[18] Bramin V.A. and Beznosyuk S.A. Mechanism of Coherence in Electrochemic and Electrodynamic Processes in Electrolytes. *Izv. Altai Gos. Univ., Issue 3, 2005.*

[19] Kaplin A.A., Bramin V.A., and Stas' I.E. Inversion Voltammetry in a High Frequency Electromagnetic Field. *Zh. Analit. Khim.,* 1988, V. 43. Issue 4

[20] Umedzova Kh., Matsumoto Kh., and Tatiki M. Thermofield Dynamics and Condensed States. *Transl. Eng., Moscow*, 1985.

[21] Beznosyuk S.A. Quantum Reology and Confinement of Electrons in Nanostructures of Condensed State. *Izv. Vuzov, Fizika,* 1994, V. 37, no. 8.

[22] Khaken G. Synergetics. Moscow 1980.