ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2007, Vol. 81, No. 10, pp. 1715–1717. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © A.A. Kolesnikov, Ya.V. Zarembo, L.P. Puchkov, V.I. Zarembo, 2007, published in Zhurnal Fizicheskoi Khimii, 2007, Vol. 81, No. 10, pp. 1914–1916.

SHORT COMMUNICATIONS

Zinc Electrochemical Reduction on a Steel Cathode in a Weak Electromagnetic Field

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Received November 24, 2006

Abstract—The influence of weak periodic electromagnetic pulses with a repetition rate of 215 kHz on the process of zinc electrochemical reduction at a structural-steel cathode under the conditions of working galvanic production was studied experimentally. The results of studying zinc coatings using scanning electron microscope and X-ray microanalyzer are presented. The effects are discussed in the context of external synchronization of the self-organized dissipative structures in the reaction zone.

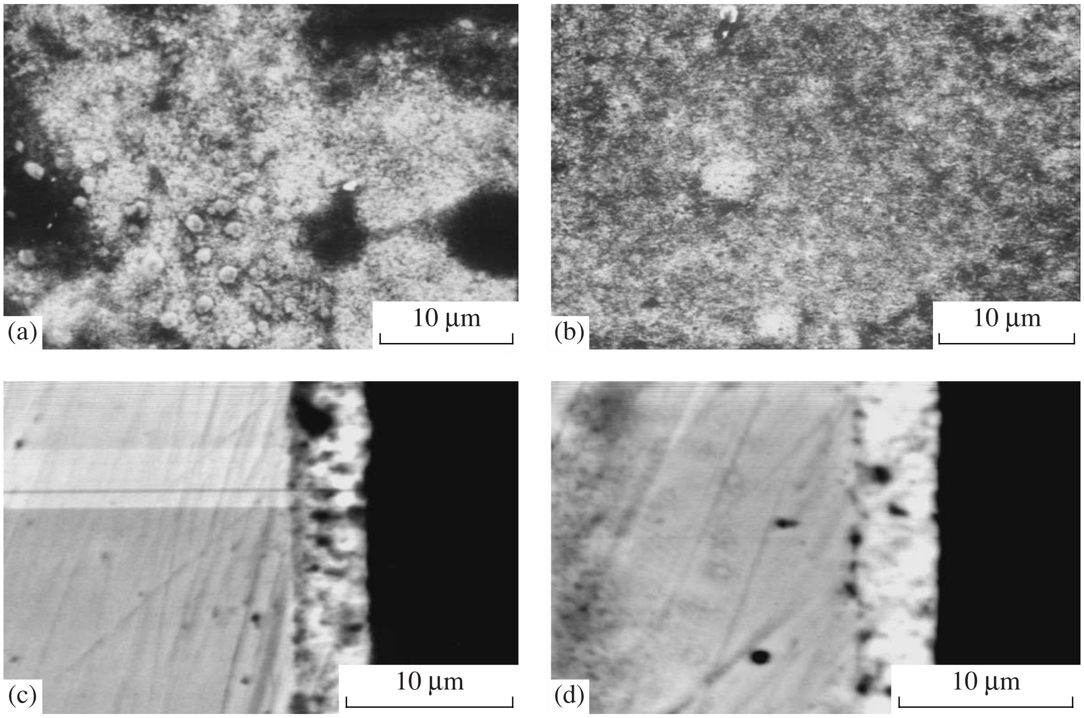
DOI: 10.1134/S0036024407100330

For the practical problems of electroplating, the formation of a defectless electrode coating is of prime interest. This is particularly important for the application of cathode-type decorative metallic films to corrosion-nonresistant metals (steel plating with tin, nickel, chrome, and gold). The anode "zinc-steel" coatings, despite the good film adhesion and corrosive insensitivity to film porosity (especially in alkaline cyanide baths), suffer from hydrogen embrittlement because of the attendant hydrogen reduction. The decorative properties of zinc layers are highly sensitive to the compositions of electrolyte and zinc anodes. The possibilities of heterogeneous control in electroplating are well known. These are the general-action methods with limited possibilities of local and selective effects, such as the preparation of electrodes and an electrolyte, variation of temperature and current density, and convection in a solution.

The spatiotemporal ordering effects in the regime of feeding weak (background) electromagnetic pulses into the galvanic system can remove the disadvantages of the existing methods without radical modification of technology [1–5]. It should be emphasized that the choice of the galvanochemical processes as the object of background control was not accidental but predictable on the basis of the effect of background acoustic resonance self-organization control (BARSC) theory that was put forward and cited in the literature for nonequilibrium nonlinear systems. Among the systems with perpetually arising dissipative structures is an electroplating reactor under real technological conditions for performing electrode processes.

We checked these presumptions in actual galvanic production by direct experiments on zinc electrocrystallization on the surfaces of steel (St. 8) cathode plates (4-dm^2 group) in a standard acid sulfate bath with a volume of $3 \times 2 \times 1$ m^3 (electrolyte composition (g/l): $ZnSO_4 \cdot 7H_2O$ (100), NH_4Cl (100), H_3BO_3 (25); dextrin as brightener) at pH 5.0–5.5, room temperature, cathode current density $j = 1$ A/dm^2, and after preparing electrodes and electrolyte according to the technological requirements. Electrolysis time was 20 min without forced convection. In the experiments, a short-circuit magnetic-dipole loop isolated from electrolyte by galvanization was used as a load of a pulsed electrical-current oscillator with a total power of 10 V A. The electromagnetic-field power (milliwatts) delivered by the oscillator to the surrounding medium is vanishingly small compared to the heat flows. The pulse repetition rate in a dipole wire was 215 kHz at an amplitude of 1 A.

The plates were plated with zinc in the standard and background regimes (with electromagnetic pulse feeding) and subjected to a comparative analysis. The comparable parameters were as follows: the visual overall coating thickness (H); "atomic" thickness of zinc layer (h) reduced to crystal close packing and characterizing the current output and surface molar density of coating; estimated coating density (ρ) with allowance for its porosity; and diameter (D) of distinct pores. In addition, microscopic visual control of the character of the resulting zinc layers was performed. Visual investigations, including measurement of the overall thickness (H), were carried out by scanning electron microscopy (SEM JSM-35CF (JEOL)) with an accelerating field of 25 kV and a probe current of 0.6 nA. The reduced coating thickness (h) was measured on a Link 860 (Link) X-ray microanalyzer (XMA) of the energy-dispersion type by the Jacovitz-Newbery method [6] in a field of 25 kV with a probe current of 10 nA during 100 s followed by the TFOS-program computation [6]. The elemental composition of coating was determined also using microanalyzer. The experimental SEM results obtained in different regimes for the planar and profile views of zinc coatings are presented in the figure.



Planar (a, b) and profile (c, d) SEM photographs of the zinc coatings at steel cathodes, as obtained in the standard (a, c) and background with 215-kHz CPs and (b, d) zinc-coating regimes. Photography in reflected electrons, 3000×. Zinc coating: porous, pore size 5–15 μm (a, c); (b, d) dense homogeneous, pore size 1–4 μm.

The visual estimate of the results of background regime of steel zinc-plating indicates, in both planar and profile photographs, that, at a CP frequency of 215 kHz, the coating is considerably more homogeneous and dense with a smaller size of zinc grains, smaller number and size gas lacunas, which, besides, become isolated contrary to the through channels appearing in the standard regime.

The quantitative computational results for the SEM and XMA data are presented in the table.

The analysis of these results suggests that the action of weak electromagnetic pulses in the electrochemical zinc plating of steel products modifies substantially the coating parameters, although the approved standard technology does not suffer noticeable changes. In addition, the data obtained above are in complete agreement with the BARSC theory [1–5], according to which, in conducting media (electrodes, electrolytes) reactive toward electromagnetic fields and dispersive toward mechanical vibrations, acoustic waves can propagate in such media under given conditions to synchronize the periodic motion (vibration and rotation) of the distributed self-excited generators representing dissipative structures (DSs) that form and govern the final properties of the reaction product.

The regulation acoustic wave forms as a result of the well-known electromagnetic-acoustic transformation effect in a wire of a magnetic-dipole current loop. For the CP shape and rate characteristic of such a condensed energy-saturated medium, a weak regulation signal is not damped but, rather, strengthens due to the energy of physicochemical processes to become a plectrum—a peculiar kind of “guide” that provides amplitude-phase coherence in the motion of the normally sto-

Comparison of the parameters of zinc coatings obtained for steel cathodes in the standard regime and under the action of weak electromagnetic pulses

CP frequency f, kHz	Zn, %	Fe, %	h(XMA), μm	H(SEM), μm	ρ, kg/m^3	D_1, μm	D_2, μm
0	90.1	4.7	1.6	4.5	2500	0.20	0.15
215	94.8	2.6	2.1	5.0	3000	0.10	0.10

Note: h(XMA) is the thickness determined by the TFOS method for ρ(Zn) = 7100 kg/m^3; H(SEM) is the thickness determined from the SEM data for the profile sections of the samples; $\rho = 7100h/H$ is the estimated coating density with allowance for its porosity; D_1 and D_2 are the mean sizes of zinc grains in the profile and planar view of coating, respectively.

chastic DSs, thereby increasing cardinally the correlation length of their parameters.

As a result, a nonequilibrium system stabilizes (the external regulation signal can be switched off), and the distribution over the DS parameters for the nonequilibrium system narrows drastically to smooth out both intensive and extensive properties of the reaction zone.

For high currents in the voltaic circuit, chaotic diffusion (described by the equation of the parabolic type) can no longer provide adequately fast charge transfer. An essentially nonequilibrium drift of current carriers in near-electrode areas of electrolyte organizes convective Rayleigh-Benard cells, which afford high velocity of the convective (perpendicular to the electrode) and advective (tangential) ion transfer and equalization of the concentrations, temperatures, and chemical potentials, favoring the dominant role of the target reaction and suppression of the side processes, in particular, the hydrogen reduction reaction. Parametrically, such scenario inevitably manifests itself in the buildup of the load voltage, current, and efficiency.

In the context of the percolation theory, DS synchronization amounts to the elimination of dislocations and disclinations in the convective cells to form the so-called infinite percolation cluster that affords the "short-circuit" regime in the chain of charge-density, mass, and temperature transfer in the zone of forming synchronous DSs. In the context of the nonequilibrium nonlinear thermodynamics, DS synchronization amounts to lowering the stationary nonequilibrium structural entropy of the DS system and decreasing the global entropy production at all hierarchy levels in the system and thermostat, which enhances the energetic efficiency of the technological process, its velocity, and the degree of spatial inhomogeneity of the end product [1–4]. These theoretically substantiated model notions, at least, are contradictory to none of the observed effects occurring in the process of electrochemical steel zinc-coating, which allows the BARSC in electroplating to be considered as a predictable, reproducible, and stable way of control and opens up prospects for applying this method in other electrochemical technologies.

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