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KINETICS OF CONTACT DISPLACEMENT PROCESS IN CITRATE-PYROPHOSPHATE ELECTROLYTES ON NdFeB

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Contact exchange of metals is widely used in PCB technology, metallization and nanostructuring of semiconductor surfaces, catalyst, sensor and battery fabrication, as well as recovery of metals from liquid wastes. Knowing the kinetics of contact exchange is essential both to size target processes and to set maximum permissible exposure when contact exchange is detrimental. In plating baths, e.g. a more electropositive alloy component may deposit on an anode made of an electronegative metal, causing extra anode dissolution and sludge formation; on workpieces left in electrolyte without current, contact exchange can reduce adhesion and induce blistering. Mitigation includes loading under current, low-concentration electrolytes, and addition of suitable surfactants and complexing agents.

The electrochemical analysis of contact exchange is based on Evans diagrams (cathodic and anodic polarization curves in the same potential window). The method includes calculation of kinetic parameters by analytically solving the $j(E)$ equations for the coupled dissolution of the negative metal and deposition of the positive metal, under assumptions of stationarity and an equipotential electrode surface.

Determining the contact exchange rate requires: (1) the time dependance of the stationary potential $E(t)$ of the electronegative metal in a working solution containing electropositive ions; (2) the polarization curves, free of side reactions, for the coupled processes (reduction of the electropositive ions in the working solution $j_k(E)$ and anodic process on electronegative metal $j_a(E)$ in a background solution.

Polarization curves are approximated by theoretical expressions appropriate to the reaction mechanisms; because the contact exchange potential region lies far from the pure-metal equilibrium potentials, reverse reactions in the kinetic equations can be neglected. Using $j_k(E)$ and $j_a(E)$, the current densities rate is obtained as $j_o(E)$ and $S_k(E)$, while $E(t)$ gives time dependences of j_o and S_k. In the limiting case, programming a nonlinear potential scan [1] according to $E(t)$ allows regulation of the sweep rate in time.

Contact exchange kinetics were studied in pyrophosphate-citrate electrolytes for copper-zinc alloy deposition with different ratio of copper and zinc ions. The parameters were calculated both for nonlinear and linear polarization. Current density of contact exchange is maximal in the first second and at 80s of the process (0,46 mA cm^{-2} for $[Cu^{2+}]:[Zn^{2+}]=1:5$ and 0,85 mA cm^{-2} for $[Cu^{2+}]:[Zn^{2+}]=1:2$).

References:

1. *Patsay I.* Nonlinear potential scanning as a novel approach to calculation of the time variable galvanic displacement reaction rate / *I. Patsay, Z. Maizelis, A. Maizelis* // ChemElectroChem. 2022. Vol. *9*(4). e202101274.