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Adipate adsorption and its incorporation into NiP coatings from citrate electroless nickel plating solutions

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Abstract

Adipate, which is used as a buffer in a citric electroless nickel plating solution, adsorbs on the NiP surface and incorporates into coatings when the plating process takes place. The quantity of adipate incorporated into NiP coatings decreases with increase in hypophosphite and citrate concentrations in plating solution, similarly to the quantity of adipate adsorbed from corresponding solutions without Ni(II) on a freshly plated NiP surface. An increase in Ni(II) ion concentration in plating solution also diminishes the quantity of adipate incorporated into coatings, though any decrease in its adsorption on NiP coatings is not observed from the corresponding solutions without hypophosphite (when plating does not occur). The adsorption of adipate and citrate leads to the decrease in the rate of catalytic hypophosphite oxidation. The deposition of smoother and brighter NiP coatings in the presence of adipate together with Cu(II) ions, which act as a stabilizer, is determined by a stronger adipate interaction with Cu as compared with NiP.

Keywords: Electroless nickel; Adipate; Hypophosphite; Adsorption

1. Introduction

Citrate is one of the most widely used ligands in electroless nickel (EN) plating solutions. These solutions may be regenerated and easily decontaminated—that is a valid reason stimulating their employment. The alkaline citrate EN plating solutions are used more frequently [1–5]. A frequent use of such solutions in practice has stimulated many works devoted to the investigation of EN plating mechanism [5–7].

However, NiP coatings of finer structure, containing more than 9 wt.% P and, therefore, particularly corrosion resistant, are usually deposited in acidic solutions (pH<5). A rather cheap acetic EN plating solution, which unfortunately cannot be used with adjustment of its composition, is not suitable for advanced practical purposes from an ecological viewpoint. However, due to its simplicity it is often used to investigate the plating mechanism in more detail [8,9]. The acidic glycinate EN plating solution, which is stable enough and may be used for a long time by continuous replenishment with the components required, enables to deposit smooth and corrosion-resistant coatings containing up to 12 wt.% P [10,11]; however, the presence of glycine complicates the decontamination of spent solutions. Meanwhile, the removal of citrate from EN solutions may be performed in a much simpler way [12]. In accordance with Ni(II)–citrate complex distribution in aqueous solution, NiL^- predominates at pH 4.5 when the ratio Ni(II)/citric acid=1:1 [13]. However, the rate of coating deposition in the corresponding EN plating solution at pH 4.5 is insufficiently high. The stability of solution decreases with increase in pH to 5. Our earlier investigations have shown that the use of adipic acid together with a stabilizer Cu(II) ions in the acidic citric EN plating solution increases the deposition rate, improves the stability of solution and also makes it possible to deposit smooth and bright coatings [14].

Investigations of the EN plating mechanism in different solutions have shown that the plating process is initiated by adsorption of hypophosphite ions on the active substrate, resulting in formation of intermediate derivatives and radicals

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[6,7,15]. $H_2PO_2^-$ adsorption capacity depends not only on the substrate nature and its activity, but also on the organic compounds present in solution. Since the plating rate is proportional to the active surface, covered by Ni(II) and $H_2PO_2^-$ ions, the adsorption of other components indirectly influences the kinetics of EN plating [9]. This point of view allows critical assessment of the hypothesis, according to which the decrease in plating rate with increase in concentration of organic acids in solution is caused by formation of stronger complexes.

The aim of this work was to assess the factors affecting EN plating by investigation of adipate adsorption and incorporation in NiP coatings and to elucidate the causes of smooth and bright coating formation when Cu(II) ions are present in solution together with adipate.

2. Experimental

Nickel coatings of 3–5 μm used as a substrate were freshly deposited onto activated Cu plates (1×1 cm^2) at a temperature of 85 °C in solution containing (mol/l): $NiSO_4 \cdot 7H_2O$—0.1; $Na_3C_6H_5O_7 \cdot 5.5$ H_2O—0.1; $NaH_2PO_2 \cdot H_2O$—0.25; $(CH_2)_4(COOH)_2$—0.07. 0.2 mmol/l $CuSO_4 \cdot 5H_2O$ was added to this solution in the indicated cases. Cu plates without a NiP coating were also used in some cases.

Adipate adsorption and its incorporation into nickel coatings were investigated at 85 °C by means of the radioactive tracer method using ^{14}C in adipic acid. Each pattern was rinsed thoroughly before radiometric measurements. The radioactivity was measured in a UMF-1500M system with an SBT-13 counter. The thickness of coatings was determined gravimetrically.

Catalytic (electroless) oxidation of $H_2PO_2^-$ at 85 °C on a freshly deposited NiP surface was estimated according to a decrease in $H_2PO_2^-$ concentration determined titrimetrically [16].

Electrochemical measurements were also carried out at 85 °C using a PI-50-1 potentiostat, a PR-8 programmer and two digital B7-43 voltmeters for automatic registration of voltammetric characteristics at a potential scan rate of 50 mV/s. The working electrode was a NiP coating (2 cm^2), the reference electrode—Ag/AgCl/KCl_{sat} and the counter electrode—platinum (potential values are given vs. the SHE).

The pH of all solutions was adjusted to 4.5 at room temperature with NaOH or H_2SO_4 solutions. Each experiment was repeated 3–5 times, and the average values are shown in the figures.

3. Results and discussion

3.1. Adipate adsorption on NiP

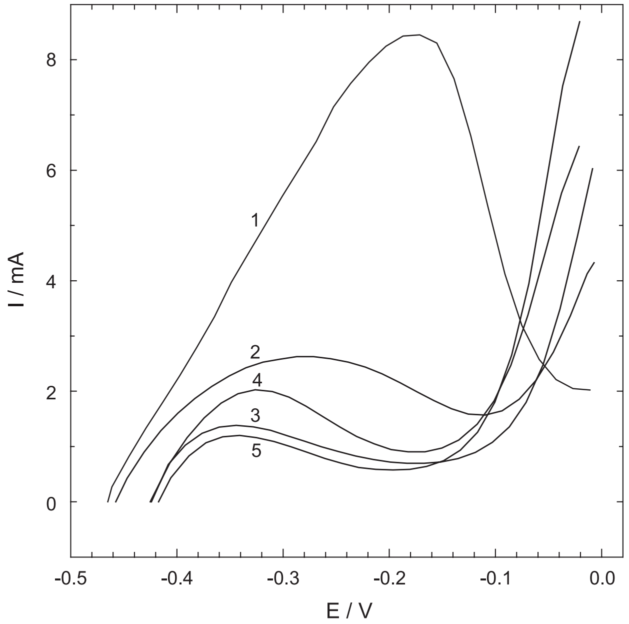

Fig. 1. Anodic oxidation of hypophosphite (0.25 mol/l) on the NiP electrode without additives (1) and with additives (mol/l): citrate 0.01 (2) and 0.1 (3); adipate 0.07 (4); citrate 0.1 and adipate 0.07 (5).

As is seen in Fig. 1, the presence of organic additives, citrate and adipate, significantly decreases the anodic current of hypophosphite oxidation on the NiP electrode, and the passivity of electrode is observed at less positive potential values. Cyclic voltammograms, recorded on the NiP electrode have shown that the anodic current of hypophosphite oxidation is considerably higher in the case of the complete EN plating solution in which nickel surface recovers as compared to the analogous solution without Ni(II) ions (Fig. 2). Organic additives present in solution block the active NiP surface and, in this way, decrease the current of hypophosphite oxidation under conditions when the renewal of NiP surface does not occur.

The investigation of hypophosphite catalytic (electroless) oxidation at 85 °C on the freshly deposited NiP coating gave similar results. Over a period of 2 h homogeneous oxidation of 0.2 mol/l $H_2PO_2^-$ (without NiP surface in the solution) was not observed. In the presence of NiP surface (load was 1 dm^2/l) 9.6% of the initial $H_2PO_2^-$ was oxidized during the same time. When 0.1 mol/l of citrate and/or adipate was added to the solution the decrease in $H_2PO_2^-$ concentration (under the same load of NiP) was only 4.5–4.8%. These data show that the catalytic effect of NiP coating on electroless hypophosphite oxidation is weakly expressed when organic additives are added to the solution. This adipate peculiarity to reduce hypophosphite oxidation rate seems paradoxical—the increase in NiP plating rate in citric acidic EN plating solution at 85 °C with an adipate additive (0.07 mol/l) reached about 29% (4.1 μm/h without adipate; 5.3 μm/h in the presence of adipate). When adipate was present in EN plating solution together with 0.2 mmol/l Cu(II), this increase reached 40% (5.9 μm/h). It has been established that the accelerating effect of adipate on EN plating rate is related to its buffering action [14]. The data indicate that the