Electrodeposition of nickel–zinc alloy coatings with high nickel content

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ABSTRACT

The electrodeposition of Ni–Zn alloy coatings with high nickel content from a Watts type bath was studied. The investigation was performed by means of cyclic voltammetry, potentiostatic electrodeposition, X-ray diffraction, energy dispersive X-ray analysis, scanning electron microscopy and transmission electron microscopy. The effect of the experimental parameters (deposition potential, bath temperature, zinc concentration, presence of additives) on the coating composition, morphology and structure was studied. The obtained results show that the addition of Zn^{2+} to the deposition bath leads to a strong decrease in the cathodic current density indicating a remarkable inhibition of Ni reduction. Even if anomalous codeposition was observed for all the studied experimental conditions, nickel rich alloys were obtained due to the mass transport control of zinc deposition. A strong decrease in the current efficiencies was observed when Zn percentage in the deposit was higher than 7 wt.%. The incorporation of Zn in the fcc Ni lattice leads to a remarkable decrease in the grain size. The presence of nanocrystalline Ni–Zn β-phase was observed in the alloys having Zn content higher than about 8 wt.%.

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1. Introduction

Electrodeposition of nickel and nickel–zinc alloy coatings is of interest because these materials have an important role in many application fields. Zinc-rich alloys are used primarily for corrosion protection of steel [1–4]. Ni and its alloys are used for their magnetic properties, for corrosion protection and electrocatalysis of several industrially relevant processes [5]; for example, they are used as active layers on the electrodes for H_2 production [6–8], for electrochemical decomposition of urea [9] or for methanol oxidation in alkaline medium [10].

The electrodeposition of Ni–Zn alloy from aqueous solutions is classified as anomalous co-deposition, according to the Brenner definition [11], because the less noble metal deposits preferably on the cathode with respect the nobler one; therefore zinc-rich alloys are generally obtained. Many attempts have been made to explain the anomalous co-deposition of alloys, but there is still no universally accepted theory. At first, anomalous co-deposition was attributed to the pH increase at the cathode surface, which leads to zinc hydroxide precipitation and to the inhibition of the more noble metal discharge [12]. Swathirajan suggests that the anomalous codeposition is due to the underpotential deposition of zinc [13]. Other authors attribute the Ni–Zn anomalous co-deposition to the slow kinetics of nickel deposition [14,15]. Landolt demonstrated that anomalous codeposition of iron group metals involves both inhibiting and accelerating effects [16,17]. However, Zn–Ni codeposition in aqueous solution is not always anomalous, as

there are particular experimental conditions, which allow the electrodeposition of nickel-rich alloys [18].

In order to avoid the electrodeposition of alloys with high zinc content from aqueous solutions, some authors used low temperature molten salts [19,20] or eutectic-based ionic liquid [21–23].

The electrodeposition of zinc-rich Zn–Ni alloys from aqueous solutions has been widely studied, but few works have been performed on nickel-rich alloys [15,24,25]. In particular, a study of the electrodeposited phases and their structures has not been carried out.

The aim of this work was to study the electrodeposition of nickel-rich Ni–Zn alloy coatings from a Watts type bath. The investigation was performed by means of cyclic voltammetry and potentiostatic electrodeposition. The effect of the experimental parameters (deposition potential, bath temperature, zinc concentration, presence of additives) on the alloy composition, morphology and structure was studied.

2. Experimental

Ni–Zn alloy codeposition was studied by means of cyclic voltammetry and potentiostatic electrodeposition carried out in a Watts type bath. The bath composition used is shown in Table 1. All the solutions were prepared with doubly distilled water and analytical grade reagents.

Cyclic voltammetry was performed in a standard ASTM three-electrode cell, 1 dm^3 in capacity. The working electrode was a glassy carbon cylinder embedded in epoxy resin leaving an exposed circular area of 7.1 mm^2; before the tests, the electrode surface was smoothed with emery paper down to 1200 grit, degreased with acetone and rinsed with distilled water. The counter-electrode was a platinum spiral and

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Table 1
Composition of the bath and electrodeposition conditions used for the potentiostatic tests.

$NiSO_4 \cdot 6H_2O$	300 g dm^{-3}
$NiCl_2 \cdot 6H_2O$	35 g dm^{-3}
$ZnSO_4 \cdot 7H_2O$	1–100 mM
H_3BO_3	40 g dm^{-3}
Saccharin	0 or 5 g dm^{-3}
Sodiumdodecylsulphate (SDS)	0 or 1 g dm^{-3}
pH	4.0
Temperature	30 or 50 °C
Deposition potential range	−700/−1400 mV

the reference was a Ag/AgCl electrode (E = 0.208 V vs. SHE), mounted inside a Luggin capillary, whose tip was placed next to the working electrode surface. Before each experiment, the solution was deaerated with a N_2 flux inside the cell. The potential was linearly swept starting from 500 mV to −1100 mV vs Ag/AgCl and then reversed to 500 mV. The scan rate was 20 mVs^{-1}.

Potentiostatic electrodepositions were carried out under constant magnetic stirring (about 250 rpm) of the solution in the potential range from −700 to −1400 mV vs Ag/AgCl by using a beaker of 800 ml in capacity as electrochemical cell. The working electrode was a mild steel disc (1 mm thick) mounted in a flat specimen holder leaving an exposed area of 314 mm^2. Before each experiment, the disc was smoothed by emery paper (from 300 to 1000 grit) and degreased by anodic electrolysis in a 60 g dm^{-3} NaOH at 4 V against graphite anodes; it was then neutralised in a 2 wt.% HCl solution and rinsed with distilled water. The disc was weighed before and after the electrodeposition to obtain the amount of the deposited alloy. For the electrodeposition experiments, the anode was a nickel sheet and the reference was an Ag/AgCl electrode. The cathode and anode were kept parallel at a distance of 40 mm. The electrodeposition time was chosen in order to obtain deposits with a thickness ranging from 7 to 10 μm.

Both the cyclic voltammetry and the potentiostatic electrodeposition were performed at 30 and 50 °C by using an EG & G Princeton Applied Research potentiostat/galvanostat Mod. 273 controlled by a personal computer.

Morphology and chemical composition of the coatings were studied by scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX). A Zeiss Supra 40 microscope and a Bruker Quantax serie 5000 L N_2-free XFlash device were used.

Three electrode reactions occur on the cathode:

$$Ni^{2+} + 2e^- \Rightarrow Ni \tag{1}$$

$$Zn^{2+} + 2e^- \Rightarrow Zn \tag{2}$$

$$2H^+ + 2e^- \Rightarrow H_2. \tag{3}$$

Ni and Zn partial current densities were calculated from the weight of deposited metal by means of the following equation, derived from Faraday's law:

$$i_m = \frac{W_m nF}{M_m tA} \tag{4}$$

where m is Zn or Ni, i_m is partial current density (mA cm^{-2}); W_m is the weight of deposited metal (mg); n is the number of moles of electrons transferred in the reaction; F is the Faraday constant (96,485 C mol^{-1}); M_m is the molar mass of Ni (58.71 g mol^{-1}) or Zn (65.38 g mol^{-1}), t is the deposition time (s); A is the working electrode area (cm^2). The hydrogen partial current density (i_{H_2}) was calculated as the difference between total current density and $i_{Ni} + i_{Zn}$; the current efficiency was calculated as percentage of $i_{Ni} + i_{Zn}$ with respect to the total current density.

The alloy structure was analysed by means of X-ray diffraction analysis (XRD), using a Philips PW 1730 diffractometer with Cu Kα radiation (λ = 0.154 nm).

The phases of the alloy containing 49.2 wt.% Zn were analysed by a Philips CM 200 transmission electron microscope (TEM). The plan-view samples were prepared with the following procedure: firstly the mild steel substrate was thinned by means of abrasive papers with different grades in order to obtain a sheet ~70 μm thick; from the sheet some discs with a diameter of 3 mm were cut and then thinned from the steel side down to ~20 μm using the Dimple Grinder by Gatan; finally the samples were thinned by low-angle ion milling (Precision Ion Polishing System by Gatan), leaving the Ni–Zn side untouched.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows the cyclic voltammetry curves obtained at 30 °C by adding different concentrations of Zn^{2+} to the bath; the cathodic potential sweep was reversed at −1100 mV. Nickel deposition from the bath without zinc starts at about −850 mV (Fig. 1a, curve 1), in agreement with the results of Lin and Selman [15]. As pointed out by the same
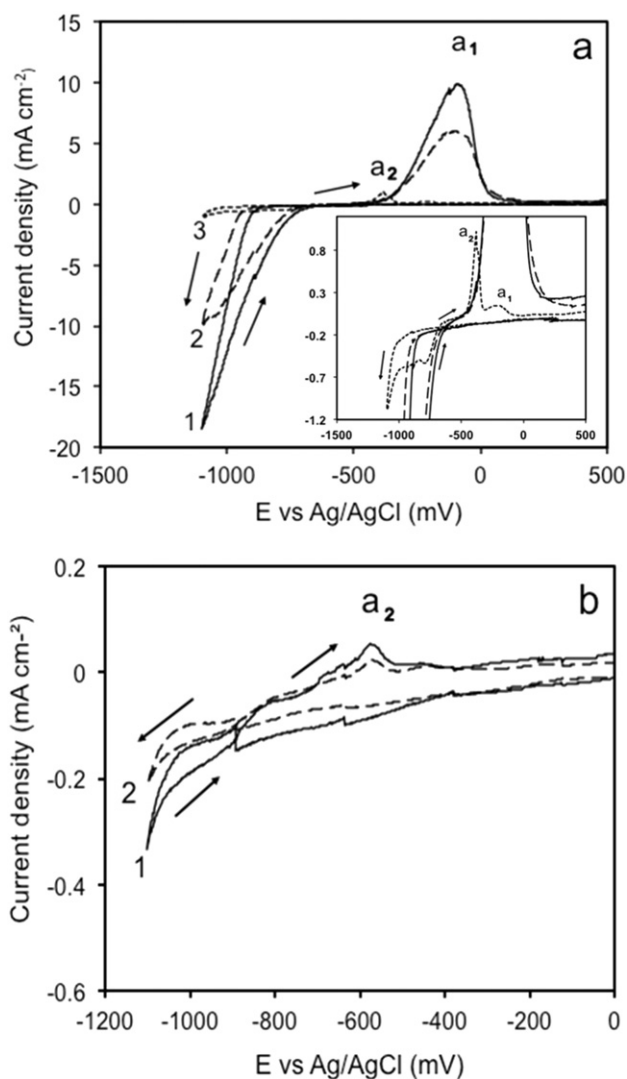
Fig. 1. Cyclic voltammetry obtained on glassy carbon from a Watts type bath without additives, with increasing concentrations of Zn^{2+}. (a): 1) Zn^{2+} 0 mM; 2) Zn^{2+} 1 mM; 3) Zn^{2+} 10 mM, inset: magnification of the curve 3. (b): 1) Zn^{2+} 50 mM; 2) Zn^{2+} 100 mM. T = 30 °C. Scan rate: 20 mV s^{-1}.