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CORROSION RESISTANCE AND SURFACE TOPOGRAPHY OF ELECTRODEPOSITED Zn-Ni-Fe ALLOY

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ABSTRACT

In electroplating of ternary Zn-Ni-Fe alloy from the acidic chloride baths, the influence of iron codeposition on corrosion resistance and surface topography of the electrodeposits were investigated in comparison with Zn-Ni alloy deposits. It was found that the ternary Zn-Ni-Fe alloy showed better corrosion resistance in comparison with binary Zn-Ni alloy, even though both Zn-Ni-Fe and Zn-Ni deposits contained approximately the same nickel content. The best corrosion resistance, in 3% neutral sodium chloride solution, observed from the deposit having 16.74% nickel and 3.95% iron. The surface topography of the deposits was characterized by using scanning electron microscopy (SEM) in order to give more information about corrosion behaviors. It was found that the deposits with iron had finer grain size and more homogenous structure in contrast to that of Zn-Ni deposits.

KEY WORDS

Electrodeposition, Zn-Ni-Fe alloy, Zn-Ni alloy, Surface topography, Corrosion.

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1. INTRODUCTION

Numerous changes in characteristic have taken place in the production of zinc coatings on steel and many efforts have been made to improve the corrosion resistance using multilayered electrogalvanizing coatings [1-3], composite zinc films [4-7] and, especially, zinc alloy coatings [8-15]. Increasing interest has been directed towards zinc-iron [7,9] and, especially, zinc-nickel [10-15] alloy coatings that appeared to be particularly attractive since these deposits exhibit better physical and electrochemical properties than a pure zinc layer. The electrodeposition of zinc-nickel alloy is a codeposition of anomalous type according to the definition of Brenner [16]; that is the less noble metal deposited preferably on the cathode with respect to the more noble one.

Various electrolytes have been reported for the electrodeposition of Zn-Ni alloys. However most of the published work concerns the electrodeposition from sulfate or chloride baths. A Boeing process has been described by Hsu [15] for deposition of Zn-Ni alloys from a non cyanide chloride bath. Most of the authors pointed out that the best corrosion resistance behavior is exhibited by electrodeposited Zn-Ni alloys containing 10-20% of nickel, because they consist of a single phase structure (γ phase).

This report is an extension for our investigations on the electrodeposition of Zn-Ni-Fe alloys to study the corrosion behavior of these deposits in comparison with Zn-Ni deposits. The study, also, included the surface topography of both Zn-Ni-Fe and Zn-Ni deposits.

2. EXPERIMENTAL PROCEDURE

In order to study the surface topography and corrosion resistance of Zn-Ni-Fe and Zn-Ni deposits, these deposits were prepared on mild steel plates using the process of separated anodes, as explained in our previous paper. Also, both Zn-Ni-Fe and Zn-Ni deposits were produced under constant conditions (at 30 mAcm^{-2} , $43 \text{ }^\circ\text{C}$ and pH 3), in order to get the same nickel content in these deposits.

The surface topography of the deposits was examined by using scanning electron microscopy (SEM). The samples for aqueous corrosion testing were mounted in an electrode holder which exposed one cm^2 of the sample area to the electrolyte. Electrolytes were made using distilled water and reagent grade sodium chloride. The sample holder was inserted in an electrochemical cell for potentiodynamic and potentiostatic corrosion experiments. For potentiodynamic testing, an anodic over-potential was added and the resulted current density

was recorded. Corrosion experiments were performed at room temperature (23 to 25 °C). The reference electrode was saturated calomel electrode (SCE) and the counter electrode was platinum wire.

3. RESULTS AND DISCUSSION

3.1) Surface Topography

Concomitant changes in the structure, as found from X-ray diffraction analysis through our previous work, can be observed by SEM analysis. Figures 1 and 2 show the surface topography of the deposits containing different percentages of nickel and iron contents.

The Zn-Ni deposits showed a homogeneous structure formed of crystallites with columnar growth of pyramidal form; these grain sizes are slightly finer with increasing nickel content from 14.17% to 17.26% as shown from case (a) in Figs. 1 and 2. While with iron codeposition, the ternary Zn-Ni-Fe alloys still show a pyramidal columnar structure, but the grain size is very fine and more homogeneous in comparison with those of binary Zn-Ni deposits, as shown in Figs. 1 and 2.

For instance, the binary Zn-Ni deposits that contained (14.17 % nickel) had a coarse grain size than those of Zn-Ni that contained (17.26 % nickel), as shown in Figs. 1(a) and 2(a), respectively. However, the ternary Zn-Ni-Fe that contained (13.92% Ni and 2.64% Fe) had a finer grain size and more homogeneous in comparison with those of binary Zn-Ni that contained (17.26% Ni), as shown in Figs. 1(c) and 2(a), respectively. Iron deposits better with increasing ferrous ion concentration in the baths as an adsorbent to inhibit the crystal growth, and the nucleation may occur a little more frequently without iron in bath. Then the grain size obtained in baths with iron becomes finer than that without iron.

3.2) Corrosion Resistance

The corrosion behavior of electrodeposited Zn-Ni thin films has been studied from an electrochemical standpoint by Kurachi *et al.* [17]. They measured the corrosion potentials (E_{corr}) over the full range of Zn-Ni alloy compositions in a sulfate bath. Their results showed that the corrosion potentials become more negative with increasing Zn content until the $\gamma+\eta$ phase alloy was reached. The corrosion resistance of electrodeposited Zn-Ni alloys was studied, also, by [17,18,19] and they concluded that the best corrosion resistance of these

alloy coatings was obtained from the deposits containing 11-18% Ni, because these alloys contained a single γ phase alloy.

In the present work, the corrosion potentials ($E_{\text{corr.}}$) vs. SCE were measured; as for different compositions of Zn-Ni-Fe deposits, after four minutes dipping in 3% neutral sodium chloride solution. Table 1 shows the results of the influence of iron codeposition on the ($E_{\text{corr.}}$) of the deposits. The results may be summarized as follows: (1) the $E_{\text{corr.}}$ of the deposits without iron shifted to the positive direction (from -1350 to -1247 mV) with increasing of Ni content (from 15% to 17.26% Ni, respectively); (2) the deposits with iron codeposition have nobler $E_{\text{corr.}}$ in comparison with $E_{\text{corr.}}$ of the Zn-Ni deposits (having approximately the same Ni content). From group D in Table 1, the $E_{\text{corr.}}$ of only Zn-Ni deposits shifted to more positive direction (from -1247 to -1135 mV) with iron codeposition and (3) the $E_{\text{corr.}}$ of Zn-Ni-Fe deposits approximately did not changed with increasing Fe content, as shown in group D of Table 1.

Table 1. The corrosion potential ($E_{\text{corr.}}$) of the deposits after four minutes dipping in neutral 3 wt% sodium chloride solution.

Alloy No.	Alloy Type	Deposit analysis, wt%			$E_{\text{corr.}}$ (mV vs. SCE)
		Zn	Ni	Fe	
A. 1	Zn-Ni	85.83	14.17	0.00	-1365
	Zn-Ni-Fe	83.27	14.60	2.13	-1290
B. 1	Zn-Ni	85.26	14.74	0.00	-1355
	Zn-Ni-Fe	83.44	13.92	2.64	-1260
C. 1	Zn-Ni	84.99	15.01	0.00	-1350
	Zn-Ni-Fe	82.44	15.08	2.48	-1260
D. 1	Zn-Ni	82.74	17.26	0.00	-1247
	Zn-Ni-Fe	81.69	16.84	1.47	-1140
	Zn-Ni-Fe	81.51	15.91	2.58	-1135
	Zn-Ni-Fe	79.31	16.74	3.95	-1140
	Zn-Ni-Fe	78.50	16.30	5.20	-1130

To make a clear comparison for corrosion resistance of both Zn-Ni and Zn-Ni-Fe deposits, the corrosion behavior was measured by polarization resistance method. Figures 3 to 6 show the potentiodynamic polarization data for the deposits in 3% neutral NaCl. From curve 1 in these figures, it can be seen that the polarization resistance of Zn-Ni deposits increases with increasing of Ni content.

Under the same plating conditions, it has been found that the polarization resistance of Zn-Ni-Fe deposits is higher than that of Zn-Ni deposits. Figure 3, for example, illustrated the polarization resistance of the deposits as a function of iron content. From this figure, the polarization resistance of Zn-Ni-Fe deposits (curves 2 to 5) is higher in comparison with that of Zn-Ni alloy (curve 1). The passive region of Zn-Ni-Fe deposits is slightly increased with increasing of iron content in the alloy up to 3.95%.

For Zn-Ni-Fe deposit; the passive region extended from the rest potential to approximately -1100 mV and the current density (at -1100 mV) was of 0.05 mAcm^{-2} (curve 4 in Fig. 3). On the other hand; the passive region of Zn-Ni deposit extended from the rest potential to approximately -1180 mV and the current density (at -1180 mV) was of 0.1 mAcm^{-2} (curve 1 in Fig. 3).

The increase in corrosion resistance of Zn-Ni-Fe alloys is not only due to the formation of a single high nickel γ alloy phase but also due to codeposition of iron. Codeposition of iron changed the γ phase structure to prefer (442), (600) and/or (444) orientation instead of (330) and (411) orientation of Zn-Ni alloy. Also, iron codeposition in the alloy tends to produce a finer grain size and increases in the lattice space of crystals as already observed by SEM and X-ray diffraction analysis.

4. CONCLUSION

SEM showed that the grain size of ternary Zn-Ni-Fe alloys was finer and more homogeneous in comparison with those of binary Zn-Ni alloys. The ternary Zn-Ni-Fe alloys had better corrosion resistance than binary Zn-Ni alloys and the best corrosion resistance was observed from the deposit containing 16.74% Ni and 3.95% Fe. The increase in corrosion resistance of ternary deposits is not only attributed to formation of single high nickel γ phase but also due to iron codeposition, which causes clearly change of crystal orientation with increases in the lattice space of crystals and obtains finer grain size with addition of iron.

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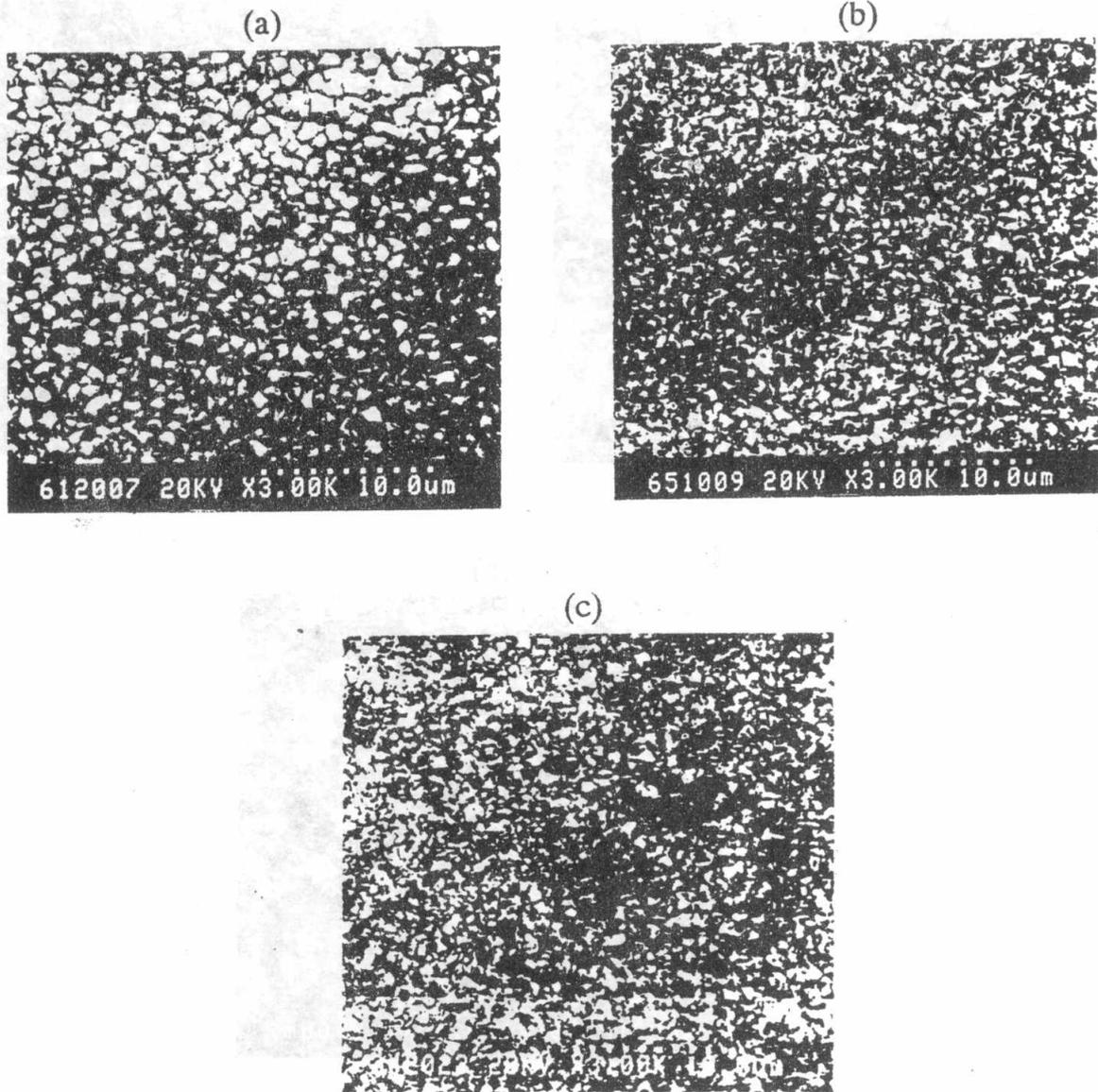


Fig. 1. SEM photographs of Zn-Ni-Fe deposits containing: (a) 14.17, 0, (b) 14.6, 2.13, and (c) 15.92, 2.64 of Ni% and Fe%, respectively.

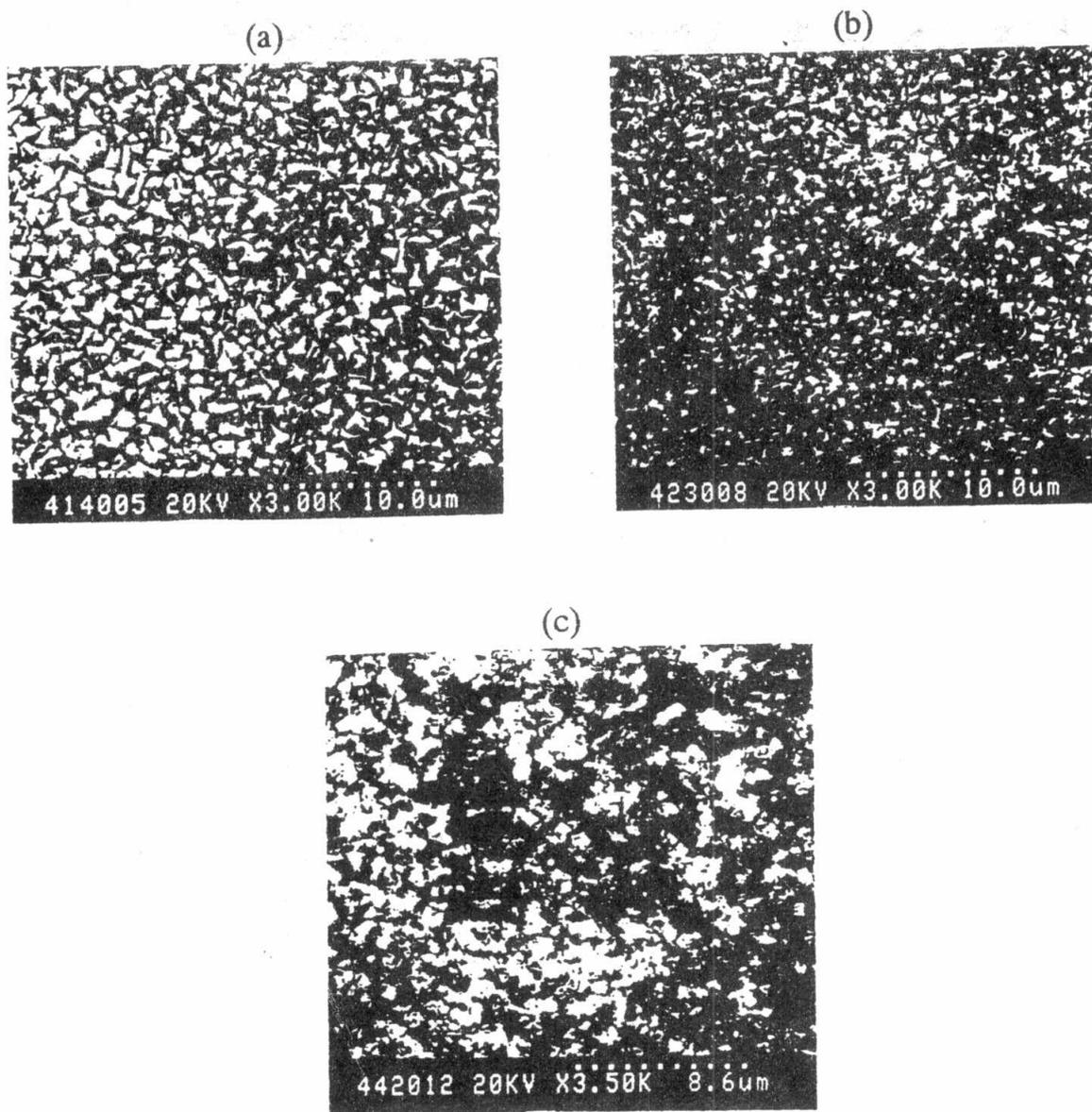


Fig. 2. SEM photographs of Zn-Ni-Fe deposits containing: (a) 17.26 g, (b) 16.54, 1.47, and (c) 16.54, 5.95 of Ni²⁺ and Fe²⁺, respectively.

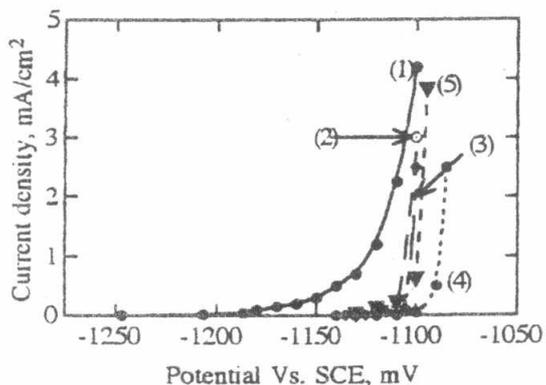


Fig. 3. Polarization resistance in neutral 3% NaCl solution for Zn-Ni-Fe deposits containing: (1) 17.26, 0, (2) 16.84, 1.47, (3) 15.91, 2.58, (4) 16.74, 3.95 and (5) 16.3, 5.2 of Ni% and Fe%, respectively.

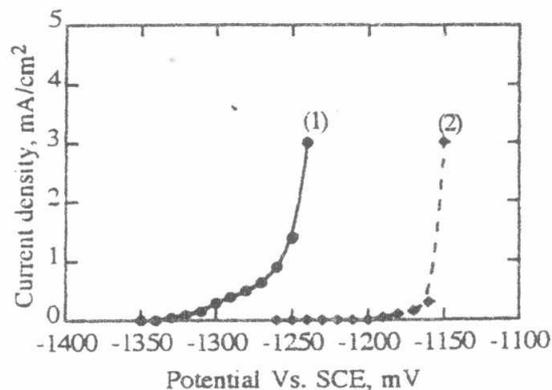


Fig. 4. Polarization resistance in neutral 3% NaCl solution for Zn-Ni-Fe deposits containing: (1) 15.01, 0 and (2) 15.08, 2.48 of Ni% and Fe%, respectively.

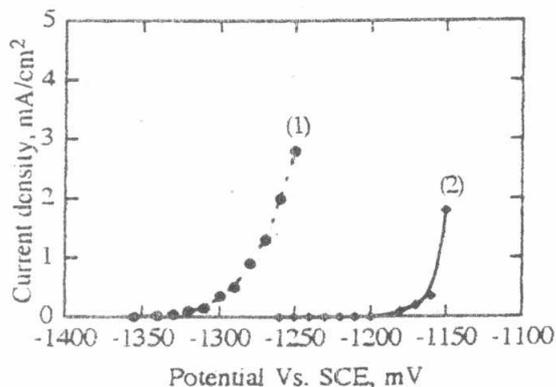


Fig. 5. Polarization resistance in neutral 3% NaCl solution for Zn-Ni-Fe deposits containing: (1) 14.74, 0 and (2) 13.92, 2.64 of Ni% and Fe%, respectively.

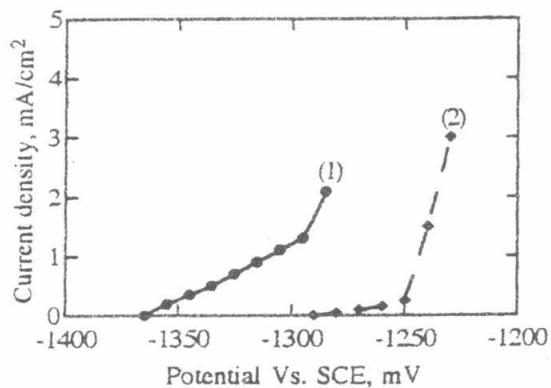


Fig. 6. Polarization resistance in neutral 3% NaCl solution for Zn-Ni-Fe deposits containing: (1) 14.17, 0 and (2) 14.6, 2.13 of Ni% and Fe%, respectively.