Polarization Behavior of Zn-Ni-Fe Alloy Electrodeposition

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Zn-Ni-Fe 合金析出の分極挙動

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Key Words: Zn-Ni-Fe Alloy Plating, Electrodeposition, Polarization Curve, $\text{Ni}^{2+}/\text{Zn}^{2+}$ Molar Ratio

Introduction

Zn-Ni alloy coatings had usually dull and gray unattractive finish, and a brightener system had to be developed to obtain bright deposits¹⁾. Recently, it is found that the bright Zn-Ni-Fe alloy electrodeposits were obtained in acidic chloride baths without any organic brightener^{2), 3)}. Also, this alloy exhibited better corrosion resistance and finer grain size in comparison with Zn-Ni deposits⁴⁾.

This work is carried out to determine the effect of Fe codeposition on the polarization behavior of Zn-Ni-Fe alloy electroplating. Therefore, the cathodic polarization of binary Zn-Fe, Ni-Fe and Zn-Ni alloys deposition are also measured.

Experimental

Zn-Ni-Fe alloy electrodeposit was obtained at $40 \pm 2^\circ\text{C}$ and pH 3 using the following bath composition: 0.4 M ZnCl_2 , 0.4 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.06 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 2.5 M NaCl, 0.3 M $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, 0.5M H_3BO_3 and 0.5g/L dodecyl sodium sulfate. Also the electrodeposits of binary Zn-Fe, Ni-Fe and Zn-Ni alloys were obtained using the above plating parameters only with the required metal ions. All experiments were done in a glass beaker of 0.2L.

The cathodic polarization was measured using potentiostat at the scanning rate of 5mV/sec. The cathodic potential was measured against saturated calomel electrode (SCE). The counter electrode was platinum wire, while the working electrode was copper disk (1.5cm diameter).

Results and Discussion

Fig. 1 shows the polarization curves of Ni-Fe, Zn-Fe, Zn-Ni and Zn-Ni-Fe alloy deposition. The curves of Ni-Fe and Zn-Fe alloy deposition increased monotonously with cathodic potential

Fig. 1 Cathodic polarization curves of binary Zn-Fe, Ni-Fe and Zn-Ni, and ternary Zn-Ni-Fe alloys electrodeposition.

in a similar manner as generally been observed in single metal deposition. On the contrary, there existed peculiar potential region in the curves of Zn-Ni and Zn-Ni-Fe alloy deposition.

Zn-Ni plating is one of the well-known anomalous type codeposition according to Brenner's definition^{5), 6)}. The anomalous codeposition behavior of Zn-Ni and Zn-Co are attributed to the formation of zinc hydroxide film on the electrode surface, which suppresses the discharge of Ni or Co ions^{7), 8)}. In the polarization curve of Zn-Ni deposition in Fig. 1, there is a sharp potential increase at a certain current density, which is called transition critical current density from normal to anomalous region⁶⁾. And there is also a sudden current density jump at a certain potential. In these cathodic potential region, Zn-Ni alloy deposition changes in phase from α to γ solid solutions⁹⁾.

The polarization behavior of Zn-Ni-Fe alloy deposition was similar to the Zn-Ni plating. This reveals that the Zn-Ni-Fe alloy deposition may proceed by similar mechanisms to the Zn-Ni plating. However, the anomalous potential region of Zn-Ni-Fe alloys shifted to negative

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Fig. 2 Cathodic polarization curves of electrodeposited Zn-Ni alloys from baths containing ; (1) 0.4, 0.3, (2) 0.4, 0.4, (3) 0.4, 0.5 and (4) 0.5, 0.4M of Zn^{2+} and Ni^{2+} respectively.

values in contrast to the Zn-Ni plating.

Fig. 2 shows the effect of Ni^{2+}/Zn^{2+} molar ratio on the polarization of Zn-Ni deposition. With increase of Ni^{2+}/Zn^{2+} molar ratio in the bath, the transition critical current density Zn-Ni deposition increased slightly, and the anomalous potential region shifted to negative values. These may be attributed to the slight pH decrease on the electrode surface with increase of the molar ratio which causes the reduction of hydrogen overpotential. This consideration was confirmed by the results that the current efficiency for the alloy deposition decreased with increase of the molar ratio³⁾.

The polarization curves of ternary Zn-Ni-Fe alloy deposition from the bath of different Ni^{2+}/Zn^{2+} molar ratio with 0.06M $FeCl_2$ are shown in Fig. 3. The transition critical current density was not affected by the addition of $FeCl_2$. However, as mentioned previously, the anomalous potential regions shifted to negative values in contrast to those of Zn-Ni deposition. These shifts became larger with increase of the molar ratio, and simultaneously, the iron contents in the alloy deposition increased³⁾. These may also be resulted from the reduction of hydrogen overpotential and the increase of charged Fe ions in the bath.

Fig. 3 Cathodic polarization curves of electrodeposited Zn-Ni-Fe alloys from baths containing 0.06M of Fe^{2+} and (1) 0.4, 0.3, (2) 0.4, 0.4, (3) 0.4, 0.5 and (4) 0.5, 0.4M of Zn^{2+} and Ni^{2+} respectively.

Conclusion

The electroplating of ternary Zn-Ni-Fe alloy exhibited the anomalous type codeposition. The transition from normal to anomalous codeposition was observed at low critical current densities. The transition critical current density was not affected by addition of 0.06M $FeCl_2$ and just as it was in Zn-Ni deposition. The anomalous potential region of Zn-Ni-Fe alloy was shifted to negative values in contrast to these of Zn-Ni alloy.

(Received December 26, 1995 ; Accepted February 28, 1996)

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