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Electrodeposition behaviour of zinc-iron group metal alloys from a methanol bath

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Electrodeposition of zinc–iron-group metal alloys is carried out in a methanol bath. The effects of different parameters, such as bath composition and current density on current efficiency and alloy composition are investigated. Partial polarization curves of zinc and nickel are measured for both alloy and single metal deposition to evaluate the codeposition behaviour of zinc–iron-group metal alloys. Attempts are also made to confirm the proposed hydroxide suppression mechanism explaining the anomalous type of codeposition of zinc–iron-group metal alloys by investigating the role of water in the electroreduction process of zinc and iron-group metal ions.

1. Introduction

Zinc and zinc alloys are widely used to electroplate steel sheet to provide corrosion resistance, mainly in the automobile industries. The corrosion resistance of pure zinc coating over steel is not satisfactory and not acceptable under severe atmospheric conditions. Several methods and materials, such as different organic paints and zinc alloys, are being examined for improved corrosion resistance and better economical means of protection of steel sheets for longer times under severe atmospheric conditions [1–14]. It is observed that the zinc alloyed with iron-group metals show better corrosion resistance behaviour than individual zinc metal. Therefore, there is an incentive to investigate the electrodeposition of zinc alloys from aqueous sulfate and chloride baths. Several researchers [1–3, 10–12, 15] are investigating the possibility of electrodepositing such alloys under different operating conditions to achieve the optimum conditions for production of more corrosion resistant alloys with zinc metal.

It is well known that the codeposition of zinc with iron-group metals, such as iron, nickel and cobalt, is of an anomalous type in which preferential deposition of zinc is observed over a wide range of electrolysis conditions [16]. Efforts are being made to explore the possible mechanism by which zinc is preferentially codeposited. The anomalous codeposition behaviour has been explained by different workers [17]. However, the zinc hydroxide suppression mechanism to facilitate the codeposition of zinc with iron-group metals seems to be more logical and acceptable [18]. In the present paper, the electrodeposition of such alloys from nonaqueous methanol bath is reported to confirm the proposed hydroxide suppression mechanism. The present communication mainly reports our findings on the electrodeposition behaviour of zinc–iron-group metal alloys. The effects of various parameters affecting the codeposition behaviour are studied to critically examine the possibility of anomalous codeposition of such alloys from a nonaqueous bath.

2. Experimental details

2.1. *Apparatus and material*

An air sealed electrolytic cell was used for conducting the electrolysis at galvanostatic and coulostatic conditions (Fig. 1). The cathode was of Cu and the anode of Pt. For all experiments, an Ag/AgCl electrode was used as a reference.

2.2. *Electrolysis*

Table 1 shows the standard electrolysis conditions employed in this experiment. Electrolytic solution was prepared from high pure hydrated nickel chloride, cobalt chloride, ferric chloride and anhydrous

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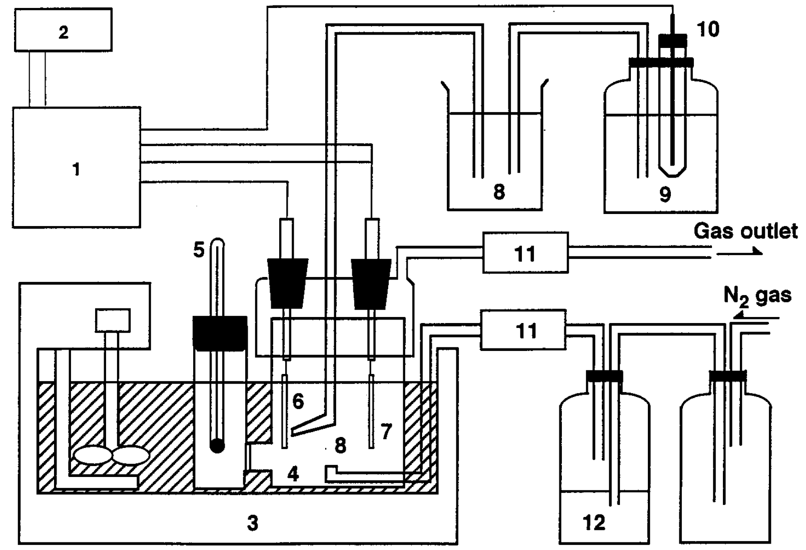

Fig.1 Apparatus: (1) potentio/galvonostat, (2) recorder, (3) heating bath, (4) electrolytic cell, (5) thermometer, (6) cathode, (7) anode, (8) electrolyte, (9) sat. KCl solution, (10) Ag/AgCl electrode, (11) silica gel, (12) pyrogallol solution. (When pH in cathode layer was measured, Sb electrode and capillary tip of reference electrode were placed at a fixed distance from cathode surface using micrometer.)

zinc chloride. Ferric chloride was used in zinc-iron system because of the low solubility of ferrous chloride in methanol solvent. Purified methanol was used as solvent for the experiments. Boric acid was added to uniformly maintain the hydrogen ion concentration in the baths and for the better codeposition of zinc–iron-group metal. Deionized water was used as additive in the methanol bath to observe its effect on the electrodeposition behaviour. Electrolysis was carried out in a stagnant solution with required concentrations of zinc ion, iron-group metal ion, methanol and water at constant temperature 50 °C. Polarization curves for the electrodeposition of alloys and individual metal were measured under potentiostatic condition.

The pH of the bath in the vicinity of cathode was also measured using a self-made antimony microelectrode during electrolysis [19, 20].

2.3. *Deposit analysis*

Electrodeposited alloys were dissolved by aqua regia and zinc and iron-group metals in the deposits were determined quantitatively by atomic absorption spectrophotometer (AAS). The current efficiency and the partial current density of individual metal were then determined from the analysis data.

Table1. Standard electrolysis conditions

Bath composition		Operating condition
$ZnCl_2$	0.25 mol dm^{-3}	Cathode: Cu
$NiCl_2{\cdot}6H_2O$	0.25 mol dm^{-3}	Anode: Pt
$CoCl_2{\cdot}6H_2O$	0.25 ,mol dm^{-3}	Current density: 250, 1000 A m^{-2}
$FeCl_3{\cdot}6H_2O$	0.25 mol dm^{-3}	Temperature: 50 °C
H_3BO_3	1.0 mol dm^{-3}	Stagnant bath
Water	0–20 vol%	
Methanol	100–80 vol%	

3. Results and discussion

3.1. *Effects of bath composition and current density*

At constant current density, the ratio of Zn^{2+}/Ni^{2+}, Zn^{2+}/Fe^{3+} and Zn^{2+}/Co^{2+} in the methanol bath was varied to observe the effect on current efficiency and alloy composition. The percentage of iron-group metal ion (M^{n+}: iron-group metal ion) in the baths was calculated as follows from the relation defined by Brenner [21];

$$\text{Percentage } M^{n+} = \frac{\text{mass \% } M^{n+}}{\text{mass \% } M^{n+} + \text{mass \% } Zn^{2+}} \times 100$$

The results of the effect of the concentration of iron-group metal ion in the baths on the alloy composition and the current efficiency at two different current densities viz. 250 Am^{-2} and 1000 Am^{-2} are presented in Fig. 2. The compositional reference line (CRL) is used to predict a normal or an anomalous type of codeposition of zinc alloys with iron group metals. The content of iron-group metal in the deposits above the CRL indicates the normal type of codeposition in which the preferential deposition of more noble iron-group metal occurs. On the other hand, the points below the CRL represent the anomalous type of codeposition because the alloys contain larger ratio of less noble zinc than the baths.

The content of iron-group metal in the deposits was found to increase with an increase in the metal percentage of the iron-group metal ion in the baths at both current densities. In the cases studied, the content of iron-group metal lay above the CRL, indicating that the normal codeposition occurred in the whole range of bath composition.

The dependence of the current efficiency for alloy deposition on the bath composition did not show a definite pattern among the systems of zinc–iron-

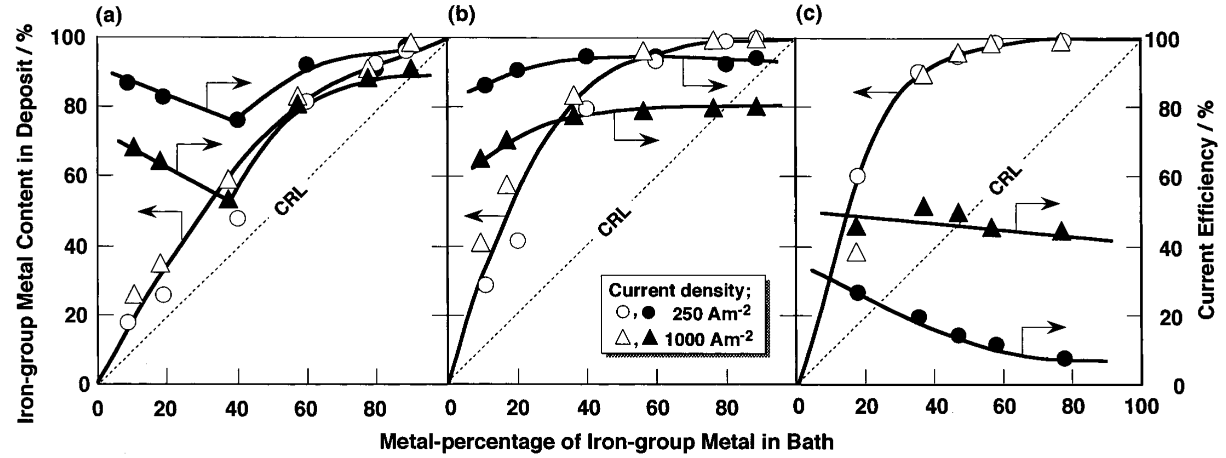

Fig. 2. Effect of metal percentage of iron-group metal in bath on alloy composition and on current efficiency at 250 (○, ●) and 1000 (△,▲) A m^{-2} (a) Zn–Ni, (b) Zn–Co, (c) Zn–Fe.

group metals. The current efficiency for zinc–nickel alloy deposition initially decreased and then increased gradually. In the electrodeposition of zinc–cobalt alloy, the current efficiency was found to be marginally increased with an increase in the initial metal-percentage of Co^{2+} in the baths. In the case of codeposition of zinc–iron alloy, the current efficiency showed relatively low values and continuously decreased with an increase in the metal percentage of Fe^{3+} in the baths. This is probably due to the unfavourable conditions for zinc–iron alloy deposition from the baths containing ferric ion.

Figure 3 shows the effect of current density on the alloy composition and on the current efficiency for alloy deposition. It was found that the contents of iron-group metals in the deposits are higher than those at the CRL over the whole range of current density studied. In the electrodeposition of zinc–iron-group metal alloys from aqueous sulfate solutions, the anomalous type of codeposition is observed in a wide current density, except the lower region where iron-group metal is preferentially deposited with extremely low current efficiency [22, 23]. However, as shown in Fig. 3, no anomalous codeposition occurred in the codeposition of zinc with iron-group metals from the methanol baths.

The current efficiency for zinc–nickel alloy deposition kept higher value of about 80% at lower current density and decreased beyond 100 Am^{-2}. For the zinc–cobalt and zinc–iron alloy depositions, the current efficiency increased with an increase in current density.

Figure 4(a) shows the partial polarization curves of zinc and nickel for the alloy deposition as a representative case. It was found that the deposition of zinc as well as nickel initiated at about −0.5 V vs Ag/AgCl and their deposition rates continuously increased with a cathodic shift of the potential. Figure 4(b) also shows the partial polarization curves of zinc and nickel for the single deposition. The potential for the initiation of the single deposition of nickel was almost the same as for the alloy deposition. However, zinc began to deposit at about −1.0 V vs Ag/AgCl for the single deposition. It is therefore found that the deposition potential of zinc is significantly shifted to positive direction for the codeposition of zinc with nickel. In aqueous solutions, on the other hand, the underpotential deposition of zinc is known to be induced under a certain electrolysis condition [23, 24]. When an electrolysis is carried out in the high

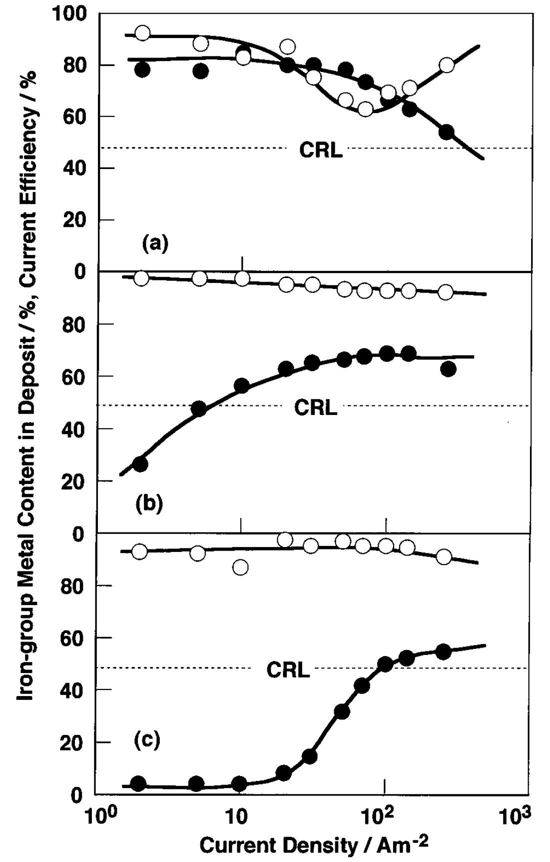

Fig. 3. Effect of current density on alloy composition and on current efficiency for zinc–iron-group metal alloy deposition. (Bath composition; Zn^{2+} 0.25 mol dm^{-3}, no water added.) Key: (●) current efficiency and (○) iron–group metal content. (a) Zn–Ni, (b) Zn–Co, (c) Zn–Fe.

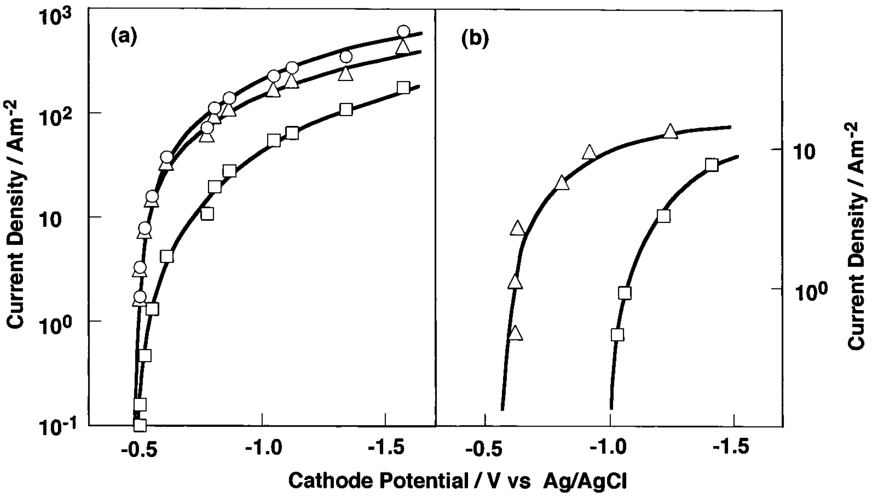

Fig. 4. Partial polarization curves of nickel (△) and zinc (□) for alloy deposition (a) and for single deposition (b) from methanol bath. [(○) Total Ni+Zn] (Bath composition; Zn^{2+} 0.25 mol dm^{-3}, iron-group metal ion 0.25 mol dm^{-3}, H_3BO_3 1.0 mol dm^{-3}, no water added.)

chloride concentration baths and/or at high temperature, the deposition behaviour of zinc–iron-group metal alloys tends to change from the anomalous to the normal type. Therefore, iron-group metal deposition proceeds with high current efficiency around its equilibrium potential. At the same time the deposition potential of zinc is shifted toward those of iron-group metals and the codeposition of zinc occurs at potentials a few hundreds millivolts more positive than the equilibrium potential of zinc. The mechanism of the underpotential deposition of zinc accompanied by the depolarization of iron-group metal has been still unclear. However, as shown in Fig. 4, it is interesting that the preferential deposition of iron-group metal and the large positive shift of the deposition potential of zinc are simultaneously observed using the methanol electrolytes.

3.2. *Effect of water addition*

According to the hydroxide suppression mechanism proposed for the electrodeposition of zinc–iron-group metal alloy from aqueous solutions [22, 23], the anomalous codeposition is caused by the zinc hydroxide formed and adsorbed on the cathode due to pH rise in the cathode layer. On the other hand, the electrodeposition behaviour of zinc–iron-group metal alloys from methanol baths can be classified into normal type and no anomaly appeared in the electrolysis condition studied here. Then, a certain amount of water was added to methanol electrolytes and the behaviour of the codeposition of zinc with nickel was investigated.

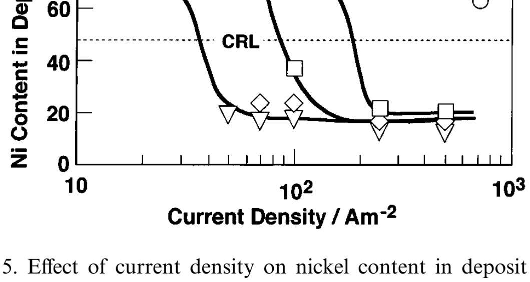

Fig. 5. Effect of current density on nickel content in deposit obtained in baths containing: (○)0. (□)5, (◇)10 and (▽) 20 vol% H_2O.

Figure 5 shows the effect of water on the dependence of the nickel content in the deposit on the current density. In the bath containing 5 vol% water, the nickel content in the deposits abruptly decreased to the anomalous region at about 200 Am^{-2} when increasing the current density, and the transition current density where the codeposition behaviour changed from the normal to the anomalous type appeared. Moreover, the anomalous codeposition was observed over a wider range of current density with an increase in water content in the baths. This indicates that some water is necessary to bring about the anomalous codeposition in the methanol solutions. Further, pH in the vicinity of the cathode was simultaneously measured at various current densities using the antimony microelectrode which was placed near the cathode surface. When less noble zinc was deposited in preference to nickel, the pH in the vicinity of cathode increased to around 6.

Figures 6 and 7 show the partial polarization curves of nickel and zinc for alloy deposition and their single metal deposition, respectively, from the baths containing 20 vol% water. These figures also include the polarization curves of these metals in the water-free solutions. The nickel deposition from the water-containing alloy plating bath began to occur at about −0.5 V vs Ag/AgCl which was the same potential as in the water-free solutions, but it was remarkably depressed at about −1.0 V vs Ag/AgCl. Then, with a cathodic shift of the potential, the deposition rate of nickel became higher again. On the other hand, zinc was deposited massively at potentials less positive than −1.0 V vs Ag/AgCl, while the underpotential deposition of zinc was observed to a small extent at the more positive potentials.

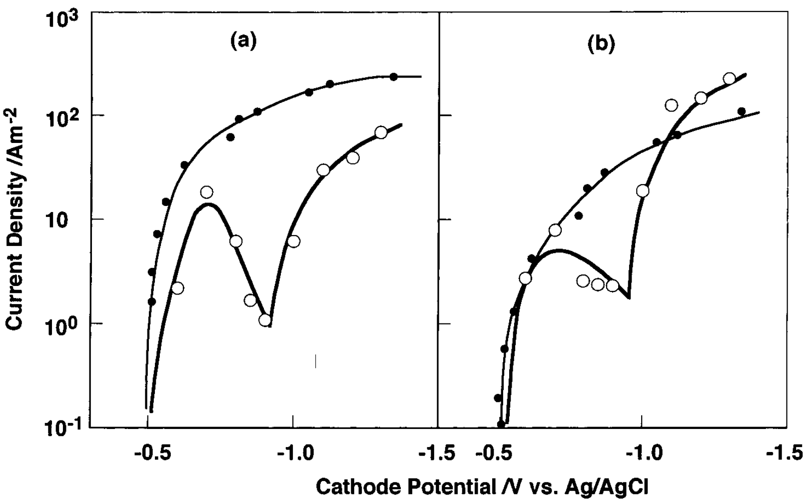

Fig. 6. Effect of addition of water on partial polarization curves of nickel (a) and zinc (b) for alloy deposition. H_2O content: (○) 20 and (•) 0 vol%.

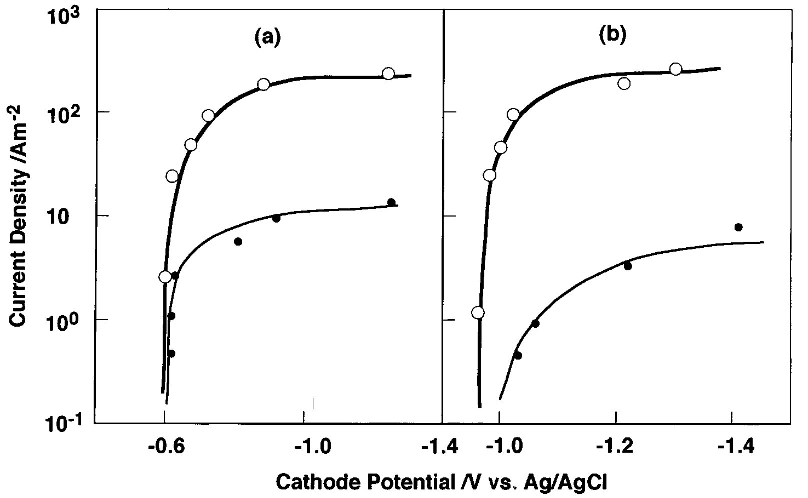

Fig. 7. Effect of addition of water on partial polarization curves of nickel (a) and zinc (b) for their single deposition. (○) 20 and (•) 0 vol%.

For the single metal deposition, both nickel and zinc began to deposit at the same potentials as in the water-free baths. However, the limiting current densities for both metal depositions from the water-containing baths were enormously different from those from the water-free baths. It is suggested that the solvated ionic species of nickel and zinc ions change with an increase in water content in the baths to affect significantly the diffusion rates of both ions.

The polarization behaviour of nickel and zinc in the alloy plating baths containing water was very similar to those in the aqueous sulfate solutions [22, 23] and reasonably explained by the hydroxide suppression mechanism. It has been reported that the electrodeposition of iron-group metals from aqueous solutions, which have the inherent property of not beginning to deposit at their equilibrium potentials, proceed by a multistep reduction mechanism through a transient intermediate containing hydroxyl species [25, 26], and their deposition sites from the intermediate are considerably limited on the cathode. Further, the deposition of iron-group metals is easily polarized by other foreign adsorptive substances. In the electrodeposition of zinc–iron-group metal alloys, the deposition sites for iron-group metals are blocked by zinc hydroxide formed due to pH rise in the cathode layer to suppress the iron-group metal deposition and the preferential deposition of less noble zinc is induced. Using methanol electrolytes, water added to the baths causes the hydrolysis reaction with zinc ion to form zinc hydroxide as a product at the cathode surface. Then the suppression of nickel deposition occurs and zinc apparently behaves as a more noble metal than nickel.

4. Conclusions

The electrodeposition behaviour of zinc–iron-group metal alloys was studied using nonaqueous methanol baths. The content of iron-group metals in the deposits was always higher than the metal percentage of iron-group metals in the baths over the whole range of electrolysis conditions studied. Accordingly the codeposition of this system from methanol baths was classified as the normal type in which more noble metal is deposited in preference to less noble metal.

Addition of water to the methanol baths induced the appearance of anomalous codeposition in which the nickel deposition was significantly suppressed.

The results obtained can be explained on the basis of the hydroxide suppression mechanism.

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