



Effects of copper and anions on zinc–nickel anomalous codeposition in plating and electrowinning

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Abstract

Anomalous codeposition describes inhibition of the reduction of a metal such as Ni by the presence of a less noble metal such as Zn. This phenomenon is observed in two important industrial applications. In the case of plating, it is shown that the addition of Cu leads to the formation of a ternary alloy which is enriched in Ni in the chloride bath, whereas little enrichment is observed in the sulfate, and none in the nitrate and acetate baths. In the case of Zn electrowinning with diluted metallic impurities, a description of the anomaly based on limiting current density is given, and once again the effect of Cu, which is to increase the content of the Ni impurity in the Zn, is much more important in the chloride than in the sulfate media.

1. Introduction

The codeposition of Zn and Ni is said to be anomalous, because the deposition of Ni, which is the more noble metal, is inhibited by the presence of Zn [1]. It can be observed in two important applications: the plating of Zn–Ni alloys for the protection of carbon-steel from corrosion [2] and the electrowinning of Zn from acidic solutions in the presence of Ni impurity [3].

The Zn–Ni alloy has already been shown to be superior to the traditional Zn coatings applied for the protection of steel, and it is currently in use in the automotive industry [4]. The best alloy has a Ni content of about 12%. Detailed studies of the effects of electrolysis parameters on alloy composition have been made, and a mechanism for alloy formation has been proposed [5–10]. However, no research has been conducted on the effects of Cu on the anomalous codeposition of Zn and Ni. It is possible that the resulting ternary alloy could have a very different composition which could offer a new insight into the mechanism. This is the subject of the present investigation.

Primary Zn is produced by a roasting, leaching, electrowinning process. Costly purification steps are required in the preparation of the acidic sulfate electrolyte in order to control the level of metallic impurities which arise from the ores [11]. If the impurities are present in the bath, they contaminate the Zn and decrease the current efficiency by facilitating H₂ evolution.

This detrimental effect of impurities has been well documented in the literature [12–15]. Nickel, which is

the most deleterious, has already been studied [12]. A detailed mechanism of its effect has been proposed [13, 14]: after codeposition with Zn, Ni acts as a site for H₂ evolution, since it offers a lower overvoltage for this reaction than Zn. Cu is also detrimental to the Zn current efficiency, and it acts by a similar mechanism. However, its effect is less pronounced than that of Ni, because it offers a higher overvoltage for H₂ evolution.

The detrimental effects of combinations of impurities have also been studied [15]. In cases such as Ni + Cu, synergy occurs: the combinations are more detrimental than the individual impurities. However, there has been no explanation for this behaviour.

It has already been observed [16] that the addition of Cu increases the content of Ni in the Zn deposit in acidic chloride solutions, which implies more sites for H₂ evolution. Thus, the characteristics of Ni + Cu combinations in acidic sulfate solutions typical of the industrial process were investigated in terms of the contents of impurities in the Zn deposits. These characteristics will then be compared here with those observed in the chloride media in order to gain a new understanding of the role of anions in anomalous codeposition.

2. Experimental details

Two kinds of tests were conducted: Zn–Ni alloy deposition and Zn electrowinning in the presence of Ni as an impurity. Both tests were conducted using a Kepco MSK 20-5M power supply and Fluke 8010A multimeter.

For alloy deposition, the cell was a 1 L beaker maintained at 25 °C on a heating plate. The cathode was a carbon-steel sheet polished with 600 grit paper and activated by dipping for 3 min in 25% volume HCl. The anode was a Ni block. The current density was 100 A m⁻².

For Zn electrowinning, the cell was a 2 L beaker immersed in a water bath to maintain the temperature at 40 °C. One aluminium cathode and two lead-0.5% silver anodes were used. The total current was 0.8 A, and the current density was 500 A m⁻². The electrodes were held in place by inserting them in a teflon stand, and the anode-cathode distance was 3.3 cm.

In both cases, electrodes were partially covered with electroplating tape (Scotch 3M no. 484). The duration of each test was 45 min, and no agitation was provided.

The electrolytes were prepared from reagent grade chemicals and from water that was both deionized by reverse osmosis and distilled. For alloy deposition, the composition of the electrolytes is indicated on the figures with the other electrolysis parameters. The pH was always 4. For Zn electrowinning, the electrolyte contained 60 g dm⁻³ Zn and 200 g dm⁻³ H₂SO₄. The NiSO₄ and CuSO₄ impurities were added from stock solutions.

In both tests cases, the current efficiency was obtained by weighing deposits. The deposits were washed with distilled water and methanol prior to drying. Samples cut from each deposit were analysed by atomic absorption spectrophotometry to determine their Zn, Ni and Cu content.

3. Results

In the case of plating, Figures 1–4 clearly show that there is anomalous codeposition in all media (Cl⁻, SO₄²⁻, NO₃⁻ and CH₃COO⁻): the Ni content of the alloys is always much less than that of the bath. This happens despite the fact that Ni is the more noble metal. It can also be seen that for the chloride bath, the addition of Cu resulted in a large increase in the Ni content of the alloys, the increase being from 9 to 34%. The Ni-rich deposits were also prone to H₂ evolution, which explains the considerable drop in current efficiency with the addition of Cu also observed in the Cl⁻ solution. In the sulfate bath, Cu only increased the Ni content slightly, while no change was observed in the nitrate and acetate solutions.

In the case of zinc electrowinning (Figures 5 and 6), comparison of the results previously reported for Cl⁻ media [16] with those obtained in acidic SO₄²⁻ solution in the presence of individual Ni and Ni + Cu combinations indicates that Ni was only slightly detrimental to the current efficiency. In the sulfate media, Ni was, as expected [12], more detrimental than Cu (at 9.5 ppm, Cu in the bath corresponds to a C_E of 88.8%), and this deleterious effect is more pronounced than in the chloride media (since the acid concentration is much

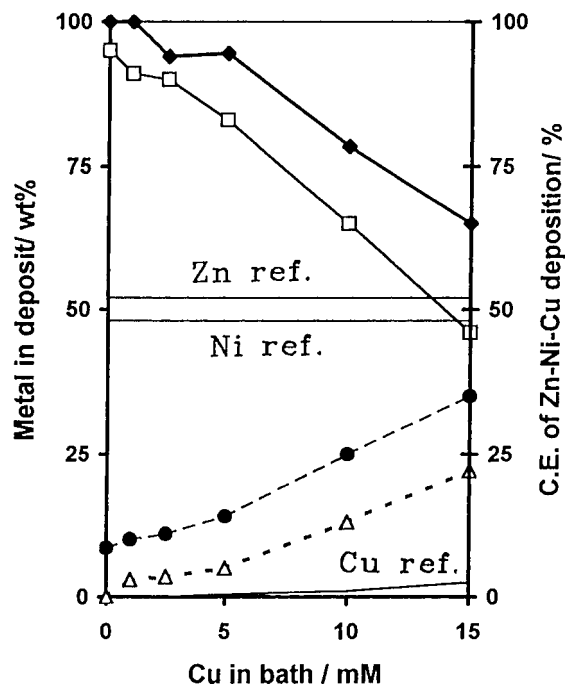


Fig. 1. Codeposition of Zn–Ni in the presence of Cu in chloride bath. Chloride bath: 0.5 M Zn + 0.5 M Ni + Cu. $T = 25\text{ }^{\circ}\text{C}$, pH 4, CD 100 A m⁻² and $t = 45$ min. Key: (◆) CE, (□) Zn, (●) Ni and (Δ) Cu.

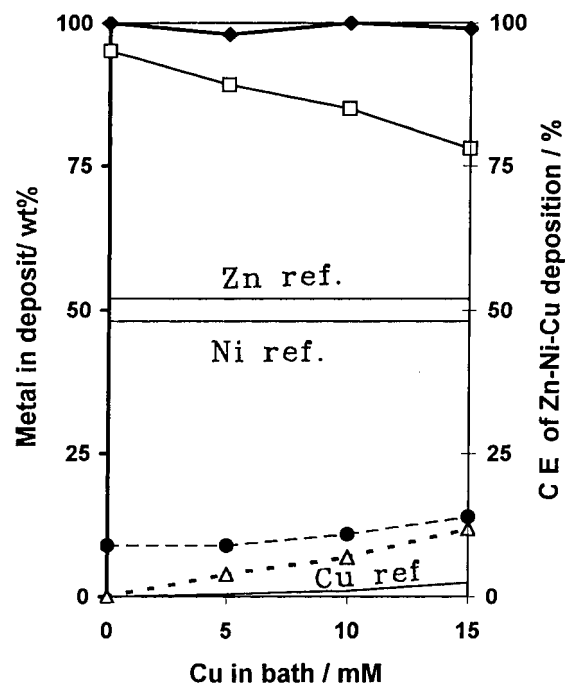


Fig. 2. Codeposition of Zn–Ni in the presence of Cu in sulfate bath. Sulfate bath: 0.5 M Zn + 0.5 M Ni + Cu. $T = 25\text{ }^{\circ}\text{C}$, pH 4, CD 100 A m⁻² and $t = 45$ min. Key: (◆) CE, (□) Zn, (●) Ni and (Δ) Cu.

stronger). Figures 5 and 6 also show that the combinations were more detrimental to the current efficiency in both baths. The more Cu or Ni there is in the Zn, the more sites there are to evolve H₂, as explained below. Once again, the bigger drop in C_E observed in the sulfate media results from the higher acid concentration.

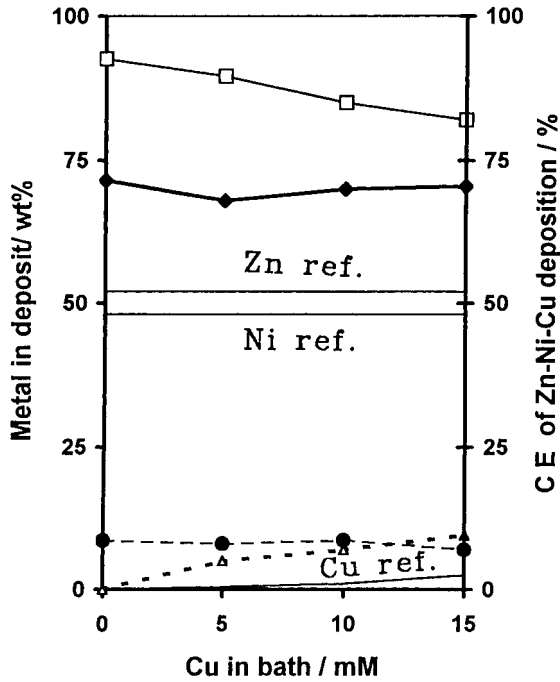


Fig. 3. Codeposition of Zn-Ni in the presence of Cu in nitrate bath. Nitrate bath: 0.5 M Zn + 0.5 M Ni + Cu. $T = 25\text{ }^{\circ}\text{C}$, pH 4, CD 100 A m^{-2} and $t = 45\text{ min}$. Key: (◆) CE, (□) Zn, (●) Ni and (△) Cu.

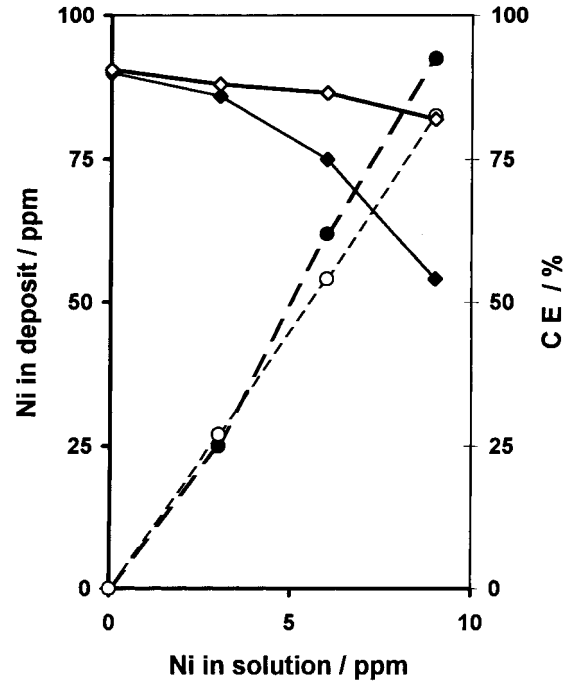


Fig. 5. Changes of the concentration of Ni in deposit and current efficiency (C_E) against Ni concentration in solution with and without presence of Cu in sulfate bath. Concentration Zn 60 g dm^{-3} , $T = 40\text{ }^{\circ}\text{C}$, concentration of H_2SO_4 200 g dm^{-3} , CD 500 A m^{-2} and $t = 45\text{ min}$. Key: (●) Ni content with 9.5 ppm Cu, (○) Ni content without Cu, (◆) CE with 9.5 ppm Cu and (◇) CE without Cu.

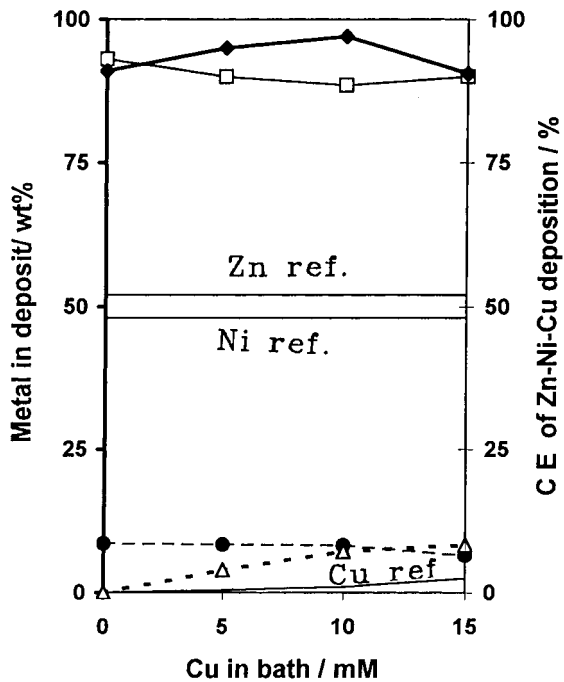


Fig. 4. Codeposition of Zn-Ni in the presence of Cu in acetate bath. Acetate bath: 0.5 M Zn + 0.5 M Ni + Cu. $T = 25\text{ }^{\circ}\text{C}$, pH 4, CD 100 A m^{-2} and $t = 45\text{ min}$. Key: (◆) CE, (□) Zn, (●) Ni and (△) Cu.

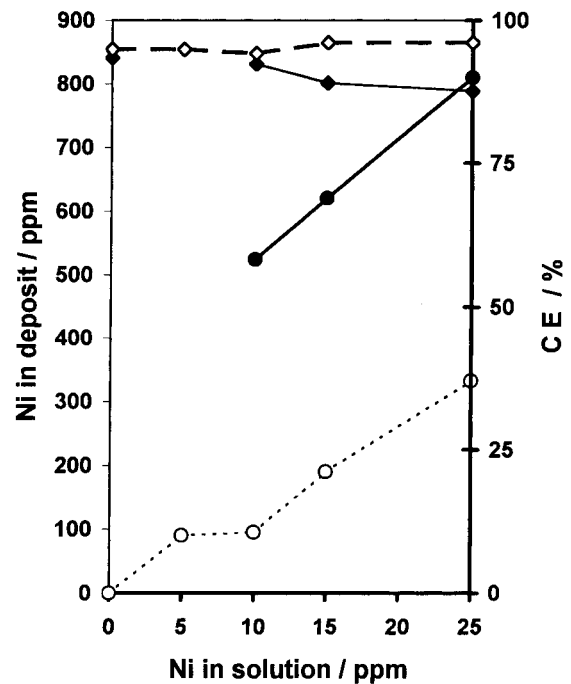


Fig. 6. Changes of the concentration of Ni in deposit and current efficiency (C_E) against Ni concentration in solution with and without presence of Cu in chloride bath. Concentration Zn 30 g dm^{-3} , $T = 35\text{ }^{\circ}\text{C}$, concentration of HCl 4.4 g dm^{-3} , CD 500 A m^{-2} , $t = 6\text{ h}$ and air sparging $5.3\text{ dm}^{-3}\text{ min}^{-1}$. Key: (●) Ni content with 20 ppm Cu, (○) Ni content without Cu, (◆) CE with 20 ppm Cu and (◇) CE without Cu.

The results of atomic absorption analysis are also shown in Figures 5 and 6. In both the SO_4^{2-} and Cl^- solutions, there is anomalous codeposition of Ni, since there is much less Ni than Cu in the Zn (9.5 ppm Cu in the sulfate solution corresponds to 365 ppm Cu in the deposit, and 20 ppm Cu in the chloride solution corresponds to 2440 ppm Cu in the deposit). At these

low concentrations, both Ni and Cu are expected to codeposit at their limiting current density [17], because diffusion coefficients do not differ very much [18]. Another proposed explanation of the anomaly is that the Ni impurity at a very low concentration codeposits with Zn at a rate below the limiting current density, which corresponds to the mass transfer conditions. The codeposition of Cu is said to be regular [1], and indeed it deposits at its limiting current density.

It should be emphasized that the difference in the individual Ni contents between the two solutions is caused mainly by the fact that the mass transfer resulted from natural convection in the SO_4^{2-} media (as in industrial conditions) while it was enhanced by air sparging in the Cl^- media (as part of an original operating practice for that alternative technology for Zn electrowinning [16]). However, this does not prevent comparison of the behaviour of the combinations of impurities in the two solutions. It can be seen that the addition of Cu resulted in a large change in the Ni content of the Zn deposits in the Cl^- media, while the change was slight in the SO_4^{2-} . To see if the difference between the two media did not result from the difference in copper and acid concentrations, more tests were conducted in SO_4^{2-} solution. At higher concentrations of Cu (31.5 mg dm⁻³ Cu + 8.8 mg dm⁻³ Ni), only a slight increase in the Ni content of the Zn deposit (1160 ppm Cu + 119 ppm Ni) was obtained, and no increase in the Ni content resulted from a decrease in the H_2SO_4 concentration (down to 2 g dm⁻³). Thus the difference in the behaviour of combinations of impurities can be attributed to an interaction with the anion of the solution.

4. Discussion

To explain the effect of a third element, copper, on Ni enrichment in Zn–Ni anomalous codeposition, it is necessary to review briefly the different mechanisms proposed for the anomalous codeposition of Zn–Ni alloys. The models can be classified into three groups: (a) the formation of a Zn(OH)₂ layer on the deposit due to a superficial pH increase, with the layer acting as a barrier to Ni reduction [5, 6]; (b) the underpotential deposition and electrocrystallization mechanisms, where the energy of formation of Zn–Ni alloys is taken into account and which favors the higher rate of Zn deposition in the alloy [7, 8]; and (c) a kinetic explanation for the change in the deposition rate [9, 10].

Several authors have reported anomalous behaviour for different alloy deposits, such as Ni–Fe, Ni–Co and Ni–Zn [19–22]. A similar phenomenon was also discussed for zinc electrowinning in acid bath [23] and in alkaline solution [24]. All of these cases of anomalous codeposition can be explained by kinetic effects.

For the Zn–Ni alloy studied here, the presence of Zn in the solution has an inhibiting effect on the reduction rate of Ni which decreases the content of that metal in

the deposit. However, the presence of nickel favours the kinetics of Zn deposition. Nickel can then be considered to have a catalytic effect which results in an increase of Zn in the deposit.

The influence of copper observed here can also be explained as a kinetic effect. Copper's presence in the solution increases the rate of Ni reduction and consequently the Ni content in the deposit alloy (Figure 6). Copper has an effect opposite to that of Zn; it decreases anomalous behaviour in Zn–Ni electrodeposition.

Copper has only a small detrimental effect on current efficiency in chloride media; it has a more significant impact, however, in sulfate bath where it reinforces the negative effect of Ni by decreasing the current efficiency (up to a concentration of 8 ppm Ni). In the absence of copper, previous results [23] indicate that the current efficiency is not significantly affected by Ni content in the electrolyte (up to 8 ppm). However, a strong decrease of current efficiency is observed above 10 ppm, and at 12 ppm the current efficiency drops to only 25%. It is also to be noted that the presence of both copper and chloride has the effect of increasing the nickel content in the alloy deposited.

The addition of Cu in the SO_4^{2-} media has only a slight effect on the Ni content of the alloy. The reason for this is probably to be found in the differences in specific adsorption or intrinsic catalytic properties of the species present in the solutions.

5. Conclusion

The anomalous codeposition of Zn–Ni is significantly affected by the presence of Cu in chloride solutions, while the effect is much less important in sulfate media. This has been clearly established in both applications of anomalous codeposition: Zn–Ni alloy plating and Zn electrowinning in the presence of Ni as an impurity. It should be emphasized that in the second case, the anomaly was that Ni was depositing much below the expected limiting current density unless both Cu and Cl^- were present. The presence of Cu, specially Cl^- media, induces an acceleration of Ni reduction and consequently increases its content in the deposited alloy. It should be emphasized that in the case of Zn electrowinning, this could provide an explanation for the detrimental synergistic effect of combinations of impurities.

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