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Effect of additives on anomalous deposition in zinc–cobalt alloy electrogalvanizing

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Alloys of Zn–Co were deposited from sulphate electrolytes containing various additives to study their influence on the anomalous behaviour of the reactions. The effects of antimony, germanium and arsenic on the Zn–Co alloy composition and structure were examined. The results showed that the composition and structure of Zn–Co alloys deposited could be dramatically changed by antimony, and to a lesser extent by germanium and arsenic. A concentration of Sb(III) as low as 5 mg dm^{-3} increased the cobalt content by a factor of approximately 3; however, the deposit morphology was very dendritic. Germanium additions nearly doubled the cobalt content and the morphology was somewhat improved. The effects of process parameters such as agitation and current density in the presence of the additives were also investigated.

1. Introduction

The development of high current density electrogalvanized steel of superior quality has resulted primarily from requirements evolving from the automotive industry [1–3]. Although corrosion resistance remains one of the most desired properties, others, such as formability, paintability, and weldability, also receive serious attention [4, 5]. The chemical composition and structure are the characteristics most likely to influence the properties and ultimate performance of the coating during extended use.

The corrosion resistance of electrogalvanized steel has been shown to increase by alloying with small amounts of cobalt [6]. Manufacture of alloys containing less than 1% Co using acid sulphate or chloride solutions has been reported [7, 8]. However, control of the composition of alloys made in sulphate electrolyte is more complicated due to the anomalous nature of the Zn–Co codeposition, a phenomenon commonly encountered in the electrodeposition of iron group metals (Fe, Co, Ni) with zinc [9]. In anomalous codeposition, the less noble zinc deposits preferentially to the more noble cobalt. Considerable research has been conducted to determine the cause of the anomalous phenomenon; currently, the hydroxide suppression mechanism appears to be the most widely accepted explanation [10–12]. In this scheme, anomalous deposition occurs due to the formation and adsorption of a zinc hydroxide film which inhibits the cobalt while favouring zinc reduction. The formation of the hydroxide is possiby a result of the pH rise in the double layer due to the simultaneous evolution of hydrogen gas resulting in a localized increase in the hydroxyl ion concentration.

One distinct characteristic of the anomalous deposition system is its sensitivity to the catalytic effects of codeposited species capable of modifying the deposition order. Previous research has shown that the addition of parts per million Sb(III) decreased the anomalous behaviour of Zn–Ni codeposition [13]. Antimony ions are well known as promoters for catalyzing cathodic reactions, such as hydrogen evolution, in acid zinc plating. Thus, it was felt that antimony might be capable of modifying the anomalous deposition of cobalt as well. Germanium and arsenic were also considered as possible additives because they behave in a similar manner to antimony in the acid zinc sulphate system [14–17].

The objective of this study was to gain a better understanding of the fundamental aspect of the role of low concentrations of additives on the anomalous behaviour of Zn–Co electrodeposition. The effects of antimony, germanium and arsenic on Zn–Co alloy composition and structure were examined. The effects of process parameters such as agitation and current density on the alloy composition and structure were also investigated. Additional tests were performed to confirm the effect of glue additions on the structure of alloys deposited from electrolytes containing Sb(III).

2. Experimental details

A stock solution of neutral purified solution containing 200 g dm^{-3} Zn(II) ions and pH 5 was prepared by dissolving high purity zinc oxide powder in reagent grade sulphuric acid. A stock solution containing 50 g dm^{-3} Co(II) was prepared by dissolving cobaltous sulphate in deionized water.

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Antimony(III) and arsenic(III) solutions of 10 g dm^{-3} were prepared by dissolving antimony potassium tartrate and As_2O_3 in deionized water. Germanium metal was dissolved by placing it in 5 ml of conc HF and adding HNO_3 dropwise until dissolution was complete before diluting with deionized water to give a level of 1 g dm^{-3} Ge(IV). A 1 g dm^{-3} glue solution was prepared by dissolving a solid protein glue in deionized water and storing under refrigeration to minimize degradation.

The deposition cell consisted of a 250 ml jacketed beaker fitted with a slotted plexiglass lid to allow for electrode placement. The distance between cathode and anode was 30 mm. The platinum mesh anode was held in a glass tube which had a fritted disc membrane to minimize anodic effects on the electrolyte components, for example the oxidation state of the additives. The cathode substrate used for electrogalvanizing was low carbon steel. The substrate was cleaned with laboratory grade detergent in an ultrasonic bath and degreased with trichloroethylene but was not polished. It was then anodically cleaned in 15 g dm^{-3} of Penwalt 395M alkaline cleaner at 60 °C using 100 mA cm^{-2} for 30 s, rinsed with distilled water, dip pickled in 200 g dm^{-3} sulphuric acid solution at room temperature for 30 s followed by a water rinse. The cleansed substrate was then masked with electroplaters tape to expose a circular working area of 1 cm^2.

The cell was connected to a controlled temperature circulating water bath with a constant temperature of 55 °C. Electrodepositions were carried out under galvanostatic conditions using a PAR Model 273 potentiostat/galvanostat as the power supply, usually at a current density of 250 mA cm^{-2}. To investigate the effects of current density, additional tests were conducted at 500 mA cm^{-2}. To provide a qualitative estimation of the effects of agitation, some tests were made using nitrogen gas sparging. The electrolysis was conducted for a sufficient time, in accordance with the current density used, to obtain a deposit with a thickness of about 7 μm. After electrolysis, the cathode was washed with distilled water, then dried under a stream of nitrogen gas prior to chemical and morphological analysis. The morphology and composition of the deposit were observed by means of scanning electron microscopy (JSM 35CF) and energy dispersive spectrometry (Tracor Northern 5502). An average of readings from four locations, consistent for each sample, was used in obtaining the approximate cobalt content of the films.

3. Results and discussion

3.1. *Zn–Co alloys*

Figure 1 shows the cobalt content of Zn–Co alloys obtained from electrolytes containing 80 g dm^{-3} Zn(II) and up to 5 g dm^{-3} Co(II). The composition of the alloy and the metal ratio of the solutions are expressed on the weight percentage basis as employed by Brenner [9]. However, in Fig. 1, the cobalt weight percentage has been converted to g dm^{-3} but reflects the Brenner convention. The composition reference line represents the condition when the weight percentage of metal in the deposit would be the same as its weight percentage in the electrolyte. Alloys whose cobalt contents lie above the composition reference line indicate that deposition is of the normal type, while alloys with cobalt contents below the composition reference line represent anomalous deposition behaviour. As seen in Fig. 1, increasing the concentration of Co(II) in the electrolyte led to an increase in the weight of cobalt codeposited with zinc. However, electrodeposition of the Zn–Co alloy was anomalous and the ratio of weight of cobalt to weight of zinc in the deposits was much lower than the respective ionic concentration in the electrolyte. Similar results have been reported by Higashi [7], and the hydroxide suppression mechanism was proposed to explain this anomaly.

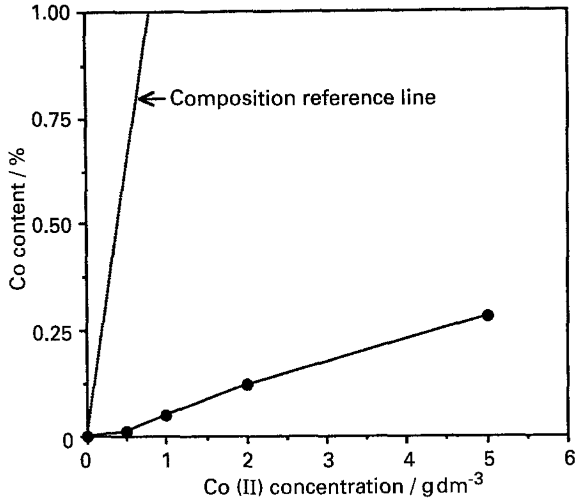

Fig. 1. Effect of cobalt concentration in the electrolyte on the deposition content compared to predicted content. (80 g dm^{-3} Zn(II), pH 1.5, 250 mA cm^{-2}, 60 s, 55 °C).

A representative morphology of a pure zinc deposit obtained at 80 g dm^{-3} Zn(II), 1.5 pH, 250 mA cm^{-2} for 60 s at 55 °C is shown in Fig. 2, and an orientation of (1 0 3) was found. With the

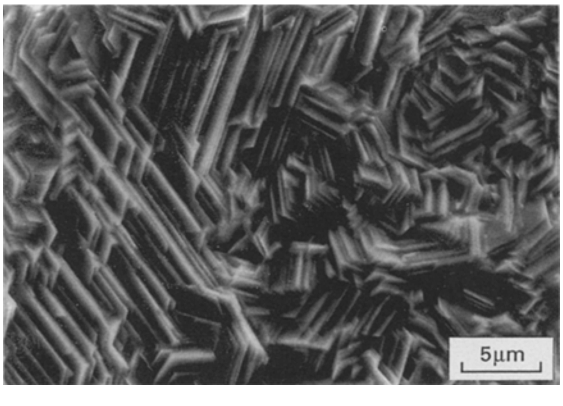

Fig. 2. Morphology of the deposit using 80 g dm^{-3} Zn(II), pH 1.5, 250 mA cm^{-2}, 60 s, 55 °C.

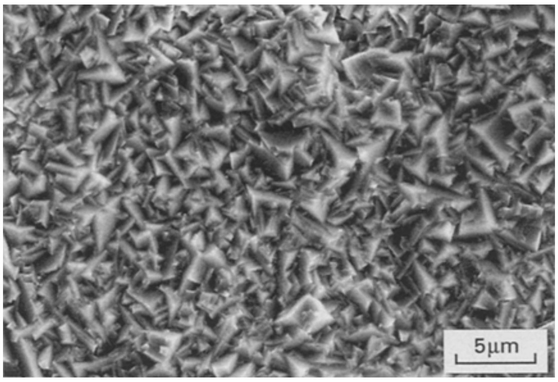

Fig. 3. Morphology of alloy deposit using 80 g dm^{-3} Zn(II), 5 g dm^{-3} Co(II) pH 1.5, 250 mA cm^{-2}, 60 s, 55 °C, 0.3% Co content.

addition of 0.5 or 2 g dm^{-3} Co(II) to the electyrolytes, the cobalt contents were negligible to approximately 0.1%, respectively, and there was no substantial difference in the deposition morphology; however, hexagonal platelet size was reduced. At 5 g dm^{-3} Co(II), the cobalt content was about 0.3% and the hexagonal platelets were replaced by the more angular crystals shown in Fig. 3. Crystallite orientation of the deposit changed from (1 0 3) for pure zinc to (1 0 1) for the Zn–Co alloys and were determined using standard X-ray diffraction techniques on a GE XRD5 unit.

3.2. *Effect of antimony*

The addition of antimony changed the cobalt content (Table 1) and modified the structure of the deposit. At 1 g dm^{-3} Co(II), the cobalt content increased progressively from less than 0.1% with no additions to 0.7% with 10 mg dm^{-3} Sb(III). The deposition morphology obtained with 1 mg dm^{-3} Sb(III) was similar to that obtained with no addition. With 5 mg dm^{-3} Sb(III), the morphology was less uniform and faceted, possibly showing signs of fine pitting which is characteristic of localized zinc dissolution. With 10 mg dm^{-3} Sb(III), the grains were rounded and the nonuniformity was more severe. The deposit showed a range of crystallite sizes, indicating a progressive nucleation and growth mechanism, a condition reported previously where antimony additions in electrogalvanizing were studied [18]. At 2 g dm^{-3} Co(II), up to 0.9% Co could be obtained by the addition of 10 mg dm^{-3} Sb(III). At 5 g dm^{-3} Co^{2+}, the cobalt content of the deposit produced using an addition-free electrolyte was 0.3%; 1 mg dm^{-3} Sb(III) did not significantly change the cobalt content but the morphology difference was obvious. The crystallite size became finer and some irregular growth with isolated needle-like crystals was evident. The cobalt content of the deposit obtained with 5 mg dm^{-3} Sb(III) was about 0.7%. The morphology was not uniform, consisting of fine powdery grains and some large nodules. With 10 mg dm^{-3} Sb(III), the Co content increased to 1.4%; however the deposit was very powdery. Specific current efficiencies were not calculated, but estimations indicated a decrease of 5% to 10% occurred at the higher antimony levels.

Previous studies on Zn–Ni alloy deposition have indicated that the nickel content can be increased significantly by the presence of very low concentrations of antimony. The effect of antimony was attributed to the possible disruption of the zinc hydroxide layer that formed on the cathode surface, thereby decreasing blockage and enhancing nickel ion discharge [13]. Comparatively, the cobalt contents in the Zn–Co alloys were lower than nickel contents for alloys deposited using similar concentration levels and plating conditions. The results showed that codeposition of cobalt with zinc was more difficult than codeposition of nickel with zinc despite the fact that cobalt and nickel are considered similar electrochemically, i.e. approximately the same exchange current density and Tafel coefficient. Other investigators have reported similar results in zinc electrowinning, and attribute the difficulty of cobalt deposition as possibly due to the existence of the cobalt complex $(Co(SO_4)_n)^{(2n-2)-}$ in sulphate solution [19]. However, further research is required to verify this behaviour in the electrogalvanizing system.

The alloy morphologies show that the deposit structure is very sensitive to the antimony content of the electrolyte. Increasing the antimony concentration gave a less uniform and more dendritic deposit although the cobalt content of the deposits increased substantially. Increasing cobalt concentration also increased the cobalt content of the alloys, but the deposits tend to become more powdery. As for 5 g dm^{-3} Co(II), 10 mg dm^{-3} Sb(III), the cobalt content was about 1.4%; unfortunately, the structure of the deposit was not satisfactory.

The results show conclusively that very low concentrations of Sb(III) can effectively minimize anomalous deposition. However, the mechanism responsible appears to substantially modify the electrocrystallization of zinc as well. Thus, additional research is needed to develop means to optimize both the composition and the structure simultaneously.

Table 1. Effect of antimony concentration on the cobalt content (Co wt %) of alloys using 80 g dm^{-3} Zn(II), pH 1.5, with 1, 2, and 5 g dm^{-3} Co(II), at 55 °C, 250 mA cm^{-2}, 60 s, no agitation

Co Content	*No Sb(III)*	*1 mg dm^{-3} Sb(III)*	*5 mg dm^{-3} Sb(III)*	*10 mg dm^{-3} Sb(III)*
1 g dm^{-3} Co(II)	< 0.1	0.1	0.3	0.7
2 g dm^{-3} Co(II)	0.1	—	0.5	0.9
5 g dm^{-3} Co(II)	0.3	0.3	0.7	1.3

Table 2. Effect of various additives on the cobalt content (Co wt %) of alloys deposited in solutions containing 80 g dm^{-1} Zn(II), 5 g dm^{-3} Co(II), at pH 1.5, 250 mA cm^{-2}, 60 s, 55 °C

Additives/5 mg dm^{-1}	*Co content (wt %)*	
	No agitation	*Agitation*
No additives	0.3	0.1
Sb (III)	0.7	1.4
Ge (IV)	0.5	0.3
As (III)	0.3	0.2

3.3. *Germanium and arsenic*

Germanium and arsenic were also considered as possible additives to modify the anomalous codeposition of cobalt with zinc. Table 2 compares the effect of 5 mg dm^{-3} Sb(III), Ge(IV) and As(III) on the cobalt content of the deposits from an electrolyte containing 80 g dm^{-3} Zn(II) and 5 g dm^{-3} Co(II) at pH 1.5. The increase in cobalt content was most significantly changed by the addition of antimony, followed by germanium, and then arsenic.

Without agitation, the cobalt content increased from 0.3% with no additions to 0.7% with Sb(III), 0.5% with Ge(IV), and only 0.3% with As(III) additions. The morphology of the Zn–Co alloy obtained with Sb(III) was not uniform, consisting of fine, rounded grains with some large nodular growths as indicated previously. Germanium increased the cobalt content by a factor of 2 and the morphology is quite similar to that obtained for the no-addition deposit. The effect of arsenic on increasing the cobalt content of the deposit was not significant and the morphology resembled that obtained from an addition-free electrolyte.

3.4. *Agitation*

The effect of agitation on the alloy composition is shown in Table 2. In the absence of the additives, agitation decreased the cobalt content from 0.3 to about 0.1%. In the presence of antimony, agitation caused the cobalt content to increase from 0.7% to 1.4%. Examination of the morphology showed that the nodules obtained with agitation were smaller and fewer in number compared to the ones obtained without agitation. However, dendritic and powdery grains were quite evident as seen in Fig. 4. For a solution containing germanium, agitation decreased the Co content of the deposit from 0.5% to 0.3%. The deposit showed signs of corrosion, Fig. 5, and noticeable pitting of the deposit was observed. The behavior of arsenic was similar to that of germanium; the cobalt content of the deposit obtained from the arsenic-containing electrolyte decreased from 0.3% to 0.2% with agitation. The morphology was quite similar to that obtained from the germanium-containing electrolyte and pitting of the deposit also occurred. The cobalt content of the deposit increased by agitating the solution containing antimony, but decreased in the other solutions, indicating that change in the reaction rate of each species by agitation was different.

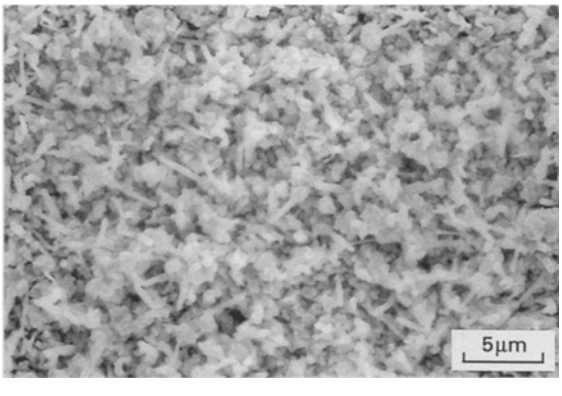

Fig. 4. Morphology of alloy using 80 g dm^{-3} Zn(II), 5 g dm^{-3} Co(II), 5 mg dm^{-3} Sb(III), pH 1.5, 250 mA cm^{-2}, 60 s, 55 °C, agitation, 1.4% Co content.

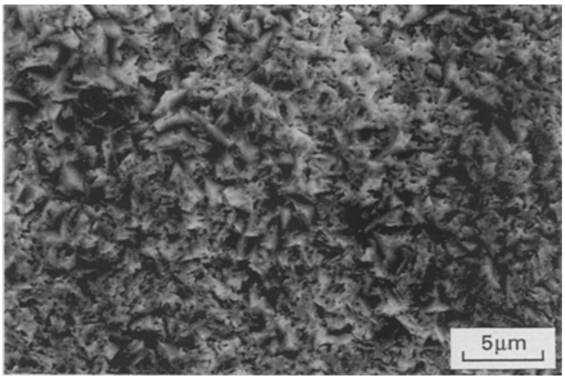

Fig. 5. Morphology of alloy using 80 g dm^{-3} Zn(II), 5 g dm^{-3} Co(II), 5 mg dm^{-3} Ge(IV), pH 1.5, 250 mA cm^{-2}, 60 s, 55 °C, agitation, 0.3% Co content.

A flow cell has now been constructed for use in future studies on agitation to provide better definition of the system hydrodynamics.

3.5. *Current density*

Tests were also conducted to determine the effect of plating current density on the cobalt content of the Zn–Co alloys. Depositions were carried out at 80 g dm^{-3} Zn(II), 5 g dm^{-3} Co(II), pH 1.5, 55 °C and with agitation. In all cases, increasing the current density from 250 mA cm^{-2} to 500 mA cm^{-2} resulted in a decrease in the cobalt content. For example, with 5 mg dm^{-3} Sb(III) the cobalt content decreased from 1.4 to 1.1; with no additives the values were approximately 0.1. At such a low concentration, the reaction of the additives may be under diffusion control. With constant agitation, the limiting current density of the additives was constant; while the deposition rate of zinc increased with increasing current density and was probably under activation control. Also, the morphology of the deposits made using Sb(III) improved at the higher current density, Fig. 6, but isolated dendrites were still

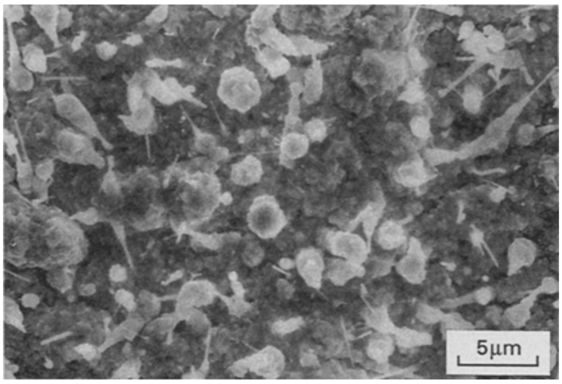

Fig. 6. Mophology of alloy using 80 g dm^{-3} Zn(II), 5 g dm^{-3} Co(II), 5 mg dm^{-3} Sb(III), pH 1.5, 500 mA cm^{-2}, 60 s, 55 °C, agitation, 1.1% Co content.

in evidence and additional study is needed in this area.

3.6. *Effect of glue*

Glue is often added to zinc electrolyte to aid in the control of the growth and electrocrystallization process of the cathode deposit. In addition, proteins are known to counteract the effect of inorganic species such as antimony and arsenic, particularly in changing the amount of hydrogen evolved during deposition. One common practice in electrowinning to assist in minimizing dendrite formation is to make additions of about 2 to 40 p.p.m. of glue to the electrolyte [14–17]. In this study, glue was added to the antimony-containing electrolyte to try to improve the structure of the deposit. The morphology of the deposit obtained at 80 g dm^{-3} Zn(II), 5 g dm^{-3} Co(II), 5 mg dm^{-3} Sb(III) and 10 mg dm^{-3} glue showed a reduction in nodular growth and the surface was more uniform. Glue diminished the effect of antimony on the composition of the deposit, decreasing the value from 0.7% to 0.3%. Increasing the glue concentration to 40 mg dm^{-3} eliminated the powdery nature of the deposit, producing a morphology similar to the one with no addition; unfortunately, the cobalt content was also reduced to only 0.1%.

4. Conclusions

The electrodeposition of Zn–Co alloys was anomalous under the conditions employed in this study. However, the composition and structure of Zn–Co alloys could be changed using additives such as antimony, germanium and arsenic. Concentrations of Sb(III) as low as 5 mg dm^{-3} caused the cobalt content to increase by a factor of approximately 3, but deposition was still anomalous. Antimony additions also produced powdery and less uniform deposits containing large nodules.

The effects of process parameters such as agitation and current density also caused changes in the alloy composition and structure. Agitation increased the cobalt content of the alloys and reduced the degree of nodulation with antimony additions. For electrolytes containing Ge(IV) or As(III), agitation decreased the cobalt content and pitting of the deposit was observed. With agitation, the cobalt content of the deposit decreased with increased current density. The effect of current density on the structure of the deposit was obvious only in the electrolyte containing antimony, where the deposit obtained at the lower current density was more powdery.

The addition of up to 40 mg dm^{-3} glue appeared to improve the uniformity and density of the deposit produced from the electrolyte containing Sb(III). However, the increase in the cobalt content of the deposit was eliminated by the glue addition. When organics are used, it appears that a proper balance of the concentration of additives must be found.

The results of this study have shown that very low concentrations of Sb(III) can substantially increase the cobalt content, but does not completely eliminate anomalous behaviour. Fundamental studies are needed to further develop the electrocrystallization aspects of the process and optimize the concentrations of the additives used. The process parameters are also important factors affecting the alloy composition and structure. Additional research to further study the influence of oxidation state of the additive and compare Sb(III) to Sb(V) or As(III) to As(V) would also now be desirable. Overall, the results are promising, not only for practical applications of enhancing the alloy content of the deposit, but also in gaining a better understanding of the fundamental aspects of anomalous deposition mechanism.

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