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Effect of pH on the deposition properties of electrodeposited Zn-Co coatings formed by potentiostatic technique on AISI 4140 stainless steel

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The effects of pH of an sulphate bath on the quality of Zn-Co coatings formed on AISI 4140 stainless steel by using the potentiostatic polarization technique at E = -3 V was investigated in order to improve uniformity and corrosion protection performance of the coating films. It was found that the uniformity and corrosion resistance of coating films deposited by potentiostatic polarization were closely associated with pH of the coating electrolyte. The pH to obtain the best coating film were investigated as a function of corrosion protection performance evaluated by curves of potentiodynamic anodic polarization conducted in NaCl 3% solution. Scanning electron microscope observation and electrochemical corrosion tests of the ZnCo samples confirmed significant improvement in uniformity and corrosion resistivity of coating films deposited by the potentiostatic technique by modifying the pH of the coating bath. It was also found that uniformity and corrosion resistivity of the coating films were firstly improved towards to pH=3 and then decreased with increasing pH values of the coating bath.

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1. Introduction

Cadmium (Cd) has been extensively used as a barrier and sacrificial coating for steel applications in aerospace, automotive, electrical and fasteners industries because of its excellent corrosion resistance and mechanical engineering properties [1–3]. There is increased pressure, both domestically and internationally, for reduced usage, or even elimination of cadmium plating for health, safety, and environmental reasons. There have been several zinc alloy baths developed that work for specific applications, but none duplicates all the properties of cadmium. There are many instances, however, where the use of cadmium plating is not essential and zinc or zinc alloy deposits could be substituted, because both give adequate anodic protection, and there was no functional purpose when cadmium was chosen in the first place [4]. Zinc and zinc alloys are widely used to electroplate steel to provide corrosion resistance, mainly in the automobile industry. The corrosion resistance of a pure zinc coating on steel is not satisfactory and unacceptable under severe atmospheric conditions [5]. It has been observed that when alloyed with iron-group metals, zinc shows better corrosion resistance than the pure metal [6-8]. The electrodeposition of Zn-Co alloys is interesting because these alloys exhibit a significant higher corrosion resistance than pure zinc [9-12].

Recently, many efforts on electrodeposition and characterization of Zn-Co alloys are reported, however, only a few works are focused on the effect of electrolyte pH on the structure and corrosion properties of Zn-Co alloys. The electrodeposition of zinc-cobalt alloys with controlled morphology and composition has been studied extensively. Kalantary [13] investigated the corrosion performance of four types of commercially used zinc alloy coatings, namely zinc–cobalt, zinc–iron, zinc–nickel and zinc–manganese. He concluded that zinc–cobalt alloy coatings containing one percent cobalt demonstrate optimum corrosion resistance, similar to those of zinc–nickel alloy electrodeposits.

Mouanga et. al. [14] studied the influence of coumarin on Zn-Co alloy obtained from an acidic chloride bath. They found that Zn-Co alloys with a finer grain size and well structured were obtained in the presence of coumarin. Lodhi et. al. [15] investigated the mechanism of anomalous electrodeposition of ZnCo alloys. Ortiz-Aparicio [16] studied the influence of cobalt on zinc electrodeposition from alkaline glycinate solutions. However, the optimum content of cobalt in the coating and their protection mechanism are still controversy. Most results reported on the electrodeposition of Zn–Co alloy coatings showed that the maximum amount of cobalt in their deposits was about 6–7 wt.% [17,18]. Although the deposits of Zn–Co alloys with cobalt content of more than 6 or 7 wt.% have not been much studied [19,20], Fei et. al. was obtained Zn-Co alloy deposits with a wide cobalt content range of 10-90 % [21]. As a result, depending on the preparation conditions, i.e. electrolyte composition, temperature, current density and pH of the solution, different morphological and structure properties can be obtained. Therefore, it is necessary to explore systematically the effect of pH on the structure and corrosion properties of Zn-Co alloys.

In this study, the effect of the coating bath for obtaining the best coating in terms of uniformity and corrosion resistivity by using the potentiostatic electrodeposition technique was investigated. The dependence of the composition and structural properties of the electrodeposited Zn-Co alloys on bath pH was researched.

2. Experimental

2.1 Electrodeposition of Zn–Co alloys

$Zn_{1-x}Co_x$ alloys were prepared by electrodeposition under potentiostatic conditions on aluminum and AISI 4140 steel disk substrates from a chloride sulfate plating bath at room temperature (Table 1). The chemical composition of AISI 4140 steel is given in Table 2. The electrolytes were prepared using (18 MΩ cm) twice distilled water.

The pH value of the bath was varied in the range 2-6 using hydrochloric acid and NaOH. The area of the deposits was (1.5cm x 1.5cm). The employed electrolyte was prepared using p.a. chemicals (Merck). Before the deposition, the substrates are prepared in the standard industrial way: chemical then electrolytic degreasing in sodium hydroxide solution (40 gL^{-1}; 64.5 ^{o}C), for 2 min. followed by water wash, mechanically grinding with silicon carbide papers from 3 to 0.5 Am and velvet, chemical pickling and activation in an acid medium (Hydrochloric acid; 30 % in vol.) for 10 s, rinsed with the twice distilled water and then dried in air. So the wettability and therefore the reactivity of the substrate surface are increased. After these preparation steps, it is necessary to operate quickly to realize the electrodeposition, because the substrate surface may be spontaneously oxidized. Counter electrode was a platinum electrode. The reference electrode used in all experiments was a saturated calomel electrode (SCE).

Table 1. Solution compositions for the alloy electrodeposition.

Solution compositions	ZnCo
$ZnSO_4$ (M)	0.5
$CoSO_4$(M)	0.1
$C_6H_5Na_3O_7{\cdot}2H_2O$ (gl^{-1}) (sodium citrate)	25
H_3BO_3 (gl^{-1})	40
NH_4Cl (gl^{-1})	45
Na_2SO_4 (gl^{-1})	0.5
Solution pH	2,3,4,5,6
Temperature (^{o}C)	Room temperature
Deposition time (min)	10
Voltage (V)	-3

Table 2. Chemical composition of AISI 4140 low alloy steel (%).

Element	C	Mn	Si	Cr	Ni	Mo	V	S	Cu	P
Wt. %	0.36	0.80	0.005	0.914	0.30	0.85	0.075	0.07	0.143	0.034

The quantitative composition analysis of the electrodeposits at the surface was examined by using JEOL 6400 scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) working at 15-30 kV. The preferred orientations of the deposits were determined by X-ray diffraction (XRD) analysis, using a Philips PANalytical X'Pert Pro X-ray diffractometer with CuK-α radiation (lamda=1.5418A). The 2θ range of 10–90° was recorded at a rate of 0.02° 2θ/0.5 s. The crystal phases were identified comparing the 2θ values and intensities.

2.2 Corrosion measurements

The electrochemical behaviors of the electrodeposited ZnCo alloys were analyzed in 3 wt. % NaCl aqueous solution at room temperature in a Pyrex glass cell. The corrosion behaviors of the samples were investigated by a potentiodynamic polarization technique. Polarization measurements were performed with an electrochemical analyzer/workstation (Model 1100, CH Instruments, USA) with a three-electrode configuration. The exposed areas of the specimens were about 1 cm^2. The specimens were covered with a cold setting resin and immersed into the solution until a steady open circuit potential (ocp) was reached. After equilibration, polarization was started at a rate of 1 mV/s.

3. Results and discussion

To define the effect of electrolyte pH on the Zn-Co alloy deposition process cyclic voltammetry technique was used. Fig. 1 shows the typical voltammograms obtained in the four solutions. The scans were initiated at near open circuit potentials. In solutions, during the forward scan towards the negative direction, the cathodic current increased sharply when the deposition begins.

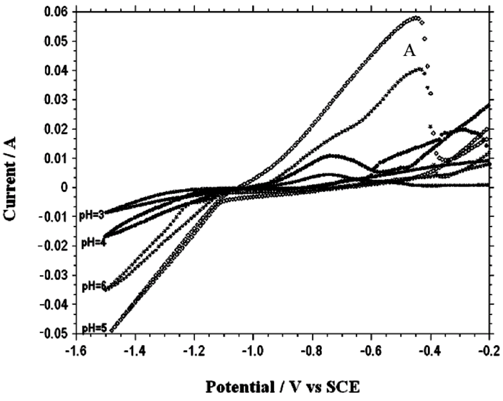

Fig. 1. Cyclic voltammograms for different pH values.

In Fig. 1 it can be seen from the cyclic voltammetry curves that the increase of the electrolyte pH, caused a decrease of the dissolution peak (A) except for pH=6. This peak corresponds to the preferential dissolution of zinc, so the decrease of dissolution peaks can be related to the composition of the dissolved deposit. It can be considered that an increase in the bath pH causes a decrease in the rate of zinc deposition except pH=4, causing the observed decrease in size of dissolution peaks.

Brenner [22] classified the electrodeposition of Zn–Co alloys as anomalous. Codeposition of Zn and Co is, however, not always anomalous since at low current densities, it is possible to obtain normal deposition, where Co deposits preferentially to Zn.

Table 3. Compositions of the films.

Electrolyte pH	2	3	4	5	6
Co at%	1.5	2.2	4.3	4.68	4
Zn at%	98.5	97.8	95.7	95.3	96.0

Table 3 shows the dependence of the Co and Zn concentrations in the films on the pH value of the electrolyte. Co concentration of the coatings increased with increasing bath pH between pH values 2-5, but more increasing in the bath pH caused a decreasing.

Fig. 2 shows XRD patterns of the electrodeposited Zn-Co alloys. In Fig. 2, with pH value of the electrolyte changing from 2 to 5, the intensity of (1 0 1) preferred orientation was strengthened, which led to the improvement of corrosion resistance of the alloys.

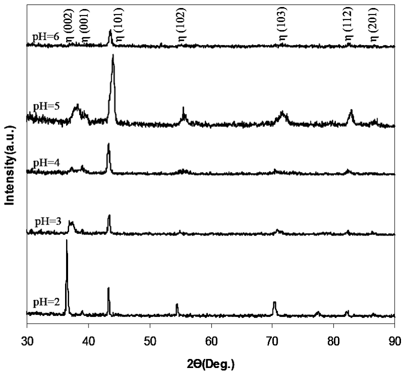

Fig. 2. XRD patterns of the electrodeposited Zn-Co alloys obtained at different pH values.

We can understand from the figure that increasing the pH increased the (1 0 1) peaks until pH=5, then it decreased depending on the Co content. As the electrolyte pH value increases the signals belonging to the η phase when it becomes more intense. At pH=6, the peaks associated with the characteristic crystallographic planes for zinc were observed, the peak associated with plane (1 0 1) having the highest intensity. When the deposit was formed at pH= 2, a considerable increase of the (0 0 2) and lower increase of (101) peaks were observed. When the pH of the electrolyte was increased to 6, all peaks diminished suddenly and the peaks of (002), (100), (102) (103) and (201) were disappeared. At pH 3, 4 and 5, the peaks associated with the planes (1 0 2), (1 0 0) and (1 0 3) shifted a bit towards to right, indicating that the ZnCo alloy crystal lattice was deformed.

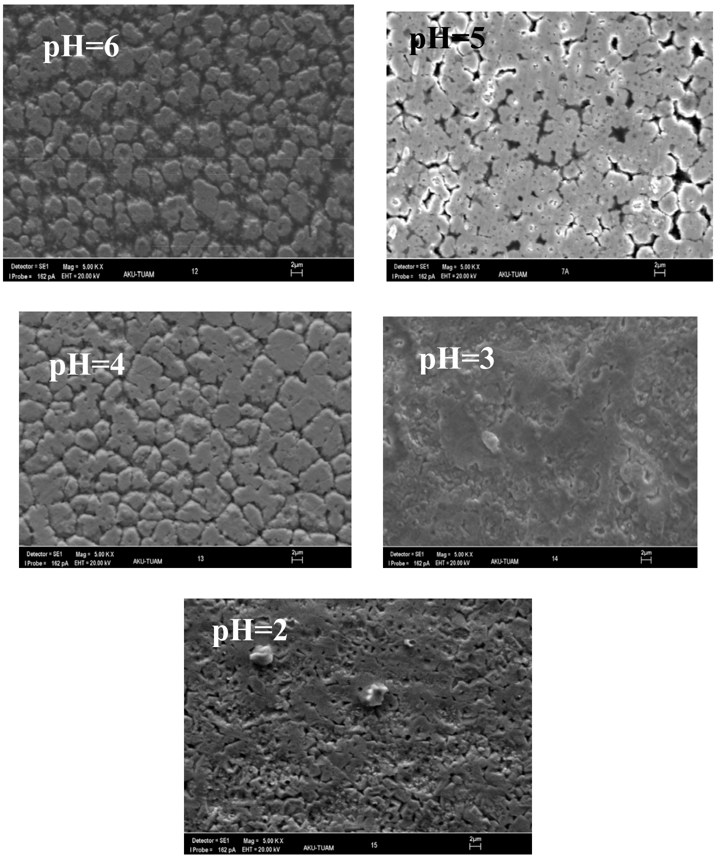

Fig. 3. SEM images of the samples electrodeposited at different pH values of the electrolyte.

After coating, samples were washed and dried with air for SEM observations. Figure 3 shows the SEM images of the samples electrodeposited at different pH values of the electrolyte. As can be seen in the figure, the average size of the coating particles increases with increasing pH of the electrolyte. Enlargement of film particles seems to lower the density of the coating films, i.e., the number of particles per unit surface area.

For the deposits obtained in the pH value of 2 and 3, compact deposits morphology was observed a (Fig. 3d-e). With further increases in the pH value, deposit with even larger grain size was observed (Fig.3a-b-c). The increase of bath pH apparently modified the growth of cobalt nuclei, leading to the larger-grained deposits obtained under potentiostatic deposition. This result is in accord with the study of Elsentriecy et.al. [23]. They observed that the average size of the coating particles increased when the electrolyte pH was increased. It is understand from the figures that bath pH plays the role of a grain-size refiner at zinc-cobalt alloys. These results suggest that pH of the electrodeposition bath is closely associated with deposition properties such as average size of particles and density and compactness of resultant coating film. From the results described above, it can be concluded that the best coating film in terms of uniformity and compactness is obtained from bath pH is 3 electrolyte.

Fig. 4 shows the corrosion property of electrodeposited Zn–Co alloy from sulfate bath in a 3 wt.% NaCl aqueous solution. As can be seen in the figure, biggest decrease in the anodic current density was observed in the electrolyte pH=3 coating. The corrosion potential (Ecorr) of the smallest corrosive at pH value of 6 coating and the biggest corrosion resistive coating pH value of 3 alloy are −1.065 VSCE and −0.946 VSCE, respectively. Compared with pH=6 coating, it is found that the corrosion potential of the deposited at pH=3 alloy is 13% nobler. It is thus further concluded that the cobalt content of the Zn–Co alloy coating up to pH value of 3 (cobalt content is 2.2 %) possesses superior anti-corrosion behaviors than that of Zn-Co coating having less than 4%. An increase of Cobalt content up to 4 wt.% reduced the reactivity of the zinc alloys and, thereby, ZnCo alloys presented a lower degree of corrosion. Ennoblement of the corrosion potential for the sample of pH value of electrolyte of 3 was confirmed.

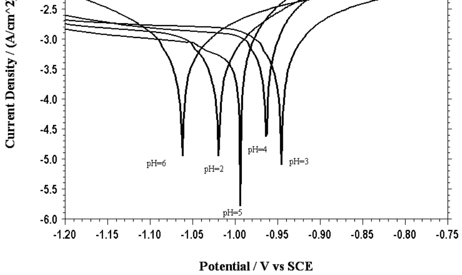

Fig. 4. Potentiodynamic polarization measurements of electrodeposited Zn-Co alloys in a 3 wt.% NaCl aqueous solution.

This outstanding corrosion resistance is attributed to the deposition of dense particles accompanied by small particles blocking the crevices as shown in Fig.3d. the deposition of such small particles resulted in formation of the most protective coating film in this study. Zinc is a good anti-corrosive material and the fundamental function of cobalt in the coatings is to make the corrosion potential more positive. In this case, the alloy coatings become nobler than zinc coatings and the Zn-Co alloy coatings become more corrosion resistant. Zn-Co alloys have more positive corrosion potentials as the electrolyte pH and so the Co content increases, which indicates that the Zn–Co coating is an ideal anodic protective coating for cobalt or steel products, and can provide longer protection for iron or steel products than pure zinc coatings due to the smaller free corrosion potential difference between the Zn-Co coating and that of iron-base substrate.

4. Conclusions

In this study we investigated various Zn–Co alloys obtained from different pH values. The corresponding electroplating behavior and corrosion properties of Zn-Co alloys were investigated using cyclic voltammetry and linear sweep voltammetry methods. The effect of bath pH was investigated on the structure of Zn-Co alloys, and the corrosion behaviour of AISI 4140 steel substrates. The average size of the coating particles increased with increase in pH of the electrolyte. pH of the coating bath were closely associated with uniformity and, thus, corrosion resistance of coating films. The most coating film produced in this work was that deposited at pH of the electrolyte was 3.

References

[1] H. Morrow, Cadmium Council Inc. Reston, Va. 201 (1995).

[2] K. R. Baldwin, C. J. E. Smith, Trans. IMF **74** (6), 202 (1996).

[3] ASM Handbook on Plating and Surface Finishing, chapter 13, 36 (2005).

[4] ASM Handbook on Surface Engineering, **5,** 496 (1994).

[5] T. Tsuru, S. Kobayashi, T. Akiyama, H. Fukushima, S. K. Gogia, R. Kammel, J. Appl. Electrochem. **27,** 209 (1997).

[6] A. Brenner, Electrodeposition of Alloys — Principles and Practice, Academic Press, New York, USA, 1963.

[7] E. Budman, R. Sizelove, www.metalfinishind.com.

[8] A. Jimenéz, H. Schmidt, Tratamento de Superfícies **120,** 26 (2003).

[9] P. Y. Chen, I. W. Sun, Electrochim. Acta **46,** 1169 (2001).

[10] E. Grunwald, A. Ziman, Cs. Varhelyi, Cs. Juhos, Galvanotechnik **85,** 3274 (1994).

[11] A. Stakeviciute, K. Leinartas, G. Bikulcius, D. Virbalyte, A.Sudavicius, E. Juzelunas, J. Appl. Electrochem. **28**, 89 (1998).

[12] S. M. Rashwan, A. E. Mohamed, S. M. Abd El-Wahaab, M. M. Kamel, J. Appl. Electrochem. **33,** 1035 (2003).

[13] M. Kalantary, Plating Surface Finishing **81,** 80 (1994).

[14] M. Mouanga, L. Ricq, P. Berçot, Surf. Coat. Technol. **202,** 1645 (2007).

[15] Z. F. Lodhi, J. M. C. Mol, A. Hovestad, H. Terryn, J. H. W. de Wit, Surf. Coat. Technol. (2007), doi: 10.1016/j.surfcoat.2007.04.070

[16] J. L. Ortiz-Aparicio, Y. Meas, G. Trejo, R. Ortega, T. W. Chapman, E. Chainet, P. Ozil, Electrochimica Acta **52,** 4742 (2007).

[17] H. Yan, J. Downes, P. S. Boden, S. J. Harris, J. Electrochem. Soc. **143,** 1577 (1996).

[18] I. Kirilova, I. Ivanov, J. Appl. Electrochem. **29,** 1133 (1999).

[19] N. R. Short, A. Abibsi, J. K. Nennis, Trans. Inst. Met. Finish. **67**, 73 (1989).

[20] M. E. Bahrololoom, D. R. Gabe, G. D. Wilcox, J. Electrochem. Soc. **150**(3), C144 (2003).

[21] J.-Y. Fei, G. D. Wilcox, Electrochimica Acta **50,** 2693 (2005) 2693.

[22] A. Brenner, Electrodeposition of Alloys, vol. II, Academic Press, New York, 1963,

[23]H. H. Elsentriecy, K. Azumi, H. Konno, Electrochimica Acta (2007), doi:10.1016/j.electacta.2008.01.009

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