

Electroplating and Corrosion Properties of Binary and Ternary Zinc Alloys with Nickel, Cobalt and Iron

Ramesh S. Bhat^{1*}, Venkatakrishna K.², A. Chitharanjan Hegde³

Abstract

The anti-corrosive three binary (Zn-Ni, Zn-Co, Zn-Fe) and two ternary (Zn-Ni-Co, Zn-Co-Fe) alloy coating films on mild steel from acid chloride bath using sulphanilic acid and gelatin as additives for the electroplating technique. The normal Hull cell method was used to optimize the bath compositions, temperature and pH of the bath solutions for coating performance against corrosion. The cause of current density (CD) on metal weight percentage ($M = \text{Ni, Co, Fe}$), thickness (t), hardness (VH), and throwing power (TP) has been investigated. The corrosion resistance of binary and ternary alloy coating films was determined using the potentiodynamic polarization technique. The metal content in the coatings were determined by colorimetric method. Under optimal conditions, the corrosion rate of Zn-Ni-Co was approximately ~8 times, ~10 times higher than Zn-Ni, and Zn-Co coating films. Also Zn-Co-Fe coating film was approximately ~8 times, and ~13 times higher than Zn-Co and Zn-Fe coating films. Thus ternary zinc-nickel-cobalt and zinc-cobalt-iron coatings can replace usual binary alloy deposits for many industrial applications such as automobile, machinery items like tools, bolts, and nuts, etc.

Keywords: Additive, Thickness, Corrosion, Zinc-based alloy coatings, Co-deposition, Hull cell

INTRODUCTION

Alloy depositions are commonly used in the manufacture of advanced materials and coatings that require certain properties like mechanical, chemical, and physical etc. Zinc alloys have been demonstrated to offer superior corrosion resistance than pure zinc when used on steel substrates. Zn-Ni [1–3], Zn-Co [4, 5], and Zn-Fe [7–8] are the most regular zinc alloys. Zn-Ni and Zn-Co alloys provide significantly better corrosion resistance and physical properties than pure Zn alloy coatings.

However, binary zinc alloys, which have strong alloy properties, also have an irregular, non-uniform, and non-attractive finish, as a result, additives are frequently employed in plating solutions to improve surface brightness. The corrosion is one of the main causes of equipment break down and safety in marine operations. Anti-corrosive deposits are a valuable means of protecting steel structures or machinery from oxidation [9]. Significant efforts have been made to boost its anti-corrosive qualities in order to improve mild steels corrosion-resistant properties in a severe climate [10]. Many studies have tried to understand the characteristics of the Zn-Ni coatings. Zn-Fe coating film has become more popular because of its low cost, brightness and

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good levelling ability and found to show excellent corrosion resistance [11]. Brenner [12] has described the electroplating of the zinc-based metal alloys as an anomalous co-deposition, where zinc, preferably deposited.

The properties of zinc-nickel and zinc-cobalt alloys could also be merged into a single alloy that could be accomplished by electroplating of Zn-Ni-Co and Zn-Ni and Zn-Fe alloys into a single alloy by electroplating of Zn-Co-Fe. Therefore a variety of literature results on Zn-Ni-Co alloys. Deposition of such alloys in the presence of additives has been investigated by Younan [13], Eliaz et al. [14], Hegde et al. [15], Abou Krisha et al. [16] and Bhat RS et al. [17] for increased corrosion resistance with respect to corresponding binary alloy coatings. Experimental investigations have revealed better electrochemical properties of ternary Zn-Ni-Co alloys compared to the binary alloys [18]. In addition, Zn-Ni-Co electroplating are distinguished by better corrosion resistance as compared with binary alloys [19] and also in particular, the bath additives helps to improve the corrosion resistance and brightness of the coatings, even at small metal composition. Hoen-Velterop et al. [20] tested the corrosion properties of zinc-cobalt-iron deposits on steel substrates with 3.5 weight percent of sodium chloride solution and compare the study of Zn and Cd films with various electrochemical methods.

In the present work, sulphanilic acid and gelatin have been used as additives to optimize the bath constituents and operating conditions for the development bright zinc-nickel, zinc-cobalt, zinc-iron, zinc-nickel-cobalt, and zinc-cobalt-iron alloy films on mild steel (MS) substrate using direct current (DC) methods. The purpose of this study is to compare the corrosion rates of binary and ternary alloy depositions.

Investigation results are provided for engineering applications, with a focus on its use as protective coatings for mild steel (MS). The impact of current density on nobler metal contents (M = Ni, Co and Fe) in the deposit, as well as hardness, thickness, throwing power, and corrosion rates has been examined.

EXPERIMENTAL PROCEDURE

Electroplating baths were made using research grade chemicals and purified water. The bath constituents were set up using the usual Hull cell approach, with a 1A cell current and a 30°C temperature. With the same surface area, the cleaned MS and zinc sheet were used as a cathode and anode. The pH of the bath was maintained at 3.0–3.5 with dilute Hydrochloric acid (HCl). The 250 ml capacity of polyvinyl chloride (PVC) cell was used and anode-cathode space of 5 cm. All coating films were made at 30°C and 10 minutes time for coating. Gavanostatic electro deposition has been achieved using a DC power supply (N6705C, Key sight technology).

The corrosion test was performed using Potentiostat (CH instrument), in tri-electrode cell, MS substrate as working electrode, Calomel as reference and Platinum as counter electrode. The 3.5% sodium chloride solution was used as a corrosion medium. In a theoretical potential ramp of ± 200 mV around the open circuit potential, the polarization analysis was performed at a scan rate of 1 mV/s (OCP). It was established the corrosion current (i_{corr}), corrosion potential (E_{corr}), and corrosion rate (CR). Faraday's law was used to calculate the thickness of the coatings.

The validity of measured thickness was cross examined using digital thickness tester (Coat measure M&C) [21]. The coating hardness (at a thickness of 20 μm) was determined using the Vickers micro hardness tester. The nobler metal contents in the coating film were assessed using the colorimetric method [22]. The plating baths throwing power was calculated using the Haring Blum cell and is provided by the equation [23].

$$\text{Throwing power \%} = \frac{A-B}{A+B-2} \times 100 \quad (1)$$

Where; A is the ratio of distance from anode of far and near cathodes and B is the ratio of mass of coatings on near and far cathodes.

DATA, VALUE AND VALIDATION

Bath composition and electrodeposition conditions of zinc-based binary and ternary (Zn-Ni, Zn-Co, Zn-Fe, Zn-Ni-Co, and Zn-Co-Fe) alloy baths have been optimized by a normal Hull cell system [23] to achieve a uniform deposit over a broad range of current densities ($10\text{--}50\text{ mA dm}^{-2}$). For the Hull cell test, the one salt varied, withholding other salts at fixed concentrations. This method was carried out for the other salts in the bath. At the ideal concentration, a smooth and bright coating was seen. Based on their smoothness and brightness of the coating film, the consequence of bath constituents on the Hull cell plates was recorded. This method was repeated with different salts in other baths. Table 1 lists the optimal bath compositions and working conditions for further research on Zn-based binary and ternary alloy films.

The three binary and two ternary Zn-based alloy baths developed, with white deposit at low applied CD and porous deposit at high CD. A sound deposit was found at optimal CD. The influence of CD on weight percentage of metal contents, thickness, hardness, throwing power (TP), and corrosion rate of zinc-based binary and ternary alloy deposits are listed in Table (2–6). All five alloy systems, the concentrations of noble metal content (Ni, Co, and Fe) in the coatings were increased with applied CD's (Table 2–6). At low CD (10 mA cm^{-2}) wt.% of metal contents acts as an anomalous co-deposition. In all CDs, the mass percentage of nickel in zinc-nickel-cobalt alloy coatings was higher than that of cobalt (Co), when compared to zinc-nickel and zinc-cobalt coatings and the mass percentage of Co, in Zn-Co-Fe coatings were higher than that of iron (Fe), when compared to Zn-Co and Zn-Fe coatings. In the case of Zn-Ni-Co and Zn-Co-Fe coatings, the concentration of Ni, Co, and Fe were increased with increase in CD as listed in Table (2–6). Furthermore, the compositions of both metals were higher than that of the resulting Zn-based binary coatings.

The data shown in Table (2–6) indicates that the thickness of all five Zn-based (Ni, Co, and Fe) coatings increased with applied CDs, and that we have obtained different thickness of the coatings with same CD. This may be due to the adsorbed metal hydroxide layer at cathode (due to decrease of pH by the evolution of hydrogen during the electroplating). The bath temperature also plays a key role on thickness, composition of metal contents and the surface appearance of the coatings as exhibited by the Zn-based coatings.

Table 1. The operating parameters and bath compositions for binary Zn-Ni, Zn-Co, Zn-Fe and ternary Zn-Ni-Co, Zn-Co-Fe alloy coatings

Bath composition	Zn-Ni	Zn-Co	Zn-Fe	Zn-Ni-Co	Zn-Co-Fe
ZnCl ₂ (M)	0.37	0.29	0.37	0.37	0.37
NiCl ₂ .6H ₂ O (M)	0.34	-	-	0.34	0.34
CoCl ₂ .6H ₂ O (M)	-	0.04	-	0.04	-
FeCl ₂ .4H ₂ O (M)	-	-	0.04	-	0.04
NH ₄ Cl (M)	2.24	2.24	2.24	2.24	2.24
KCl (M)	1.61	1.48	1.61	1.61	1.61
Sulphanilic acid (M)	0.03	0.06	0.06	0.03	0.03
Gelatin (gL ⁻¹)	7	5	5	7	7
Ascorbic acid (gL ⁻¹)	-	-	10	-	5.0
pH	3.0	3.0	3.0	3.0	3.0
T (°C)	30	30	30	30	30
i (mA cm ⁻²)	30	20	30	40	40

Table 2. The effect of CD on the wt.% Ni, hardness and thickness and TP of Zn-Ni coatings, and its corrosion parameters in 3.5 wt.% NaCl.

i (mA cm ⁻²)	wt.% Ni	VHN	TP	t (μ m)	$-E_{\text{corr}}$ (V vs. SCE)	i_{corr} (μ A cm ⁻²)	CR (μ m y ⁻¹)
10	6.02	172	16	7.6	1.063	39.54	567
20	3.43	97	19	15.9	1.083	31.69	455
30	3.82	220	25	20.5	1.142	14.91	214
40	5.45	214	23	25.0	1.117	17.98	258
50	10.0	205	21	27.8	1.089	36.38	552

Table 3. Effect of applied CD on wt.% of Co, thickness and hardness and corrosion rates of the Zn-Co coatings in 3.5 wt.% NaCl.

i (mA cm ⁻²)	Co (wt.%)	VHN	TP	t (μ m)	$-E_{\text{corr}}$ (V vs. SCE)	i_{corr} (μ A cm ⁻²)	CR (μ m y ⁻¹)
10	2.34	150	15	5.4	1.119	32.32	467
20	1.74	160	18	10.5	1.081	9.021	138
30	2.45	175	26	15.5	1.129	9.434	148
40	3.06	180	21	20.2	1.119	15.84	229
50	3.75	160	19	24.9	1.106	28.24	408

Table 4. Effect of applied CD on wt.% Fe, thickness and hardness of Zn-Fe coatings, with corrosion rates in 3.5 wt.% NaCl.

i (mA cm ⁻²)	Fe (wt.%)	VHN	TP	t (μ m)	$-E_{\text{corr}}$ (V vs. SCE)	i_{corr} (μ A cm ⁻²)	CR (μ m y ⁻¹)
10	2.31	145	13	5.2	1.128	38.82	559
20	2.18	171	17	10.5	1.194	26.44	380
30	3.16	175	23	15.1	1.206	22.63	325
40	3.79	177	20	19.9	1.144	28.75	414
50	4.99	189	18	24.2	1.127	34.94	502

Table 5. Effect of applied CD on wt.% noble metal content, thickness, hardness and corrosion rates of Zn-Ni-Co coatings in 3.5 wt.% NaCl.

i (mA cm ⁻²)	Ni (wt.%)	Co (wt.%)	VHN	TP	t (μ m)	$-E_{\text{corr}}$ (V vs. SCE)	i_{corr} (μ A cm ⁻²)	CR (μ m y ⁻¹)
10	8.76	0.96	146	19	8.6	0.959	14.72	212
20	7.68	3.59	164	23	13.6	0.773	3.015	43.6
30	11.80	5.61	186	25	18.4	0.702	2.224	31.2
40	14.36	6.39	204	32	22.2	0.687	1.465	20.4
50	18.25	6.90	218	30	26.8	0.736	1.913	28.1

Table 6. Effect of applied CD on wt.% noble metal content, thickness and hardness of Zn-C-Fe coatings, with corrosion rates in 3.5 wt.% NaCl.

i (mA cm ⁻²)	Ni (wt.%)	Fe (wt.%)	VHN	TP	t (μ m)	$-E_{\text{corr}}$ (V vs. SCE)	i_{corr} (μ A cm ⁻²)	CR (μ m y ⁻¹)
10	11.05	4.64	148	17	6.2	1.298	8.414	122
20	9.43	4.98	178	20	11.8	1.287	5.323	77.2
30	16.12	5.43	185	27	16.2	0.726	3.057	43.4
40	19.61	5.70	197	31	20.6	0.812	1.836	26.4
50	21.19	5.80	205	29	25.5	0.977	2.412	35.2

The hardness of all Zn-based alloy coatings, increased with CDs, as listed in Table (2–6). This may be attributed to the high density of Ni, Co, and Fe. At high CD, however, the deposit was dense, porous due to the production of metal hydroxide cause by the rapid evolution of hydrogen through plating [7]. The throwing power of all Zn based alloy coatings, increased with increase in applied CD to a maximum value, and then decreased at higher CD (Table 2–6). This may be due to adsorbed $M(OH)_2$ at the cathode substrate during the electrode position.

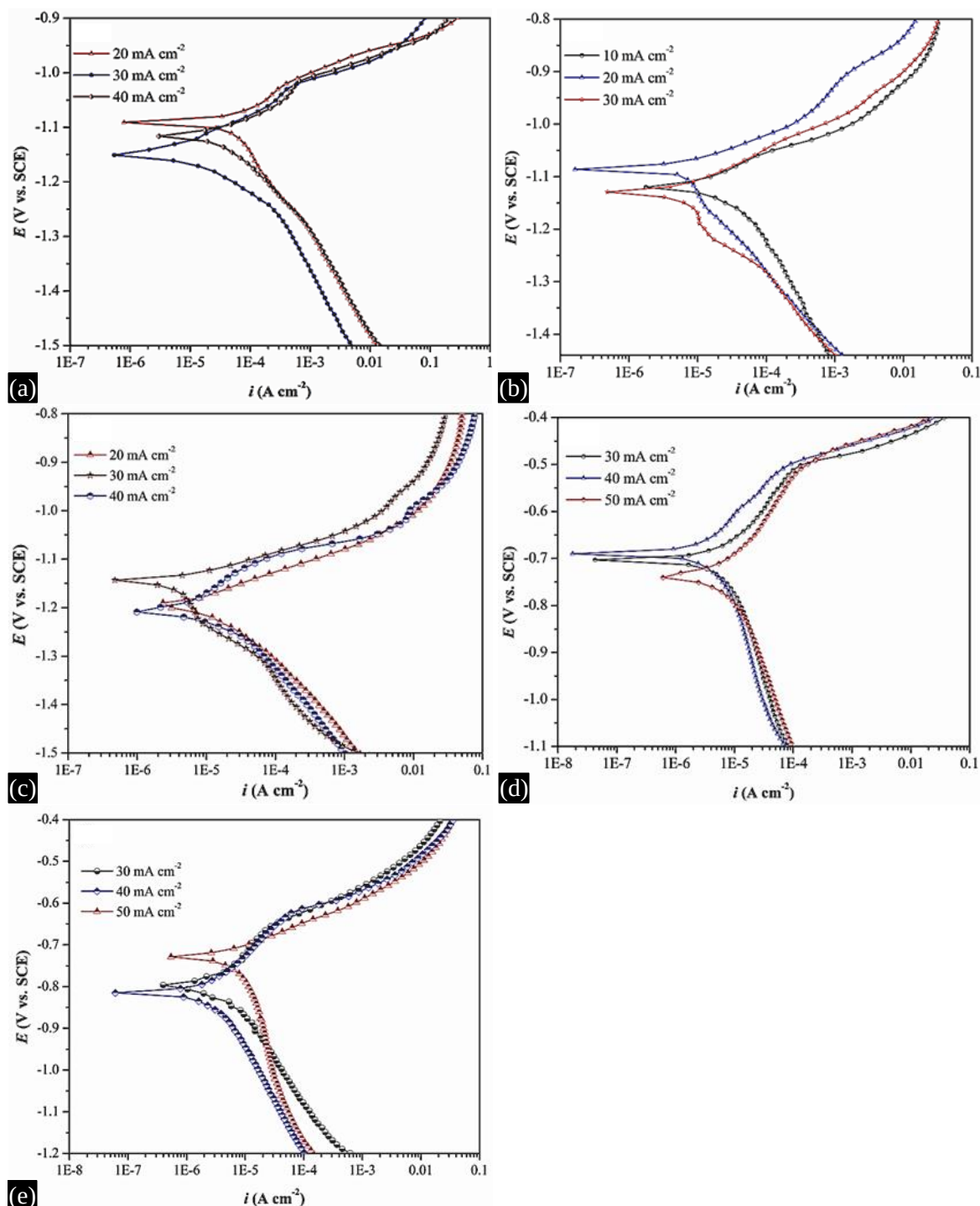


Figure 1. Potentiodynamic polarization curves of Zn-Ni (a), Zn-Co (b), Zn-Fe (c), Zn-Ni-Co (d) and Zn-Co-Fe (e), alloy coatings at different CDs.

The experimental corrosion data of zinc-based alloy films were tabulated in Table 2–6. The Zn-Ni coating films displayed, a minimum CR of $214 \mu\text{m y}^{-1}$ at 30 mA cm^{-2} and an overall difference in corrosion potential (E_{corr}) of 79 mV. In the case of Zn-Co alloy film, the CR at 20 mA cm^{-2} was $138 \mu\text{m y}^{-1}$ and the overall difference in E_{corr} of the coating was 48 mV. The Zn-Fe alloy deposit displayed a low CR of $325 \mu\text{m y}^{-1}$ at 30 mA cm^{-2} and the average difference in the E_{corr} was 78 mV. The improved corrosion efficiency with lower CRs (Tables 5 and 6) and the most nobler corrosion potential (less negative) at 40 mA cm^{-2} was seen in the case of Zn-Ni-Co and Zn-Co-Fe alloy films. The data indicated that, the zinc-nickel-cobalt coating at optimal CD (Table 5) is having the lowest CR ($20.4 \mu\text{m y}^{-1}$), which was 10 times; 7 times lower than zinc-nickel and zinc-cobalt (Tables 2 and 3) films and also Zn-Co-Fe film at optimal CD is having, least CR (Table 6), which was 8 times, 12 times lower than Zn-Ni and Zn-Fe (Tables 2 and 4) alloy films. The potentiodynamic polarization curves of Zn-Ni (a), Zn-Co (b), Zn-Fe (c), Zn-Ni-Co (d) and Zn-Co-Fe (e) alloy coatings at different CDs are shown in Figure 1. In conclusion, at optimized CD, zinc-nickel-cobalt and zinc-cobalt-iron alloy films have greater corrosion resistance compared to zinc-nickel, zinc-cobalt, and zinc-iron deposits.

The lowest CR of Zn-based alloy films could be described with the theory of barrier protection mechanism. Zinc dissolves preferably, during corrosion, leaving an upper layer with high composition of nobler metal content (Ni, Co, and Fe). The maximum corrosion potential (E_{corr}) of zinc-nickel-cobalt and zinc-cobalt-iron alloy and the beginning (at less negative potential) of its passivity regime [14, 15]. The increase in noble metal content in the alloy films was required to shift the deposit protection from a sacrificial to a protective one in all the alloys [7]. It is also inferred that the homogeneity of coatings increased and the CR decreased with the addition of additives.

CONCLUSION

In all five alloy systems, the baths have been optimized with electroplating techniques for the development of Zn-Ni, Zn-Co, Zn-Fe Zn-Ni-Co, and Zn-Co-Fe alloy films on mild steel surface using sulphanic acid and gelatine as additives. In all five alloy films, the metal content (M) was increased with applied CDs. With applied CD's the thickness, hardness, and throwing power was increased. In all optimal CD's, Zn-Ni-Co coatings ($\sim 14.36 \text{ wt.}\%$ nickel and $\sim 6.39 \text{ wt.}\%$ cobalt) has a least corrosion rate of $20.4 \mu\text{m y}^{-1}$, which was around ~ 10 times lesser than zinc-nickel ($214 \mu\text{m y}^{-1}$) and ~ 07 times lesser than zinc-cobalt alloy films ($138 \mu\text{m y}^{-1}$) and Zn-Co-Fe coating films ($19.61 \text{ wt.}\%$ Ni and $5.70 \text{ wt.}\%$ Fe) has a minimum corrosion rate of $26.4 \mu\text{m y}^{-1}$, which is ~ 08 times lesser than Zn-Ni ($214 \mu\text{m y}^{-1}$) and 12 times lesser than Zn-Fe ($325 \mu\text{m y}^{-1}$) film. Thus, among all five alloy systems, Zn-Ni-Co alloy film showed better CR, due to increase in metal contents (M= Ni and Co).

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Conflict of Interest

The authors declare that there is no conflict of interest.

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