

CONVERSION COATINGS FOR ZINC-COBALT ALLOY ELECTRODEPOSITS

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The chromating solutions suitable for zinc-cobalt alloy electrodeposits has been developed and evaluated in the context of improving the corrosion performance of the above alloy deposits. The performance evaluation has been carried out by means of chemical (immersion test) and electrochemical (polarisation) measurement methods and the test results are compared with zinc and zinc-nickel alloy deposits.

Keyword: Corrosion, electrodeposition, zinc-cobalt alloy chromating, immersion test and polarisation measurement

INTRODUCTION

Over the years electroplated zinc has been accepted by the automotive industry to provide an economical and good corrosion protection for steel substrates. While zinc plating is still used for this purpose intense market competition has caused automobile manufacturers to turn their efforts to provide increased service life to zinc plated components. The results of extensive research [1-5] on this subject reveal that alloys of zinc with iron group metals are highly corrosion resistant and cost effective. Passivation of the alloy deposits, further enhances the corrosion resistance and also meets colour requirements.

The small amount of iron group metals present in these alloys makes passivation treatments difficult, while zinc deposits easily accept a variety of passivating coatings [6,7]. Special passivating solutions should be developed to produce acceptable chromate films.

Our previous work in this line dealt with the passivation treatments for zinc-nickel alloys [8]. This paper presents our results on the corrosion behaviour of passivated zinc-cobalt alloy deposits.

EXPERIMENTAL

Zinc and zinc-cobalt alloy (0.4%, 0.8% and 1.8% cobalt) electrodeposits of 12 μ thickness were obtained from a sulphate-chloride bath under galvanostatic conditions on 5x7.5x0.1 cm cold rolled steel panels as per the conditions reported earlier [9]. Necessary precautions were taken to obtain alloys of uniform composition and thickness. The deposits were chromated in the solutions of compositions and conditions as given in Table I. The treated panels were allowed to dry in air for 24 hours.

1.5 x 2.0 cm area specimens were cut from the above panels and their edges were masked suitably so as to expose an area of 1 cm² for the polarisation experiments.

A conventional H-cell was used for the above studies with a platinum foil counter electrode, the deposited panel as the working electrode and a saturated calomel reference electrode. Experiments were conducted in deaerated 0.01 M sodium chloride solution prepared using triple distilled water. The polarisation measurements were carried out in an electrochemical analyser BAS 100 A.

TABLE I: Composition of passivating solutions and their operating conditions

Solution No.	Conc of Na ₂ Cr ₂ O ₇ ^(a) or CrO ₃ ^(b) (g/l)	Chrom alum (g/l)	NaCl (M)	H ₃ PO ₄ (m/l)	pH	Time of immersion (sec)	Colour
1.	a: 200	—	0.75	—	1.5	60	Yellow
2.	a: 200	5	0.50	—	1.0	30	Khaki
3.	a: 200	—	0.75	—	1.5	15	Iridescent
4.	b: 30	—	0.50	10	1.0	60	Green

The working electrode was water rinsed and equilibrated in the test solution for about 30 minutes to establish stable rest potential. The potential was scanned from -150 mV to +150 mV from the open circuit potential in a single sweep at a scan rate of 1 mV/sec. From the intersection of the anodic and cathodic Tafel slopes the I_{corr} and E_{corr} values were estimated. The tests were conducted in triplicate.

The chromated specimen of 5 x 7.5 x 0.1 cm size with an exposed area of 3 x 4.5 x 2 cm were immersed in 5% sodium chloride solution to determine the weight loss which was expressed in mils per year (mpy). The times taken for white and red rust formation were also observed.

RESULTS AND DISCUSSION

The presence of cobalt on the deposit surface makes the chromating difficult and only darker shades could be obtained with the conventional chromating solution. Hence special chromating solutions (Table I) were developed to produce different colours viz., iridescent, yellow, khaki and green.

Table II summarises the results of polarisation experiments. The E_{corr} values of zinc-cobalt alloy coatings shifted slightly towards more noble potentials and their corrosion rates decreased considerably when compared to values obtained for zinc deposits. The corrosion rate gradually decreased with the increase in cobalt content of the deposit and varied with the nature of passivation treatment given.

TABLE II: Polarisation behaviour of chromated deposits

Deposit	Chromating Solution	E_{corr} (mV)	I_{corr} (μA)
Zn	Unchrom	-1142	9.1
	Yellow	-1010	6.7
	Green	-1042	6.2
Zn-0.4% Co	Unchrom	-1018	7.9
	Yellow	-999	3.2
	Khaki	-997	3.4
	Iridescent	-1004	3.8
Zn-0.8% Co	Green	-992	2.9
	Unchrom	-1011	6.8
	Yellow	-984	2.4
	Khaki	-984	2.7
Zn-1.8% Co	Iridescent	-988	3.2
	Green	-978	1.8
	Unchrom	-1000	6.4
	Yellow	-970	2.2
	Khaki	-976	2.6
	Iridescent	-989	3.1
	Green	-966	2.0

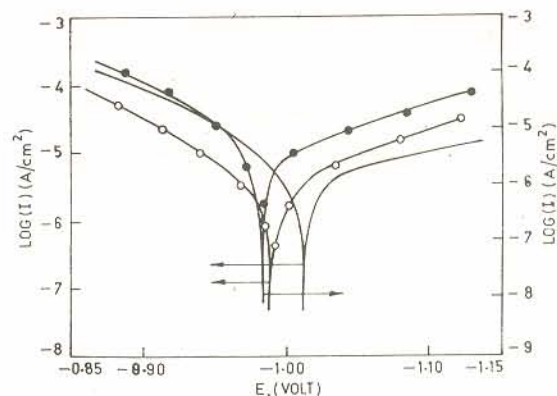


Fig. 1: Polarisation behaviour of zinc-0.8% cobalt alloy deposits in deaerated 0.1 M NaCl solution

— Unchromated deposit
 ○ Yellow colour chromated deposit
 ● Iridescent colour chromated deposit

As it is expected, the thicker chromating film offers improved corrosion resistance compared to the light transparent coatings. Also the results given in Table II indicate that the green passivated films are more protective than the other films.

I_{corr} values of zinc cobalt alloy deposits were found to lie between those of zinc and zinc-nickel alloy deposits [8].

Figs. 1 and 2 give a comparison of E_{corr} and I_{corr} values of unchromated Zn-0.8% Co with chromated deposits. Though an increase in Co-content from 0.4 - 0.8% resulted in decreasing the I_{corr} values, further increase in cobalt content is not effective in decreasing the corrosion rate. The same trend is observed with 1.8% cobalt even in the unpassivated state.

A comparison of the results observed in immersion test of Zn-0.8% Co alloy systems with zinc and Zn-15% Ni alloy

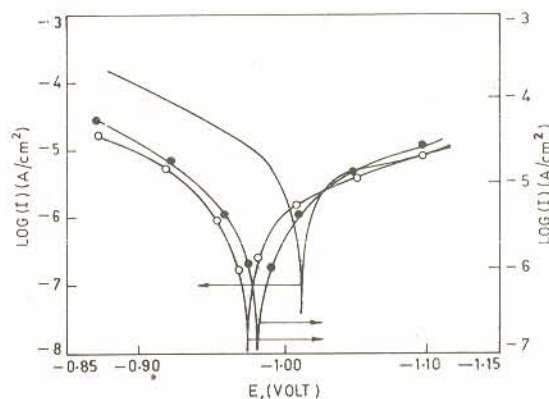


Fig. 2: Polarisation behaviour of zinc-0.8% cobalt alloy deposits in deaerated 0.01 M NaCl solution

— Unchromated deposit
 ○ Khaki colour chromated deposit
 ● Green colour chromated deposit

TABLE III (a): Results of immersion test in 5% NaCl solution at 303 K

Chromating solution	Hours to white and red rust formation		
	Zn	Zn-15% Ni	Zn-0.8% Co
Unchrom	114 (325)	240 (498)	170 (440)
Yellow	233 (590)	*384 (1100)	285 (970)
Khaki	—	*377 (1100)	240 (920)
Iridescent	—	*306 (1028)	215 (730)
Green	281 (696)	*408 (1124)	365 (1000)

* Thin film of white rust () Red rust formation

system is made in Tables III a and b. Zinc deposit showed signs of white rust in 114 hours and red rust in 325 hours compared to 170 and 440 hrs respectively observed for Zn-0.8% Co system. Red rust formation started in the yellow and green passivated zinc after 590 and 696 hours respectively whereas in the Zn-0.8% Co alloy it started only after 970 and 1000 hours respectively. In the case of Zn-15% Ni alloy the signs of white rust and red rust formation were further delayed and the onset of white corrosion was less prevalent in the alloy coating especially after passivation.

The corrosion rates as determined by the weight loss in the case of immersion tests were in accordance with the above visual observations. The two alloy systems showed nearly twice the corrosion resistance of pure zinc deposits. However, the dissolution rate offered by Zn-Ni alloy deposits were much less than that of Zn-Co deposits. Hence it can be inferred that Zn-Co alloy system can be recommended for moderate service conditions and Zn-Ni for severe conditions though both of them out perform zinc deposit in the respective conditions. Zinc-cobalt baths are simple to operate and the alloy system is more economical.

CONCLUSION

The newly developed passivating solution improves the corrosion resistance of the zinc-cobalt alloy. Zinc-nickel

TABLE III (b): Weight loss measured in 5% NaCl solution with immersed condition

Chromating solution	Corrosion rate (mpy)		
	Zn	Zn-15% Ni	Zn-0.8% Co
Unchrom	15.53	11.48	13.14
Yellow	11.67	5.56	6.47
Khaki	—	5.56	6.55
Iridescent	—	6.66	7.57
Green	8.11	5.41	5.64

alloy coating provides protection for longer period than zinc-cobalt alloy coating. For milder environments Zn-Co alloy system is favoured from the cost point of view, when compared to Zn-Ni system.

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