

Corrosion behaviour of electrodeposited zinc-nickel alloys

M. PUSHPAVANAM, S. R. NATARAJAN, K. BALAKRISHNAN, L. R. SHARMA*

Central Electrochemical Research Institute, Karaikudi 623 006, India

*Department of Chemical Engineering and Technology, Panjab University, Chandigarh 160014, India

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Improved corrosion resistance requirements, higher production costs and stringent pollution regulations have led researchers and commercial platers to study and develop new types of coatings for protection of steel components. Deposition of zinc-nickel alloy is of particular interest to the automobile industry where the coatings should satisfy many vital requirements such as formability, weldability, paint adhesion. This paper discusses the corrosion behaviour of zinc-nickel alloy coatings of various thicknesses and different compositions in the chromated and non-chromated condition on steel. The corrosion resistance was tested by various electrochemical methods and an industrially adopted salt spray test and the results indicate that an alloy deposit containing 15–18% nickel can efficiently replace zinc and cadmium deposits.

1. Introduction

Improved corrosion resistance requirements, higher production costs and stringent pollution regulations have intensified developmental investigations with regard to newer types of coatings for steel components. Multilayer alloy galvanizing, alloy zinc plating etc., are of particular interest to the automobile industry where the coatings are expected to have higher corrosion resistance, paint adhesion, etc.

Recently increasing interest has been directed towards zinc-nickel alloy coatings [1, 2] as they exhibit better physical and electrochemical properties than pure zinc deposits. Zinc-nickel alloys exist in various phases and it is well known that the corrosion resistance of a deposit is also determined by its structure and morphology [3, 4]. Along with corrosion resistance, the deposit should also possess the required ductility and pleasing appearance and must be capable of favourably responding to the chromating treatment which helps by enhancing the service life of the plated components.

This paper discusses the corrosion behaviour of zinc-nickel alloy deposits of various compositions on the basis of results obtained from the industrially accepted salt spray and electrochemical tests.

2. Experimental

Zinc-nickel alloy deposits of various compositions were applied on either side of mild steel substrates from a citrate based electrolyte as used in the earlier work [5]. Cadmium and zinc deposits were also produced respectively from the conventional cyanide and sulphate electrolytes and nickel from a Watts' bath [6].

Dissolution rates of the deposits of 7.5 cm × 2.5 cm area on either side of the steel specimens were deter-

mined by the weight loss method, by suspending them in 5% neutral sodium chloride solutions separately for a period of 15 days.

The corrosion currents and potentials in respect of the different deposits were measured by the potentiodynamic polarization technique, using a conventional three electrode cell assembly containing deaerated sodium chloride. The experiments were carried out with the help of potentiogalvanoscan (Wenking, Model PSG 81), connected to a voltage scan generator (Wenking Model VSG 71) and a $X-Yt$ recorder.

The effect of coupling each of the coated specimens with bare steel was examined by measuring the galvanic current using a zero resistance ammeter for a period of 7 days and determining their weight loss. The specimen to steel area ratio was maintained 2:1.

Steel specimens of 7.5 cm × 5.0 cm × 0.1 cm area and plated to 6 μm and 12 μm thickness with zinc, cadmium or zinc-nickel alloy were subjected to chromate passivation in dichromate based solutions with a view to comparing their corrosion resistance with unpassivated specimens. The corrosion resistance was assessed by means of the salt spray test with a 5% neutral sodium chloride solution and conducted by spraying for 8h with 16h rest for a total period of 360 spraying hours.

The observed behaviour was also examined by carrying out anodic stripping voltammetry with the different specimens with the same set up as used for potentiodynamic polarization [7]. Solutions with nickel sulphate 0.5 M–0.1 M, zinc sulphate 0.5–0.1 M, boric acid 0.4 M, trisodium citrate 0.1 M in which the Ni/Zn ratio was varied as 5:1, 4:2, 3:3 and 0.1:0.5 were used for deposition of alloys of different nickel contents. The solutions were operated at pH 4, 30°C and at –1.2 V (4.0 A dm⁻²). Under these conditions deposits of 30%, 20%, 18% and 12% Ni could be pro-

Table 1. Open circuit potentials, dissolution rates and corrosion current values for zinc, cadmium, nickel and zinc-nickel alloy in 5% neutral sodium chloride

Deposit (Steel substrate)	OCP (V)	Dissolution rate (mpy)	Corrosion current (mA cm ⁻² × 10 ⁻²)
Matte nickel	-0.28	0.45	0.0145
Zinc	-1.01	7.87	3.2
Zinc-12% nickel	-0.91	3.77	2.75
Zinc-18% nickel	-0.80	3.08	2.50
Zinc-25% nickel	-0.76	2.90	2.20
Cadmium	-0.72	4.51	2.10
Steel	-0.53	9.77	-

duced at cathode efficiencies of 80%, 90%, 93% and 96%, respectively. SEM micrographs of deposits were taken for studying their surface characteristics.

3. Results and discussion

It has been observed that, in general, deposits having up to 20% nickel are ductile with greyish white colour and those having above this limit are somewhat brittle. Alloys become yellowish white in colour with increasing nickel content, probably indicating the existence of the α -phase alloy.

Results shown in Table 1 indicate the rate of self dissolution of the alloy in the test medium decreases with increasing nickel content. It is also observed that the 18% alloy has a rate of dissolution which is nearly 40% of that of zinc and 70% of that of cadmium deposits. But when compared to nickel, it is 7 times as much as with the latter and this is certainly due to the higher activity of the alloy being rich in zinc. The lower dissolution rate of the alloy compared to zinc and cadmium helps reduce the excessive loss of the coating, still maintaining the same order of protection to steel.

The increasing equilibrium potential of the alloy deposits with increasing nickel content are in accordance with their dissolution rates. Being cathodic, nickel confers less protection to steel and permits substrate oriented pitting attack. On the other hand, zinc is highly anodic to steel and thus offers good sacrificial protection. However, the higher difference in the open circuit potentials of steel and zinc results in excessive dissolution of the latter. By alloying, the difference in the open circuit potentials is considerably narrowed with reduced metal loss coupled with sufficient protection to steel.

The anodic polarization data given in Fig. 1 and Table 1 indicate increased corrosion currents for zinc and zinc rich alloys in agreement with the dissolution rates observed. Since oxygen reduction occurs at potentials for more negative than open circuit and is usually preceded by some cathodic reaction, only the anodic dissolution part has been considered.

When specimens of 15 μ m thickness on either side are coupled to bare steel, the zinc-steel couple is found to be associated with a higher galvanic current and a

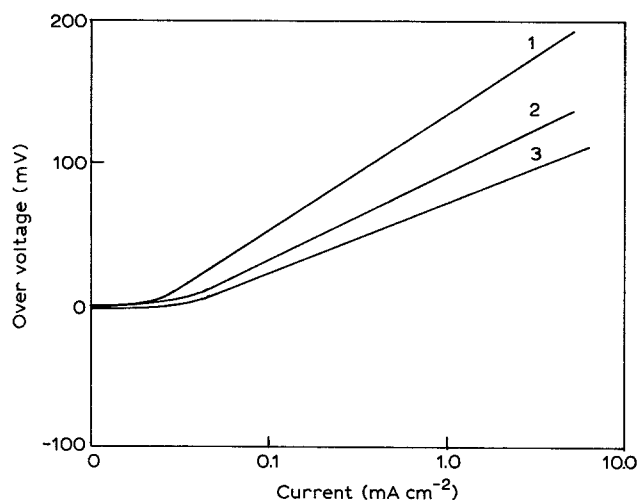


Fig. 1. Potentiodynamic polarization curves of (1) Zn-25% Ni, (2) Zn-18% Ni and (3) Zn-12% Ni.

higher zinc loss as shown in Table 2. Nickel becomes cathodic to steel when coupled. These results are in agreement with the previous findings. However, the experiments do not clearly prove whether the alloy deposits can effectively replace cadmium deposits which are widely used under severe marine conditions. Replacement of cadmium is important since more and more stress is now being laid on prevention of pollution due to the poisonous nature of cadmium salts. To what extent zinc-nickel deposits can be of use from the view point of corrosion performance is to be determined on the basis of salt spray tests.

Figures 2-4 and Table 3 illustrate the corrosion behaviour of zinc, cadmium, nickel and alloy deposits of 6 and 12 μ m thicknesses and in passivated and unpassivated conditions. The nickel and nickel-rich alloy deposits were not found to be highly corrosion resistant, the major reason being the formation of substrate oriented deep rust pits giving an unsightly appearance to the deposits. On the other hand, the zinc rich deposits formed white corrosion products, whose rate of formation decreased with increase in the nickel content of the alloy. The 12 μ m alloy deposits developed white rusting only after 72-96 h of exposure whereas those of 6 μ m thickness developed white rust at an early time. This is due to the high galvanic current prevailing between the exposed substrate and deposit at a lower thickness. The zinc deposit developed red rust only after 72 and 160 h for thicknesses of 6 and 12 μ m, respectively, whereas zinc-18% nickel

Table 2. Galvanic current and dissolution rate of zinc and the alloy when coupled to steel

Deposit	Average galvanic current (mA)	Weight loss (mpy)
Matte nickel	0.60 (cathodic)	0.77
Zinc	0.71 (anodic)	42.48
Zinc-12% nickel	0.54 (anodic)	33.51
Zinc-18% nickel	0.51 (anodic)	16.93
Cadmium	0.11 (anodic)	4.62

(mpy is ml per year)

Table 3. Corrosion behaviour of zinc, cadmium and zinc-nickel alloy deposits in salt spray test

Condition and thickness (μm)	Test duration for the appearance of white/red rust (h)					
	Cd	Zn	Zn-5% Ni	Zn-12% Ni	Zn-15% Ni	Zn-18% Ni
A. White rust formation						
As Plated:						
6	64	24	32	40	48	56
12	104	48	56	72	80	96
Passivated:						
6	210	72	96	120	160	176
12	320	160	200	240	288	288
B. Red rust formation						
As Plated:						
6	160	72	88	112	132	144
12	272	160	172	192	216	240
Passivated:						
6	280	136	184	216	264	280
12	Nil	280	296	Nil	Nil	Nil

deposits formed red rust only after 144 and 240 h, which is almost similar to that exhibited by cadmium deposits. The passivated alloy deposits were found to be more resistant to white as well as red rust formation than the unpassivated ones. Alloys containing more than 25% nickel failed to respond to the passivation treatments. Alloys containing more than 25–30% nickel resembled nickel deposits in developing red rusting without white rust formation.

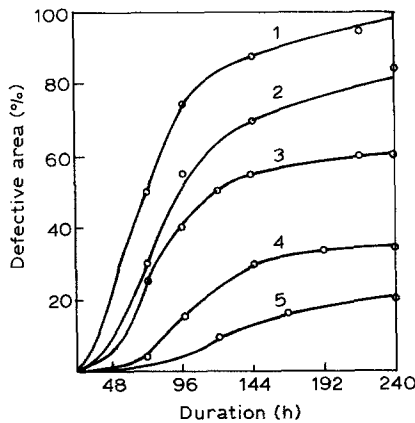


Fig. 2. Corrosion resistance of zinc-nickel alloy in 5% sodium chloride. Resistance to white rust formation. Zinc deposits ($6\ \mu\text{m}$) with nickel (%): (1) 0, (2) 5, (3) 12, (4) 18 and (5) cadmium deposit.

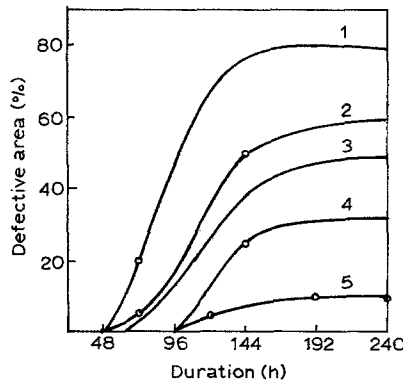


Fig. 3. Corrosion resistance of zinc-nickel alloy in 5% NaCl. Resistance to white rust formation. Conditions as in Fig. 2 ($12\ \mu\text{m}$).

The change in the corrosion behaviour of the alloys can be understood by analysing the anodic stripping curves obtained with varying zinc to nickel ratios (Fig. 5) [7]. Solutions having higher nickel ratios showed a dissolution peak potential corresponding to the α -phase, whereas for those with higher zinc content, the peak potentials shifted to less noble potentials corresponding to the γ -phase which is said to have higher corrosion resistance [3, 4].

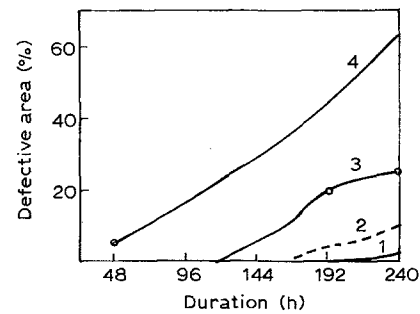


Fig. 4. Corrosion resistance of zinc-nickel alloy in 5% NaCl. Resistance to red rust formation. Zinc deposit ($12\ \mu\text{m}$) with nickel (%): (1) 18, (2) 0, (3) 30 and (4) pure nickel deposit.

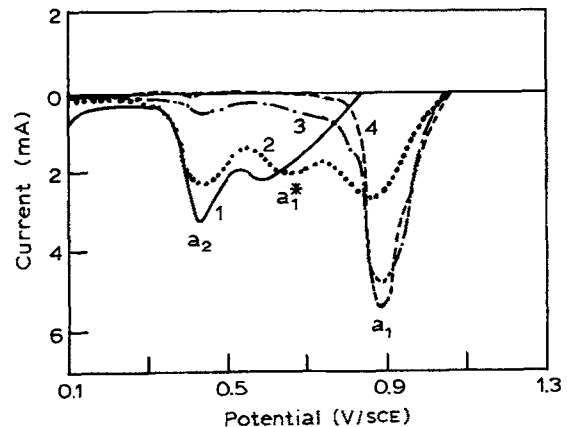


Fig. 5. Voltammetric anodic stripping curves for zinc-nickel alloy deposits. Deposition potential $-1.2\ \text{V}$, $10\ \text{mV/s}$. Time 60 s. (1) Zn-30% Ni, (2) Zn-20% Ni, (3) Zn-18% Ni and (4) Zn-10% Ni.

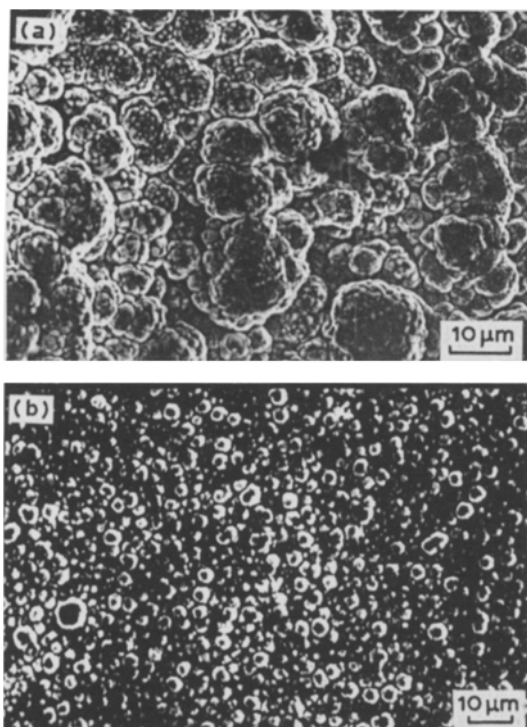


Fig. 6. SEM micrographs: (a) Zn-30% Ni and (b) Zn-18% Ni alloy.

The SEM micrographs (Fig. 6) obtained with deposits having no nickel shows bunching with coarse grain structure, whereas that for 18% nickel shows a fine grained pyramidal structure, which is responsible for the relatively better appearance, higher hardness

and lower dissolution rate than pure zinc. These structural differences, along with the anodic stripping analysis, confirm the observed corrosion behaviour of the alloys.

4. Conclusion

Salt spray test and other electrochemical tests indicate that the alloy having 15–18% nickel has corrosion resistance better than zinc. This is supported by the data on anodic stripping analysis as well as SEM analysis.

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