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Zn- Ni Alloy Deposit for Cadmium Replacement Applications

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Abstract

Zinc - nickel alloy was deposited from alkaline bath at a PH of 13-14 with the nickel percentage of 5-9% in our prior research. Present study dealt with the research on 10-12% of Nickel at a PH of 12-13 from Zinc – nickel alloy electrolyte and the remaining percentage of Zinc, required for corrosion resistant applications to be used for reliable alternative of cadmium. Hull cell studies was carried out to optimize current density, temperature, agitation etc., for getting a deposition of 10-12% of Ni & 88-90 % of Zn. SEM, EDAX, XRD measurements characterize the deposit properties and structure. Corrosion resistance measurements such as polarisation, corrosion impedance spectra of zinc-nickel alloy were evaluated.

Keywords: Zinc – Nickel alloy deposit, Cadmium alternative, Zincate electrolyte, Surface morphology, Corrosion resistance.

Introduction

New environmental regulations over the world encourage the use of alternatives to cadmium plating for corrosion-protection of steels. Initially zinc was considered as good substitute for cadmium due to its superior corrosion resistance properties than cadmium. Nowadays , the electro deposition of zinc alloys with group eight metals (Ni, Co and Fe) has recently attracted interest due to their high corrosion resistance than zinc and considered to be as suitable alternative to hazardous cadmium for most of the industrial applications. Zn - Ni alloy deposition is an anomalous co deposition since the less noble metal zinc, deposit preferentially and its percentage in the deposit is higher than that in the electrolyte and is explained by Brenner. Normal Zn – Ni Co deposition is also possible in particular experimental conditions. The presence of nickel in zinc - nickel alloy of 8-15% is required as optimum elemental percentage for corrosion resistance applications. Zinc-nickel alloys from acidic solutions shows the presence of nickel of about 12-15% with good current efficiency. Alkaline electrolyte of zinc-nickel deposit shows a better corrosion resistance due to good throwing power than other electrolytes. Zinc – nickel alloy coatings normally shows high impact in corrosion resistance after post treatment by chromating and is quite applicable for automotive industries. Hydrogen embrittlement is also less as compared to other alloy systems and was considered to be suitable substitute for cadmium applications. Research was done previously in Co deposition of zinc –nickel alloys using chloride bath at direct and pulsed current. Conversion of anomalous to normal co-deposition was identified at low current densities in direct as well as pulse current. Anomalous co deposition of under potentially deposited zinc forms the sub monolayer which inhibits the nickel deposition to some extent (1-6). The Ni content in the deposition layer was suppressed from low current density to high current density where Zn deposition was predominant (7). Complexing agents based on amine group such as TEA (tri ethanolamine) was to be considered as one of the best complexants in alkaline electrolyte (8).

Methods & Materials

Electrode

Mild Steel Strips 1× 1Cm^2 of area was exposed to deposit Zinc-nickel alloy was used as cathode and Zinc metal with 99% purity grade was used as anode. Mild steel cathode was pre treated by using trichloroethylene and the followed by cleaning with alkaline detergents to remove oil and other impurities. Alkaline electro cleaning using caustic soda and sodium hydroxide solution was used to remove organic and inorganic contaminants.

Electrolyte

Electrolyte for zinc-nickel alloy deposition was prepared as in the following composition

1. Zinc Oxide	: 9 -12 g/l
2. Sodium Hydroxide	: 75-120 g/l
3. Nickel Sulphate	:10-15 g/l
4. TEA	: 120-150 ml/l
5. pH	: 12-13
6. Temperature	: 30 ± 2

7 .Current Density : 1- 8 A/dm^2

A known amount of sodium hydroxide was weighed and dissolved in water. Then a known amount of Zinc Oxide was weighed and added to dissolved sodium hydroxide and this was made up to 1 litre. A known amount of nickel sulphates was weighed and dissolved in water (5-10 g/l) and then with complexant(tri ethanol amine) was added to it until the clear solution was obtained (50-100 g/l) and then it made up to 2 liter. To prepare zinc-nickel bath equal amount of zincate bath and nickel sulphate (5-10 g/l) baths are mixed together. The experiments were carried out by using the electrolyte to identify Hull cell study, current efficiency, surface morphology & microstructure, elemental percentage, corrosion resistance measurements.

Results and Discussions

Hull cell studies was carried out to optimize the electrolyte , current density (CD), temperature, agitation etc (i.e. operating conditions) for getting a deposition of 10-12% of Ni & 88-90 % of Zn.

Hull cell Studies

Fig 3.1 shows the codes for recording **Hull cell** patterns and the Hull cell diagram obtained with the plain bath for a duration of 5,10 minutes.

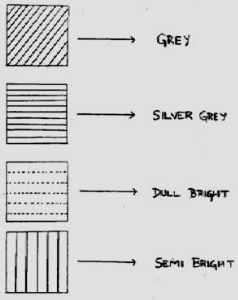


Figure 3.1 Codes For Recording Hull Cell Pattern

Fig 3.1.1 to Fig 3.1.4 shows the Hull cell diagrams obtained with and without additive in the bath with 2 and 3 A for 5, 10 minutes duration.

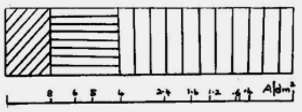


Figure 3.1.1
WITHOUT ADDITIVE 2A 5mins

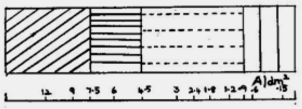


Figure 3.1.2
WITHOUT ADDITIVE 3A 10 mins

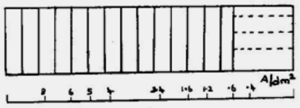


Figure 3.1.3
WITH ADDITIVE 2A 5mins

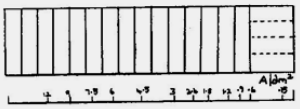


Figure 3.1.4
WITH ADDITIVE 3A 10mins

It is seen from the figure **3.1.1** that semi bright deposits were obtained only at low current density areas i.e up to 1 A/dm^2. Increasing the CD results in dull bright, silver grey and grey coloured deposits. A variety of additives are usually added to bath depositions to improve the efficiency of the deposition and the characteristics of the deposit. Among the additives added is gelatin leads to a high cathode overvoltage in a wide range of concentrations causing the grain size to decrease and the nucleation rate to increase. However, the effect of this additive on the deposition of Zn–Ni alloys is not yet clearly understood. Hence in the present study gelatin was used as an additive and Hull cell studies were carried out in the bath. It is seen from the figures **3.1.3** to **3.1.4** that addition of gelatin at a concentration of 0.5 g/L improves the brightness of the deposits over the entire range of 3A Hull cell. The increased brightness may be due to increase in nickel content of the deposits. Hence for further studies the operating CD was fixed from 1.25 to 8 A/dm^2.

Current efficiency studies

Current efficiency is the ratio of the actual weight of the deposit to the theoretical weight. Actual weight could be found out by either weight gain at the cathode or weight loss at the anode. Anode and cathode current efficiencies are calculated from the weight loss or weight gain of the anode and cathode plates respectively and the charge passed for the deposition. In the present system total charge was found out using a coulometer connected in series to the circuit. Theoretical weight was calculated from the electrochemical equivalent weight and the charge passed.

Effect of current density (CD) on the current efficiency of the bath

Table 1 shows the effect of current density on the current efficiency of the bath obtained at room temperature and at 45ºC with and without gelatine

Current density A/dm^2	Current efficiency % At RT without addiitve	Current efficiency % At RT with additive	Current efficiency % at 45ºC
1.25	22.49	22.12	37.02
2.5	96.21	92.22	32.52
4	97.4	93.26	27.60
8	91.88	94.53	15.22

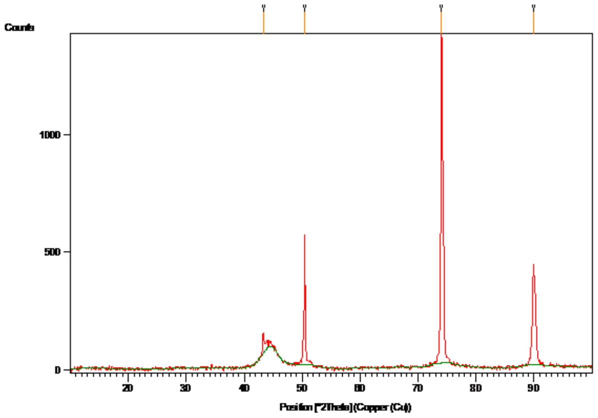
Table 2 Effect of current density on the current efficiency of the bath as well elemental percentage obtained at different current densities at room temperature

Current density A/dm^2	Current efficiency %	Zn%	Ni%
1.25	22.49	12.21	87.79
2.5	96.21	89.29	10.71
4	97.4	87.25	12.75
8	91.88	87.83	12.17

In presence of additive there is a slight decrease in current efficiency of the bath at the same time there is an increase in the brightness of the deposits as observed in the Hull cell pattern. The decrease in current efficiency at higher temperature of the bath without any additive may be due to increased rate of ionic diffusion and migration in plating solution. It is seen from the **table 1** nickel content in the alloy is high at low CD. Nickel is nobler than zinc and hence at low current densities nickel preferentially deposits than zinc thereby increased percentage of alloy in the deposits. At higher CD's due to anomalous deposition zinc content of the deposits is more than the noble metal ie nickel and is not significantly affected by increased current densities. This enables a uniform alloy composition even on a complex surface on which the current densities at different zones differ considerably. This feature provides a potential industrial application of the alkaline Zn-Ni bath. This cannot be expected from an acid alloy plating bath where the variation of nickel content with current density is very high.

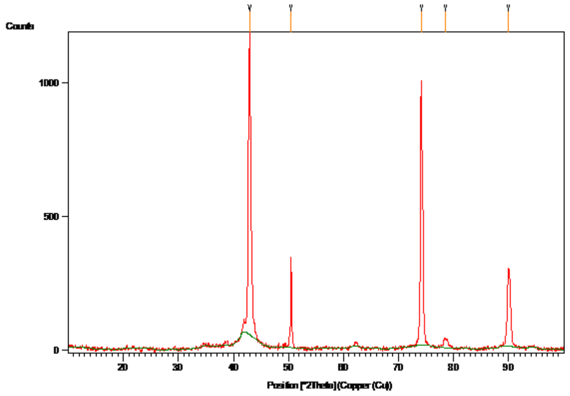
XRD

Fig 4.1 Shows the XRD spectrum obtained for the deposits obtained at a CD of 1.25 A/dm2. It is seen from the figure that the intensity nickel peaks is higher than that of zinc. This is in conformity with the nickel content in the deposits obtained by analysis and EDAX studies



4.1 XRD pattern of zinc - nickel alloy at 1.25 a/dm2

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
43.2454	86.34	0.2676	2.09214	6.30
50.3608	544.46	0.2844	1.81197	39.70
74.0429	1371.35	0.2509	1.28038	100.00
89.8778	410.67	0.4896	1.09053	29.95



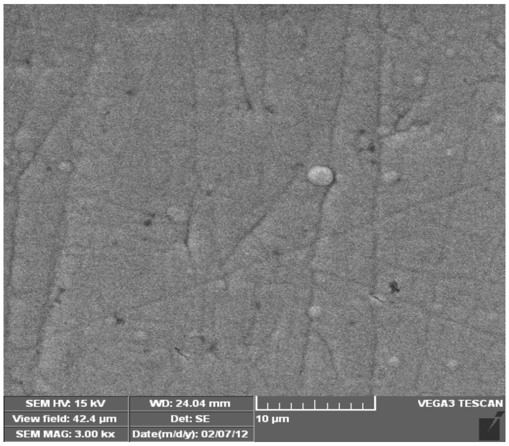
4.2 XRD Pattern of Zinc- nickel alloy deposits at 4 A/dm2

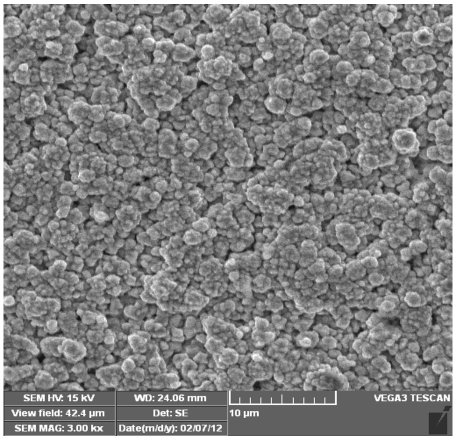
Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
42.8340	1118.16	0.3346	2.11127	100.00
50.3846	305.29	0.2342	1.81117	27.30

74.1035	965.52	0.2175	1.27949	86.35
78.5293	33.19	0.9368	1.21810	2.97
89.8556	260.27	0.5712	1.09074	23.28

Figure 4.2 shows the XRD spectra obtained for the deposits at 4 A/dm2 .In this diagram in addition to nickel and zinc peaks corresponds to zinc oxide ,copper and sulphur are observed. At higher current densities as observed by the analysis and EDAX measurements the intensity of zinc is higher than nickel. Copper peak obtained may be due to substrate effect. Sulphur may be present as an impurity present in the bath which is incorporated during deposition. Electrodeposited zinc–nickel alloy has different phases: α-phase, a solid solution of zinc in nickel with an equilibrium solubility of about more than 79% nickel; γ -phase, an intermediate phase with a composition Ni5Zn21; η-phase, a solid solution of nickel in zinc with less than 5% nickel; δ-phase (Ni3Zn22) appeared from η-phase to α-phase with increasing content of nickel. The fact that the zinc from γ -phase is oxidized at two different potentials is related to the phase composition of the alloys. When the deposit contains high amount of η-phase, this is dispersed among the intermediate of γ -phase, and after the stripping of zinc from the solid solution, the remaining deposit is porous and easy to oxidize. However, in the absence of, or with low amounts of, the solid solution, the γ -phase forms a more compact structure with a lower value of exchange current density, and it is more difficult to oxidize. The composition of the alloy might suggest a pure γ -phase between 11% nickel and 14% nickel, with the result that the zinc–nickel alloy coatings have very good corrosion resistance (9-12).

SEM





SEM Zn-Ni alloy at 1.25 A/dm^2 5.2 SEM Zn-Ni alloy at 4 A/dm^2

Figures 8.1 and 8.2 shows the surface morphology of the Zn-Ni alloy deposits at 1.25 and 4 A/dm^2. Nodular structure was obtained in the deposit corresponds to 1.25A/dm2 whereas in the figure 8.2 the deposits are coarse grained and corresponds to zinc nickel alloy deposits with more of zinc than nickel.

EDAX

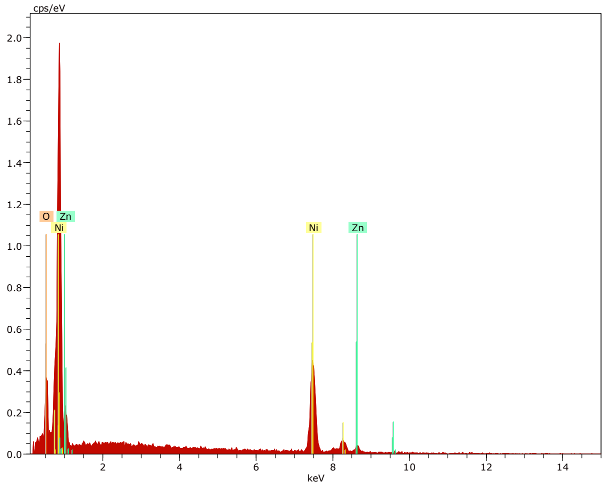


Figure 6.1 EDAX analysis of Zinc- Nickel alloy at 1.25 a/dm2

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Acquisition        Date:2/7/2012 12:38:59 PM          HV:15.0kV        Puls th.:0.75kcps
El AN  Series  unn. C norm. C Atom. C Compound Comp. C norm. Comp. C Error (1 Sigma) K fact. Z corr. A corr. F corr.
             [wt.%]  [wt.%]  [at.%]          [wt.%]       [wt.%]         [wt.%]
-----------------------------------------------------------------------------------------------------------------------
Ni 28 K-series  71.78   69.17   44.45     NiO   88.03        91.34          2.54   0.581   1.132   1.000   1.051
O  8  K-series  22.01   21.21   50.00           0.00         0.00       4.38   0.000   0.000   1.000   0.000
Zn 30 K-series   9.98    9.62    5.55     ZnO   11.97        12.42          0.73   0.108   0.847   1.000   1.049
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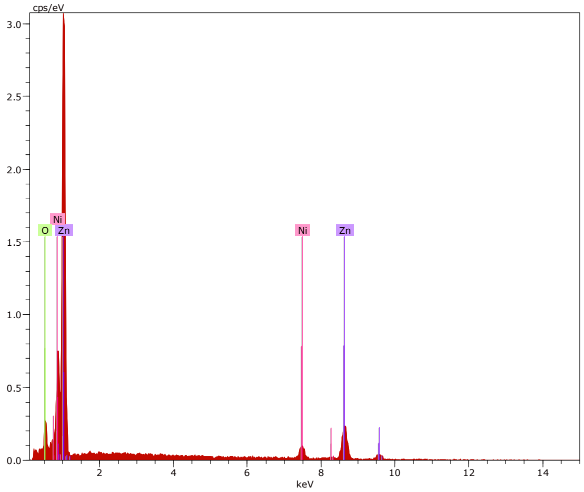

Figure 6.2 EDAX analysis of Zinc-nickel alloy deposited at 4 A/dm2

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Acquisition        Date:2/7/2012 12:43:53 PM          HV:15.0kV        Puls th.:0.86kcps
El AN  Series  unn. C norm. C Atom. C Compound Comp. C norm. Comp. C Error (1 Sigma) K fact. Z corr. A corr. F corr.
            [wt.%]  [wt.%]  [at.%]    [wt.%]       [wt.%]        [wt.%]
-----------------------------------------------------------------------------
Zn 30 K-series  76.57   69.89   42.99     ZnO   86.99        95.30          3.12   0.707   0.944   1.000   1.047
O  8  K-series  21.79   19.89   50.00           0.00         0.00       4.72   0.000   0.000   1.000   0.000
Ni 28 K-series  11.20   10.22    7.01     NiO   13.01        14.25          0.56   0.060   1.263   1.000   1.341
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It is seen from the EDAX results that at low CD's there is more nickel than at higer current densities. The above results are in good agreement with other studies.

Corrosion Behaviour of the Zinc Nickel Alloy Deposits

Table 3 shows the corrosion behaviour of the deposits obtained with gelatin at various current densities.

Current density A/dm^2	E corr Mv/SCE	I corr UA	R ct ohms cm
1.25 Zn-Ni	-550	11.4	1.838
4 .00 Zn-Ni	-518	6.4	4.011
4 .00 Zinc	-661	23.4	0.891

It is seen from the table that corrosion resistance of the Zinc nickel alloy coating is very much improved when compared to bare zinc for the coatings deposited at the same conditions. Improved Corrosion resistance is noticed in the case of Zn-Ni deposits obtained at very lower CD's. This may be due to the increased nickel content present in the low CD levels. The results obtained are in concordance with impedance studies.

Corrosion Impedance Spectra

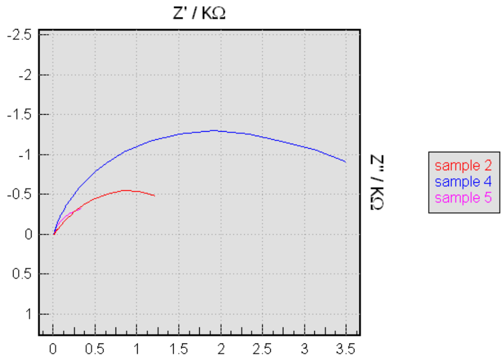

Figure 8.1 Impedance spectra for the three different coatings (sample 2- Zn –Ni (1.25 dm^2) (sample 4 –zn Ni at 4 A/dm^2) (sample 5 –Zn 4 A/dm^2)

Corrosion impedance spectra shows peaks corresponding to the different deposits for zinc, zinc-nickel at different current densities according to the corrosion resistance of the deposits . Zn-Nickel alloy deposition at 4 A/dm^2 shows the highest peak relates to higher corrosion resistance than pure zinc and zinc- nickel alloy deposit at 1.25 A/dm^2

Conclusion

A new bath has been developed to deposit Zn-Ni alloy from alkaline bath. The optimum bath composition for getting Zn-Ni (10-12%) is given below

Zinc oxide	:	9-12 g/ L
Sodium hydroxide	:	75-120 g/L
Nickel sulphate	:	10-15 g /L
TEA	:	120-150 ml /L
pH	:	12-13
Temperature	:	30 ±2 C
Current Density	:	1-8 A/dm^2

At this current density the deposits contain 10-12 % nickel in the deposits. Addition of gelatin improves the brightness of the deposits and increases the bright deposit range. As observed by other researches at low current densities regular type of deposition is observed and at higher current densities anomalous behaviour is observed. ie more of zinc than nickel. This enables a uniform alloy composition even on a complex surface on which the current densities at different zones differ considerably. This feature provides a potential industrial application of the alkaline Zn-Ni bath. This cannot be expected from an acid alloy plating bath where the variation of nickel content with current density is very high. Corrosion resistant measurements revealed that corrosion resistance of zinc-nickel alloy is more superior to zinc. Hence it is good replacement of cadmium for many industrial applications(13-17).

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