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Electrochemical Deposition and Characterization of Zinc-Cobalt

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Abstract: ***Various protective methods may be used to improve the corrosion resistance of steel. Electrochemical preparation of Zn-Co alloy has been investigated potentiostatically by using mild steel plate electrode. Electrodepositon of Zn-Co alloys have been applied to the production of highly corrosion resistance steel sheets for automotive body panels. Zn-Co alloy mostly used for industrial or commercial purpose. Organic additive used in Zn-Co coating to make the electroplated surface more durable, uniform and compact for better performances in terms of corrosion protection. Various concentrate solutions of HCl, H_2SO_4 and NaCl may be used for determining the corrosion rate of Zn-Co alloys. SEM, EDAX and XRD revealed the morphology, percentage composition and structure of Zn-Co coating respectively.***

Keywords: Alloy, Corrosion rate, EDAX, SEM and XRD

1. Introduction

Electrodeposition of metals and alloys has become widely used in many industries with distinct advantages compared to most other alloy coating technologies (1). Electrodeposition of binary Zn-Co alloys exhibits improved properties compared to pure zinc (2-3). Coating of Zinc-Cobalt alloys is interesting because these alloys exhibit a significant higher corrosion resistance and better surface morphology than pure Zinc (4-5). The corrosion resistance of Zinc-Cobalt alloys have been found to depend significantly on the concentration of Cobalt deposition.(6). It has been observed that the ternary alloy is characterized by enhanced corrosion resistance compared to binary alloy (7-9). Zinc and Zinc alloys coatings are increasingly being used in the automotive industry to protect the car body from both perforation corrosion and cosmetic corrosion. In recent years there has been a growing interest in replacing a pure Zn coating with thinner more corrosion resistant Zinc alloy layer (10). Cobalt and its alloys are of considerable interest from the point of view of some practical application (11-13). Electrodeposition has emerged as a simple and cost effective technique for the preparation of alloy film (14-16). Corrosion rate also decreases by adding suitable inhibitor, generally organic inhibitors play important role in decreasing corrosion rate. Nitrogen base material and Sulphur containing organic compounds reduces the corrosion rate. Organic inhibitors generally have heteroatom. Oxygen, Nitrogen and Sulphur are found to have higher basicity and electron density and thus act as corrosion inhibitor. O, N, and S are the active centers for the process of adsorption on the metal surface. The inhibition efficiency should follow the sequence $O < N < S < P$ (17).

2. Experiment Details

2.1 Material

Analytical grad $ZnSO_4.7H_2o$,$CoSO_47.H_2O$, H_3Bo_3(Boric acid), $SC(NH_2)_2$ (Thiourea), HCl, H_2SO_4, NaCl and distilled water. Three electrode assembly (calomel electrode used as reference ,1cm^2 mild steel plate used as working as well as counter electrode). Digital Multimeter, Power Supply unit and Voltage stabilizer.

2.2 Method

Electrochemical preparation is carried out Potentio-statically by using sulphate bath with three electrode configuration. Current, efficiency and potential measured using high precision Digital Multi-meters. Co-deposition potential of Zn-Co is found out by Current Vs Potential data. pH of the solution is maintained as acidic. Various concentrations of HCl, H_2SO_4 and NaCl were used as corroding solution. Thiourea used as inhibitor. Corrosion rate calculated according to Tafel plot (Polarization curve) using following equation.

$$CR = (Icorr * 0.13 * Eq.Wt.) / (F * D * A)$$

Where,
CR = Corrosion Rate
Eq.Wt. = Equivalent weight of Zn-Co
F = Faraday's constant
D = Density of Zn-Co
A = Area of the substrate

3. Results and Findings

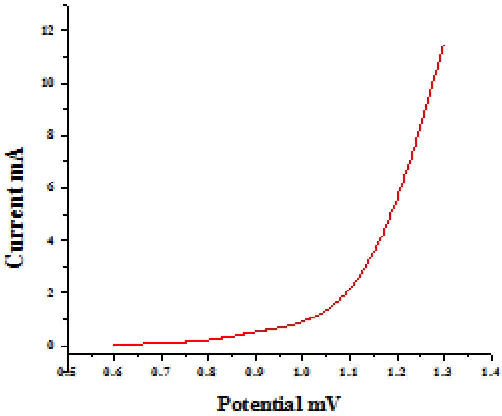
3.1 Electrochemical behavior of Zn-Co alloys

The present study deals with thin films of Zn-Co alloy. Zn-Co binary alloy prepared by electrochemically. Co-deposition potential found out by Current Vs Voltage data (Fig.1). Coating of Zn-Co alloys carried out at 1.0 mV potential Vs SCE electrode. Before applying 1.0 mV potential, the electrodes are dipped in electroplating solution of Zn-Co and equilibrium have been established in 2-5 minutes. During the deposition of Zn-Co, initially the current decreases fast up to steady state value. Thickness of thin film is calculated from Current Vs Time graph (Fig.2) using following equation.

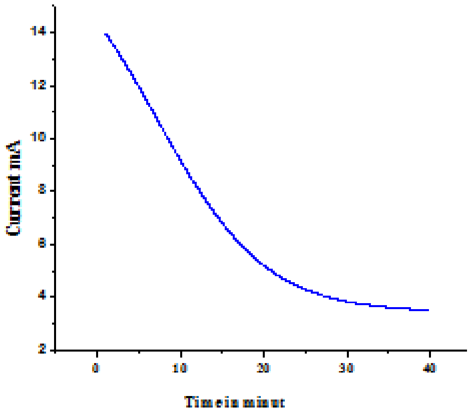
$$FT = (I * T * Ew) / (F * D * A)$$

Where,
FT= Film-thickness
T= Time
Ew= Equivalent weight of Zn-Co
F = Faraday's constant
D = Density of Zn-Co
A = Area of the substrate

Thickness of Zn-Co coating increases with increasing Cobalt concentration in electrolytic solution. Concentration of Zn was always kept constant. Zn-Co alloy film thickness decreases with addition of Thiourea as inhibitor.



Current Vs Voltage Fig. 1



Current-Time graph Fig-2

3.2 Chemical Analysis

In Zn-Co alloy, Co content in the deposited coating varies with the Cobalt concentration in electrolytic solution. Higher concentration of Cobalt is responsible for more thickness of alloys. In this work three types of Co variable solution were used in absence and presence of Thiourea as inhibitor. Boric acid was used to maintain the pH of the solution and also having great interest in deposition as catalyst and also shows significant compositional and morphological characteristics of Zn-Co deposited alloy.

3.3 Polarization Studies

After 40 minute of deposition, the deposited plate of mild steel is tested in different concentrations of corrosive solution of H_2SO_4, HCl and NaCl. The polarization study had been carried out from cathodic and anodic data. Polarization data has been used to construct the Tafel plot (Fig.3). Corrosion rates are calculated from Tafel plot. Corrosion rate decreases with decreasing concentration of Cobalt in electroplating solution. After addition of inhibitor corrosion rate become much lower than Zn-Co alloys in absence of inhibitor.

Tables

Table 1: Corrosion rate of electrodeposits in H2SO4

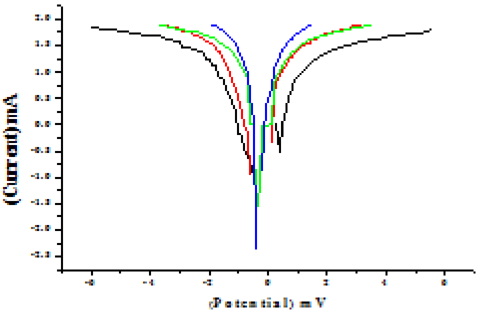
Experimental solution	*Corrosion Rate in10^{-4} mpy*							
	0.01N H_2SO_4		0.02N H_2SO_4		0.03N H_2SO_4		0.04N H_2SO_4	
Composition	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor
0.1M Zn + 0.1M Co	0.217	0.025	0.297	0.008	0.206	0.004	0.21	0.002
0.1M Zn + 0.2M Co	0.225	0.089	0.28	0.004	0.276	0.025	0.293	0.183
0.1M Zn + 0.3M Co	0.234	0.068	0.302	0.123	0.293	0.042	0.293	0.11

Table 2: Corrosion rate of electrodeposits in HCl

Experimental solution	*Corrosion Rate in10^{-4} mpy*							
Composition	0.01N HCI		0.02N HCI		0.03N HCI		0.04N HCI	
	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor
0.1M Zn + 0.1M Co	0.268	0.055	0.276	0.021	0.293	0.008	0.293	0.004
0.1M Zn + 0.2M Co	0.217	0.072	0.281	0.123	0.297	0.114	0.234	0.136
0.1M Zn + 0.3M Co	0.272	0.048	0.280	0.056	0.310	0.068	0.221	0.127

Table 3: Corrosion rate of electrodeposits in NaCl

Experimental solution	*Corrosion Rate in10^{-4} mpy*							
Composition	0.01% NaCl		0.02% NaCl		0.03% NaCl		0.04% NaCl	
	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor	With out inhibitor	With inhibitor
0.1M Zn + 0.1M Co	0.097	0.017	0.102	0.017	0.106	0.106	0.127	0.17
0.1M Zn + 0.2M Co	0.046	0.089	0.063	0.191	0.157	0.212	0.187	0.297
0.1M Zn + 0.3M Co	0.208	0.021	0.195	0.104	0.072	0.051	0.068	0.178



Tafel plot Fig.3

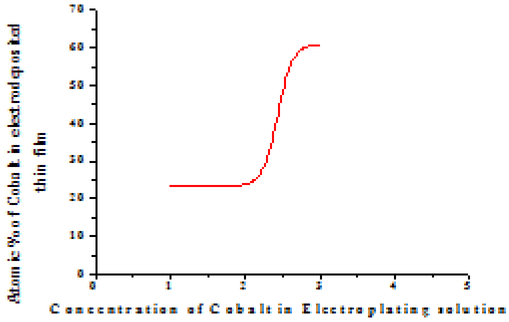
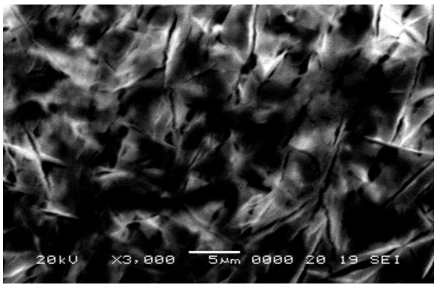
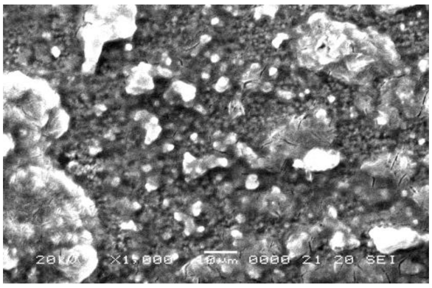


Fig.5

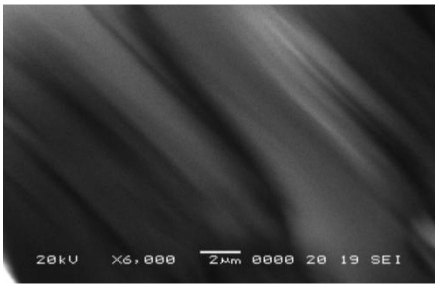
3.4 Morphology, composition and structural analysis



SEM of 0.1 M Zn-0.1Co alloy (a)

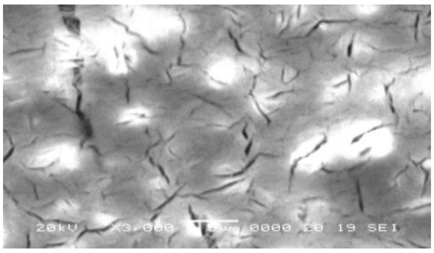


SEM of 0.1 M Zn-0.2Co alloy (b)

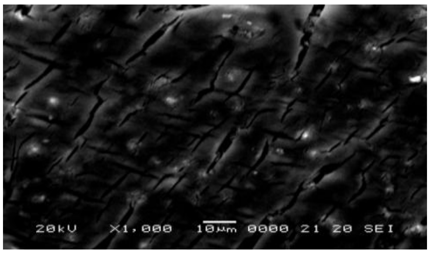


SEM of 0.1 M Zn-0.3Co alloy (c)

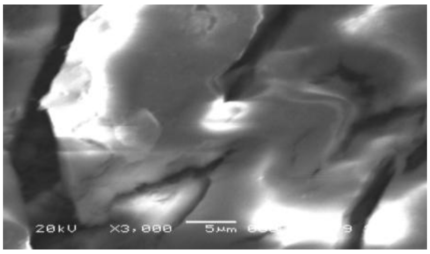
All above a,b,c SEM image in absence of inhibitor Fig.-4



SEM of 0.1 M Zn-0.1Co alloy (d)



SEM of 0.1 M Zn-0.2Co alloy (e)

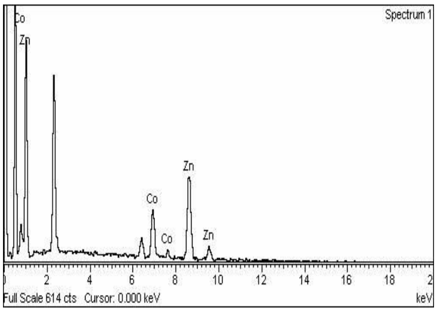


SEM of 0.1 M Zn-0.3Co alloy (f)

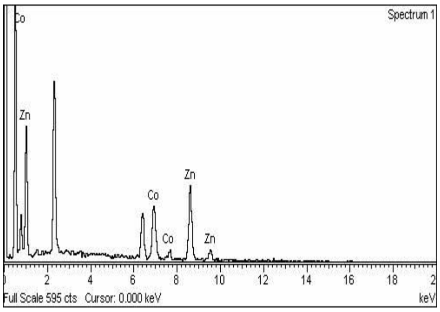
All above d,e,f SEM image in presence of inhibitor (Thiourea)

SEM images of Zn-Co alloys in absence and presence of inhibitor Thiourea at various concentration of cobalt in solution. The 1:1 ratio of Zn-Co in absence of inhibitor shows Fig.4(a) Thorn like structure, equal size of particle with homogeneous surface area and in presence of inhibitor it shows Fig.4(d) equal size of particle with homogeneous surface area. In 1:2 ratio of Zn-Co shows Fig.4(b) dendrites like structure with equal size of particle in absence of inhibitor after addition of inhibitor the SEM image of Zn-Co shows Fig.4(e) Thorn e like structure. Increasing concentration of cobalt in bath it shows smooth surface area. In 1:3 ratio of Zn-Co in absence of inhibitor and in presence of inhibitor shows Fig.4(c,f) large size of particle which tend to cover substrate surface completely.

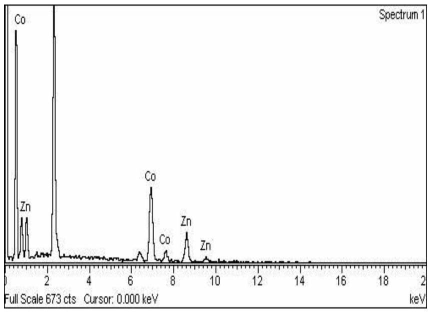
EDAX analysis shows the percentage composition of Zn-Co alloy. EDAX analysis confirm the presence of Zn-Co and atomic percentage of deposited elements(Fig.5 (above)) and (Fig.6). XRD analysis shows the structural feature of Zn-Co alloys. XRD of the electrodeposited thin film shown in (Fig.7). The peak obtained in XRD of Zn-Co compared with reference pattern of JCPDS card standard peak. Sample were index successfully to determine the crystal structure, particle size of the Zn-Co. Crystal structure of found to be Hexagonal closed packed.



EDAX of 0.1 M Zn-0.1Co alloy (a)

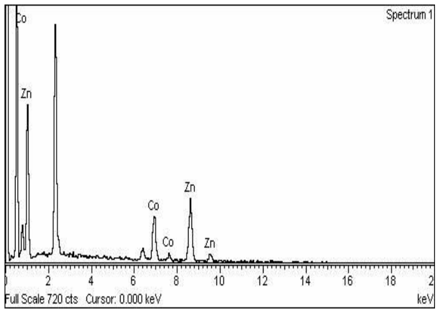


EDAX of 0.1 M Zn-0.2Co alloy (b)

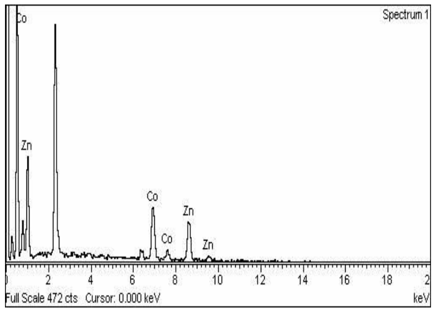


EDAX of 0.1 M Zn-0.3Co alloy (c)

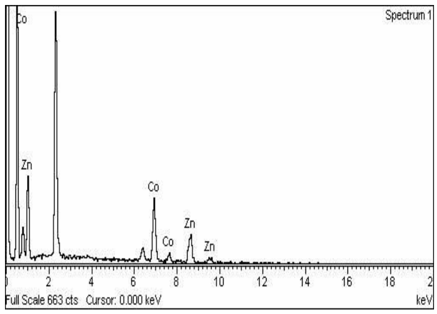
All above a,b,c EDAX data in absence of inhibitor



EDAX of 0.1 M Zn-0.1Co alloy (d)



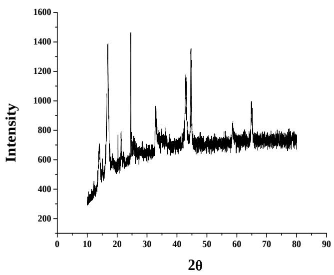
EDAX of 0.1 M Zn-0.2Co alloy (e)



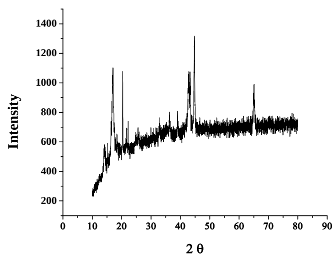
EDAX of 0.1 M Zn-0.3Co alloy (f)

All above d,e,f EDAX data in presence of inhibitor (Thiourea)

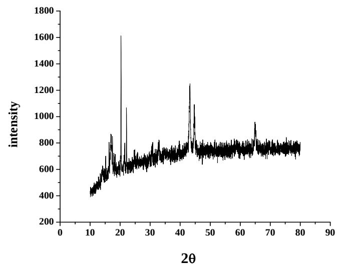
Fig.6



XRD of 0.1 M Zn-0.1Co alloy (a)

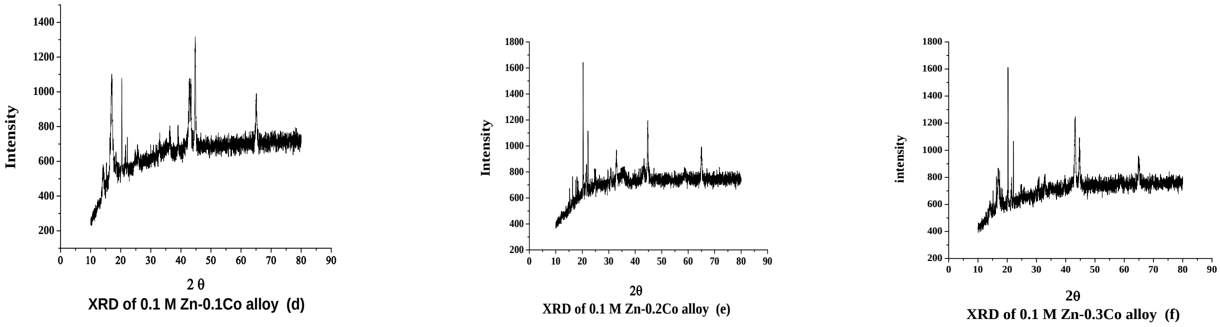


XRD of 0.1 M Zn-0.2Co alloy (b)



XRD of 0.1 M Zn-0.3Co alloy(c)

XRD data a,b,c in absence of inhibitor



XRD data d,e,f in presence of inhibitor (Thiourea)
Figure 7

4. Conclusion

Cobalt content in deposits increases with increasing the cobalt concentration in electroplating solution. The presence of Zn-Co and percentage of Zn-Co confirm the by XRD, EDAX analysis method respectively. Morphological studies of Zn-Co have been study by SEM. The presence of boric acid gives growth, perfect size of crystal and uniform arrangement of Zn-Co crystal. Corrosion rate decreases with decreasing concentration of Cobalt in bath solution. Addition of inhibitor gives better results than Zn-Co alloys absence of inhibitor

5. Acknowledgments

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