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Synthesis and Characterization of Zn-Ni Cmma Electrodeposition from Acetate Electrolytic Bath

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ABSTRACT

Compositionally modulated multilayer (CMM) coatings Zn-Ni alloy were produced on steel surface by electrochemical deposition from the acetate electrolytic bath under various cyclic cathode current densities. Multilayer deposition and its composition at different cyclic current density range are related to the corrosion resistance properties of the deposit. Anti-corrosion properties were evaluated by potentiodynamic Tafel extrapolation method in 3.5% NaCl results showed that zinc-nickel computationally modulated multilayered alloy coatings have enhanced corrosion resistant than monolayer of binary Zn-Ni alloy deposits. The Zn-Ni multilayer alloy deposit with 120 sublayers obtained at cyclic cathode current density at 2.0-3.0 A/dm^2 shows enhanced corrosion resistance and XRD confirm the presence of high intensity γ- phase.

Keywords: Compositionally modulated multilayer: Alloy electrodeposit; Corrosion rate; Current density; mild steel.

I. INTRODUCTION

Nowadays the electrodeposition of Zn-M (M=Fe, Co, Ni) group alloys are used to protect the steel components which are used in industry from the corrosion instead of pure zinc and toxic cadmium coating due to its improved corrosion resistance properties [1]. Albeit, the corrosion resistance of zinc-iron group alloys were decreased at aggressive corrosion environments. In this connection, the corrosion resistance of Zn-Fe group alloy was improved by the developing the compositionally modulated multilayered alloy (CMMA) deposit by switching the cathode current density between two potential/or current sequence. Although monolayer of Zn-Fe group alloys has the range of interest applications in the engineering sectors, the development of CMMA coatings have great interest due to the multilayer deposit has the improved properties such as hardness, mechanical strength, and corrosion resistance. Multilayer with alternate layers of two materials coated on the substrate has some specific functional properties. Numerous deposition methods such as Physical vapour deposition (PVD), Chemical vapour deposition (CVD), Sputter ion plating (SIP), Molecular beam epitaxial (MBE) and Electrochemical deposition are applied to get monolithic and multilayered coating by academic researchers as well as industrialist [2]. Among these techniques, electrodeposition technique is versatile and cost-effective one due to it can easily be handled plating parameters such as cyclic cathode current density (CCD). Multilayer deposition can be obtained by electrodeposition method in single as well as double bath technique. In a single bath technique, the electrodeposition of CMM will be carried out in a single bath itself; whereas in dual bath technique the two different baths containing different metal ion concentrations were used for the deposition, here the anode and cathode will be transferred from one bath to another bath for each switching current density. The first multilayer deposition was reported by Blum was the inventor of multilayer deposit with an alternative layer of copper and nickel [3]. The earliest single bath technique was obtained by Brenner [4]. The composition of the coating was changed progressively by tuning plating parameters such as CCCD, temperature, and agitation etc. Zn-Ni multilayered deposit has an excellent approach for improving corrosion resistance and has the commercial outstanding interest. Thangaraj *et al.* developed Zn-Ni multilayered alloy deposit with improved corrosion resistance than the coating of monolithic Zn-Ni alloy deposit obtained at the same chloride electrolytic bath [5]. Ivanov and Kirilova (2003) developed a Zn-Ni CMMA deposit from the sulfate-chloride bath with improved corrosion resistance with alternating Ni composition [6]. Rao *et al.* prepared the Zn-Ni CMMA deposit from the chloride bath and they resulted out the CMMA with 300 layers shown the high corrosion resistance and about 35 times are higher than Zn-Ni monolithic alloy coating [7]. Pavithra & Chitharanjan Hegde developed the Fe-Ni alloy deposit and they concluded that an improved corrosion property of CMMA coatings were due to the changes of an intrinsic electrical property of the multilayer [8]. Rashmi *et al.* developed Zn-Ni CMMA obtained from sulfate bath by cyclic cathode current density of 3.0-5.0 A/dm^2 with 60 sublayers shows the best corrosion resistance and about three times more than the single monolithic coating [9]. Although, Zn-Ni multilayered alloy deposit deposited from various electrolytic bath such as sulfate, chloride bath [10] reported that the Zn-Ni CMMA deposit obtained from acidic chloride bath with 20 wt% Ni does not show any red rust formation with prolonged time of 400 h and also confirm the presence of γ-phase in the alloy deposit, but no attempt have been given for the CMM Zn-Ni multilayer deposit from acetate electrolytic bath. Hence in this present investigation, the deposition conditions for Zn-Ni multilayered alloy deposits were developed by cycling the cathode current density between two current densities at a particular time interval of 10 minutes in an acetate electrolytic bath. The periodic change in the current density (c.d.) allows the growth of layers on a substrate with a periodic change in the chemical compositions. The main focuses are given to develop the new electrolytic bath and to optimize cyclic cathode current density for obtaining best corrosion resistance multi-layered coating to mitigate the corrosion damage in the industry regarding ferrous materials. Here the number of layer was changed by properly tuning the CCCD's to get the deposit with desired properties and where the pH kept as a constant and the deposits was characterized by the following test such as SEM, EDAX, XRD, Tafel Polarization to know the corrosion properties of the deposit.

II. EXPERIMENTAL

The bath composition used to deposit Zn-Ni multilayer alloy are in analytical grade of acetate electrolytic bath. Mild steel substrate with 5.0 X 2.5 cm^2 sizes was used as a cathode for Zn-Ni multilayered alloy deposit with the use of Zinc as an anode. All the deposition parameters kept as constant for optimization of cyclic current density. For optimizing the cathode current density, before the deposition, the mild steel panel were pre-treated mechanically polishing with successive grade emery paper (400, 600, 800, 1200, 2000 grits) and followed by electro cleaned cathodically for two minutes and anodically for one minute using the electro-cleaning solution containing 35 g/L NaOH and

25 g/L Na_2CO_3. After the electro cleaning, the surface of the steel was activated by using 30% HCl and immediately the pretreated substrate was subjected to electrodeposition by keeping the substrate in a electrolytic bath containing zinc and nickel constituent and the deposition were carried out in computer-controlled potentiostat / galvanostat (Biologic science instrument model no SP240). The two current density was chosen arbitrarily to fix the optimized CCCD's shown in Figure 1. After the deposition was done the multilayered Zn-Ni alloy deposit was examined by SEM, EDX and XRD and Tafel polarization for the study of surface morphology, composition, and phase nature of the Zn-Ni multilayered alloy deposit.

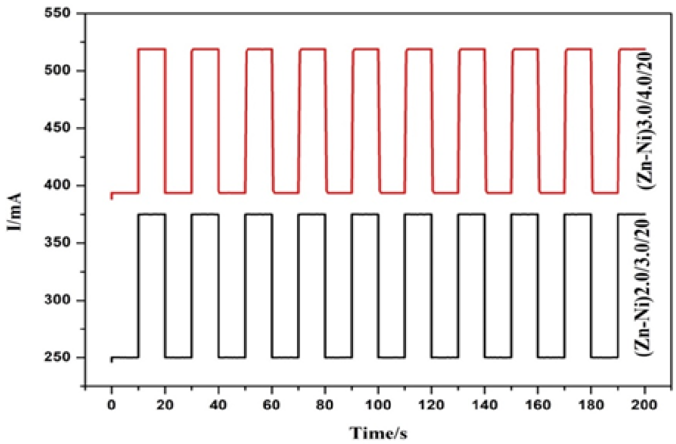

Fig 1. Model diagram for CMM of Zn-Ni alloy deposited by cycling the cathode current density between two current densities

Corrosion properties Zn-Ni multilayered alloy deposit was carried out by potentiodynamic polarization technique in 3.5 % NaCl using a potential ramp of ± 250 mV from open circuit potential (OCP) at a scan rate of 1mV per second and impedance behaviour of the deposit was analyzed by using the Electrochemical Impedance Spectroscopy (EIS).

III. RESULTS AND DISCUSSION

3.1 Cyclic Cathode Current Density (CCCD)

In order to get the uniform deposition, CCCD are optimized by varying the current density between 2.0-3.0 A/dm² and 3.0-4.0 A/dm² with 20 sublyers. From the results, the deposit obtained at CCCD's 2.0-3.0 A/dm² with 20 sublayers shows better peak performance against corrosion. Therefore, the cccd's of 2.0-3.0 A/dm² were selected as an optimized CCCD for further studies of the same with different number of sublayers.

3.2 Hardness Studies of Zn-Ni CMMA Alloy Deposit

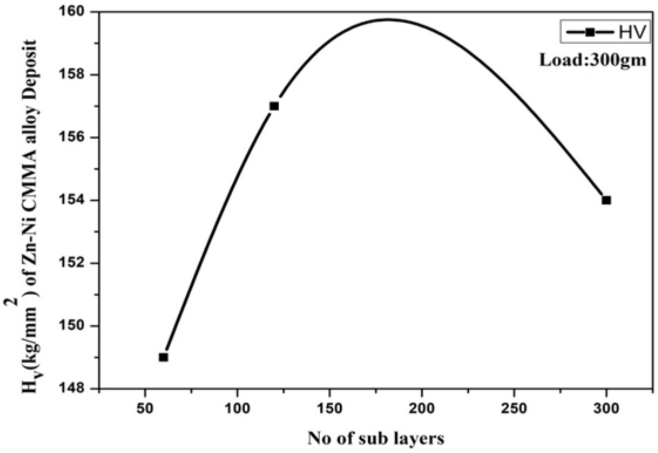

Fig 2. Vickers hardness of the Zn-Ni CMMA electrodeposit at Cyclic Cathode Current density 2.0-3.0 A/dm2 with 60,120 and 300 sublayers

Figure 2. Shown the hardness of the Zn-Ni CMMA deposit with 60,120 and 300 sublayers at cyclic cathode current density 2.0-3.0 A/dm². The Zn-Ni CMMA deposit with 120 sublayers shows the highest hardness value which is higher than the deposit obtained monolithically by direct current electrodeposition technique.

3.3 Corrosion Studies

The potentiodynamic Tafel polarization extrapolation studies are carried out for the entire Zn-Ni CMMA deposited samples to test the corrosion resistance of the Zn-Ni multilayered deposit with applying anodic polarization ramp at ±250 mV vs. OCP in 3.5% NaCl solution at scan rate 1mv/s. The results show that the lowest corrosion rate of Zn-Ni multilayer deposit obtained at CCCD's of 2.0-3.0 A/dm^2 with 120 sublayers and shown in table 1. From the Figure 3 all the zinc-nickel multilayered alloy deposit shows more negative corrosion potential than steel which indicate the sacrificial behaviour of the deposit and the zinc-nickel alloys obtained at optimized switching cathode current density with more sublayers shows more negative potential than the monolithic deposit obtained at the same acetate electrolytic bath which indicates the sacrificial action of zinc with preferential dissolution of zinc in the multilayered alloy deposit. The CMMA deposit with 120 sublayers shows the lowest corrosion rate than CMMA deposit of zinc-nickel alloy with 20, 60,300 and 600 sublayers. From these, the CMM Zn-Ni alloy deposited at CCCD's of 2.0-3.0 A/dm^2 with 120 sublayers has fixed as the desired one due to the lowest corrosion rate and beyond the 120 layers the corrosion rate was increased it may be due to the monolithic nature was developed may due to the interdiffusion of layers has occurred. This monolithic enhances to reach the corrosive medium to the substrate so highest corrosion rate. However, all the deposit of Zn-Ni CMMA has the lowest corrosion rate than the monolithic coating obtained by direct current method. Electrochemical impedance spectroscopy (EIS) of Zn-Ni CMMA deposit at optimized CCCD's with a different number of multilayers is shown in Figure 4. From the EIS capacitance loop with large semicircle confirm the high impedance due to the formation of the dielectric film in the interfacing layers due to the dezincification. This large semicircle corresponds to the charge transfer resistance. The largest semicircle of zinc-nickel CMMA deposited deposited at CCCD's of 2.0-3.0 A/dm^2 with 120 sublayers shows the lowest corrosion rate these results also supported by Tafel corrosion studies. Zn-Ni CMMA deposit with 20, 60,120,300 and 600 sublayers follow the anomalous deposition mechanism. At optimized CCCD's with 120 sublayers, the deposit showed improved corrosion resistance is due to modified composition with a different weight percentage of Ni in the subsequential layers.

Table 1. Corrosion properties of Zn-Ni multilayered alloy coatings at various CCCD's (with 20, 60,120,300,600 sublayers).

CCCD: A/dm^2	Number of Sublayers	$-E_{corr}$(V) Vs SCE	Corrosion Rate(mpy)
(Zn-Ni)2.0/3.0	20	1.098	2.97
(Zn-Ni)3.0/4.0	20	1.101	3.48
(Zn-Ni)2.0/3.0	60	1.106	2.08
(Zn-Ni)2.0/3.0	120	1.110	0.61
(Zn-Ni)2.0/3.0	300	1.156	1.87
(Zn-Ni)2.0/3.0	600	1.177	2.27

3.2 XRD Analysis

XRD pattern of Zn-Ni multilayered alloy deposit at different switching cathode current densities from the acetate electrolytic bath shown in Figure 8. The results reveals that significant improvement in the properties was obtained it may be due to the phase change with the changes of composition in the Zn-Ni multilayered alloy deposit. The strongly oriented Zn-Ni γ-phase was obtained at cyclic cathode current density (Zn-Ni)3.0/4.0/120 sublayers of the deposit. When the weight percentage of Ni is greater than 10 % the γ-phase was observed as a dominant phase.The γ phase intensity of (103) plane was increased for Zn-Ni CMMA with 120 sublayers and other planes such as (100) and (102) was reduced which indicate the γ phase predominant in the CMMA Zn-Ni alloy deposit and less chances to develop the potential difference that is local cell formation so the deposit with 120 sublayers show the lowest corrosion rate.

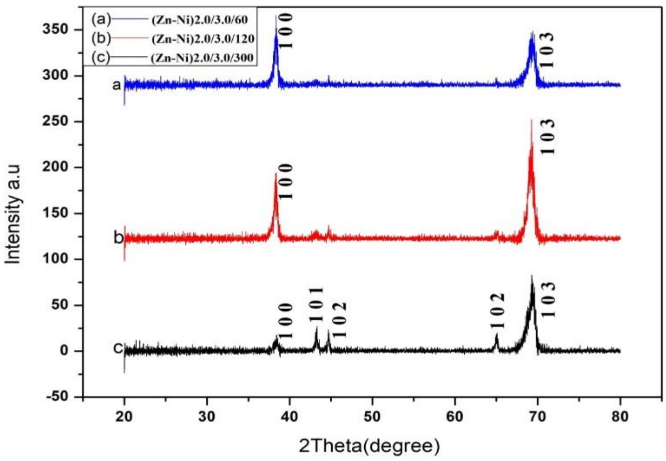

Fig 1. XRD analysis of Zn-Ni CMMA alloy deposit with 60,120 and 300 multilayer (Reference pattern no. 00-004-0831)

IV. CONCLUSION

Zn-Ni multilayered alloy coating obtained at optimized cyclic cathode current density of 2.0-3.0 A/dm^2 with 120 sublayers displayed the enhancement corrosion resistance in 3.5% NaCl medium than deposit obtained with 20, 60, 300 and 600 sublayers. It concluded due to the formation of alternate layers of the deposit with different weight percentage of nickel and different phase nature present in the Zn-Ni multilayered alloy deposit. When the noble metal percentage in the multilayered alloy deposit was increased the deposit behaves barrier between the metal and electrolytic environment and it shows the highest peak performance against corrosion. From the different surface morphology of SEM image confirms the Zn-Ni multilayer deposit formed with a different composition. The highest xcorrosion protection efficiency of multilayer coatings is due to the barrier effect with high wt.% Ni, and sacrificial effect of layers with less wt.% Ni. Newly developed acetate electrolytic bath was a suitable one to develop the Zn-Ni multilayered alloy deposit for the protection of ferrous metal from the severe corrosion environment.

V. REFERENCES

[1]. Ghaziof, S & Gao, W 2014 'Electrodeposition of single gamma phased Zn–Ni alloy coatings from additive-free acidic bath, Applied Surface Science,vol.311, pp.635-642.

[2]. Yogesha, S & Chitharanjan Hegde, A 2011 'Optimization of deposition conditions for development of high corrosion, resistant Zn–Fe multilayer coatings', Journal of Materials Processing Technology , vol.211,pp.1409-1415.

[3]. Blum, W 1921 'The structure and properties of alternately electrodeposited metals', Transactions of the American Electrochemical Society, vol. 40, pp. 307- 320.

[4]. Brenner, A 1963 'Electrodeposition of alloys', New York, Academic Press, vol.2, p.194.

[5]. Thangaraj, V, Ravishankar, K & Chitharanjan Hegde, A, 2008, 'Surface Modification by Compositionally Modulated Multilayered Zn-Fe Alloy Coatings ', Chinese Journal of Chemistry, vol.26, pp.2285-2291.

[6]. Ivanov, I & Kirilova, I 2003, 'Corrosion resistance of compositionally modulated multilayered Zn–Ni

alloys deposited from a single bath', Journal of Applied Electrochemistry, vol.33, pp.239–244.

[7]. Rao, VR, Chitharanjan Hegde, A & Udaya Bhat, K 2013 'Effect of heat treatment on structure and properties of multilayer Zn-Ni alloy coatings',Journal of Electrochemical Science and Engineering,vol.3 (4), pp. 137-149.

[8]. Pavithra, GP & Chitharanjan Hegde, A 2013, 'Production of Layered Coatings of Fe–Ni Alloy for Enhanced Corrosion Protection, Surface Engineering and Applied Electrochemistry', vol. 49(3), pp. 261–266.

[9]. Rashmi, S, Elias, L, & Chitharanjan Hegde, A 2017 'Multilayered Zn-Ni alloy coatings for better corrosion protection of mild steel, Engineering Science and Technology, an International Journal, vol.20 pp. 1227–1232.

[10]. Ganesan, P, Kumaraguru, SP & Popov, BN 2007, 'Development of compositionally modulated multilayer Zn-Ni deposits as replacement for cadmium', Surface and Coatings Technology, vol.201, pp.7896–904.

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