An executive summary of the final report of the work done on the Minor Research Project of **Dr. Pavithra G P** entitled **"Electrodeposition and characterization of nanostructured zinc-nickel alloy: correlation between corrosion and dielectric properties"**sanctioned by UGCvide sanctioned letter no. **1438-MRP/14-15/KAMA002/UGC-SWRO** dated **04-Feb-15.**

Executive Summary Of The Report:

Surface engineering is the sub-discipline of materials science which deals with the surface of solid matter. It has applications to chemistry, mechanical engineering, and electrical engineering etc. Surface engineering involves altering the properties of the surface phase in order to reduce the degradation over time. This is accomplished by making the surface robust to the environment in which it will be used. One branch which represents the diverse nature of surface engineering is Electroplating Technology. The present work details the optimization of deposition conditions for development of nanostructured multilayer Zn-Ni alloy coatings onto mild steel (MS) for better corrosion resistance, using square current pulses. The project details optimization of a new electrolytic bath using glycerol and gelatine, as additives. The bath constituents and deposition conditions were optimized for peak performance of monolayer Zn-Ni alloy coatings (developed using direct current) against corrosion followed to the development of multilayer alloy coatings, represented as CMMA Zn-Ni, from the same bath by cyclic modulation of composition using square current pulses. The corrosion performances of CMMA Zn-Ni coatings are found to be improved many fold with increase in number of layers, up to an optimal level, and then decreased. The cyclic cathode current densities and number of layers for CMMA Zn-Ni coating have been optimized for peak performance against corrosion. The corrosion behaviours of all coatings are evaluated by Tafel's extrapolation, Electrochemical Impedance Spectroscopy (EIS), and cyclic polarization methods.

Deposition of monolayer Zn-Ni alloy

Different types of Zn-Ni alloy formed on Hull cell panel showed that current density (c.d.) bears a strong relation with the deposit characters, in terms phase structure consequent to noble metal content. Monolithic (monolayer) Zn-Ni alloys were developed galvanostatically on to pre-cleaned mild steel (MS) at different c.d.'s and were tested. The effects of c.d. on wt. % Ni, thickness, corrosion resistance and appearance of the coatings were reported. The corrosion data showed that at 4.0 A/dm^2, the coating shows least corrosion rate (20.9×10^{-2} mm y^{-1}) with bright appearance and was taken as its optimal corrosion rate. The least corrosion current (i_{corr}) value of the coating deposited at 4.0 Adm^{-2}, having ~ 8.07 Ni, revealed that (gelatine + glycerol) modified the deposit character by their preferential deposition on the cathode.

Optimization of cyclic cathode current densities (CCCD's)

By proper manipulation of cathode current densities (CCCD‟ s) it is possible to develop alternate layers of alloys with different compositions to exhibit advanced material properties. In other words, by interposing distinct interface between layers it is possible to improve the properties of nanocoatings. Hence multilayer coatings having different combinations of CCCD's may have to develop for optimizing the coating configuration for best performance. Hence, to begin with multilayer coatings having 10 layers were developed at different set of CCCD's to increase their corrosion resistance. Among the various sets tried, the less corrosion rate was reported in the coatings produced at difference of 2.0A/dm^2 between CCCD's.

Optimization of overall number of layers

Various material properties of CMA coatings, including their corrosion resistance, may often be increased substantially by increasing the degree of layering (usually, up to a certain limit), without sacrificing the demarcation between each layers. Therefore, one set of CCCD such as 1.0/3.0 has been selected for layering. Zn-Ni CMA coatings with 10, 30 and 60 layers were developed; and their corrosion rates were measured by Tafel's extrapolation method. The corrosion rate (CR) of coatings was found to decrease with number of layers in each set of CCCD‟ s as shown in **Table 1**.

Table 1: *Decrease of Corrosion rate (CR) of CMA Zn-Ni Coatings with increase of layers*Optimization of layer thickness of CCCD"s of 1.0/3.0.

CCCD's A/dm^2	Number of layers	$-E_{Corr}$ mV vs SCE	I_{Corr} μA/cm^2	CR×10^{-2} mmy^{-1}
$(Zn\text{-}Ni)_{1.0/3.0/10}$	10	1004.2	11.0	14.8
$(Zn\text{-}Ni)_{1.0/3.0/30}$	30	874.0	8.2	11.7
$(Zn\text{-}Ni)_{1.0/3.0/60}$	60	809.0	5.3	7.1

However, at 1.0/3.0 A/dm^2, the coating with 60 layers showed minimum CR of 7.1 x 10^{-2} mmy^{-1} relative to 20.9 x 10^{-2} mmy^{-1} for monolithic Zn-Ni alloy coatings. $(Zn\text{-}Ni)_{1.0/3.0/60}$ has been proposed as the optimal configuration of CMA coating from the proposed bath for peak performance against corrosion.

Tafel's polarization study

The polarization behavior ofmonolithic Zn-Ni coatings developed at different current densities are shown in Fig. 1 and it shows the increase in corrosion resistance with increase in c.d. from 1 A/dm^2 to 4 A/dm^2.

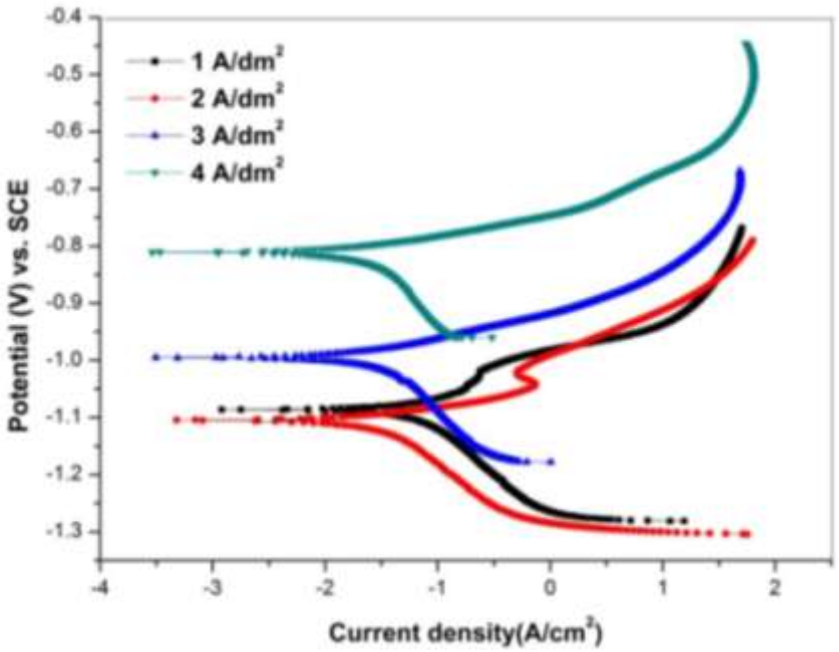

Fig 1 - *Potentiodynamic polarization curves of monolithic Zn-Ni coatings developed at different current densities.*

The polarization behavior of $(Zn\text{-}Ni)_{1.0/3.0}$ CMA coatings with different degree of layering are shown in Fig. 2.It was observed that the corrosion resistance of the coatings increased with number of layers as evidenced by their i_{corr} values, reported. Further, the progressive decrease of corrosion current (icorr) with number of layers indicated that improved corrosion resistances are due to layering of alloys, having distinctive properties. Polarization curve shown in Fig.2. indicates that CMA coating with $(Zn\text{-}Ni)_{1.0/3.0/60}$

configuration is the most corrosion resistant. Fig 1 shows the polarization behavior of monolithic Zn-Ni coatings at different current densities.

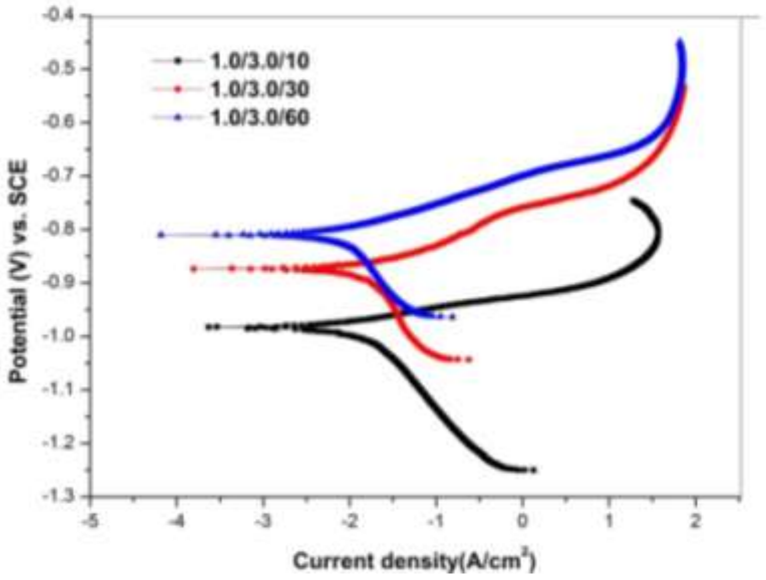

Fig.2. *Potentiodynamic polarization curves of CMA (Zn-Ni)1.0/3.0 coating with different number of layers*

Electrochemical impedance spectroscopy (EIS)

EIS, also referred to as AC impedance spectroscopy is a suitable technique to gain valuable information on the capacitance behavior of double layer responsible for improved corrosion resistance of the coatings and behavior of inhibitors. In this technique, it is common to plot the data as imaginary impedance versus real impedance with provision to distinguish the polarization resistance contribution (Rp) from the solution resistance (Rs).

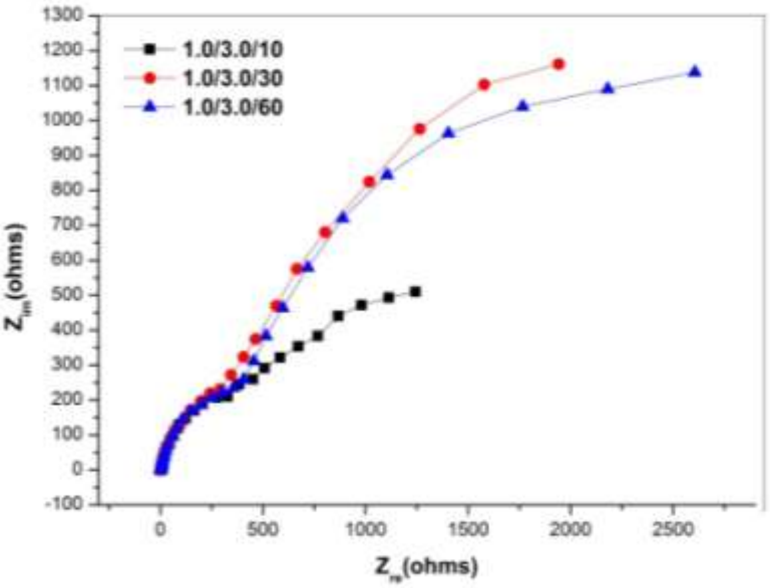

Fig. 3 - *Nyquist plots of CMA (Zn-Ni)$_{1.0/3.0}$ coatings having different number of layers*

These plots are often called Nyquist diagrams. Nyquist diagrams of (Zn-Ni)$_{2.0/5.0}$ and (Zn-Ni)$_{3.0/5.0}$ coatings with different number of layers were studied. Impedance signals showed in Fig 3 clearly indicates that the capacitance of the double layer has decreased progressively with increase of number of layers.

CONCLUSIONS

A stable Zn-Ni bath was proposed for deposition of bright, uniform coatings of Zn-Ni on to MS. Both monolayer (using DC) and multilayer coatings (using square pulsed direct current) have been developed from optimal bath. Layering of alloys at different set of CCCD's was done. Based on the experimental investigation carried out monolayer and multilayer Zn-Ni alloy coatings,the increased corrosion resistance of multilayer coating is due to increased surface area, due to layering.

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