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Development of Nanostructure Multilayer Co-Ni Alloy Coatings for Enhanced Corrosion Protection

G. P. Pavithra and A. Chitharanjan Hegde*

Electrochemistry Research Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Srinivasnagar-575 025, India

*Corresponding Author, Tel.: + 91-9980360242; Fax: +91-824-2474033

E-Mail: achegde@yahoo.in

Abstract-Nanostructure multilayer alloy coatings (NMAC) of Co-Ni were developed on copper in layered manner using different current pulses. NMAC of Co-Ni was deposited galvaostatically from acid sulphate bath under different combination of cyclic cathode current densities (CCCD's) and number of layers. Corrosion behaviors of coatings were evaluated in 1 M hydrochloric acid, as representative corrosion medium. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) study revealed that NMAC (Co-Ni) 2.0/4.0/6.0/60/three exhibits~160 times better corrosion resistance than monolayer coating, deposited from same bath for same time. Better corrosion protection was attributed to the increased effect of interface, arising from the exceptional thinness of the layers. As composition of alloys in successive layers were varied, consequent to the deposition current density (c.d.), the change in phase structure of the deposits were observed, confirmed by X-ray diffraction (XRD) study. Layer formation and surface after corrosion tests were examined by scanning electron microscopy (SEM) and optical profilometer, and reasons responsible for better protection were analyzed.

Key words- Layered Coating, Co-Ni Alloy, Corrosion Behavior

1. INTRODUCTION

The development of nano-structured materials is a subject of increasing interest in the protection, prevention and controlling of corrosion. One of the emerging areas in nano-structured materials research is electrodeposition of metals/alloys with a spatially periodic composition in one dimension, and they are called nanostructured multilayer alloy (NMAC) coating [1]. These coatings with thin layers of pure metals/alloys show wide range of applications owing to their unique technological properties, different from pure metals and homogenous alloys. Promising mechanical strength, wear, elasticity, ductility, electrical, optical and corrosion properties have been reported [2]. In addition, due to the increased effect of surface, or interface arising from the exceptional thinness of the layers, there can be large deviations from bulk behavior, and leads to totally new properties to multilayer coatings. The composition and thickness of each individual layer can be manipulated to optimize the desired property of the deposit or coating. The overall property of the deposit is then a function of the individual components, the modulation thickness, as well as the structure of the interface. In so-called single bath technique (SBT) the composition modulation in the deposit is achieved with the modulation in either current, or potential. The bath compositions applied are usually very similar to those developed for monolayer alloy coatings using direct current (d. c.). However, modulation in composition can be effected using different types of power pattern, depending on type of gradation [3].

Substantial amount of work have already been reported to support the enhanced corrosion resistance of CMMA coatings of Zn-M (where M=Fe, Co and Ni) alloy using SBT. Recently, development of multilayered Zn-Ni alloy coatings, using square current pulses for improved corrosion resistance have been reported [4,5]. But no work is reported with regard to development of corrosion resistant multilayer Co-Ni coatings using two and three current pulses. In this paper, we optimize the deposition conditions for development of layered coatings of Co-Ni alloy on copper using two and three current pulses successively; while demonstrating the better corrosion protection of the coatings due to increased effect of interface, arising from the exceptional thinness of the layers.

2. MATERIALS AND METHODS

Plating solutions were prepared from reagent grade chemicals and distilled water. Electroplating was carried out at pH 3.5 and temperature was maintained at 303 K. Copper panels having an exposed area of 7.5 cm^2 were used as cathode, and pure nickel plate having same exposed anodic area. The copper substrates were polished mechanically and then cleaned electrochemically. An acid sulfate bath having composition: cobalt sulfate (14 g L^{-1}),

nickel sulfate (131 g L^{-1}), boric acid (30 g L^{-1}), L-Ascorbic acid (8 g L^{-1}), and sulphanilic acid (1 g L^{-1}), was used as the electrolyte.

All coatings, viz. monolayer and NMAC's were accomplished for 10 minutes using sensitive power source (N6705A, Agilent Technologies), and their corrosion protection efficacy were compared. Electrochemical studies were made using Potentiostat/Galvanostat (VersaSTAT[3], Princeton Applied Research) in a three-electrode cell using a saturated calomel electrode (SCE), as reference electrode. The corrosion behaviors of the coatings were evaluated in 1 M hydrochloric acid medium by potentiodynamic polarization and EIS method. Polarization study was made in the potential limit of ±250 mV from open circuit potential (OCP), at scan rate of 1 mV s^{-1}. EIS study was carried out in the frequency range, from 100 kHz to 10 mHz with perturbing signal of 10 mV. Scanning Electron Microscopy (SEM), interfaced with Energy dispersive X-ray (EDX) facility (Model JSM-6380 LA from JEOL, Japan) was used to examine the layer formation and compositions of layers formed, respectively. The phase structures of the coatings were identified with X-ray Diffractometer (XRD) (JEOL JDX-8P), using Cu Kα (λ=1.5406 Å) radiation in continuous scan mode at scan rate of 2° min^{-1}. 3-dimensional images of the coatings were carried using optical profilometer (Wyko, Model-NT9100).

The objective of improving the corrosion resistance of multilayer alloy coatings are guided by the principles*: 1.Successive change in current density (c.d.) allows the growth of layers having successive change in its chemical composition. 2. Formation of distinct interface is due to different noble metal content of the alloy, deposited at different c. d's. 3. Better corrosion protection of multilayer coatings are due to increased effect of interface, arising from the exceptional thinness of the layers.* Having guided by the above principles of nanostructured multilayer coatings, the NMAC's of Co-Ni were deposited using square current pulses, by making the current density to cycle between two and three values.

Thus the instrument was set to cycle between two and three different cathode current densities, called cyclic cathode current densities (CCCD's). The power pattern having two and three current pulses used in the present layered coatings is shown in Fig. 1. The thickness of each layer was controlled by the duration of each current pulse; and total number of layers was fixed by adjusting time for each cycle. Thus, NMAC's of different configurations were produced. Such nanostructure multilayer alloy coatings are hereafter represented as (Co-Ni)$_{1/2/n,}$ where (Co-Ni) represents alloy of cobalt and nickel, and 1 and 2 represent cathode c.d. that is made to cycle, and 'n' represents the number of layers formed in total time of deposition(10 min).

3. RESULTS AND DISCUSSION

3.1. Monolayer Co-Ni alloy coatings

It should be noted that in the present Co-Ni alloy bath, the wt. % of nickel and cobalt in the bath are found to be 91 and 9, respectively. Neglecting a small deviation, an increase in nickel wt. % in the deposit was observed with increasing applied c.d., this is supported by the deposition principle of mutual alloys of iron-group metals. i.e., an increase in the c.d. or temperature results in an increase of more noble metal in the deposit [6]. Hence it may be inferred that, the bath follows anomalous type of codeposition of Co^{+2} and Ni^{+2} ions at all conditions of c.d. employed in this study.
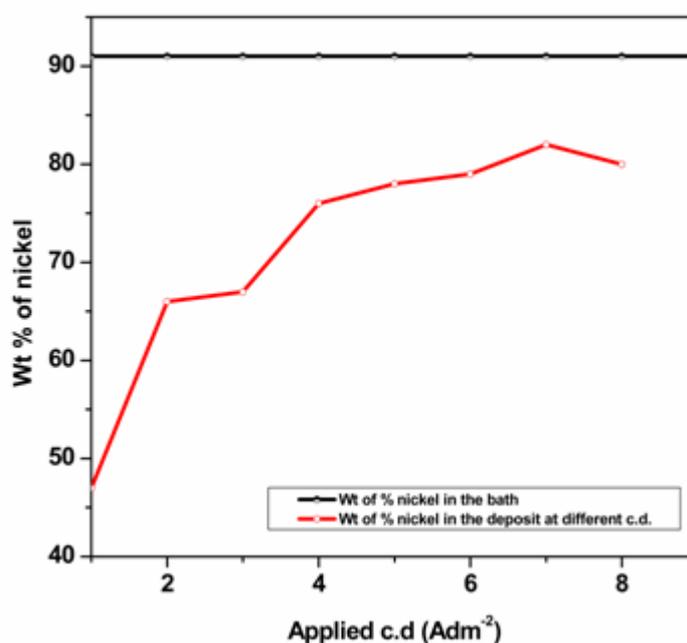

Fig. 1. Variation in wt. % nickel in the deposit with c.d., deposited from optimal Ni-Co bath at 303 K and pH=3.5

Further, it was observed that at c.d. larger than 2.0 A dm^{-2}, the wt.% of nickel in the deposit was found to increase with c.d. At 4.0 Adm^{-2}, the bath produced a sound and bright deposit having ~76 wt. of %Ni. This increase of nickel wt.% with c.d. indicates that the deposition process is tending towards normal type, as shown in Fig. 1. The crystal orientations of electrodeposited Co-Ni alloys at different applied c.d. were characterized by XRD analysis. The identification of the phases of the deposits was obtained from the peak profiles of the X-ray reflection plotted as a function of 2θ as shown in Fig. 2.
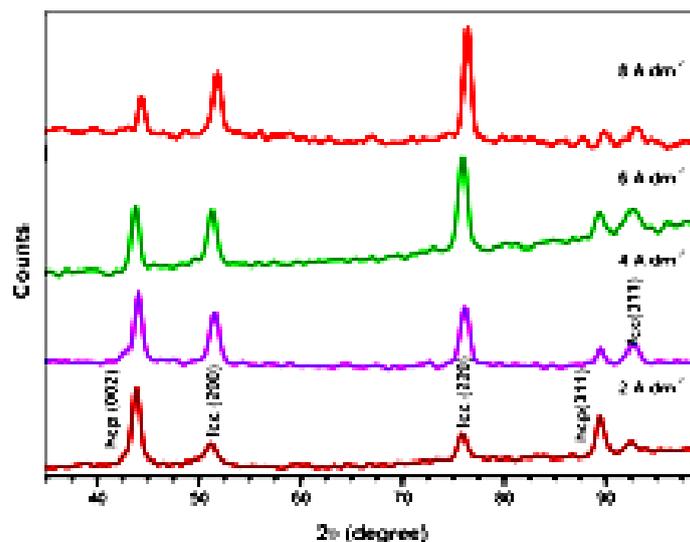
Fig. 2. X-ray diffraction patterns of Ni-Co alloys electrodeposited from the optimized bath at different c.d.'s

With no exception to mutual alloys of Fe-group metals, the electrodeposited NMAC's explores the potential use of nanotechnology in corrosion control [7]. i.e. a small change in the deposition c.d. and layer thinness were found to bring significant change in the corrosion behavior of the coatings. It is supported by the difference in phase structure of the coatings in alternate layers, evidenced by XRD peaks shown in Fig. 2. It is observed that the intensities of hcp peak decreases while the fcc peak increases as the c.d. has increased, as function of increased nickel content in the alloy. XRD signals of Co-Ni coating at 2.0 Adm^{-2} showed hcp predominant phase related to Co crystal structure. As cathode c.d. increased, the wt. % of nickel in the deposit increases, accordingly an increase in fcc phase structures was observed. The XRD signals corresponding at 4.0 Adm^{-2} shows a mixed crystalline structure domination of fcc and hcp phase structure. In this mixed crystalline structure, the cobalt content tends to decrease and nickel content tends to increase. Nickel being nobler compared to cobalt, a decrease of corrosion rate (CR) was observed, shown in Table1. But, further increase of c.d. resulted in decrease of CR. This is attributed to high porosity of the coatings, due to increase in nickel content of the deposit. Therefore, cathode c.d. as tool for modulation in composition, NMAC's of Co-Ni was deposited using successively two and three current pulses, and experimental procedure for optimization of deposition conditions is illustrated below.

3.2. Deposition of layered Co-Ni alloy coatings

3.2.1. Optimization of cyclic cathode current densities (CCCD's)

After deposition of monolayer Co-Ni alloy using direct current, the layered Co-Ni coatings were deposited at different set of c.d's, known as CCCD's. To optimize the CCCD's, the coatings with 10layers (arbitrarily chosen) were developed, and the one showed the least CR was considered for further layering. Among the various sets tried, the less CR was observed in the coatings at 2.0-4.0 A dm^{-2} and 2.0-4.0-6.0 A dm^{-2} as reported in Table 2. Hence, same has been taken as optimal CCCD's for further thinning of layers.

Table 1. Effect of current density on the deposit characters of monolayer Co-Ni coatings

c.d. /A dm^{-2}	$-E_{corr}$ /V *vs.* SCE	i_{corr} /μA cm^{-2}	CR /mm y^{-1}
1. 0	0.6759	2297.8	25.56
2. 0	0.6442	1974.9	21.97
3. 0	0.6259	1816.3	20.20
4.0	0.5838	1586.1	17.64
5.0	0.5138	1770.8	19.70
6.0	0.4638	1843.5	20.50
7.0	0.4438	1986.7	22.10
8.0	0.5123	2178.9	24.23

3.2.2. Nano-structuring of layers

The properties of NMAC's including their corrosion behavior can be improved by increasing number of interfaces with successive deposition of layers with distinct interface. The modulations in deposition current density thus interpose more number of interfaces. After optimizatoinof CCCD's, the NMAC of Co-Ni have been developed with n=20, 60, and 75 etc. It was found that that in both two and three current pulses, the corrosion protection efficacy of the coatings decreased with increase in number of layers only up to n=60, and then increased as reported in Table 3. Further, in case of three current pulses, the alloy coating was found to be more corrosion resistant than the one developed using two current pulses. It is attributed to the combined effect of increase in the number of interfaces, due to three pulses and composition of layers. The average thickness of the each layer under optimal condition of n=60 was found to be ~120 nm.

3.3. Potentiodynamic polarization studies

The corrosion data of layered coatings of Co-Ni alloy with different number of layers, reported in Table 3 shows that the CR decreases as the degree of layering increased. But at very high number layers, i.e. when n=75 the corrosion rate was found to be decreased. The potentiodynamic polarization curves corresponding to the coatings with different number of layers are shown in Fig. 4. It may be observed that the corrosion current, i_{corr} is found to be decreased with increase in the number of layers, and then increased, when n=75. The decrease of CR at higher degree of layering may be attributed to the less relaxation time for redistribution of metal ions (Co^{2+} and Ni^{2+}) at the diffusion layer, during deposition. At high degree of layering, the deposition time for each layer is very small. With the result, the metal ions could not relax (against the influence of applied c.d.), and get deposit on cathode with changed composition [8]. In other words at higher degree of layering the deposit is tends to become monolayer, due to exceptional thinning of layers. From Table 3, it is observed that (Co-Ni) $_{2.0/4.0/60}$ and (Co-Ni)$_{2.0/4.0/6.0/60}$ coating shows respectively ~88 and ~160 times better corrosion resistance than (Co-Ni) $_{4.0 A dm}{}^{-2}$ alloy coatings.
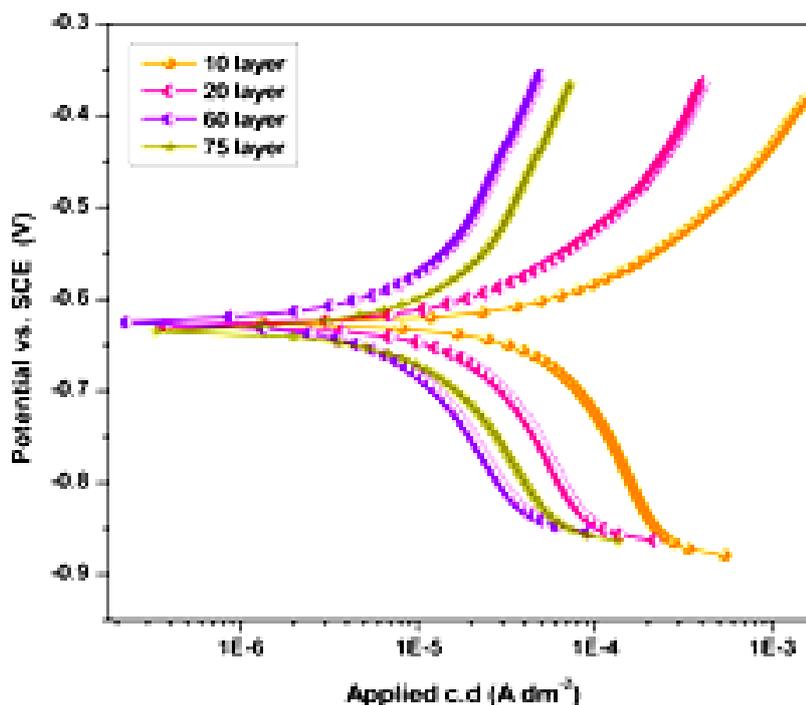

Fig. 3. Polarization behavior of CMMA (Co-Ni) coating deposited using three current pulses having different number of layers

Table 2. Corrosion rates of layered Co-Ni coatings at different set of CCCD's (with 10 layers each)

Coating configuration	$-E_{corr}$ *vs.* SCE V	i_{corr} /μA cm^{-2}	corrosion rate (CR) mm y^{-1}
CMMA coatings using dual pulses			
2 A dm^{-2} difference			
(Co-Ni)$_{2/4}$	0.647	185.3	2.06
(Co-Ni)$_{4/6}$	0.677	230.9	2.56
(Co-Ni)$_{6/8}$	0.687	313.7	3.49
(Co-Ni)$_{3/5}$	0.597	370.1	4.11
4 A dm^{-2} difference			
(Co-Ni)$_{2/6}$	0.511	297.5	3.30
(Co-Ni)$_{4/8}$	0.582	381.0	4.23
(Co-Ni)$_{3/7}$	0.647	596.0	6.63
CMMA coatings using triple pulses			
2 A dm^{-2} difference			
(Co-Ni)$_{2/4/6}$	0.625	62.9	0.70
(Co-Ni)$_{1/3/5}$	0.642	144.2	1.60
(Co-Ni)$_{3/5/7}$	0.682	173.5	1.93
(Co-Ni)$_{4/6/8}$	0.605	234.5	2.60
3 A dm^{-2} difference			
(Co-Ni)$_{2/5/8}$	0.650	187.1	2.08
(Co-Ni)$_{1/4/7}$	0.632	202.8	2.25

The improved corrosion resistance of layered coatings may also be explained in terms failures like pores and crevices occurring in the single layer, which will be covered by the successively deposited coating layers. Thus the corrosion process is blocked or delayed [9]. That is why, as the number of layers increased, the corrosive agent needs more time to penetrate through coating defects into the substrate material, than in case of monolithic coating. Overall potentiodynamic polarization study reveals that the CMMA coating, when designed properly with distinct modulation in composition, better corrosion stability is possible.

Table 3. Corrosion data of multilayer Co-Ni alloy coatings developed using two and three current pulses in comparison with monolayer alloy coating

Coating configuration	$-E_{corr}$ vs. SCE/V	i_{corr} /$\mu A\ cm^{-2}$	CR mm y^{-1}
(Co-Ni)$_4$	0.583	1586.1	17.64
CMMA coatings using two current pulse			
(Co-Ni)$_{2/4/10}$	0.642	144.2	1.60
(Co-Ni)$_{2/4/20}$	0.650	59.7	0.66
(Co-Ni)$_{2/4/60}$	0.644	18.8	0.20
(Co-Ni)$_{2/4/75}$	0.650	36.5	0.40
CMMA coatings using three current pulse			
(Co-Ni)$_{2/4/6/10}$	0.625	62.9	0.70
(Co-Ni)$_{2/4/6/20}$	0.628	34.9	0.38
(Co-Ni)$_{2/4/6/60}$	0.625	10.0	0.11
(Co-Ni)$_{2/4/6/75}$	0.624	29.6	0.33

3.4. Electrochemical impedance study

Fig. 4 shows the Nyquist plots obtained for NMAC of Co-Ni with different number of layers at their respective open circuit potentials. All the curves appear to be similar (Nyquist plots), consisting of a single capacitive loop signifying the charge transfer resistance, R_{ct}. However, it should be noted that though these curves appear to be similar with respect to their shape, they differ considerably in their size. This indicates that the same fundamental processes are responsible for improved corrosion protection. Progressive increase in the values of R_{ct} with number of layers imply that the better corrosion protection of layered coating is due to enhanced resistance for transfer of charge across the double layer.

Further, the relative impedance response of multilayer (Co-Ni) coatings developed using both two and three current pulses in comparison with that of monolayer coating (all under optimal conditions) is shown in Fig. 5.
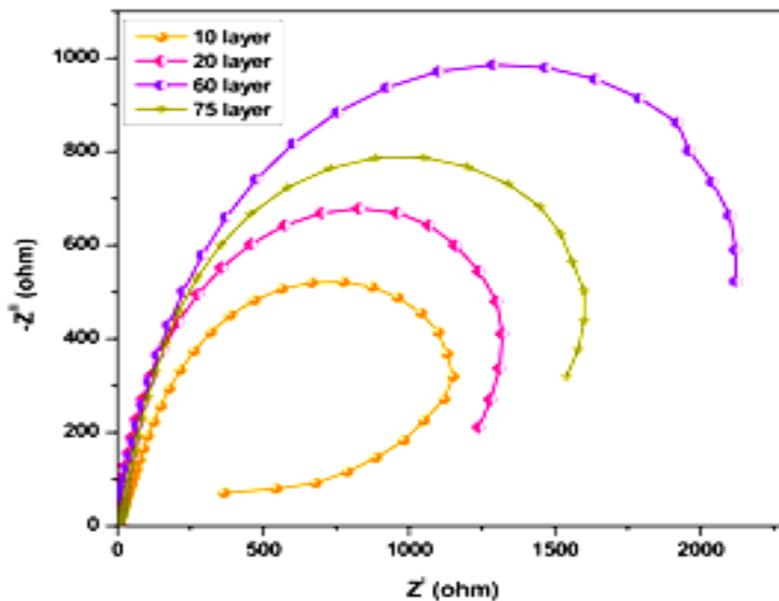
Fig. 4. Relative EIS response of multilayered (Co-Ni) alloy coatings having different number of layers, developed using three current pulses
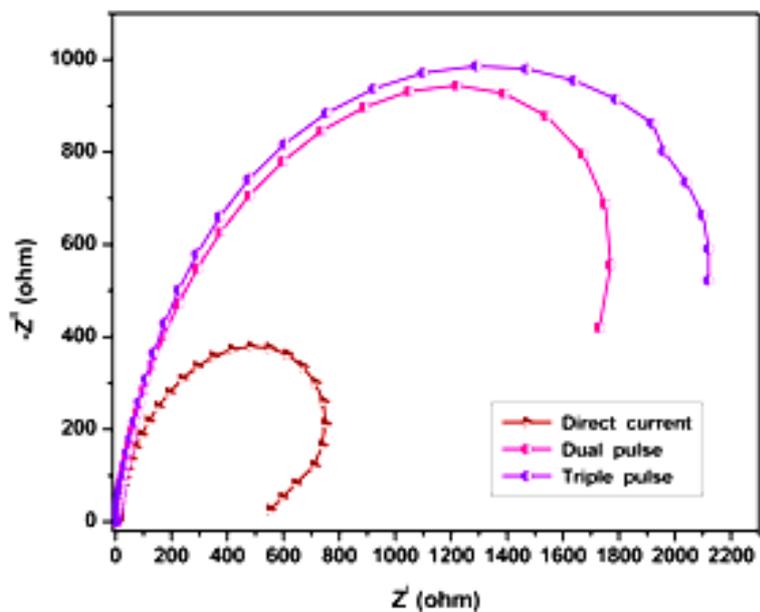

Fig. 5. Comparison of EIS response of multilayer (Co-Ni) coatings, developed, using different current power patterns, (All under optimal conditions)

3.5. Dielectric properties of layered coatings

EIS data points can also be used to study the dielectric properties of layered coatings, and the technique is called dielectric spectroscopy. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. This technique measures the relative dielectric constant of a system over a range of frequencies, and the frequency response of the system, including the energy storage and dissipation properties can be identified. In the presence of a material having dielectric constant, ε_M the surface charge density on the plates of a capacitor is represented by [10],

$$\sigma = \varepsilon_M E + P \tag{1}$$

Where 'σ' is the surface charge density , or quantity of charge per unit area of capacitor plate (C m^{-2}), is proportional to the electric field, E and polarization, P or the increase in the electric charge density, above that for a vacuum because of the dielectric material. For many dielectric materials, P is proportional to E through the relationship,

$$P = \varepsilon_0 (\varepsilon_r - 1) E \tag{2}$$

Where, ε_0 is the dielectric constant of vacuum, and ε_r is the relative dielectric constant of the medium. The equation for the dielectric constant, ε_r can be shown as [11,12],

$$\varepsilon_r = \frac{Z_I}{\omega C_0 \left(Z_R^2 + Z_I^2 \right)} \tag{3}$$

Here $C_0 = \varepsilon_0 A / t$ and ε_0 is the permittivity of free space, A is the electrolyte-electrode contact area and t is the thickness of the dielectric medium and ω, the angular frequency $= 2\pi f$, f being the frequency in Hz. Where, Z_R and Z_I are real and imaginary parts of complex impedance spectra, $Z^* = Z_R + j Z_I$.

The enhanced corrosion protection efficiency of multilayer coatings can also be described by changed dielectric property of the coatings due to layering. The equation relating the relative dielectric constant, ε_r with real and imaginary component of impedance, Z_R and Z_I, respectively is given by equation (3). The variation of relative dielectric constant, ε_r with frequency (from 10 mHz to 100 kHz) for different coatings, namely, (Co-Ni)$_4$, (Co-Ni)$_{2/4/60/two}$, and (Co-Ni)$_{2/4/6/60/three}$ are shown Fig. 6.

From Fig.6, it is observed that ε_r is more sensitive to the number of current pulses used for their deposition. In low frequency limit, the variation in ε_r is small in case of coatings developed using three current pulses, and more in case of monolayer Co-Ni coatings. At high frequency limit, the variation of ε_r is small in all three type of coatings. This means to say that at higher frequency limit, the imaginary component, Z_I reduces to zero.

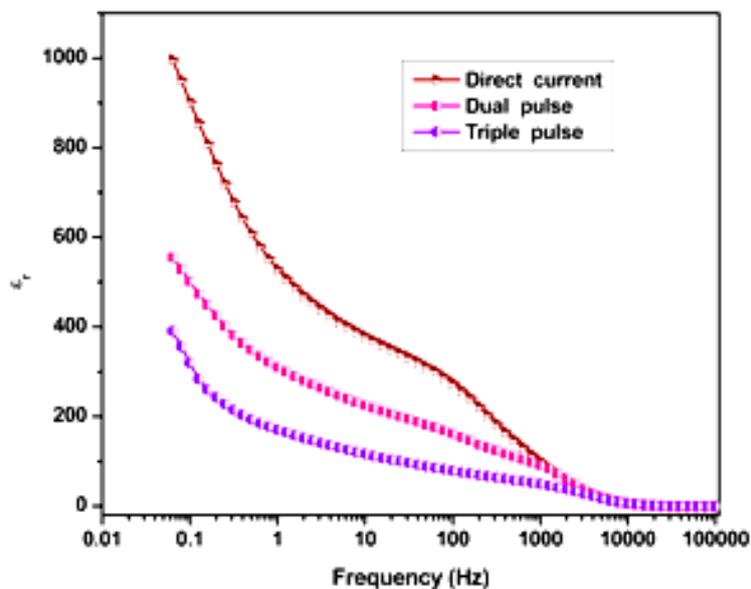**Fig. 6.** Change of relative dielectric constant, ε_r over range of frequency for (Co-Ni) monolithic and multilayer coatings

Hence, ε_r is same for all coatings irrespective of the deposition conditions. At low frequency limit, the capacitor being charged and discharged slowly, and it effectively constitutes a open circuit [13,14]. Under this condition, depending on the relative dielectric constant value of the electrical double layer (EDL) capacitor, it allows the charges to transfer through the capacitor plates. This attributes to the increased interfacial polarization effect, caused by the heterogeneous media consisting of phases with different dielectric permittivity. Thus the value of ε_r for CMMA (Co-Ni)$_{2/4/6/60/three}$ is least compared to that for other coatings. This supports the fact that the enhanced corrosion protection is due to decreased dielectric property of the coating due to layering.

3.6 Morphological studies

The scanning electron microscopy (SEM) image of (Co-Ni)$_{2/4/6/20/three}$ shown in Fig.7(a) evidences the formation of alternate layers of alloys, and Fig.7(b) shows leached multilayer coatings after corrosion test. The inspection of the microscopic appearance of the surface allows the understanding of corrosion mechanism; with possible reasons for improved corrosion resistance. The high corrosion prevention is due to fact that one layer of alloy having one type of failures (like pores, crevices or columnar structure) will be covered successively by the another layer of alloy with different type of failures than the earlier one (due to deposition at some other c.d). Thus the coating having alternate layers with different degree of failures are responsible for longer or blocked pathway for the corrosion medium.

That is why in multilayer coating, the corrosive agent needs more time to penetrate through, than in monolayer coating.

A comparison of three dimensional (3–D) optical profilograms of monolayer and multilayer coatings after corrosion test is shown in Fig.8. It may be noted that the deformation of monolayer and multilayer coatings occurs uniformly and graded manner, respectively. This supports the selective breaching of layers alternatively, and is responsible for better corrosion protection.
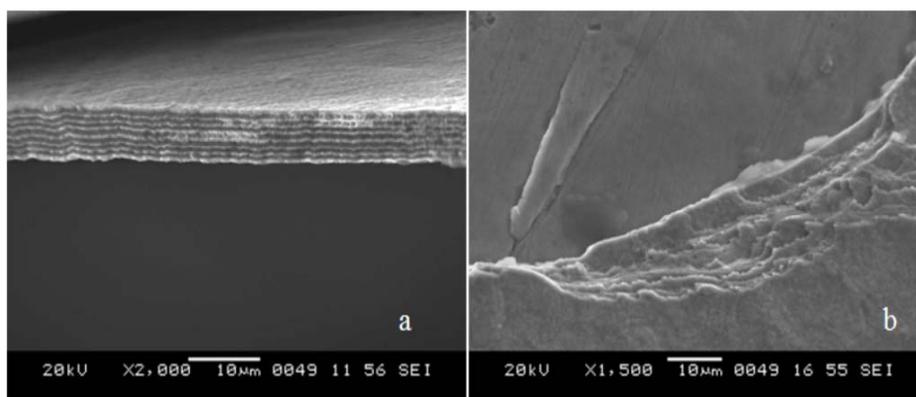

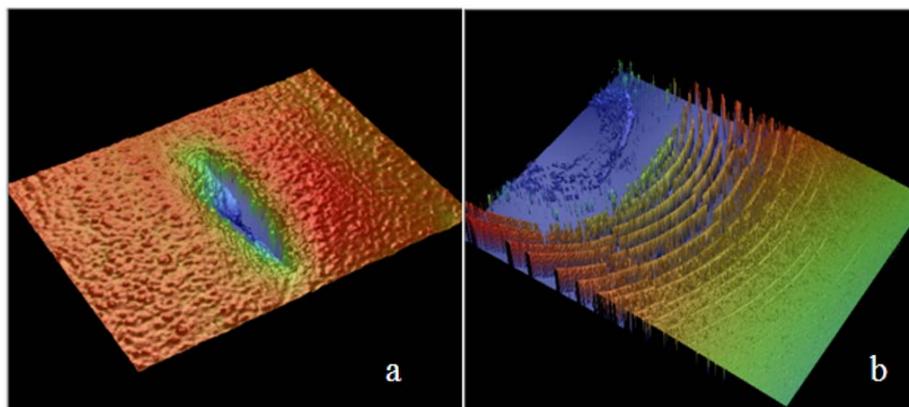**Fig. 7.** SEM images of CMMA Co-Ni alloys: Cross sectional view, (a) and deformed multilayer after corrosion test, (b)

Fig. 8. Three dimensional (3-D) image of monolayer (a) and multilayer coatings (b), after corrosion test

4. CONCLUSIONS

i)   The multilayered coatings of Co-Ni alloy was developed on copper galvanostatically from acid sulphate bath using successively two and three current pulses.

ii)   The corrosion resistance of layered coatings increased with number of layers, up to an optimal level and then decreased in both types of current pulses.

iii) An effort to increase the corrosion resistance by increasing the layering beyond 60 has resulted in increase of CR. It is due to diffusion of interfaces on exceptional thinning of the layers.

iv) Drastic increase in the corrosion protection of multilayer Co-Ni coatings is due to decreased dielectric property of the coatings due to layering, supported by dielectric spectroscopy.

v) Under optimal conditions, the coatings developed using two and three current pulses were found to be respectively, about 88 and about 160 times more corrosion resistant than monolayer coating, deposited from same bath for same time. It may be attributed to progressive increase in number of interfaces interposed during deposition.

vi) The SEM and Optical Profilogram study confirmed the formation of multilayer during deposition and have justified the reasons responsible for enhanced corrosion protection of layered coatings.

Acknowledgement

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