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Ultrasound Induced Co-deposition of Ni-co Alloy for Better Corrosion Protection

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Abstract:
Bright, uniform and low cost Ni-Co alloy coatings are highly desired for many corrosion protection applications. Here we demonstrate the that corrosion stability of Ni-Co alloy coatings can be increased to many fold of its magnitude by inducing the ultrasound effect, parallel to the process of electrodeposition. Ultrasound effect of known power density (p.d.) has been affected to bring the modulation in mass transfer process at cathode. Ni-Co alloy coatings with significant change in composition, phase structure and surface morphology have been developed, under ultrasound effect of different p. d. Corrosion performances of ultrasound-assisted Ni-Co alloy coatings have been evaluated by electrochemical methods. Corrosion data revealed that sonolectrodeposited Ni-Co alloy coatings developed at current density (c.d.) and p. d. of, respectively 4.0 Adm^{-2} and 1.2Wcm^{-2}(represented as $(Ni\text{-}Co)_{4.0/1.2}$) is about 3times more corrosion resistant than its conventional coating deposited at 4.0 Adm^{-2}(represented as $(Ni\text{-}Co)_{4.0}$), using same bath. Corrosion protection efficacy of sonoelectrodeposited Ni-Co alloy coatings were attributed to increase of Co content in the alloy, due to change in its limiting c.d. (i_L). Improved corrosion resistance of sonoelectrodeposited Ni-Co alloy coatings has been discussed in the light of changed composition, surface morphology and phase structure, supported by Scanning electronmicroscopy (SEM) Energy dispersive spectroscopy (EDS)and X-Ray diffraction (XRD) study.

Keywords: *Ni-Co alloy, sonoelectrodeposition, corrosion behaviour, limiting current density*

1. Introduction

In recent years, sonoelectrochemistry has become an active research field, and few research group have pointed out the benefits of ultrasound field on the electrode processes [1]. In this regard we have tried to take the advent of sonication for improving the properties of alloy coatings. Literature review reveals that Ni-Co alloy is one of the most important coating material because of its special properties high hardness, good wear resistance. Due to this properties, these coatings have been used in rocket technology, sound signal recording, die casting and as an anticorrosive coating [2,3] There are enough literature on Ni-Co alloy coatings, where it has used as a good anti-corrosion materials. The corrosion performance of Ni-Co alloy coatings can be improved further by varying the Co content of alloy, by altering the mass transport process at the electrode-electrolyte interface, parallel to the process of electrodeposition. This can be accomplished by taking the advantage of sonication effect, called sono-electrodeposition. *i.e.*by modulating the ultrasound effect parallel to the process of electrodeposition. Accordingly, the corrosion performance of Ni-Co alloy coatings were tried to improve drastically by bringing the change in the mass transport process at the electrical double layer (EDL), by periodic modulation of ultrasound effect by varying the power density (p.d.).

2. Experimental

The composition of Ni-Co alloy bath, used throughout the study is given in Table 1. The optimal conditions, like composition and operating variables (c.d., pH and temperature) were arrived by the standard Hull cell method. The mixture containing, Cobalt sulphate ($CoSO_4.7H_2O$), Nickel sulphate ($NiSO_4.6H_2O$) as salts, ascorbic acid as antioxidant, prepared in distilled water was used. All reagents used were of LR grade (Merck, Mumbai, India). The bath at constant pH (3.5) was used, by addition of either NH_4OH or HCl, depending on the requirement using Micro pH Meter (Systronics,362). All depositions were carried out at room temperature, under condition of constant agitation on polished copper substrate (7.5×3.0 c m), used as cathode. The substrate was polished metallurgically to get the mirror polish, degreased with trichloroethylene, and then pickled in 1:1 HNO_3. The deposition was carried out on known active surface area (3×3cm), leaving the other region of substrate covered by cellophane tape. Pure nickel plate was used as anode for electrodeposition, with same exposed surface area as that of cathode. The cathode and anode were placed parallel 5cm apart during

deposition. All coatings were cleaned using distilled water, followed by air drying. The deposited coatings were further analyzed for the composition, phase structure and surface morphology.

Electrodeposition of Ni-Cocoating both in the presence and absence of the ultrasound effect have been carried out, and deposition conditions were optimized for coatings of maximum corrosion protection. The electrodeposition was carried out at different c.d.'s using DC power analyzer (Agilent Technologies, N6705A, USA) and sonoelectrodeposition was carried out using an ultrasound generator (SONIC Vibra-cell^{TM} VC 750, 20 kHz, maximum power 750 W, with sonicator probe(electrode) of 13 mm tip diameter) coupled with DC source. All depositions were carried out for constant time (10 min), for comparison. Sonoelectrodeposition was accomplished with the combined effect of two driving forces: one is c.d., expressed in A dm^{-2}, and the other one is p.d., expressed in W cm^{-2}. Here, c.d. acts as the driving force for reduction of metal ions, and p.d. for modulation of mass transfer at EDL.

Bath composition	Amount, g/L	Operating parameters
Cobalt sulfate	14	p^H: 3.5
Nickel sulphate	131	Temperature: 303K
Sulphanilic acid	0.75	Anode: Nickel
Ascorbic acid	2.5	C.d. range: 1.0 A dm^{-2}- 7.0 A dm^{-2}
Boric acid	30	
Glycerol	15 m/L	

Table 1: Bath composition and operating parameters used for electrodeposition of Ni-Co alloy coatings

2.1. Electrochemical Characterization

The electroplated surface of Ni-Co alloy were subjected for electrochemical measurements, using potentiostat/galvanostat (Gill AC, ACM instruments, with version-5 software) in a three-electrode configuration cell, using saturated calomel electrode (SCE), as the reference electrode and platinum electrode as counter electrode. The corrosion tests were carried out, taking 1 cm^2 exposed surface area of the coatings in 5% HCl at 298K.Potentiodynamic polarization study was carried out in a potential ramp of ±250 mV around equilibrium potential, at a scan rate of 1 mV s^{-1}. Electrochemical impedance spectroscopy(EIS) study was made using 10 mV perturbing AC voltage, and corresponding Nyquist plots were analyzed. The corrosion rates(CR) were expressed in $mmyear^{-1}$, determined by the Tafel extrapolation method [4].

2.2. Characterization

The surface morphology of sonoelectrodeposited Ni-Co alloy coatings were analysed under Scanning electron microscope (SEM, Model JSM-6380 LA from JEOL, Japan). The composition and phase structure of coatings were analyzed using Energy dispersive X-ray spectroscopy (EDX, Oxford EDS(X-act)) and X-ray diffraction study(XRD) (Rigaku- miniFlex 600), respectively.

3. Results and Discussions

3.1 Sonoelectrodeposition of Ni-Co coatings

Basically, standard Hull cell method was used to set optimal electrolytic conditions for the deposition of bright, uniform and corrosion resistant Ni-Co alloy coatings over wide range of c.d., using procedure described elsewhere [5]. The experimental results revealed that under optimal conditions of c.d. =4.0 A dm^{-2}, the bath produced good coating showing the least CR (22.4×10^{-2} mm $year^{-1}$). *i.e.* with no ultrasonication effect. Keeping this c.d. as the optimal, the corrosion protection of Ni-Co alloy coating was tried increase by taking the benefit of ultrasound effect. Accordingly, Ni-Co alloy coatings were deposited under different conditions of p.d. (at 0.6,0.9 and 1.2 Wcm^{-2}), and their corrosion performance were evaluated, and corresponding corrosion data are reported in Table 2 and Table 3.From the CR data, it may be noted that sonoelectrodeposited Ni-Co alloy coatings are more corrosion resistant compared to the one, deposited without ultrasonic effect (p.d.=0 W cm^{-2}). Further, it was found that Ni-Co alloy at p.d. of 1.2 Wcm^{-2} exhibits the least CR (7.9×10^{-2} mm $year^{-1}$). It is more important to note that wt. % Co in the deposit increased drastically when deposition was carried out under the effect of ultrasound. A drastic increase in the wt.% Co in the deposit may be attributed to an increase of limiting c.d. (i_L) of Co by thinning of EDL [6]. The variation in the thickness of EDL is mainly associated with the geometry of sonoelectrode, and the p.d. of ultrasonic effect. Hence, it may be noted Co content of the alloy has increased drastically (due to increase of its i_L) due to effect of ultrasonication. Hence, it may be concluded that ultrasound effect has decreased the CR of Ni-Co alloy coatings by increasing its Co content by increasing its i_L

3.2. SEM Study

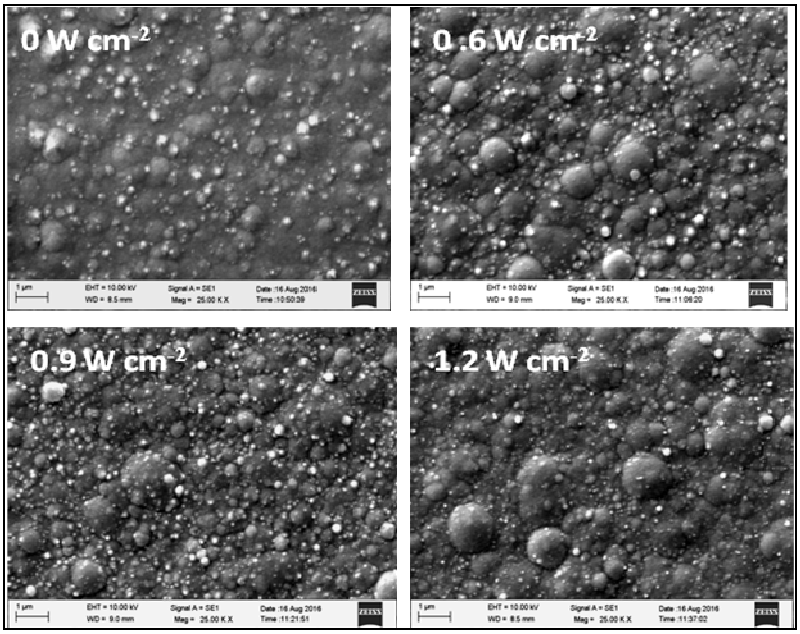

Figure 1: SEM image of Ni-Co alloy coatings deposited at different power densities

The surface topography of Ni-Co alloy coatings, deposited at different p.d.'s areas shown in the Figure 1, in comparison with that of conventional Ni-Co alloy (0 Wcm^{-2}). It may be noted on increasing the p. d. from 0 W cm^{-2} to 1.2 W cm^{-2}, the Co content of the alloy increased from about 21.82wt.% to 43.52wt.%. It may be attributed to action of cavitation and ultrasonic microstreaming generated by ultrasonic vibration [7]. The decrease of Ni content may be reasoned by the fact that nickel ion being a smaller in size compared to cobalt ions, kinetic movement of Ni ions towards the cathode leads to creation of bubbles, during ultrasonic streaming [7]. Hence, a large difference in the surface morphology of sonoelectrodepoisted Ni-Co alloy coatings, with p. d. may be attributed to an increase of Co content of the alloy, due to ultrasonic steaming effect.

3.3. X- ray Diffraction Study

XRD patterns of sonoelectrodeposited Ni-Co alloy coatings obtained at different p.d.'s (0 W cm^{-2} to 1.2 W cm^{-2}) are shown in the Figure 2. It may be noted that the orientations of all phases are same in all coatings developed in both presence and absence of ultrasonic field effect. However, the intensity of reflection corresponding to (220) phase of fcc Ni structure (JCPDS 04-0850) decreased drastically with increase of p. d. as shown Figure 2. The intensity of distinct peak of conventional Ni-Co alloy, observed at $76.4^0$for (220) plane decreased with increase of p. d. The Ni-Co alloy coatings exhibiting peritectic phase structure of (112) and (311) reflections are corresponding to the combination of both fcc and hcp structures. The wt. % Co in the deposit was found to be increased (or wt. % Ni decreased), when the ultrasound field is applied, which is evidenced by (002) (JCPDS 05-0727). Hence, from XRD study it may be inferred that p. d. has vital role on the composition, and hence the phase structure of Ni-Co alloy coatings.

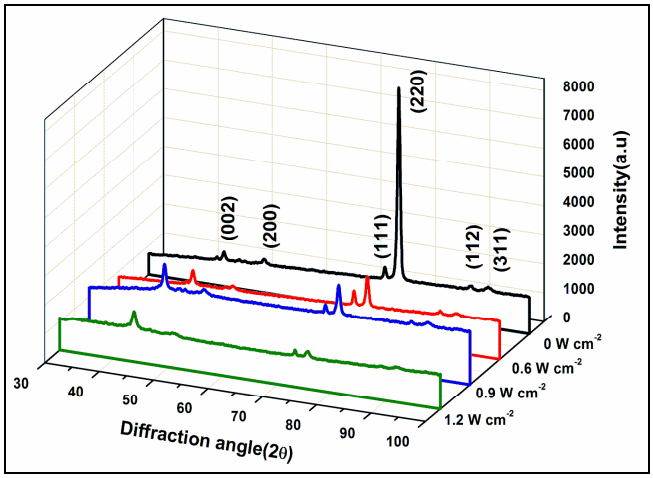

Figure2: XRD patterns showing crystallographic orientation of Ni-Co alloy coatings deposited at different p.d., at same c.d. of 4.0 A dm^{-2}

3.4. Potentiodynamic Polarization Study

The potentiodynamic polarization method was used to study the corrosion behaviour of Ni-Co alloy coatings, and CR's were evaluated by Tafel extrapolation method. The corrosion data of Ni-Co alloy coatings deposited at different c.d. are shown in Table 2.

c.d. ($A\ dm^{-2}$)	Wt. % Co in the deposit	$-E_{corr}$ (mV vs SCE)	i_{corr} ($\mu A\ cm^{-2}$)	$CR\times10^{-2}$ ($mm\ year^{-1}$)
1.0	44.4	218.52	24.4	41.1
2.0	42.9	228.56	14.6	24.6
3.0	37.7	237.6	17.62	23.42
4.0	21.8	273.19	20.81	22.4

Table 2: corrosion data of Ni-Co alloy coatings deposited at different c.d.'s using optimal bath

It may be noted that Ni-Co alloy deposited at 4.0 Adm^{-2} shows the least CR, and hence it has been considered as optimal c.d. for sonoelectrodeposition. Then, sonoelectrodepostion of Ni-Co alloy coatings were carried out at different p. d. (0, 0.6, 0.9 and 1.2 Wcm^{-2}) and their CR were evaluated, and are reported in Table 3. A comparison of Tafel's plots of sonoelectrodepoisted Ni-Co alloy coatings, deposited at different p. d. are shown in Figure 3, in relation to that of conventional Ni-Co alloy coating. The corrosion data reported in Table 3 demonstrate that $(Ni\text{-}Co)_{4.0/1.2}$ alloy coating exhibits the least CR compared to all other coatings. The least CR (7.9×10^{-2} mm $year^{-1}$) of $(Ni\text{-}Co)_{4.0/1.2}$ alloy coating may be attributed to highest Co content of the alloy, evidenced by EDX analysis (reported in Table 3) due to effect of induced ultrasonic effect as discussed earlier sections.

p.d. ($W\ cm^{-2}$)	Wt. % Ni in the deposit	Wt. % Co in the deposit	$-E_{corr}$ (mV vs SCE)	i_{corr} ($\mu A\ cm^{-2}$)	$CR\times10^{-2}$ ($mm\ year^{-1}$)
0 $W\ cm^{-2}$	78.18	21.82	229.7	20.81	22.4
0.6 Wcm^{-2}	68.67	31.33	215.48	9.3	10.4
0.9 $W\ cm^{-2}$	62.17	37.83	241.25	8.3	9.0
1.2 Wcm^{-2}	56.48	43.52	247.07	7.4	7.9

Table 3: corrosion data for Ni-Co coatings deposited at different p.d.'s at same c.d. (4.0 Adm^{-2})

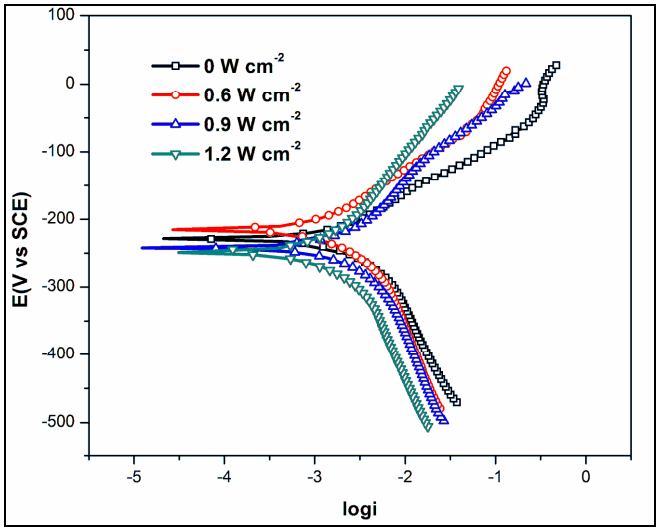

Figure 3: Potentiodynamic polarization behaviour of sonoelectrodeposited Ni-Co alloy coatings, deposited different p.d., at same c.d. (4.0 Adm^{-2})

3.5. Electrochemical Impedance Spectroscopy Study

EIS is a non-destructive method for studying the interfacial interaction of test material very accurately. The ability of the technique to segregate various processes, like Ohmic conduction, charge transfer, interfacial charging, mass transfer etc., and made it as an elegant technique for electrochemical study [8]. Their representation is popularly called as Nyquist diagrams. The impedance response of Ni-Co alloy coatings deposited at different p. d. are shown in Figure 4. The impedance responses showed incomplete depressed semicircle in the studied frequency range, in addition to an increase of axial radius of the semicircle with increase of p. d. was found. Nature of Nyquist plots clearly shows that the charge transfer resistance (R_{ct}) of the coatings has increased progressively with of p.d. used for deposition. The impedance response of $(Ni\text{-}Co)_{4.0/1.2}$ alloy coatings is characterized by high polarization resistance (R_p) as shown in Figure 4, indicates that this particular coating is more corrosion resistant compared to coatings at other p. d. (including its conventional alloy coatings). This observation is in compliance with Tafelplots, shown in Figure 3, and corrosion data given in Table 3.

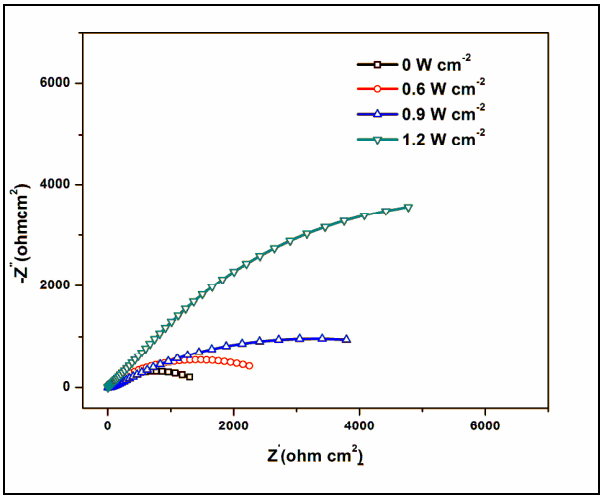

Figure 4: EIS response of sonoelectrodeposited Ni-Co alloy coatings, deposited different p.d., at same c.d. (4.0 Adm^{-2})

Thus, a drastic decrease of CR's was observed mode of Ni-Co alloy coating is changed from conventional electrodeposition type to sonoelectrodeposition type. This is confirmed by the data summarized in Table 2 and Table 3.In case of sonoelectrodeposited Ni-Co alloy coatings, an increase of R_p was found with increase of p. d., supported by impedance response shown Figure 4.Thus from corrosion data, it may be inferred that under optimal conditions magnetoelectrodeposited Ni-Co alloy coating, represented as $(Ni\text{-}Co)_{4.0/1.2}$ is about 3 times more corrosion resistant (7.9×10^{-2} mm year^{-1})than its conventional alloy coating(22.4×10^{-2} mm year^{-1}), developed from the same bath.

4. Conclusions

In the pursuit of improving the corrosion resistance behaviour of Ni-Co alloy coating from a new sulphate bath through sonoelectrodeposition approach the following conclusions are drawn:

1. The corrosion rates of Ni-Co alloy coatings can be decreased drastically by inducing the ultrasound effect parallel to the process of electrodeposition.
2. In the present study, under optimal condition, $(Ni\text{-}Co)_{4.0/1.2}$ coating is about 3 times more corrosion resistant (7.9×10^{-2} mm year^{-1}) than its conventional alloy coating (22.4×10^{-2} mm year^{-1}), deposited from same bath for same duration.
3. Drastic improvement in corrosion resistance of sonoelectrodeposited Ni-Co alloy coating is attributed to an increase of Co content of alloy, due to sonication.
4. Increase of Co content in the alloy is due to an increase of its limiting c.d. (i_L), affected by induced ultrasound field.
5. The factors such as surface morphology, composition and phase structures, responsible for better corrosion resistance of the coatings were found to be mainly controlled by the power density (p. d.) used for deposition, supported by SEM, EDX and XRD study, respectively.

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