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Effect of Pyridine on the Corrosion Behavior of Electrodeposited Ni-Co Alloy Thin Films and Their Structural and Morphological Analysis

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Abstract: *Ni-Co thin films have been grown on Stainless steel substrate by galvanostatic electrodeposition from Sulphate baths containing Pyridine as Organic inhibitor. A comparative study of corrosion parameters were done in three different electrolytes; NaCl, HCl, H_2SO_4 by tafel extrapolation method. Pyridine is found as an effective corrosion inhibitor for Ni-Co alloy thin films and showed minimum corrosion rate in NaCl medium. The morphology and structural analysis of thin films were done by Scanning Electron Microscopy (SEM) and X-Ray Diffraction pattern (XRD), respectively. Elemental composition has been determined by Energy Dispersive X-Ray spectroscopy (EDAX). XRD confirmed that the films possessed a mixture of Cubic and hcp crystal structures.*

Keywords*: thin films, galvanostatic electrodeposition, inhibitor, XRD, SEM-EDAX.*

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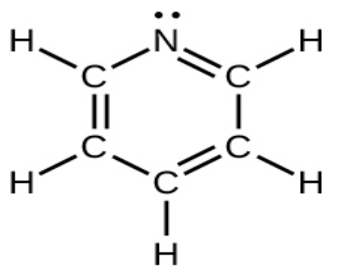
I. Introduction

Ni-Co alloys [1-3] are gaining tremendous attention of researchers due to its important applications in aviation industry, automobile industries [4], chemical process industry, marine industry etc. Ni-Co co-deposition is anomalous. Many researchers studied the corrosion behavior of Ni-Co alloys and found it suitable as anticorrosive alloy [5]. Alloys with much lower corrosion rate are anticipated for better results to apply practically. Now a days the concept of corrosion inhibitors [6-8] is achieving interest of scientific community to lower the corrosion rate of metals and alloy thin films.

A corrosion inhibitor is a substance when added in a small concentration to an environment reduces the corrosion rate of a metal or alloy exposed to that environment. It can be use either internally addition into the plating bath as additive or by addition in exposing environment. Organic compounds containing Nitrogen, Oxygen and Sulphur reduces the corrosion rate. Inhibitors act by selectively precipitating on cathodic or anodic or mixed areas to limit the diffusion of reducing species to the surface.

In present work, Ni-Co alloy thin films are galvanostatically electrodeposited from a deposition bath containing pyridine (C_5H_5N) as organic inhibitor [9]. Their effects on corrosion properties of alloy thin films have been studied.



Structure of Pyridine (C_5H_5N)

II. Experimental Procedure

The composition of deposition bath used for synthesis of Ni-Co thin films is 0.10 M $NiSO_4$, 0.10-0.30 M $CoSO_4$, 0.10 M $Na_3C_6H_5O_7$, 0.20M H_3BO_3, 0.20M Na_2SO_4 and 0.0005M C_5H_5N (pyridine). All chemicals were of A.R. grade and deposition solutions were prepared in deionised water.

All electrochemical experiments were carried out in a conventional three electrode cell without stirring and potentials were referred to the saturated calomel electrode (SCE). Mild Steel (MS) plates with surface area 1cm X 1cm were used as working as well as counter electrode. The substrate plates were cleaned with emery paper and washed successively with acetone and distilled water. For data acquisition transistor based power supply and for current density and potential measurements digital multimeters were used during electrochemical co-deposition of alloy thin films. The pH of deposition bath was maintained 3 using dilute H_2SO_4 and thin film depositions were carried out at 25°C.

Three deposition solutions were prepared by taking fix concentration of other chemicals including pyridine with different concentration of $CoSO_4$.

The electrodeposition was done using galvanostatic method on constant current density 2 mA/cm^2 for 20 minutes at 25°C. The corrosion parameters of deposited alloy thin films were determined by Tafel Polarization curve. The corrosion rate were calculated using equation (1)

C.R.= (0.13 $*$ I_{corr} $*$ eq.wt.) / (D$*$ A) __(1)

Here,

C.R.. = Corrosion rate (MPY)

I_{corr} = Corrosion current density (μA/cm^2)

Eq.wt.= Equivalent weight of deposited alloy

D = Density of alloy (gm/cm^3)

A = Area of substrate (cm^2)

The morphology and composition of thin films were investigated by FModel : JEOL JSM5600 Scanning electron microscope(SEM) and EDS model: INCA Oxford. Crystalline phase of the deposited films was characterized by Bruker D8 Advance X-Ray Differectometer (XRD) with a monochromatized CuKα irradiation (λ = 0.154 nm).

III. Result and Discussion

Ni-Co alloy thin films with pyridine were obtained from different deposition baths at constant current density of 2 mA/cm^2. The Sodium Citrate ($Na_3C_6H_5O_{7)}$ was used as complexing agent while Boric Acid (H_3BO) As buffer.

In order to obtain the suitable static current for deposition, first of all the deposition was performed at different current densities i.e. 0.5 mA/cm^2, 1mA/cm^2, 2mA/cm^2, 3mA/cm2 and 4mA/cm^2 respectively. A smooth surface and corrosion rate was observed at 2 mA/cm^2 and than all deposition experiments were carried out on this current density for 20 minutes. The variation in potential with time was noted in Fig.1. It shows the Potential Vs Time curve at fixed current density i.e. 2mA/cm^2. During the deposition, potential first increases and than it decreases very fast up to a steady state value. The steady state indicates that the coverage of working electrode surface is nearly complete.

The estimated film thickness of Ni-Co thin films is in μm range.

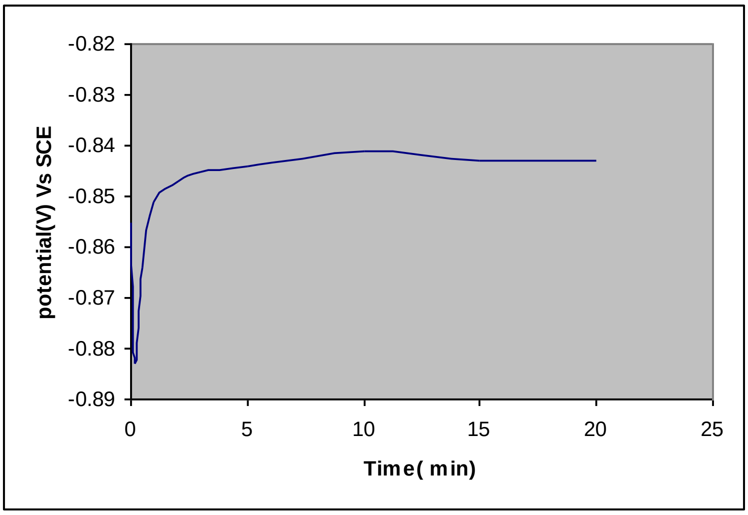


Fig. 1: Potential-Time graph of 0.10M Ni+0.20M Co alloy Thin film in presence of pyridine as inhibitor at 2 mA/cm^2

III.I Corrosion analysis

The corrosion behavior of electrodeposited Ni-Co thin films with pyridine as inhibitor on mild steel substrate was studied using Tafel polarization curve. The corrosion studies were made by cathodic and anodic polarization data shown in Fig 2(a-i)

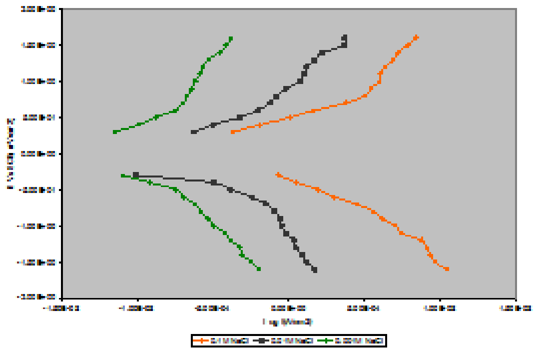


Fig 2(a): Tafel plot for 0.10M Ni+0.10M Co (with pyridine) in NaCl Medium

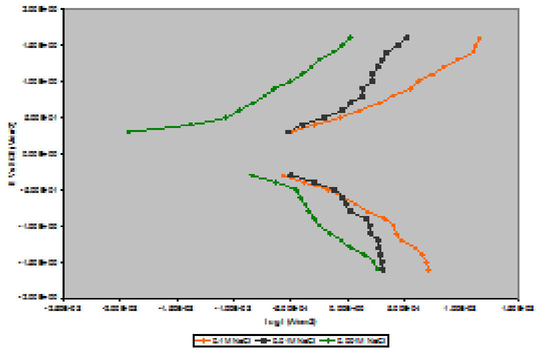


Fig2(b): Tafel plot for 0.10M Ni+0.20M Co (with pyridine) in NaCl Medium

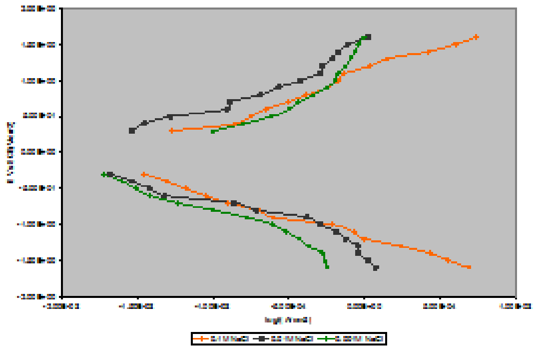


Fig.2(c): Tafel plot for 0.10M Ni+0.30M Co (with pyridine) in NaCl Medium

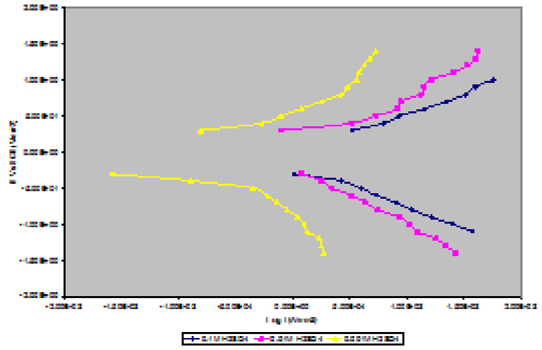


Fig2(d): Tafel plot for 0.10M Ni+0.10M Co (with pyridine) in H_2SO_4 Medium

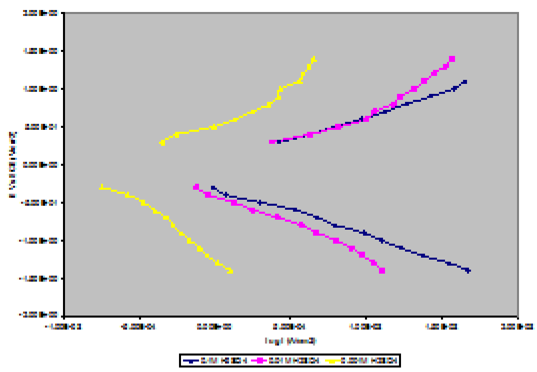


Fig.2(e): Tafel plot for 0.10M Ni+0.20M Co (with pyridine) in H_2SO_4 Medium

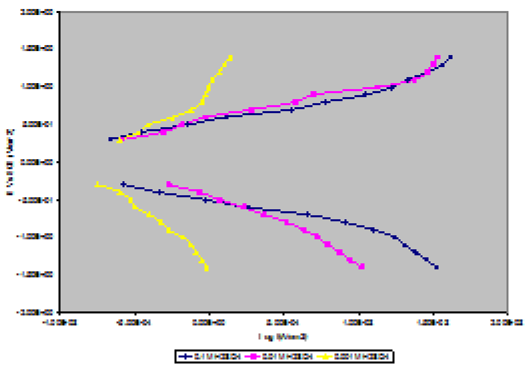


Fig2(f): Tafel plot for 0.10M Ni+0.30M Co (with pyridine) in H_2SO_4 Medium

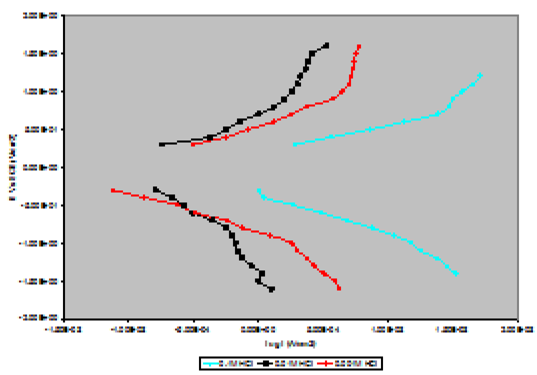


Fig.2(g): Tafel plot for 0.10M Ni+0.10M Co (with pyridine) in HCl Medium

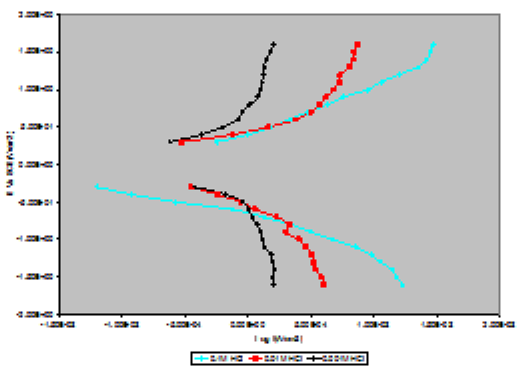


Fig2(h): Tafel plot for 0.10M Ni+0.20M Co (with pyridine) in HCl Medium

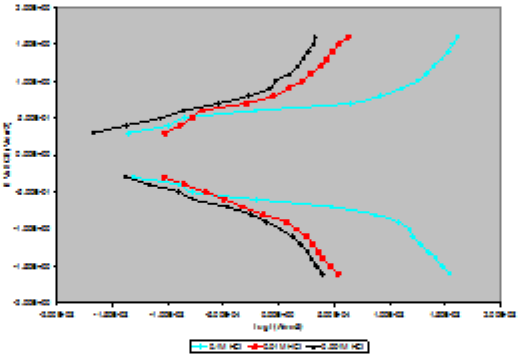


Fig2(i): Tafel plot for 0.10M Ni+0.30M Co (With pyridine) in HCl medium

The alloy thin films were tested in three different corrosive mediums i.e. NaCl, HCl and H_2SO_4 at three different concentrations. Table 1(a-c) shows the corrosion parameters of deposited films in different corrosive mediums. It was found that as the cobalt concentration increased in deposited films the corrosion rate was decreased in all mediums. The corrosion rates of Ni-Co alloy thin films synthesized in presence of pyridine as inhibitor were much lower than the Ni-Co alloys synthesized without inhibitor [10,11].

Table 1(a): Corrosion Rate of electrodeposited NiCo alloy thin films synthesized in presence of pyridine in NaCl medium

Conc. Of $NiSO_4.6H_2O$	Conc. Of $CoSO_4.6H_2O$	Conc. Of Pyridine (C_5H_5N)	0.1 M NaCl		0.01 M NaCl		0.001 M NaCl	
			I_{corr} (mA/cm^2)	Corrosio n Rate (mm/year	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)
0.10 M	0.10 M	0.0005 M	0.2113	1.2125	0.0841	0.4826	0.0237	0.1360
0.10 M	0.20 M	0.0005 M	0.1496	0.8585	0.0695	0.3988	0.0200	0.1148
0.10 M	0.30 M	0.0005 M	0.1259	0.7225	0.0531	0.3047	0.0150	0.0861

Table 1(b): Corrosion Rate of electrodeposited NiCo alloy thin films synthesized in presence of pyridine in H_2SO_4 medium

Conc. Of $NiSO_4.6H_2O$	Conc. Of $CoSO_4.6H_2O$	Conc. Of Pyridine (C_5H_5N)	0.1 M H_2SO_4		0.01 M H_2SO_4		0.001 M H_2SO_4	
			I_{corr} (mA/cm^2)	Corrosion Rate (mm/year	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)
0.10 M	0.10 M	0.0005 M	0.8404	4.8225	0.3548	2.0360	0.1496	0.8585
0.10 M	0.20 M	0.0005 M	0.6310	3.6209	0.2818	1.6171	0.1259	0.7225
0.10 M	0.30 M	0.0005 M	0.5309	3.0465	0.2113	1.2125	0.1059	0.6077

Table 1(c): Corrosion Rate of electrodeposited NiCo alloy thin films synthesized in presence of pyridine in HCl medium

Conc. Of $NiSO_4.6H_2O$	Conc. Of $CoSO_4.6H_2O$	Conc. Of Pyridine (C_5H_5N)	0.1 M HCl		0.01 M HCl		0.001 M HCl	
			I_{corr} (mA/cm^2)	Corrosion Rate (mm/year	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)	I_{corr} (mA/cm^2)	Corrosion Rate (mm/year)
0.10 M	0.10 M	0.0005 M	0.1995	1.1448	0.0944	0.5417	0.0422	0.2422
0.10 M	0.20 M	0.0005 M	0.1679	0.9635	0.0794	0.4556	0.0355	0.2037
0.10 M	0.30 M	0.0005 M	0.1413	0.8108	0.0596	0.3420	0.0282	0.1618

III.II Morphology and compositional analysis

The SEM images of deposited thin films are shown in Fig.3(a-b). The image analysis has confirmed that the thin films are homogenous with smooth surface area and evenly covered the mild steel substrate surface. The images showed the sharp thorn like structured particles which are agglomerated. The EDAX analysis (fig 4(a-b)) confirmed the oxide alloy of NiCo. The Elemental data for NiCo thin films obtained from EDAX is shown in table 2.

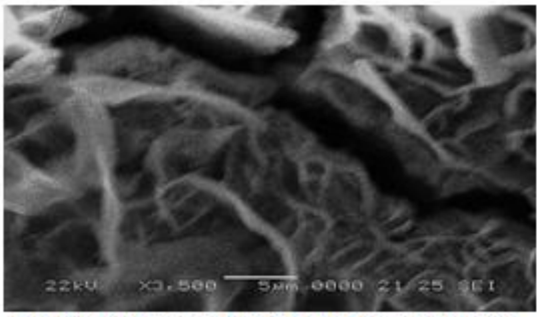


Fig 3 (a) SEM image of 0.10M Ni+ 0.20M Co In presence of Pyridine

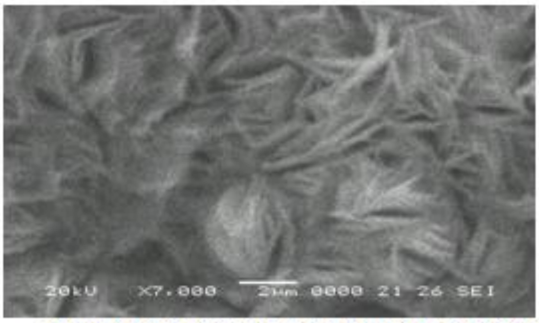


Fig 3 (b) SEM image of 0.10M Ni+ 0.30M Co in presence of Pyridine

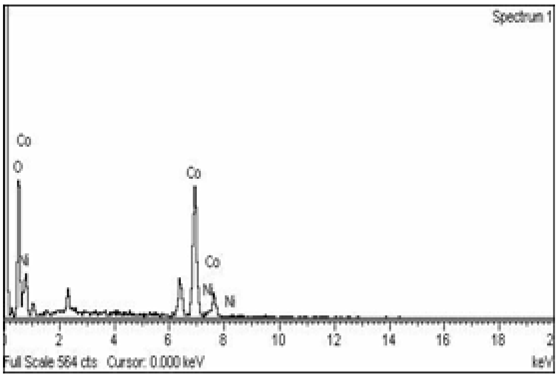


Fig 4 (a) EDAX of 0.10M Ni+ 0.20M Co In presence of Pyridine

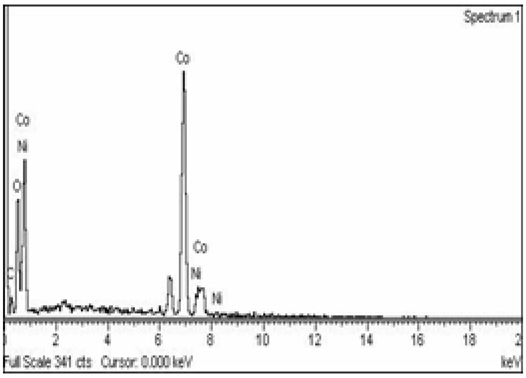


Fig 4 (b) EDAX image of 0.10M Ni+ 0.30M Co in presence of Pyridine

Table 2: percentage composition of NiCo alloy thin films

Elements (Weight %)	Bath Composition	
	0.10M NiSO4+ 0.20M CoSO4+ 0.0005M Pyridine	0.10M NiSO4+ 0.3M CoSO4+ 0.0005M Pyridine
%Ni	2.6	7.44
%Co	60.01	68.76
%O	37.39	24.09

III.III Structural analysis

XRD of NiCo alloy thin films synthesized in presence of pyridine as inhibitor is shown in fig.5(a-c). The XRD with sharp peaks indicated the crystalline nature of the films. The peaks obtained in XRD graphs are compared with the standard JCPDS data. It was found that the films are a mixture of fcc and hcp crystal structures with hcp(111) and (101) as predominant planes.

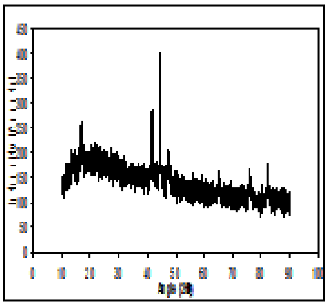


Fig.5 (a)

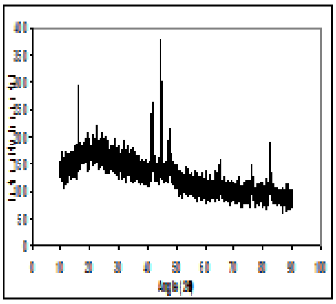


Fig.5 (b)

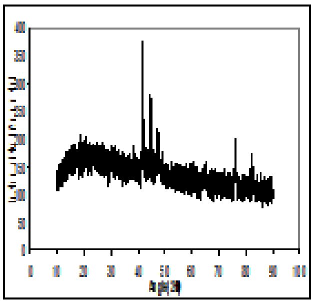


Fig.5(c)

Fig.5(a-c); (a) XRD of 0.10M Ni-0.10M Co alloy thin film in presence of pyridine, (b) XRD of 0.10M Ni-0.20M Co alloy thin film in presence of pyridine, (c) XRD of 0.10M Ni- 0.30M Co alloy thin film in presence of pyridine .

It was observed that as the cobalt content increased in the films the hcp crystal structure became predominant indicated by the increased intensities of related peaks. The crystallite size is determined by Scherer equation (equation(2)) which was found to be less than 30 nm.

Crystallite size

$$D = \frac{k\,\lambda}{\beta\ Cos\,\theta} \qquad \text{\_\_\_\_ (2)}$$

λ = Wavelength of incident beam (nm)

k = Scherrer's constant

β = Peak broadening (FWHM)

θ = Scattering angle in radian

The dislocation density of thin films was calculated by equation (3).

$$\delta = 1/D \qquad \text{\_\_(3)}$$

here, δ= Dislocation density

D=Crystallite size

The crystallite size and dislocation density of electrodeposited NiCo thin films is shown in table 3.

Table 3 : XRD parameters for (111) hcp plane

S. No.	**Conc. Of $NiSO_4.6H_2O$**	**Conc. Of $CoSO_4.6H_2O$**	**Conc. Of pyridine (C_5H_5N)**	**Angle 2 □**	**Interplaner spacing (d) (Å)**	**FWHM (β)**	**Crystallite size (nm)**	**Dislocation density (nm)**
1	0.10 M	0.10 M	0.0005 M	41.7617	2.1612	0.48768	17.1350	0.0574
2	0.10 M	0.20 M	0.0005 M	41.7998	2.1593	0.49978	17.0151	0.0588
3	0.10 M	0.30 M	0.0005 M	41.6285	2.1678	0.28980	29.3239	0.0341

IV. Conclusion

NiCo alloy thin films having oxides were lucratively synthesized from sulphate bath containing pyridine as organic inhibitor. The alloy thin film with higher cobalt content showed the best results against corrosion in all applied corrosive mediums. Deposited thin films were homogenous in nature with smooth surface area. The NiCo alloy thin films have sharp thorn like structures which slightly agglomerated on increasing concentration of cobalt. XRD analysis confirmed the crystalline nature of films having hexagonal closed packed crystal structure along with face centered cubic phase which confirmed the formation of NiCo alloy thin films. The pyridine worked effectively both in terms of corrosion protection as well as better morphology, as compared to the alloy thin films synthesized without inhibitor.

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