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Growth of Electrodeposited Ni-Co Thin Films on Cu Substrate

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Abstract : *This report is on the synthesis of Ni-Co alloy thin films by using electrodeposition methods. The crystalline characteristics have been demonstrated by deposition parameters. The current density, pH, temperature, bath concentration and deposition time have the most influence on the crystallographic structure of the thin film. The X-Ray Diffraction (XRD) measurements confirmed the crystalline behaviour of the thin film samples. The mixed phase of hexagonal close packed structure and face centred cubic structure is obtained at room temperature. For all the face centred cubic peaks, lattice parameters are a = b = c = 3.56 Å. X-Ray Fluorescence (XRF) gives the percentage of constituent element present in the deposited film on the substrate. The crystallite sizes were also measured by Scherrer equation and it lies in the range of 17.5 nm to 19.97 nm.*

Keywords: *Electrodeposition, Binary alloy, Thin film, XRD, XRF, FCC, HCP.*

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Introduction :

Electrodeposition is a film growth process that consists in the formation of metallic or semiconducting films on conductive substrates, starting from metal ion precursors in a suitable solvent and occurring via a charge transfer process (Zangari et. al., 2015). Electrodeposition is referred to a situation where the electrons reducing the metal ion come from the electrode substrate via an external power supply. The electrons needed for metal ion reduction can alternatively be provided by the oxidation of reducing compounds present in the solution, this process is generally referred as electroless or autocatalytic deposition. The term electrochemical deposition refers to both the processes described above.

Among the various film growth deposition methods, electrodeposition exhibits several distinctive and unique characteristics; in contrast to physical deposition method. Electrodeposition was made possible by the availability of the first voltage generator, the Volta Pile, and was invented shortly thereafter, in 1805 by Brugnatelli. The first materials to be deposited where Au

and Ag and consequently the initial application of this technique was limited for decorative purpose. Nowadays, electrodeposition method is used to deposit transition and coinage metals, which became widely used to coat tools in order to increase hardness, enhance corrosion resistance and improve surface finishing as well as appearance (Gamburg et. al., 2011).

In electrodeposition process, the substrate which has to be plated is made cathode (also known as working electrode) and the anode (also known as counter electrode) is made of the another metal. They both are immersed in an electrolytic solution containing one or more dissolved metal salt as well as other ions that permit flow of electricity. The rate at which anode is dissolved is equal to the rate at which cathode is plated (Gamburg et. al., 2011).

In this report, we have deposited thin films of Ni-Co by electrodeposition technique (Ma et. al., 2014). Five different series of thin film samples of Ni-Co binary alloys were deposited on the Cu substrate.

Factors Affecting Electrodeposition

1. Effect of current density and distribution
2. The effect of pH which depends upon the bath concentration
3. Temperature; an increase in temperature leads to increase in crystal size
4. Effect of bath concentration
5. Deposition time effect the thickness of deposited film.

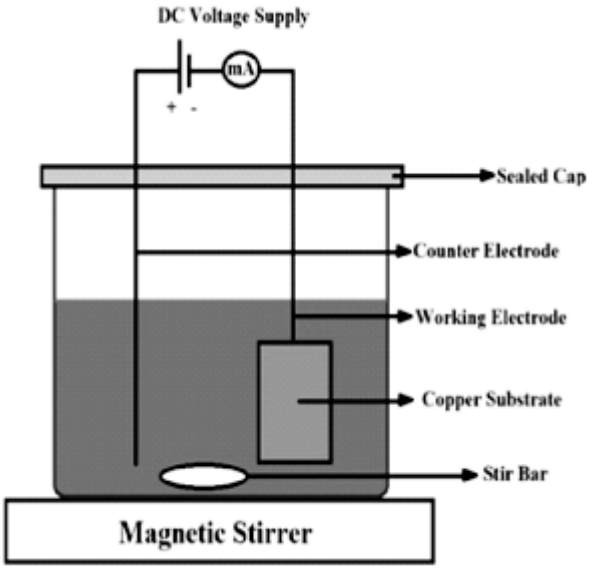

Fig. 1.The electrodeposition setup

Experimental Details

Substrate preparation and electrodeposition : The Ni-Co films were electrodeposited on copper substrate that was initially prepared for electrodeposition. The substrate were cleaned then rinsed from distilled water and then it was treated with acetone and then dried. Deposition of Ni-Co films on copper substrate were performed by using a conventional sulphate bath electrodeposition process. Fig. 1 shows the electrodeposition setup. According to table 1 the concentration were taken:

Table 1. Sulphate bath electrolyte compositions and parameters for Ni-Co films

Sample	Component Salts	Concentration ($g\ ml^{-1}$)	pH
Ni-Co	$NiCl_2 . 6H_2O$	5	
	$CoSo_4 . 6H_2O$	2.9	2-4
	H_3BO_3	3	

The pH of the electrolytic solution was controlled for different samples and the temperature was set between 100°C to 150°C. Five different samples were prepared at different values of current and voltages (Ma et. al., 2014).

Table 2. Samples of deposited of Ni-Co

Sample No.	Time of deposition	Deposition current (mA)	Voltage (V)
1	1 hour	35	1.3
2	1 hour 30 minutes	42	1.0
3	45 minutes	30	2.1
4	50 minutes	12	2.1
5	30 minutes	32	1.3

After deposition these samples were kept in vacuum desiccator. The samples were examined by X-Ray Diffraction measurements were carried out by Rigaku Miniflex 600 X-Ray Diffractometer. The composition of the prepared thin film samples was ascertained from X-Ray Fluorescence (XRF) measurements were taken on different part of the sample.

Results and Discussion :

Crystal structure : The crystographic structure of the samples were identified by X-Ray Diffraction (XRD) using a Rigaku Miniflex 600 X-Ray Diffractometer with filtered CuKa radiation of wavelength 1.54 Å. The X-ray

diffraction measurements were performed at room temperature from Diffraction angle 30° to 90°. Fig. 2 shows the XRD data of sample 1.

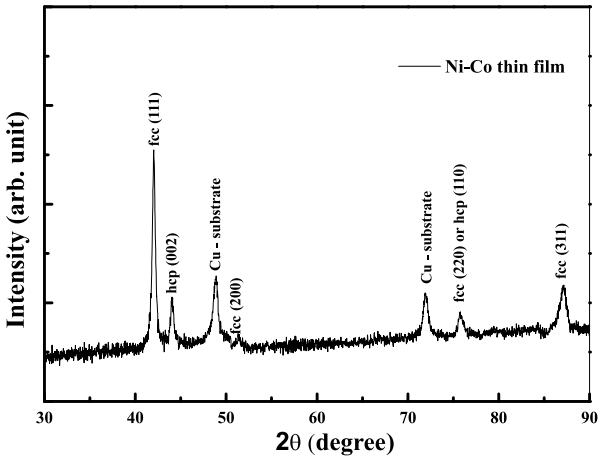

Fig. 2. X-ray diffraction data of Ni-Co alloy deposited on Cu substrate

The peak shows the texture of the deposited thin film. At angle 2q = 43.92° face cantered cubic structure is obtained whose miller indices are (111). At angle 2q = 44.42° hexagonal closed packed structure is obtained whose miller indices are (002), at 2q =51.36° face centred cubic structure is obtained whose miler indices are (200) and at angle 2q = 75.75° its miller indices are (220). Thus, it is observed that either face centred structure exists or hexagonal closed packed structure exists. We know that nickel has face centred cubic unit cell while cobalt has hexagonal closed packed structure (Puri et. al., 2010).

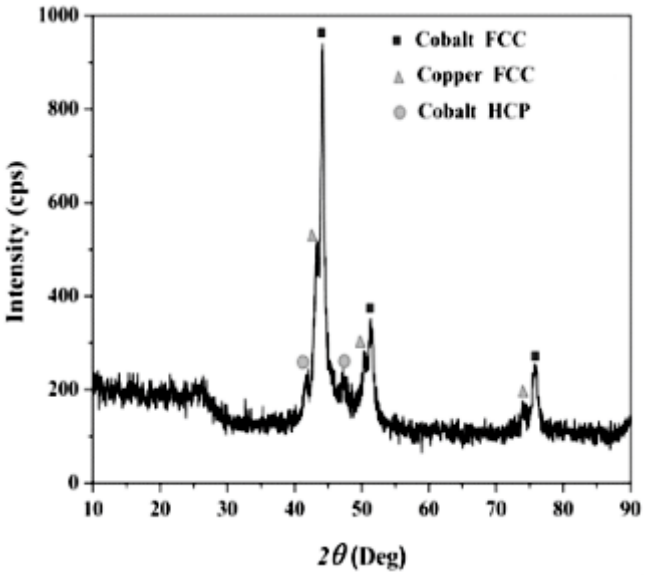

Fig. 3. X-ray diffraction data of Cobalt

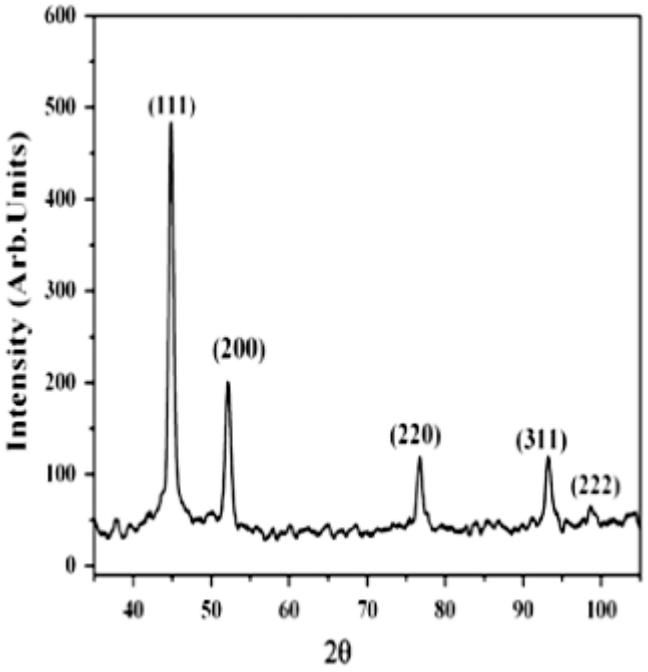

Fig. 4. X-ray diffraction data of Nickel

In Hexagonal close packing (HCP), layers of spheres are packed so that spheres in alternating layers overlie one another. As in Cubic close packing, each spheres is surrounded by 12 other spheres. In hexagonal close packing structure lattice parameters ***a*** is equal to ***b*** (***a*** = ***b***) but ***b*** is not equal to ***c*** i.e. (***b*** ¹ ***c***) and a and b is equal to 90° and g = 120°.

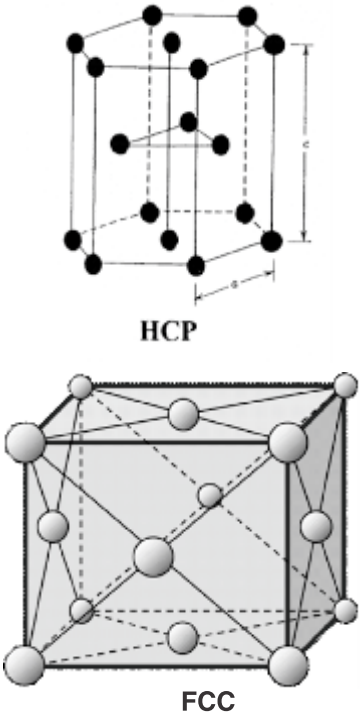

Fig. 5. The FCC and HCP structure

In a Face centred cubic structure lattice parameter a, b and c are equal and a, b, g is equal to 90°(Bai et.al., 2002).

Calculation:

From Bragg's law, we know that 2d sinθ =$n\lambda$, where d is the interplanar spacing of the crystal lattice, l is the wavelength of the incident X-ray and n = 1, 2, 3, ... (Puri et. al., 2010).

The relation between the lattice parameter and interplanar spacing is given by

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Here$(h\ k\ l)$ are the miller indices (Pillai et. al., 2018).

1. For first peak the angle is obtained as
$2\theta = 43.92^o$, $\theta = 21.96^o$

From Bragg's law, 2d sinθ =$n\lambda$

$$\therefore d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Here the miller indices are given as (111) for this $d = \frac{a}{\sqrt{3}}$

$$\frac{2a}{1.732}\sin(21.96) = n(1.54)$$

where l =1.54 Å is the wavelength of Copper kαline.

$$\Rightarrow 0.374a - \frac{2.66}{2}\text{ Å}$$

$$\Rightarrow a = \frac{1.33}{0.374}\text{ Å}$$

therfore, a = 3.56 Å

2. For second peak angle obtained is ,
$2\theta = 51.36^o$ $\theta = 25.68^o$

From Bragg's law, 2d sin θ =nλ

For miller indices (200), $d = \frac{a}{2}$

$$\Rightarrow \frac{2a}{2}\sin(25.68^0) = n(1.54)$$

$$\Rightarrow a\ (0.433) = 1.54\text{ Å}$$

$$\Rightarrow a = 3.55\text{ Å}$$

3. For third peak angle obtained is , $2\theta = 75.75^o$
$\theta = 37.875^o$

From Bragg's law, $2d\sin\theta = n\lambda$

For miller indices (220), $d = \frac{a}{2\sqrt{2}}$

$$\Rightarrow \frac{a}{2\sqrt{2}}\sin(37.875^0) = n(1.54)\text{ Å}$$

$$\Rightarrow a\ (0.61) = 2.177\text{ Å}$$

$$\Rightarrow a = 3.56\text{ Å}$$

From the above three calculations we obtain the same values of lattice parameter of 'for different values of peak angles.

Concentration of components in the electrodeposited thin films : After performing X-ray Fluorescence method the concentration of the constituent elements are obtained. The copper substrate which was used for deposition of thin film of Ni-Co alloy consists of 96.70% of copper in it.

X-Ray Fluorescence (XRF) of several different positions of four different samples are given below which shows the percentage of the substrate and the deposited Nickel and Cobalt. The information was obtained from the XRF Machine (Model Number-AI800) (Wang et. al., 2005).

Table 3. The percentage of Copper, Cobalt and Nickel present in the four samples deposited on the Cu substrate for different deposition time.

1st sample (Deposition time = 1 hour)			
Elements	**1st position (in %)**	**2nd position (in %)**	**3rd position (in %)**
Co	53.68	53.33	56.84
Cu	30.02	33.26	27.07
Ni	9.70	9.99	9.89

2nd sample (Deposition time = 1 hour 30 minutes)			
Elements	**1st position (in %)**	**2nd position (in %)**	**3rd position (in %)**
Cu	45.31	48.25	58.94
Co	43.09	40.49	30.45
Ni	8.67	8.46	5.46

3rd sample (Deposition time = 45 minutes)			
Elements 1st	position (in %)	2nd position (in %)	3rd position (in %)
Cu	77.16	71.20	70.70
Co	15.60	20.82	21.12
Ni	3.13	3.66	3.69

4th sample (Deposition time = 30 minutes)			
Elements 1st	position (in %)	2nd position (in %)	3rd position (in %)
Cu	56.50	45.19	44.28
Co	32.04	43.16	43.84
Ni	4.98	7.04	7.15

Crystallite size : Crystallite size is usually measured from X-ray diffraction patterns and grain size by other experimental techniques like transmission electron microscopy. Most of the Solid materials are polycrystalline in nature, made of a large number of small single crystallites held together. The crystallite size can vary from a few nanometres to several millimetres (Pillai et. al., 2018).

The Scherrer equation, in X-ray diffraction and crystallography, is a formula that relates the size of sub-micrometres particles, or crystallite, in a solid to the broadening of a peak in diffraction pattern. Scherrer equation for the determination of size of particles of crystals is given by:

$$\tau = \frac{k\lambda}{\beta\cos\theta}$$

where t the mean size of the order (crystallite), K is shape factor, I is the X-ray wavelength, is the Bragg's angle and is the line broadening at half the maxima intensity.

Calculation of crystallite size

1. For the calculation of crystallite size, we have

   peak angles at 75.75° and 75.24°, wavelength (λ) = 1.54 Å

   Shape factor K = 0.9

   Maximum peak = 1909, minimum peak = 1625

   $2\theta = 75.495$

   $\Rightarrow \theta = 37.74$

   Difference between angles

   $= (75.75 - 75.24)^\circ = 0.51^\circ$

   $\beta = \frac{0.51 \times 3.14}{180} = 0.0088$ radian

   Therefore, crystal size $= \frac{k\lambda}{\beta\cos\theta}$

   $= \frac{0.9 \times 1.54}{0.0088 \times \cos(37.74)} \Rightarrow 199.7$Å

2. For the calculation of crystallite size, we have

   Peak angles at 51.05° and 51.55°, wavelength (λ) = 1.54 Å

   Shape factor K = 0.9

   Maximum peak = 2053, minimum peak = 1562

   $2\theta = 51.30$

   $\Rightarrow \theta = 25.65$

   Difference between angles

   $= (51.55 - 51.05)^\circ = 0.50^\circ$

   $\beta = \frac{0.50 \times 3.14}{180} = 0.0087$ radian

   Therefore, crystallite size $= \frac{k\lambda}{\beta\cos\theta}$

   $= \frac{0.9 \times 1.54}{0.0087 \times \cos(25.65)} \Rightarrow 175$ Å

   Thus the crystallite size lies between 19.97 nm to 17.5 nm (Wang et. al., 2005).

Conclusion :

Thin films of Ni-Co alloy were successfully deposited on the copper substrate. After X-ray diffraction (XRD) we get several peaks which confirm that it is crystalline in nature. Some of the peak angles are, $2\theta = 43.92^\circ$ for which miller indices (111) and it has a face centred cubic structure, $2\theta = 44.42^\circ$ for which miller indices is (002) and it has hexagonal closed packed structure and $2\theta = 75.75^\circ$ and its miller indices is (220). Thus, it is conformed that thin film samples has mixed phase of hexagonal closed packed structure and

face centred cubic structure. For all the FCC peaks, the value of lattice parameters are similar .i.e.

$$a = b = c = 3.56 \text{ Å}$$

X-Ray Fluorescence (XRF) gives the percentage of constituent element present in the deposited film on the substrate.

The crystallite sizes were also measured by Scherrer equation and it lies in the range of 17.5 nm to 19.97 nm.

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