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Electrodeposition and characterization of Ni-Co Nano composite from glycine Bath

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Abstract
Nanostructured nickel and cobalt deposits were obtained on Cu substrates, using electrodeposition method, with different operating conditions such as: current density id, temperature **C**, time min, PH, Concentration of Ni/Co c and organic additive contents in the deposition bath. The obtained coatings were characterized using X-ray diffractometr (X RD), Scanning Electron microscope (SEM) and Energy Dispersive X-ray (EDX). Results indicated the formation of nanostructured Face centered cubic (fcc) and Hexagonal close packed (hcp) This is, due to the presence of Ni, and Co in the composite, respectively. The optimum conditions results from the presence bath is of anomalies type.

Keywords: electrodeposition, Ni-Co Nano composite, glycine bath, Ni-Cobalt deposits, Cu-substrate

1. Introduction

Many synthesis techniques for production of nanostructured materials have been developed like inert gas condensation, ball-milling, severe plastic deformation, chemical vapor deposition and electrochemical deposition. The electrodeposition technique has significant advantages compared to other methods for synthesis of nanocrystalline materials; one of them is possibility of preparation of amorphous alloys. Other important advantages are the easy preparation of materials of high purity exhibiting different structures and morphologies and the possibility of changing the composition and morphology within a broad range, adjusting only the deposition parameters (Lidija, *et al*, 2009) [12]. Alloy deposition of two or more metals has been carried out to improve properties such as grain size, hardness and corrosion resistance than the parent metals. The deposition of face centered cubic (FCC) Ni–Co alloy coatings has been widely used for recorder head materials in computer hard drives and in surface finishing industries for items such as printed circuit boards, wear resistant coating, corrosion resistance layers, electroformed laser mirrors and decorative coating. During alloy deposition, anomalous behaviour can arise when the less noble metal (cobalt) is preferentially deposited compared to the more noble metal (nickel). This phenomenon was described and classified by Brenne. (Mehdi Ebadi, 2009) [14] The thickness of the magnetic layer used in microelectrical mechanical system (MEMS) can vary from a few nanometers to a few millimeters, depending on the applications, and the magnetic thin films must have good adhesion and corrosion resistance and low-stress, and be thermally stable with excellent magnetic properties. As a kind of typical magnetic layers for MEMS, electrodeposited Ni–Co alloy coatings have been widely used as recording head materials in computer hard drive industries Since metal-matrix composite coatings usually have significantly improved mechanical strength, wear resistance and corrosion resistance, and desired chemical and biological compatibilities than the alloy coatings. (Shi, *et al*, 2005) [17]. showed that the structure of electrodeposited Co significantly depends on the level of used overpotential When electrodeposition is performed far from equilibrium conditions, *i.e.* at a higher overpotentials, FCC cobalt is deposited while at lower overpotentials HCP Co is formed with a lower rate of hydrogen evolution. Recently, several papers have been published on the effect of electrolyte composition and current density on the hardness of the electrodeposited iron group films as well as on the chemical composition, structure, electric and magnetic properties and corrosive stability of thin electrodeposited nanocrystalline film. Higher electrical resistivity of the electrodeposited Ni–Co alloys can be attributed to the smaller grain sizes, high defect densities, and impurity incorporation during electrodeposition (Lidija, *et al*, 2009) [12]. Ni-Co alloy foils can be fabricated in several methods such as smelting and electrodeposition. However, the method of electrodeposition is the simplest, most economical, reliable and reproducible technique. Experimental studies on the electrodeposition of Ni–Co alloy by DC current or pulse currents were carried out by a number of researchers (Fang, *et al*, 2011) [8] Amorphous ferromagnetic films are widely used in the microelectronics industry, magnetic media and computers. Different methods are used in the preparation of these films. Electrodeposition is a good technique for preparing highly functional magnetic recording materials. It offers the advantage of low-cost production, since producing multi-layers with a large area and arbitrary. Nickel, cobalt and their alloys are important it requires simple and inexpensive processing equipment. Moreover, electrodeposition technique is suitable for engineering materials. They have unique properties, such as magnetic, wear-resistant, heat-conductive, light-reflector and electrocatalytic activity (Kamel, 2007) [11] and also exhibits many excellent properties such as corrosion resistance, ductility, brightness, good strength, hardness and stable beneficial magnetic properties. So Ni-Co alloy foils are typical magnetic materials applicable in several fields, such as soft-magnetic and giant-magneto-resistive (GMR) materials (Fang, *et al* 2011) [8]. In addition, Ni and Co oxides are used in batteries. The physico-chemical properties of alloys are seriously affected by their composition and structure. Therefore, reliable control of their composition and structure is an important issue for their wide application. Cobalt and nickel forms a solid solution over the whole concentration range. This ability enables the potential uses of their magnetic properties in a wider range of conditions. This makes Co–Ni alloy of special interest to the microelectronics industry. Further, Co–Ni films are expected to show greater resistance to corrosion than Ni–Fe films. The electrodeposition of Co–Ni alloys, whether from simple or complex baths, is a codeposition of anomalous type. The less noble metal, Co, deposits preferably to the nobler one, Ni. The operating conditions such as current density, temperature, pH, use of organic additives, buffer capacity, concentration of all solution components, etc. lead to changes in the kinetics of electrodeposition, the composition and morphology of the coatings and their physicomechanical characteristics (Kamel, 2007) [11] The anomalous composition related to the current density, temperature, pH value, applied potential and other variables in electrolyte would affect the property of alloy (chung, *et al*, 2010) [6]. The majority of metal electrodeposition processes are carried out from baths containing complexing agent. Recently, the various complexing agents such as sulfamates, tartrates, citrates, glycinates and gluconates have been used. These complexing agents are non-toxic, easily obtained and their degradation products offer easier treatment The purpose of the present investigation is to obtain cobalt–nickel electroplates with good quality from acidic glycine baths. Such baths are not only cheap but also environmentally friendly and easily degradable (Kamel, 2007) [11].

2. Experimentals

Solutions baths listed in Table 1 were freshly prepared from Analar chemicals and doubly distilled water were used. Copper sheet cathode and pure platinum sheet anode both of dimensions 2X2 cm2 were used as electrodes. The copper sheet cathodes were mechanically polished with different grade emery papers and then immersed in pickling solution (300ml H2SO4+100ml HNO3+5ml HCl+595ml doubly distilled water) for 1min, washed with distilled water, rinsed with acetone, dried and finely weighed. The pH was measured using Microprocessor pH/mV/^{0}C Meter (Model CP 5943-45USA) and adjusted by NaOH 20% addition, the temperature was controlled by using water bath. Direct current was supplied by a d.c power supply unit (GP-4303D). The copper cathodes were weighed before and after electrodeposion for a certain period of time and at fixed current density. the surface of the as-deposited nickel and cobalt, on copper substrates was morphologically inspected using scanning electron microscopy (SEM). (JEOL-5410 attached to an EDX unit), phases of surface and phase changes of the different coated substrates investigated by using an X-Ray Diffractometer.

Whereas the different thicknesses of as deposted Co/Ni coatings were calculated according to the following equation:

$$\text{Thickness (T)} = \frac{W}{A \,.\, D}$$

Where;
W ≡ The weight of deposit.
A ≡ The Area of the deposited.
D ≡ The density of the metal.

Table 1: The bath composition and operating conditions of nickel-cobalt composite

Nickel chloride	0.2 – 0.8 M
Cobalt chloride	0.2 – 0.8 M
Boric acid	0.2 g/l
Ammonium sulfate	0.2 g/l
Ammonium chloride	0.2 g/l
Glycine	0.4 g/l
Temperature	45 - 75^0C
Current density	0.2 – 1.0A/dm^2
PH	5 – 10
Time	10 – 60 min

3. Results and Discussion

Several studies were devote to specific features of nickel deposition from glycine containing bath, However, the contemporary opinions on the mechanism of this process substantially disagree with one an other. Some authors believe that complexes of any composition formed in solutions are discharge simultaneously on both, solid nickel and dropping mercury electrode. Other show that amono glycinate complex [Ni $(H_2O)_4$ GLY] + is the electro- active species and the discharge of complexes with different composition necessarily includes a preliminary chemical dissociation stage. The notions on the nature of the diffusion nature, whereas in, certain kinetic difficulties that arise in the presence of small amino acid concentrations were mentioned, such deviations in the views on this process were first of all caused by the complex composition of the studied electrolyte for which the comparison of literature data is complicated due to the do different experimental condition used. The studies were carried out for different ratios of main solution components (their concentration could differ by an order of magnitude) in the presence or absence of supporting baths; for the constant ionic strength or supporting bath concentration. In practice, in conventional nickel – plating baths, the Ni(11) concentration is of tenmaintained constant by correcting procedures; while the glycine concentration and the solution PH vary in wide ranges during the electrolysis (Bradley, 2011) [5]. Cobalt is seem to follow the same behavior with glycine except that the formation constant of the complex of glycine with nickel is greater than cobalt as Ni/Co electrodeposition from gluconate bath (Kamel, 2007) [11].

Time effect on electrodeposition of Co/Ni from glycine bath was shown in table (2) and fig (1) respectively, it’s clear that the thickness increased with increasing time and these agreed well with Faradays law.

Table 2: Time effect of Co/Ni electrodeposition

Time (min)	Thickness (μm)
10	7.55
20	16.9
30	18
40	26.17
50	27.46

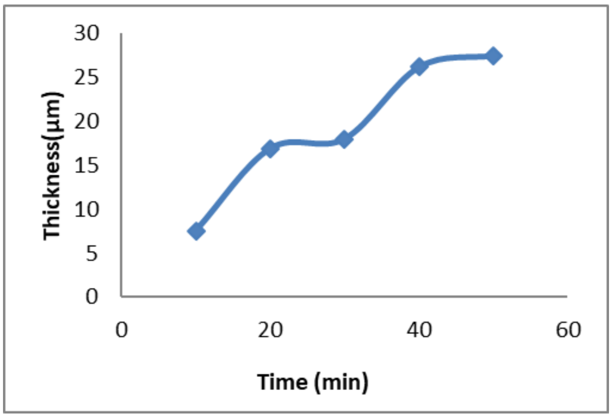


Fig 1

Fig 1: The effect of time in the deposition of Co/Ni from bath containing nickel chloride (0.2M), cobalt chloride (0.2M), Boric acid, Ammonium chloride (0.2M), Ammonium sulphate (0.2M), glycine, PH= 3, current = $0.2A/cm^2$, temperature =30^0C, time= (10, 20, 30, 40, 50 min).

- No doubt that Co/Ni electrodepositing is of anomaly type deposition in which the less noble metal Co, deposits preferably to the nobler one, Ni in any concentration of all solution components (Ali Eltoum, 2011) [2] therefore from table (3) and fig (2) one could see increasing in thickness of coatings when the concentration of cobalt increased in the bath.

Table 3: The effect of cobalt chloride in the deposition of Ni/Co alloy

Cobalt(M)	Ratio of Co/Ni	Thickness (µm)
0.2	0.5	5.59
0.3	0.6	8.389
0.5	0.71	11.189
0.7	0.78	14.54
0.8	0.8	15.66

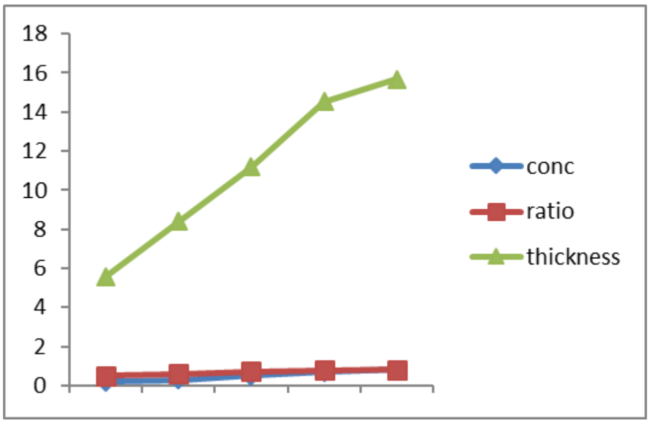


Fig 2

Fig 2: The effect of cobalt chloride in the deposition of Ni/Co from bath containing nickel chloride (0.2M), cobalt chloride (0.2-0.8M), Boric acid, Ammonium chloride (0.2M), Ammonium sulphate (0.2M), glycine, PH= 3, current = $0.2A/cm^2$, temperature =30C, time = 10.

- It's clearl from Table 4 and Fig 3 is that the thickness of plates decreased as Nickel chloride decreasing and the deposition rate was also decreased according to Faraday law's and Nernst equation.

Table 4: The Nickel Chloride effect in Co/Ni alloy deposition

Ni (M)	Ratio of Ni/Co	Thickness (µm)
0.2	0.5	13.7
0.3	0.6	10.9
0.5	0.71	10.06
0.7	0.78	10.9
0.8	0.8	12.3

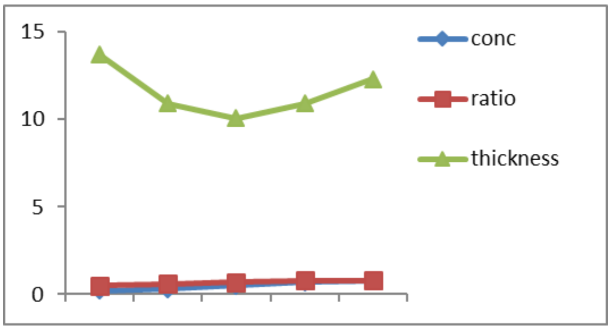


Fig 3

Fig (3): The effect of Nickel chloride concentration in deposition of Ni/Co from bath containing nickel chloride (0.2-0.8 M), cobalt chloride (0.2M), Boric acid (0.2M), Ammonium chloride (0.2M), Ammonium sulphate (0.2M), glycine (0.2M), PH= 3, current = $0.2A/cm^2$, temperature =30C, time= 10

- Most chemical reaction go faster at higher temperature so that nickel and cobalt ion will deposit from warm solution than cooler, furthermore according to Nernst equation the cathode potential is effect by temperature so that the thickness of plate increasing and after (65C) decreased due to the polarization effect as shown in Table (5) and Fig (4)

Table 5: The temperature effect in Co/Ni deposition

Temperature (°C)	Thickness(µm)
45	2.796
55	6.3199
65	10.18
75	3.02

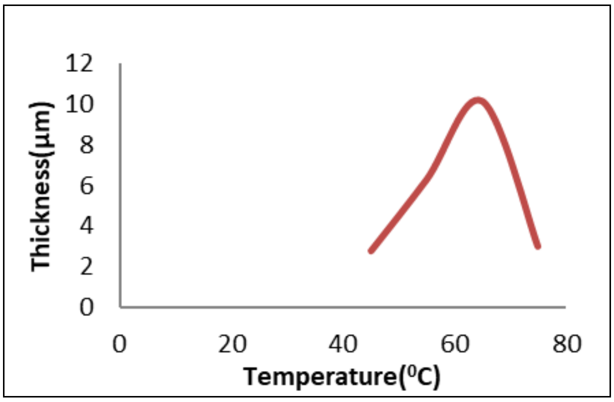


Fig 4

Fig 4: The effect of Temperature in deposition of Ni/Co from bath containing nickel chloride (0.2M), cobalt chloride (0.2M), Boric acid (0.2M), Ammonium chloride (0.2M), Ammonium sulphate (0.2M), glycine (0.2M), PH= 3, current = $0.2A/cm^2$, temperature = (45, 55, 65, 75C), time= 10.

- From table (6) and Fig (5) the thickness of plate increased as the current increasing and this in a good agreement with Faradays law.

Table 6: The current density effect in Co/Ni deposition

Current (A/cm^2)	Thickness (µm)
0.2	7.88
0.4	15.38
0.6	24.02
0.8	27.09
01	39.43

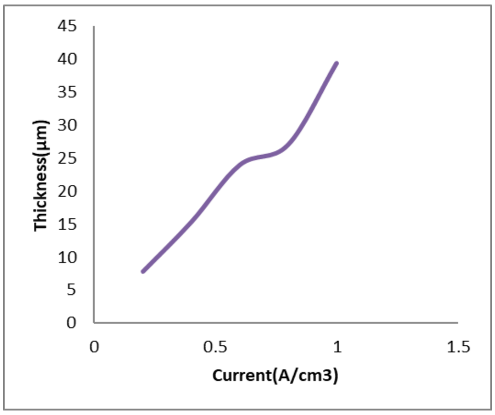


Fig 5

Fig 5: The effect of different current densities in the deposition of Ni/Co from bath containing nickel chloride (0.2M), cobalt chloride (0.2M), Boric acid (0.2M), Ammonium chloride (0.2M), Ammonium sulphate (0.2M), glycine (0.2M), PH= 3, current =(0.2, 0.4, 0.6, 0.8, 1A/cm^2), temperature = (30C), time= 10.

- From Table 7 & Fig 6 the PH is clearly affect the deposited thickness of the plate, in high acidic solution the hydronium ion transport proton to anode and created free metal particle, this charge are deposited onto cathode so that the thickness of plate decreased as a base nature of medium increasing and increases as acidic solution increasing.

Table 7: The PH effect in Co/Ni deposition

PH	Thickness(µm)
5	9.68
6	10.35
7	7.159
8	6.124
9	6.124

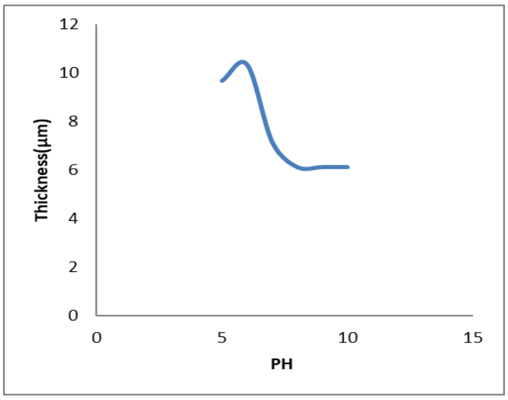


Fig 6

Fig 6: the effect of change in PH in the deposition of Ni/Co from bath containing nickel chloride (0.2M), cobalt chloride (0.2M), Boric acid (0.2M), Ammonium chloride (0.2M), Ammonium sulphate (0.2M), glycine (0.2M), PH= (5, 6, 7, 8, 9, 10) current =(0.2A/cm^2), temperature = (30C), time= 10.

3.2 Characterization of Co/Ni Coatings

- Figure (7): XRD data show that Co–Ni form solid solutions and this enables the alloys to be obtained with different proportions of the two metals. This is in agreement with previously published data on the deposits obtained from chloride and acetate electrolytes (Mehdi Ebadi, 2009) [14]. two well-defined peaks are observed. The peaks are sharp and well defined, indicating good crystallization structure. All indexed peaks correspond to formation of Ni-Co deposit.

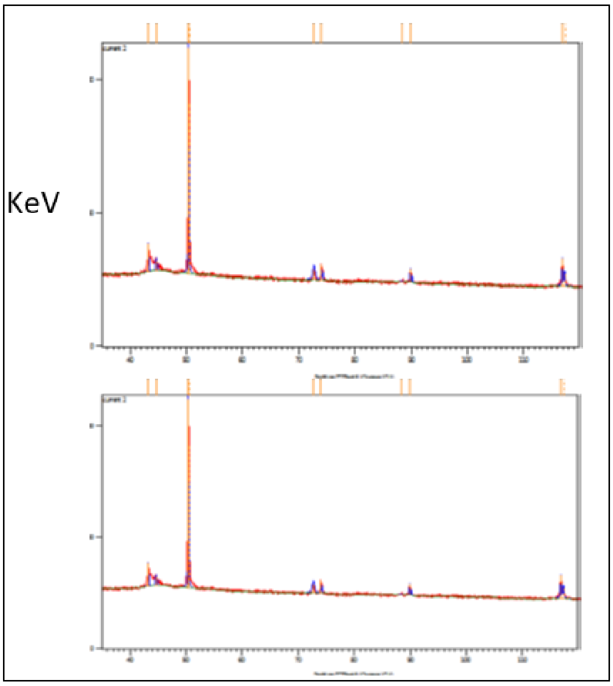
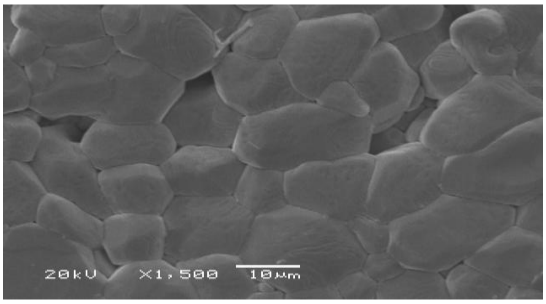


Fig 7: XRD patterns of Ni-Co alloy deposits from optimum bath conditions.

- Figure 8: shows the SEM micrographs of the Ni-Co alloy with different cobalt contents. The morphology shows uniform spherical fine-grain nodules which are characteristic of cobalt alloy deposits. Hydroxide particles are not observed and all the deposits are bright, metallic and smooth. Obvious grain boundary can be found on the deposit. Also it can be seen that the crystal size of the deposit with higher Co content is much smaller.



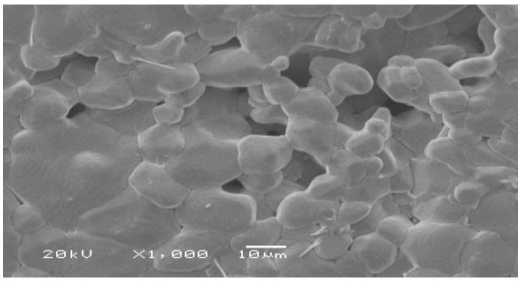
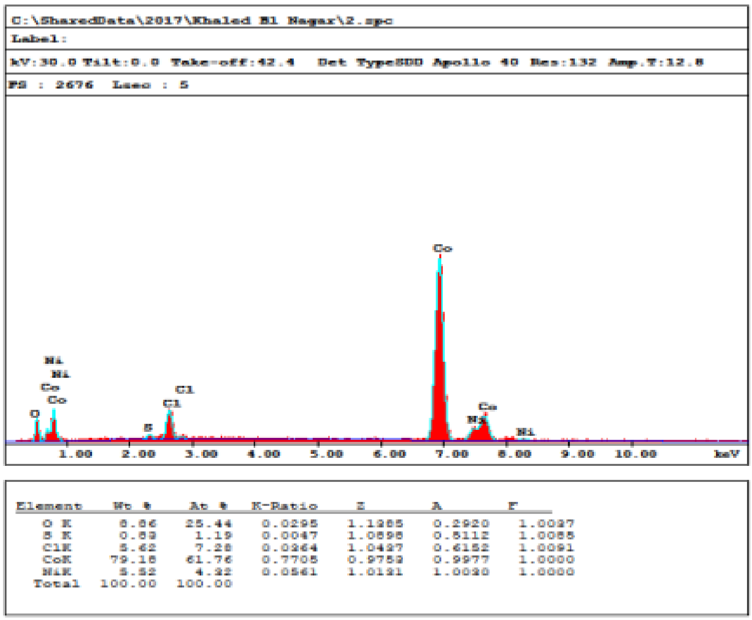


Fig 8: 3D SEM reconstructions of the surfaces of Ni−Co deposits from an electrolyte with concentration Ni2+ (0.2M): Co2+ (0.2M).

- Fig (9): Deposited Ni–Co alloys were also investigated using SEM and EDX. From EDX analysis, it was clear that the electrodeposition of cobalt was enhanced compared to nickel deposition and this can be related to nature of this deposition of this type which is of anomuls type.
- The XRD figure has illustrated at the presence of Thiourea the full width at half maximum (FWHM) of textures (200) were broadened with increasing of cobalt and applied PPMF as well. The intensity of peaks (220) was shrunk with increasing of cobalt and Magnetic flux. To controversy, the intensity of textures (200, 111) was enlarged with the enhancing of cobalt on the electrodeposited Ni–Co alloy films. The grain size changing of deposited layers could be calculated from XRD data through the Debye–Scherrer equation. (Mehdi *et al*, 2009) [14].

$$\iota = \frac{0.9\,\lambda}{\text{FWHM} \cos\theta\ c}$$

where **λ** = 1·540 A is the wavelength, full width at half maximum (in radians), ι is the grain size/nm, in applying the above calculation the grain size of the deposited layer was in the Nano sized.



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Element   Wt %    At %   K-Ratio     Z        A        F
  O K     8.86   25.44   0.0295   1.1985   0.2920   1.0027
  S K     0.69    1.19   0.0047   1.0898   0.5112   1.0085
  ClK     5.62    7.28   0.0264   1.0427   0.6152   1.0091
  CoK    79.18   61.76   0.7705   0.9759   0.9977   1.0000
  NiK     5.52    4.22   0.0561   1.0121   1.0020   1.0000
 Total  100.00  100.00
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Fig 9: EDX of Ni/Co coating

Conclusion

In the present research electrodeposition of Co/Ni from glycine bath was investigated, the different operating conditions of electrodeposition process were studied and attended and it were shown that the less noble metals in the bath (Cobalt) was always high in the alloys of Co/Ni than Nickel indicated a nomolus type deposition.

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