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Corrosion resistance and hardness characteristics of electrodeposited ternary black Ni-Cu-Co alloy coatings

S. Karthikeyan[1*], P.A. Jeeva[2], S. Narayanan[2]

[1*]Surface Engineering Research lab, Centre for Nanobiotechnology, VIT University, Vellore-632 014, India.
[2]School of Mechanical &Building Sciences, VIT University, Vellore-632 014, India.

Abstract

An attempt has been made to develop a novel ternary Ni-Cu-Co coatings with improved corrosion resistance and micro hardness values. XRD and XPS studies have proved that the enhancement of corrosion resistance and hardness by coating after annealing at 300°C could be due to the formation of Ni_3Cu_5, CuO and NiO and confirmed from the appearance of core peaks at Co $2p_{3/2}$, Cu 3p, Cu $3p_{3/2}$, Ni $2p_{3/2}$ and Ni 2p with binding energies of 785 eV, 45 eV, 933 eV, 853 eV and 839 eV respectively. The formation of uniform layer of Ni-Cu-Co coatings is evident from SEM images. The coatings offered the corrosion resistance of 40 times of uncoated mild steel surface in 3.5% NaCl. The reduction of E_{corr}, I_{corr}, C_{dl} and enhancement of R_t value from polarization and impedance measurement indicated the corrosion resistance ability of Ni-Cu-Co black coatings.

Keywords Ni-Cu-Co coatings, corrosion resistance, impedance, salt spray

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Introduction

In the field of surface treatments, black coatings are extensively used for decorative or solar absorbing functions. The films deposited should have high optical properties (absorption of solar radiations). Black coatings used for both decorative and solar absorbing functions are mostly prepared by liquid phase deposition or vapour phase deposition. Black nickel and black chromium are the most significant electrodeposited materials, whereas the films elaborated by vapour phase deposition comprise generally titanium alloys and carbon based materials. The studies on black coatings based in electrodeposition of nickel alloys in recent years are gaining much value as they discover a great range of applications in different fields like solar absorbance and gas turbines.

Electrodeposited black nickel bath was prepared from sulphate, chloride and combination of both chemicals by Dennis et.al.[1] and Ibrahim [2]. Mehra and Sharma [3] are of view that black nickel coatings for solar applications could be obtained by chemical conversion of zinc-coated aluminium. Monteiro et.al.[4] have reported that the black colour of the nickel and zinc electro coatings are due to the formation of zinc sulfide and nickel sulfide particles in the film. But, they found that these coatings did not show consistent resistant to corrosion above 75°C. Koltun [5] et.al., Peterson [6] et.al. and Bonora and his co-workers[7] have investigated that corrosion resistance of coatings using polarization techniques. These coatings showed better optical properties as compared with earlier reports. Electroless black nickel coating was first developed by Guofeng Cui et.al.[8] to improve the

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mechanical properties and corrosion resistance and they claimed that improvement in mechanical properties are due to the surface texture modification in coatings. However, the uses of black Ni-Cu-Co ternary alloys on improvement of mechanical properties on metallic objects have not been exposed. This lead to an identification of appropriate black coatings to be used for enhancing the mechanical properties in order to enable to extend life time of machineries. The performance of coatings is to be evaluated by weight gain studies, micro hardness evaluation, corrosion resistant measurement by electrochemical methods. The surface morphology of the coatings is the predominant properties of the coating which will be assessed by XRD, SEM and XPS. Salt spray analysis to be carried out to follow up the corrosion and get an idea about the performance of Ni-Cu-Co black coatings in automobile parts.

Experimental Procedure

The optimized bath used in the present study had the following composistions.

$NiSO_4.6H_2O$ = 40 g/l

$CuSO_4.6H_2O$ = 8 g/l

$CoSO_4.5H_2O$ = 15 g/l

Ammonium thiocyanate = 25 g/l

Boric acid = 30 g/l

EDTA = 3 g/l

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pH = 4.7

Current density = 400 mA/cm^2

Plating time = 180 seconds

Evaluation of black coatings through different techniques

Weight-gain method

Mild steel specimens of 99.52% purity of size 20 x 50 x 2 mm^3 were used in the plating bath. They were polished with fine grit paper and degreased using tri choloro ethylene to remove oil and greases. Mild steel panels were pretreated in acid bath followed by alkali bath and washed with tap water. They were rinsed in double distilled water and dried. The initial weight of panel was recorded using digital weighing balance machine. The same operating conditions were used for coating on radiator drain plug, lock nut and vehicle brake tube made of mild steel. Then, both metallic components and mild steel test specimens were introduced into the plating solution under optimized conditions of the bath. The rate of deposition was calculated using the following formula:

$$\text{The rate of deposition } (\mu\text{m/h}) = \frac{W \times 10^4}{D\,A\,T}$$

Where,

W – Weight of the deposit (g)

D – density of the deposit (g/cm^3)

T – plating duration (h)

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A - Surface area of the specimen (cm^2)

Micro hardness measurements

Micro hardness measurements for all the as plated specimens (20 x 50 x 2 mm^3) and also for the annealed samples at 300°C were made by Vicker's harness tester as per ASTM E-384 with a load of 100 g. A diamond shaped indentation was made on each sample at 8 different places and the average value of hardness was measured from the diagonal of indendation on Vicker's scale using the formula.

$$V.H.N = (1854 \times \text{load}) / d^2$$

where d = diagonal of the indentor

Corrosion resistance measurements

The electrochemical polarization measurement and impedance studies were made with the black coated steel surface of 10 mm^2 area (working electrode), 40 mm of platinum electrode (counter electrode) and saturated calomel as reference electrode in three electrode cell assembly.

Potentiodynamic polarization method

A constant quantity of 200 ml of 3.5% NaCl solution was taken in a 250 ml beaker. The working electrode, reference electrode and the counter electrode were assembled in position and the connections were made. Initially, the potential is noted which is recorded as OCP. From OCP, polarization studies were performed using Sinsil Model 604E Electrochemical Analyzer imported from USA. The readings

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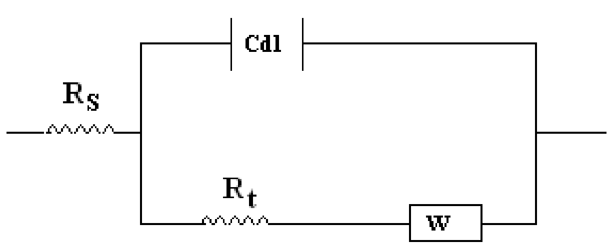
were obtained by ranging the potential values from OCP ± 1000 mV with scan rate 10 mV per second for both as plated and annealed black coated steel surfaces.

The corrosion kinetic parameters such as E_{corr}, I_{corr}, anodic and cathodic Tafel slopes (b_a and b_c) were measured. The reduction in potential values of Tafel slopes gave an idea that whether the black coatings have reduced the oxidation of metal from surface or involved in reducing cholorine gas evolution.

Impedance measurement

The SINSIL Model 604E electrochemical analyzer was used for this measurement in the frequency range of 100 kHz to 0.01 Hz under potentiostatic conditions using 3.5% NaCl as corrosive medium. The impedance measurements were carried out both as plated and annealed black coated steel surface at room temperature. The electrical equivalent circuit for the corroding system is given below:



R_S – Solution resistance

R_t – Charge transfer resistance

W – Warburg impedance

Cdl – Double layer capacitance

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The cell impedance consists of real part (Z') Vs imaginary part (Z''). A plot of real part (Z') Vs imaginary part (Z'') gives a semicircle which cuts the real axis at higher and at low frequency Z corresponds to (R_S + R_t). The difference between the two values gives R_t. The double layer capacitance can be determined from the frequency at which Z'' is maximum from the relation

$$Z''_{(max)} = \frac{1}{2\pi C_{dl} R_t}$$

Surface morphological studies of black Ni-Cu-Co coatings

X-ray diffraction studies

The X-ray diffraction patterns for the black electrodeposited mild steel specimens were made using X' pert pro XRD,(make- Panalytical, USA) both as plated as well as annealed conditions. These measurements help to explain the intermetallic phases formed in the coatings. The X-ray diffraction patterns were obtained with Cu Kα radiation in the above instrument with the step of 0.02°. XRD patters were recorded for different depth profiles employing grazing incidents X-ray technique.

Scanning electron microscopic studies (SEM)

The morphology of the black electrodeposits were examined under high magnification to assess the grain size, deposit nature, heterogeneities and pores present in the deposits using a scanning electron microscope. The scanning electron microscope, which makes use of reflected primary electrons and secondary electrons, enable one to obtain information from regions that cannot be examined by others.

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The deposited specimens of various black coatings were cut into 10 x 10 mm^2 size and mounted suitably and examined under the microscope. The SEM photographs were taken by using S-3000 model with an acceleration voltage range of 20,000 V and with the magnification range of 1000.

Surface Characterization (XPS or ESCA analysis)

The surface characterization measurements were carried out on black coated samples under annealed conditions having surface area of 10 x 10 mm^2 using X-ray photoelectron spectra also known as Electron Spectroscopy for Chemical Analysis (ESCA) in a physical electronics PHI 5600 ESCA system with Al K_α monochromatic source was used to obtain oxidation states of species along with chemical composition of surfaces. The binding energy values were calculated with a precision of ±0.2 eV. For these measurements, the samples were mounted in to an ultra high vacuum chamber at 10^{-9} Torr housing the analyzer. Prior to mounting, the black coated samples were placed in the preparation chamber for 6 hours in order to remove any volatile species exist on the surface.

Salt spray analysis for corrosion resistance of black Ni-Cu-Co coated samples

The salt spray rest of the black coated steel panels were conducted in SF 850 salt spray cabinet as per ASTM B-117 in 3.5% NaCl to understand the corrosion resistance of the coatings in aggressive environment i.e. sea water medium. The corrosion degree of the samples was evaluated by average weight loss which was visibly noted by the appearance of formation of red rust spots on the coated samples used under annealed conditions. This test has established that the

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corrosion resistance of the coatings is higher in sea water medium as a validated result for potentiodynamic polarization and A/C impedance test.

The surface morphological studies were performed using X-ray diffraction technique and scanning electron microscopic images. In order to understand the existence of metallic atoms in black coatings, X-ray photo electron spectra have been carried out for all coatings.

Results and Discussions

Weight gain studies

The results of black coatings obtained in the present study by weight gain method and eddy current tests are presented in Table 1.

It has been observed that the addition of copper into nickel-cobalt system improves the black colour in the coating. If the copper concentration exceeds 8 grams per liter the coating failed to show intense black colour which is the required colour for the present investigations.

However, the addition of cobalt did not show any significant changes in black colour. The optimum loading of copper and cobalt were found as 8 gram per liter and 15 gram per liter.

The rate of deposition for Ni-Cu-Co black coatings was observed as 31μm at the plating timing of 180 seconds. Hence, the above formulations can be used for industrial applications as high speed plating baths.

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Micro hardness measurements

The hardness of the electrodeposited Ni-Cu-Co coatings measured by Vicker's hardness tester is given in Table 2.

The higher hardness of black coatings can be ascribed to the formation of inter metallic phases of Ni-Cu, Cu-Co in the coatings. After annealing, the coatings hardness was found to increase due to the precipitation hardening mechanism formed by Ni_6Cu_6 phases. The results were in good conformity as reported by Kotnarowska [9].

Corrosion resistance studies

Potentiodynamic polarization studies

The corrosion resistance studies of black Ni-Cu-Co black coatings have been carried out potentio dynamically by shifting the potentials from ± 1000 mV from OCP vs Hg/Hg_2Cl_2/KCl(Satd.) which starts from -1474 mv to +526 mV at the scan rate of 10 mV/sec using platinum wire as a counter electrode.

The E_{corr} value for mild steel is -894 mV which is shifted to positive direction for the black Ni-Cu-Co coatings both in the as plated as well as annealed conditions at 300^{o}C. E_{corr} values for nickel based black coatings were found as -788 mV for Ni-Cu-Co in the as plated condition [10-11].

This is further shifted to more positive direction(-435 mV for black Ni-Cu-Co coatings) due to the formation of intermetallic phase precipitations resulted from annealing the coatings at 300^{o}C. The results are presented in table 3.

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It is concluded that after annealing, the coatings exhibited better corrosion resistance than as plated condition. These results are in good agreement with XRD and SEM studies.

Also the corrosion currents(I_{corr}), anodic(b_a) and cathodic(b_c) tafel slopes for coatings both in the as plated and annealed conditions have been reduced to greater extent in comparison with mild steel immersed in 3.5% NaCl confirming that the black coatings offered excellent corrosion resistance.

Electrochemical Impedance Spectroscopy (EIS) studies

The measured impedance spectra of the mild steel substrate and black coatings in 3.5% NaCl solution are shown in the table 4.

It is evident from table 4 that the R_t values increased at the expense of C_{dl} values for the black coatings. In the case of Ni-Cu-Co black coatings, R_t and C_{dl} values were obtained as 1900 Ohm.cm^2 and 3.26 μF.cm^{-2}.

The enhanced values of R_t for black coatings were noticed as 2810 Ohm.cm^2 in annealed conditions. However, the double layer capacitance values have been brought down to 2.47 μF.cm^{-2} indicating that these black coatings could offer higher corrosion resistance in annealed conditions than the as plated steel panels and mild steel [12].

Surface morphology of the Ni-Cu-Co coatings

X-ray diffraction analysis

The results of XRD analysis of Ni-Cu-Co black coatings are shown in Figure 1. The crystalline peaks are resulted from the nickel and alloys. A broad dominant peak appearing around d value of 1.98 indicated the existence of nickel in the black

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coatings. The feeble peaks at d values of 2.3 and 1.41 corresponded to the presence of copper and cobalt metals in the black coatings which accounts for the highest hardness of black coatings than mild steel substrate [13]. A thin peak at d value 7.66 corresponds to the formation of Nickel oxide in the black coatings. This result is in good agreement with results of XPS analysis.

The appearance of peaks at d values of 4.75 and 3.45 confirmed the presence of cobalt in the coatings. The formation of peaks at d values of 1.67 and 1.58 indicated [Figure 2] the formation of intermetallic phase viz., Ni_3Cu_5 which is a soft matrix due to the presence of copper (soft metal).

Scanning Electron Microscopic studies

Figure 3 shows the morphologies of Ni-Cu-Co black coatings obtained from nickel electroplating bath. It can be found that the morphology changes remarkably. For the black coatings, the best evenness and compactness can be observed and needle holes hardly appear on its surface, as evidenced from SEM images[Figure 3(a) & (b)]. The appearance of corn like structure in figure 3(b) indicated the presence of cobalt which has diffused to surface after annealing at 300^{o}C. After annealing, the surface morphologies become more even in compared with SEM images of as plated Ni-Cu-Co black coatings. In the as plated conditions, it was noticed that crowding of particles with coalescence [Figure 3(a)].

XPS analysis of black coatings

The annealed ternary Ni-Cu-Co black coatings were subjected to XPS analysis in order to determine the oxidation state of particular elements in the deposits. In

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figure 4, the core peak of cobalt appeared as $Co2p_{3/2}$ at binding energy 785 eV along with appearance of Cu3p peak at binding energy of 45 eV confirming that copper and cobalt are existing as their oxides with oxidation state of +2 [14-15].

This is further confirmed by the formation of O1s peak with binding energy value 531 eV. The traces of C1s, S1s and N1s at binding energy values 213 eV, 162 eV and 127 eV have shown the utility of ammonium thiocynate which acted as a complexing agent for nickel ions to prevent powdery deposits.

The appearance of core peaks i.e. doublet peaks for nickel as Ni $2p_{3/2}$ and Ni 2p along with a singlet strong peak of Cu $2p_{3/2}$ and O KLL at their corresponding binding energy values of 853 eV, 839 eV, 933 eV and 1008 eV establishing that at inner layers nickel is existing as NiO with oxidation state of +2. Similar is the trend with copper which existed as CuO with oxidation state Cu(II).

Analysis of Salt spray test

The results of salt spray test are shown in table 5. For steel samples, it is noticed that 30% red rust formed on uncoated sample at 30 minutes stay in salt spray chamber. 2% rust area formation on black coatings after 1200 hours stay in salt spray chamber. Therefore, it can be concluded that corrosion resistance of black Ni-Cu-Co coatings in salt spray is 40 times higher than uncoated mild steel.

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Table 1 The results of weight gain studies and eddy current test obtained for Ni-Cu-Co black coatings

S.No.	Ni-Cu-Co coating	Deposition timings (sec.)	Thickness (μm)		Colour of coatings
			Weight gain method	Eddy current test	
1	Optimized bath	180	31	31	Intensive black

Table 2 Micro hardness values for black Ni-Cu-Co coatings

S.No	Coatings	Hardness (V.H.N) Load:100g	
		As plated	Annealed at 300^{o}C
1.	Ni-Cu-Co	295	410

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Table 3 Potentiodynamic polarization studies of black Ni-Cu-Co coatings

Nature of deposit	E_{corr} (mV vs SCE)	Tafel slopes		I_{corr} (μA. cm^{-2})
		b_a (mV.dec^{-1})	b_c (mV.dec^{-1})	
Mild steel	-894	235	212	617
Ni-Cu-Co (As plated)	-788	201	192	540
Ni-Cu-Co (Annealed)	-435	165	157	472

Table 4 Impedance values of Ni-Cu-Co black coatings

Nature of deposit	R_t (Ohm.cm^2)	C_{dl} (μF. cm^{-2})
Mild steel	1710	4.56
Ni-Cu-Co (As plated)	1900	3.26
Ni-Cu-Co (Annealed)	2810	2.47

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Table 5 Results of salt spray analysis as per ASTM B-117

Time (hr)	Uncoated Steel	Black Ni-Cu-Co coatings(Annealed)
0	White	Black
0.5	30% red rust area	Black
1	100% red rust area	Black
36	100% red rust area	Black
120	100% red rust area	Black
240	100% red rust area	Black
480	100% red rust area	Black
960	100% red rust area	Black
1100	100% red rust area	Black
1200	100% red rust area	2% red rust area

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Legends for figure

1. XRD results for Ni–Cu–Co black coatings (As plated)

2. XRD results for Ni–Cu–Co black coatings (Annealed)

3(a). SEM image for Ni–Cu–Co black coatings(As plated)

3(b). SEM image for Ni–Cu–Co black coatings (Annealed)

4. XPS analysis of Ni–Cu–Co black coatings

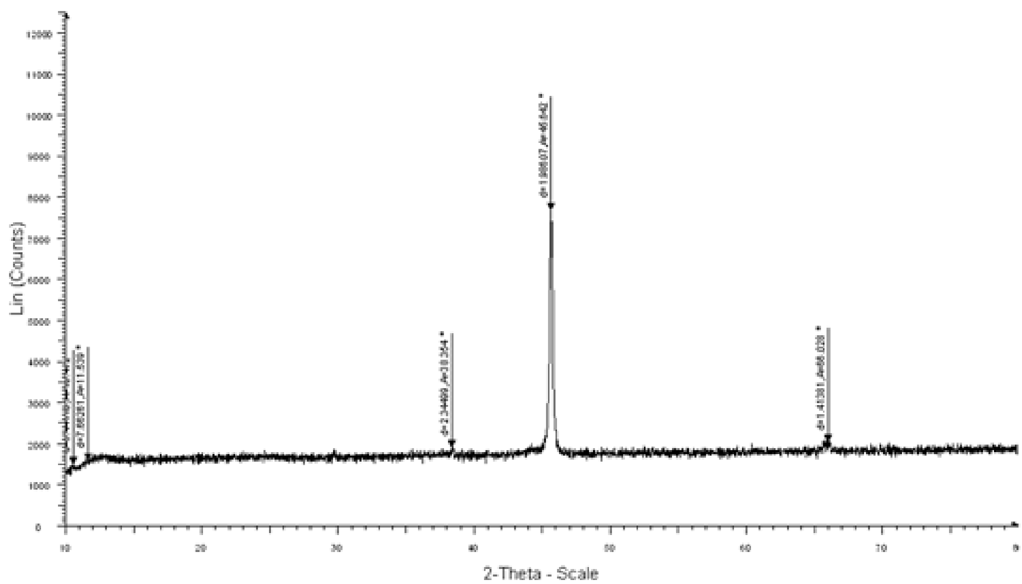

Figure 1

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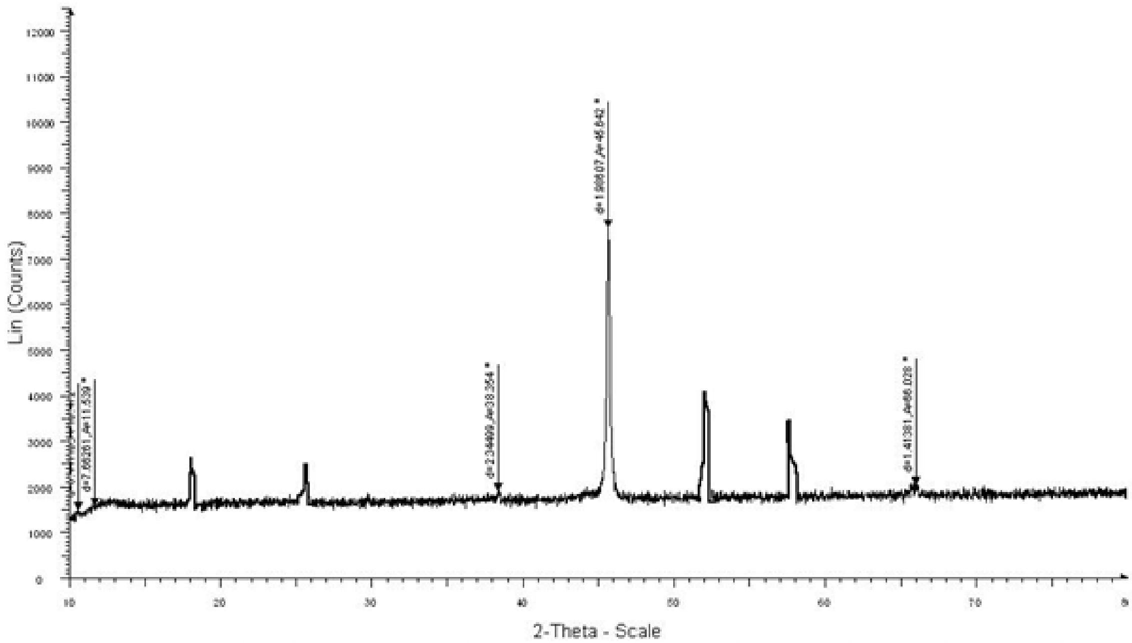
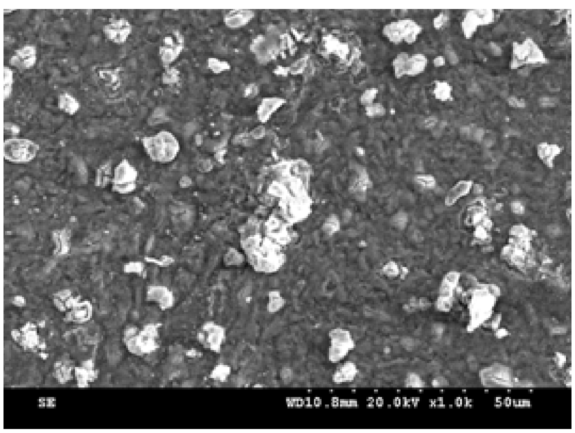


Figure 2



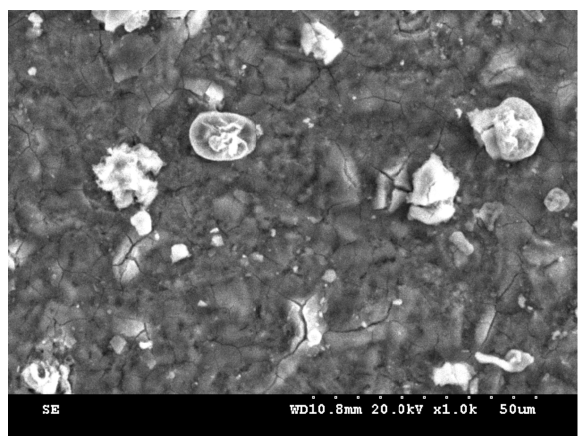


Figure 3(a) Figure 3(b)

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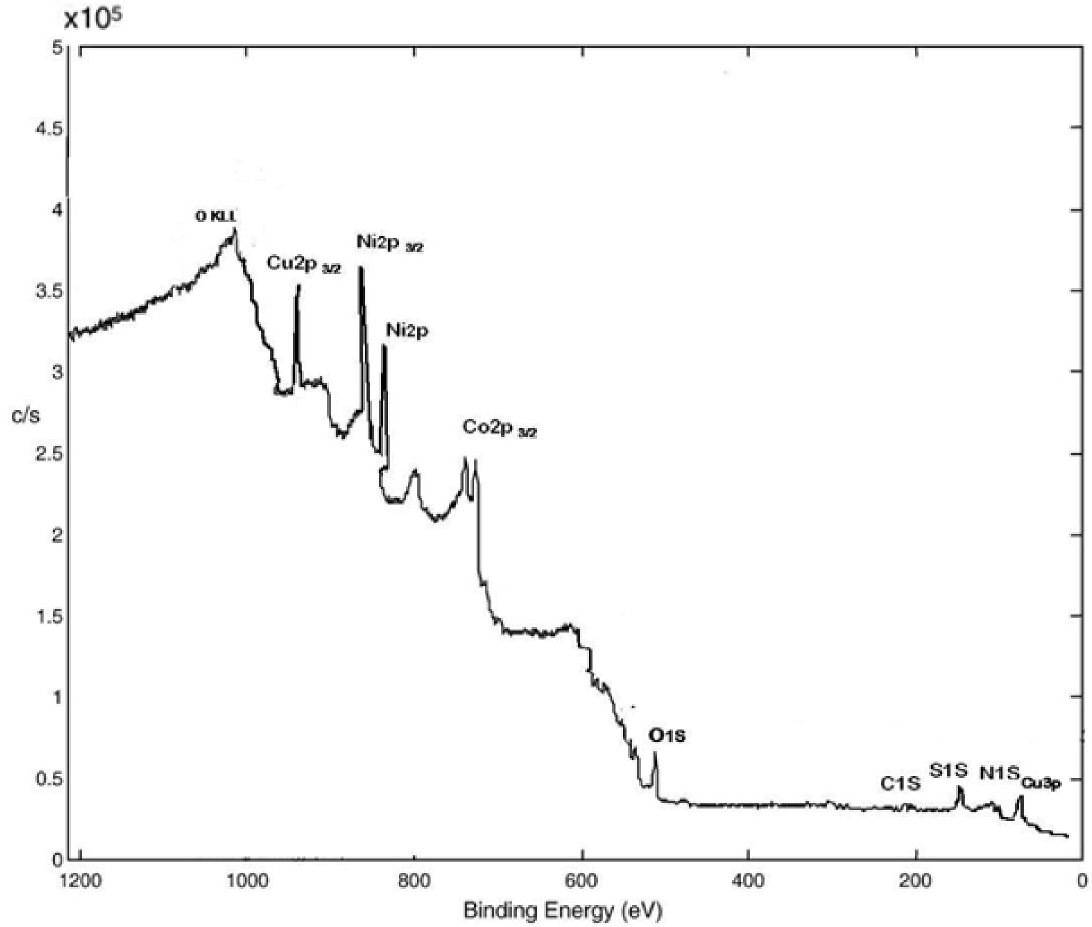

Figure 5

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