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# CHARACTERIZATION OF BLACK NICKEL SOLAR ABSORBER COATINGS ON ALUMINIUM SUBSTRATE.

**O.R.M. Khalifa[a,*], E.A. Al Hamed[a], M.A. Shoeib[b], H.A. Mohamed[a] , S.Y. Ahmed[a]**

a Chemistry department, Faculty of Girls for Arts, Science and Education, Ain shams University, Cairo, Egypt.
b Surface Coating Department, Central Metallurgical Research and Development Institute (CMRDI) , Egypt.

**ABSTRACT** *Electroless nickel alloys are applied because of their useful physical and mechanical properties. Black electroplating nickel coatings are used in optical instruments, absorbing material, decorative coatings and aerospace industries. They are specified due to their stability against sunlight exposure and electrical conductivity. Electroless plating of nickel phosphorous and nickel tungsten phosphorous on aluminium substrate were discussed. Blacking of both nickel phosphorous and nickel tungsten phosphorous by electroplating were investigated by the reflectance percent and the absorption percent for black nickel coating from the Ultra-Violet Device (UV) at different wave lengths ranging from (230-700nm) as the reflectance = (1- absorption) and by X-ray photoelectron spectroscopy (XPS). The influence of blackening was discussed by comparing it with original deposits. All coats were investigated by X-ray diffraction, scanning electron microscope (SEM) and energy dispersive X-ray analyses (EDX) Optical property and thermal stability. Corrosion resistance of both nickel phosphorous, nickel tungsten phosphorous and the black coats were studied by potentiodynamic polarization.*

**KEYWORDS:** Aluminum alloy; black nickel; solar absorber.

## INTRODUCTION

Aluminum alloys possess high mechanical strength, excellent thermal and electrical conductance, good reflectivity and low working cost [1,2] . The electroless deposition of nickel in a bath containing hypophosphite was first done by Wurtz in 1844 [3]. Electroless nickel plating coatings have been well-known as a hard coating for industrial application, due to their excellent hardness, corrosion and wear resistance properties [4–6] .

Nowadays, Black nickel coatings can be accompanied by electro- [7–9] and electroless [10] depositions. In general, metallic black appearance of electroless nickel black parts were obtained by blackened treatment, after they were electroless plated with nickel. Super black or black electroless nickel coating, as it is based on a nickel - phosphorous compound, is set to have a major application in fields, such as black decorative coatings, photo-thermal conversed material, absorbing material , and within aerospace and defense industries[10]. The phosphorus element can co-deposit with nickel, resulting in the formation of a Ni-P alloy, during electroless plating process [11–13].

## EXPERIMENT

### Material and chemicals

Aluminum alloy test specimens alloy composition is shown in Table 1:

**Table 1**

| **Element** | Si | Fe | Cu | Mn | Mg | Ni | Cr | Pd | Sn | Ti | V | Co | Al |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **wt%** | 0.327 | 0.582 | 0.00585 | 0.981 | 0.216 | 0.0091 | 0.01140 | 0.0107 | 0.00532 | 0.047 | 0.006 | 0.0004 | 97.8 |

**Chemical composition of aluminum alloy (wt %).**

The specimens of the size 20 x 40 x 8 mm were used for electroless plating of Ni-P and Ni-W-P alloys.

The coatings were deposited from the most stable bath with and without sodium tungstate. The composition and condition of the bath are shown in Table 2.

Table 2: Bath composition and operating conditions of electroless Ni-P and Ni-W-P.

**Table 2:**

**Chemical composition of Electroless Ni-P and Ni-W-P.**

| **Bath constituents and parameters** | **Quantity** |
|---|---|
| Nickel sulphate | 30 g/l |
| Sodium hypophosphite | 10 g/l |
| Citric acid | 10 g/l |
| Sodium tungstate | 2g/l |
| pH | 8.5 |
| Plating temperature(˚C) | 90 |
| Coating time | 1h |

### Blackening of Ni-P and Ni-W-P alloy (electrodeposits).

For electrical deposition to take place, the nickel is connected to the anode from both sides and the base metal coated with bright Ni-P or Ni-W-P is connected to the cathode for the deposition of black nickel on the alloy to take place.

### Characterization of Ni-P and Ni-W-P coatings.

The composition of Ni-P and Ni-W-P were analyzed using X-ray diffraction before and after heating to 400˚C for one hour. Bruker AXS, Model D8, 40 kV,40 mA, Cu Kα ADVANCE. EDX(energy dispersive X-ray analyses).EDAX GENESIS ABEX4(AMETET).Surface morphology is analyzed by using scanning electron microscope (SEM)Quanta 250 FEG.

### Characterization of black Ni-P and Ni-W-P coating.

Besides the analysis of the composition of black Ni-P and Ni-W-P by the above methods, X-ray photoelectron spectroscopy XPS is studied. Thermo SCIENTIFIC K-ALPHA.The optical properties, namely, solar absorbance and ultra violet emittance of the black samples were measured by a solar reflectometer. These instruments provide an average value of solar absorbance and emittance.a PG Instruments T80+ UV–visible double-beam spectrophotometer (PG Instruments, United Kingdom).

### Thermal cycling test:

The thermal cycling test is designed to evaluate the effect of cycling temperature on the deposit. The test was conducted in thermostatically controlled hot and cold chambers. A total of eight cycles was applied. A cycle consists of placing the samples into a water bath at 85˚C for one hour and left to cool. After thermal cycling, the optical properties were measured.

## RESULTS AND DISCUSSION: THIN FILM X-RAY DIFFRACTION

Fig.1 (a ,b) show X-ray Thin film diffraction patterns of the as plated Ni-P deposit and after heat treatment at 400˚C for 60 minutes. The diffraction pattern of the as plated coating shows broad peaks around 2Ɵ value of 44.60, 51.90 and 76.64 which is attributed to the amorphous nature of the as deposited. The reflection corresponds to III plane of face-centered cubic (fcc) phase of nickel. The grain size of the as deposited Ni-P is 5.5 nm. After heat treatment, the peaks are sharper due to formation of fine nickel and tetragonal nickel phosphide $Ni_3P$ metastable phases where the grain size is 31.8 nm. XRD for the ternary Ni-W-P as deposited and after heat treatment is shown in Fig.2 (a,b) .It was observed that three broad peaks at 2 Ɵ, at 44.16, 51.66, and76.40 corresponding to Ni (III) which are sharper than that of the as deposited binary Ni-P alloy. The grain size of the ternary alloy Ni-W-P is 21.4 nm. In our investigation the amount of tungsten present in the ternary alloy is in solid solution form since the solubility limits of tungsten in nickel is 39.9 wt%. Hence the XRD patterns of ternary coating revealed only a prominent Ni III peak. After heat treatment, sharp peaks were induced as a result of the formation of Ni(III)plane face-centered cubic(fcc) phase of nickel ,tetragonal nickel phosphide $Ni_3P$ and monoclinic nickel tungsten oxide $NiWO_4$ ,where the grain size is 46.8 nm. Phase identification of the blackened Ni-P and Ni-W-P samples, Fig.3(a, b) and Fig.4 (a, b) were carried out by x-ray Thin film diffraction. (XRD) for black Ni-P layer showed five sharp peaks at 2Ɵ at 38.49, 44.65, 52.09, 78.20 and 76.6, all corresponding to cubic nickel. Black Ni-W-P coat showed five peaks at 2Ɵ at 38.48, 44.61, 52.09, 65.24 and 76.61, all related to cubic nickel.

## MICROSTRUCTURE.

### Morphology.

The surface morphologies of Ni-P and Ni-W-P before and after blackening were shown in Fig.6 (a, b, c, d), respectively.The surface morphology of the as deposited Ni-P and Ni-W-P showed a dense coating with spherical nodular structure with very smooth and high coalescence. The diameters of nodules were 0.019 µm and 1.388 µm, respectively. The surface morphology of black coat (Ni-P and Ni-W-P) showed more dense coating with spherical nodular structure composed of particles with diameter 1.4µm and 2.857 µm, respectively. The particles are in close contact with each other which improve corrosion resistance as shown below.

### Properties of coatings (Ni-P and Ni-W-P).

### Thickness.

The cross section of Ni-P, black Ni-P, Ni-W-P and black Ni-W-P show the thickness of the layers. Fig.6 (a, b) show the cross section of Ni-P is equal to 5.845µm which become after blackening equal to 2.545 µm and black layer is equal to 3.45 µm. Fig.7 (a, b) show the cross section of Ni-W-P is equal to 4.34µm which become after blackening equal to 3.15 and black layer is equal to 5.71 nm.

## Optical properties:

The optical properties were measured via solar absorbance and ultra violet emittance of the black coating. First, black binary coat Ni-P was detected. The measured reflectance rate was 0.55 in the range of wave length 250-550 nm. The absorption percentage range of wave length 250-550 nm, was 99.45%. The high absorption indicates that the black film can be used as an absorbing material. The black colour of Ni-P is due to the formation of the oxidized alloy at the surface of the Ni-P black layer, nickel oxides (NiO, $Ni_2O_3$) and nickel phosphorus Ni-P (confirmed by composition detection of both black Ni-P and black Ni-W-P)**.**Second, nickel tungsten phosphorous with W content of 1.19% by weight was used for black treatment by electroplating .The rate of the reflectance of the black coating of Ni-W-P was 0.495 in the range of the wave length 250-550 nm. The absorption percentage range of the black Ni-W-P range was 99.51%.The presence of tungsten in the ternary coat improves the absorption percentage range by about 0.06%.

## Thermal stability test.

The black electroless coatings are used in some of the high heat dissipating parts where the temperature is likely to go around 200˚C for an extended period. The thermal stability test consists of heating of black electroless nickel test coupons in an oven for 24h., at 200˚ ± 2˚C. The test specimens were then examined visually for any degradation and their optical properties were measured. No degradation in physical appearance and no change in optical properties, before and after the test, were noticed.

## Thermal cycling test.

The thermal cycling test is designed to evaluate the effect of cycling temperature on the deposit. The test was conducted in thermostatically controlled hot and cold chambers. A total of eight cycles were applied. A cycle consists of placing the samples into a water bath at 85˚C for one hour, and left it to cool. After thermal cycling, the optical properties were measured. The initial values of absorption had a small decrease and small increase in emittance.

## Composition

XPS spectra of the black Ni-P and Ni-W-P deposit, with 1.19%W, were shown in Fig.8 and Fig.9. In case of binary black deposit (Ni-P), it was observed that Ni, P, O and C elements were contained in the black film table 3. For the ternary black deposit Ni-W-P, Ni, P, O, C and W elements were contained in the black film table 4.According to atomic ratio and valence of element, the composition of black film should be Ni-O, $Ni(H_2PO_4)_2$, $Ni_2O_3$and $WO_3$, metallic Ni and W/nickel content in binary black film (87.83) was less than that in as deposited electroless Ni-P (97.14). It can be concluded that dissolution of Ni and formation of metallic oxides are main processes during blackening.

**Table 3**

**The weight percent of the composition of Ni-P and black Ni-P.**

| Type of coating | Ni% | P% | O% | W% |
|---|---|---|---|---|
| Ni-P | 92.16 | 7.84 | - | - |
| Black Ni-P | 87.83 | - | 12.17 | - |

**Table 4**

**The weight percent of the composition of Ni-W-P and black Ni-W-P.**

| Type of coating | Ni% | P% | O% | W% |
|---|---|---|---|---|
| Ni-W-P | 93.02 | 5.79 | - | 1.19 |
| Black Ni-W-P | 89.93 | - | 10.07 | - |

## Polarization.

## Corrosion resistance

Fig.10 shows potentiodynamic curves of (a) the substrate , (b) as deposited electroless Ni-P coat and (c) black coat Ni-P in 3.5% sodium chloride solution. The potential was scanned from cathode to anode. Corresponding $I_{corr}$ and $E_{corr}$ were calculated and listed in table 5. The corrosion potential $E_{corr}$ of the black Ni-P coating was more positive than that of the as deposited electroless Ni-P coatings and substrate immersing in 3.5% NaCl solution.

**Table 5**

**The corrosion kinetic parameters Ecorr ,Icorr determined from the Tafel region from substrate Ni-P and black Ni-P in 3.5% sodium chloride solution.**

| Type of coating | $E_{corr}$(volt) | Log $i_{corr}$(μA/cm) | Polarization(mV/ mA) Rp=(βa×βc)/[2.3×Icorr(βa+βc)] |
|---|---|---|---|
| Substrate | -0.8465 | -6.2672 | 36 |
| Ni-P | -0.5291 | -6.0845 | 229 |
| Black Ni-P | -0.3695 | -7.2612 | 497 |

Fig.11 shows potentiodynamic curves of (a) the substrate ,(b) Ni-W-P coating and (c) Ni-W-P coating blacking in 3.5% sodium chloride solution. The corrosion potential $E_{corr}$ of the black Ni-W-P coatings was more positive than that of Ni-W-P coating and substrate. Table 6 shows the corresponding $E_{corr}$ and $I_{corr}$for blackening Ni-P and Ni-W-P and substrate in 3.5 % NaCl solution.

**Table 6**

**The corrosion kinetic parameters Ecorr , Icorr determined from the Tafel region from substrate Ni-W-P and black Ni-W-P in 3.5% sodium chloride solution.**

| Type of coating | $E_{corr}$(volt) | Log $i_{corr}$(μA/cm) | Polarization(mV/ mA) Rp=(βa×βc)/[2.3×Icorr(βa+βc)] |
|---|---|---|---|
| Substrate | -0.8465 | -6.2672 | 36 |
| Ni-W-P | -0.4168 | -7.1876 | 397.751 |
| Black Ni-W-P | -0.3581 | -6.6293 | 611 |

These results indicated that the black film has good corrosion resistance in 3.5% NaCl, i.e. the corrosion resistance follows the sequence black Ni-W-P>black Ni-P> Ni-W-P> Ni-P>substrate.

## CONCLUSIONS

The use of electroless nickel solution at 90˚C and pH 8.5 and 60 minutes for deposition time for the samples were the best condition for preparing Ni-P and Ni-W-P coat. An electrodeposited black nickel solar absorber coating has been produced cathodically from a low concentration bath. Optical properties of the coating produced under the optimum condition are found to be excellent absorbers. Corrosion tests indicate that all coats had a corrosion protection in 3.5% NaCl and followed the sequence black Ni-W-P> Ni-W-P> black Ni-P > Ni-P>substrate.

## REFERENCES.

[1] E.A. Stark Jr., J.T. Staley, Prog. Aerosp.Sci. 32 (1995) 131.
[2] A.K. Mukhopadhyay, A.K. Sharma, Surf. Coat.Technol. 92 (1997) 212.
[3] A. Wurtz, C.R. Hebd, Séances Acad. Sci. 18 (1844) 702.
[4] S. Kodama, M. Horiuchi, T. Kunii, K. Kuroda, IEEE Trans. Instrum. Meas. 39 (1990) 230.
[5] C.E. Johnson, Met. Finish. 78 (1980) 21.
[6] J. Hajdu, S. Zabrocky, Met. Finish. 98 (2000) 42.
[7] E. Wäckelgård, Sol. Energy Mater. Sol. Cells 56 (1998) 35.
[8] M.L. Cantú, A.M. Sabio, A. Brustenga, P.G. Romero, Sol. Energy Mater. Sol. Cells 87 (2005) 685.
[9] S. John, Met. Finish. 95 (1997) 84.
[10] R.J.C. Brown, P.J. Brewer, Martin J.T. Milton, J. Mater. Chem. 12 (2002)2750.
[11] S. John, N.V. Shanmugham, B.A. Shenoi, Met. Finish. 80 (1982) 47.
[12] L.M. Abrantes, J.P. Correia, J. Electrochem. Soc. 141 (1994) 2356.
[13] K. Parker, Plat. Surf. Finish. 74 (1987) 60.

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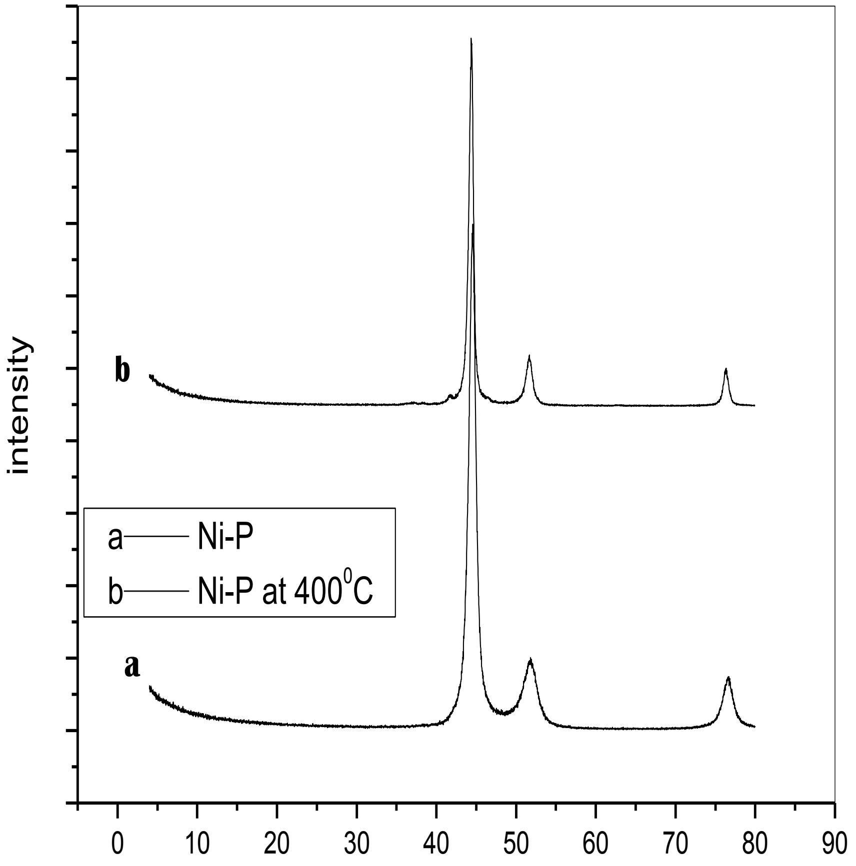


Fig.1 (a ,b) show X-ray Thin film diffraction patterns of the as plated Ni-P deposit before and after heat treatment at 400˚C for 60 minutes.

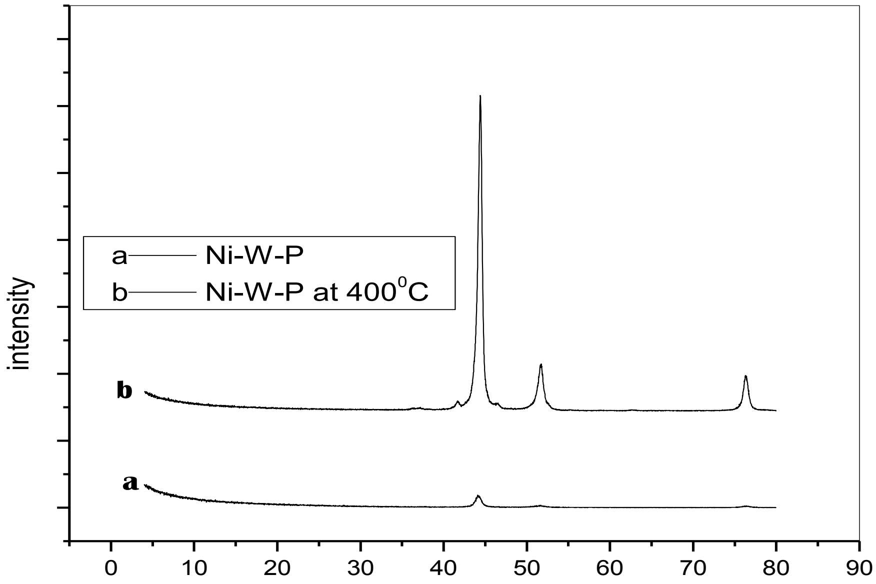


Fig.2.(a ,b) show

X-ray Thin film diffraction patterns of the as plated Ni-W-P deposit before and after heat treatment at 400˚C for 60 minutes.

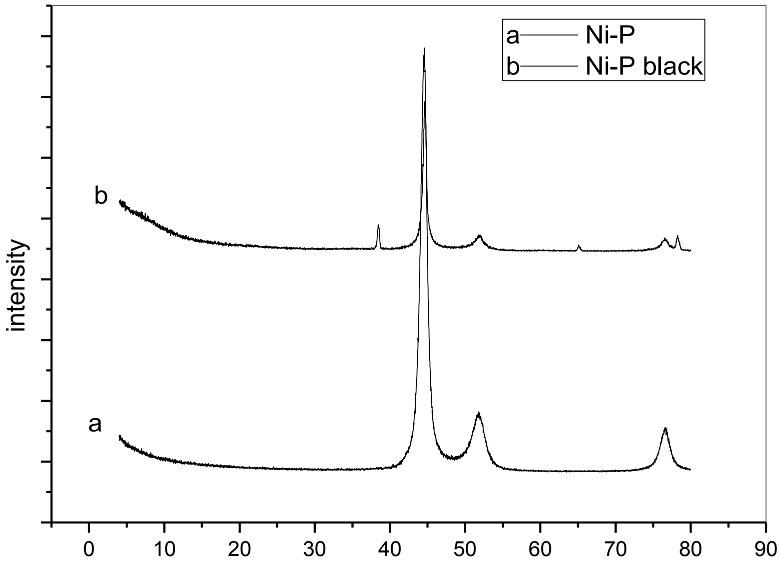


Fig.3.(a,b) show X-ray

Thin film diffraction patterns of Ni-P and black Ni-P.

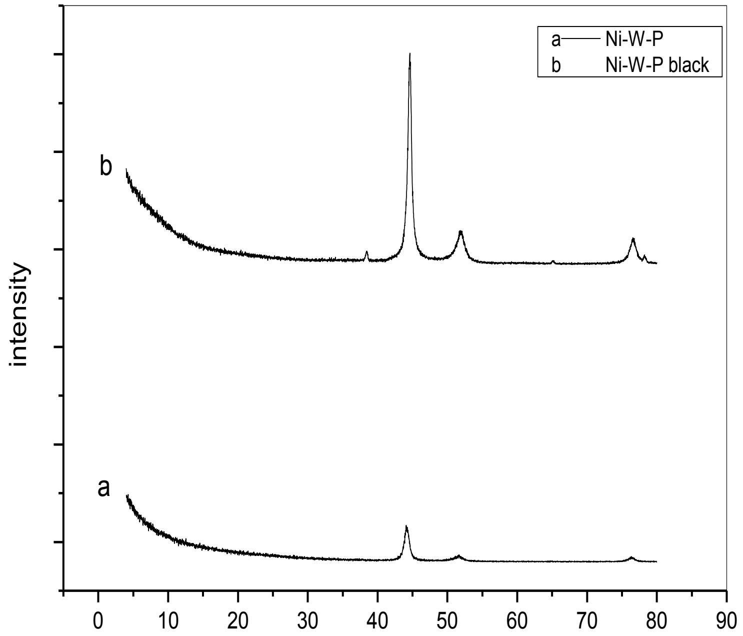
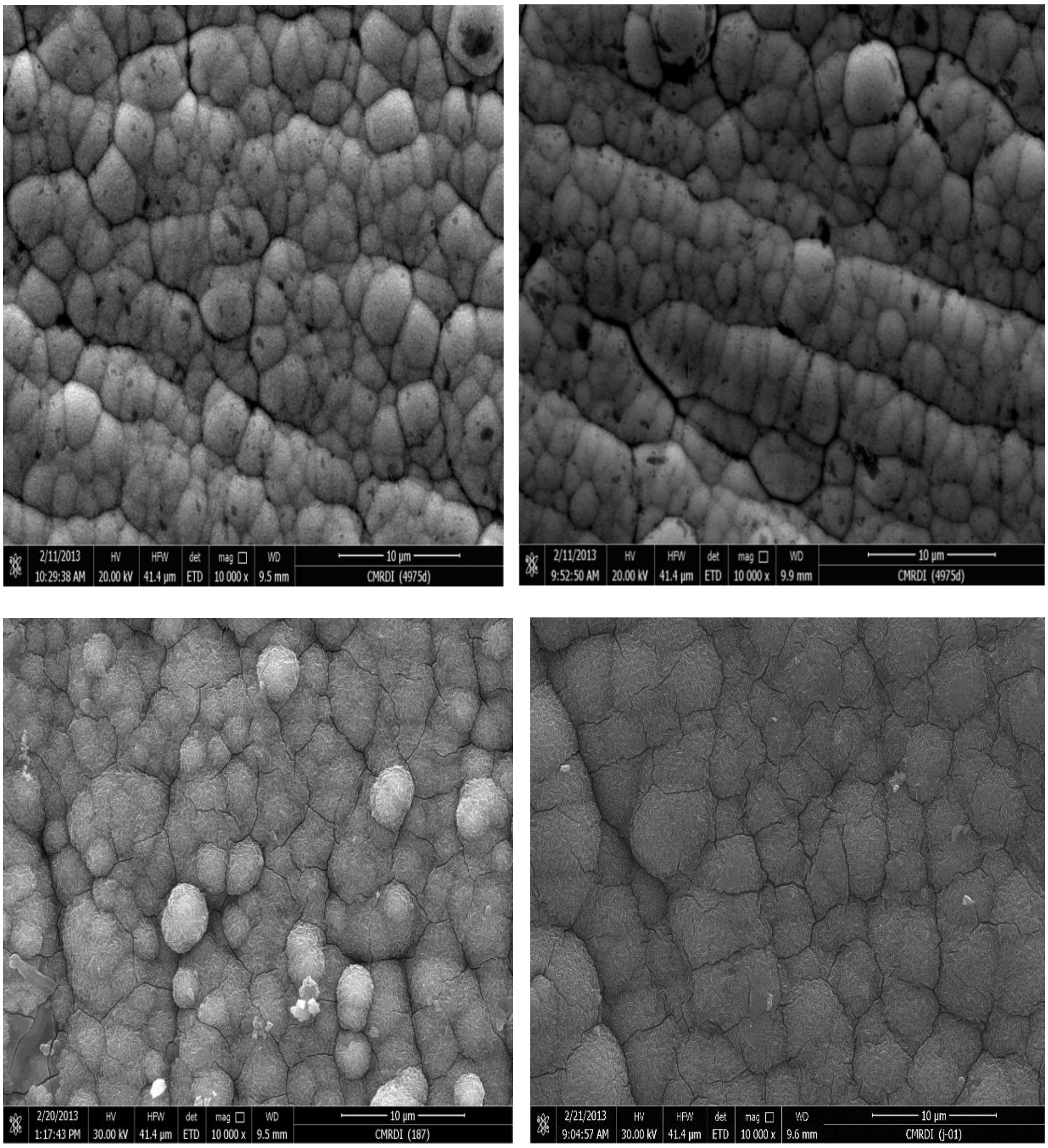


Fig.4.(a,b) show X-ray Thin film diffraction patterns Ni-W-P and black Ni-W-P.



Figs.5.: Scanning electron microscope of as plated electroless (a) Ni-P (b) Ni-W-P before blackening and (c) Ni-P (d) Ni-W-P after blackening.

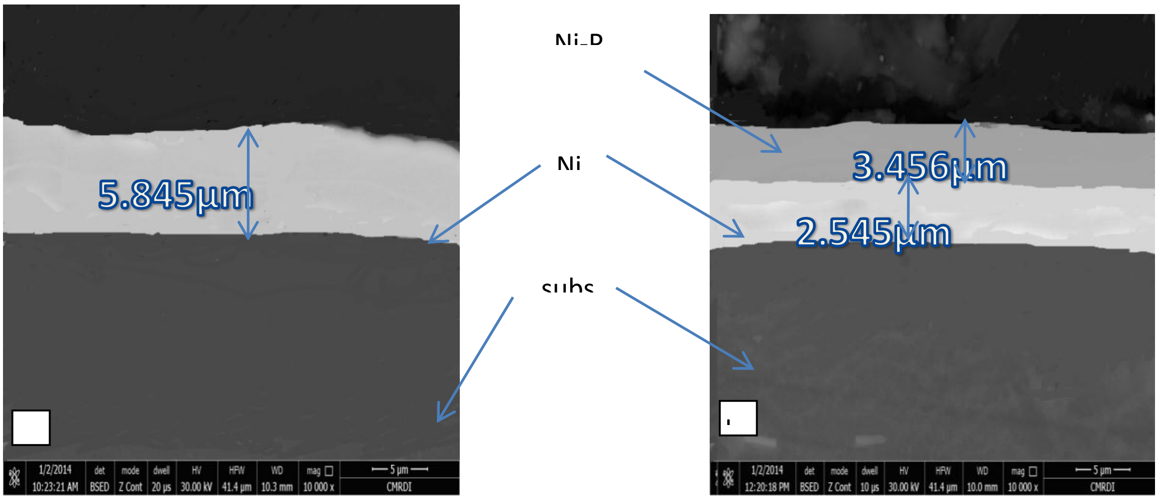


Fig.6. (a, b) Cross section of Ni-P and Ni-P black layers.

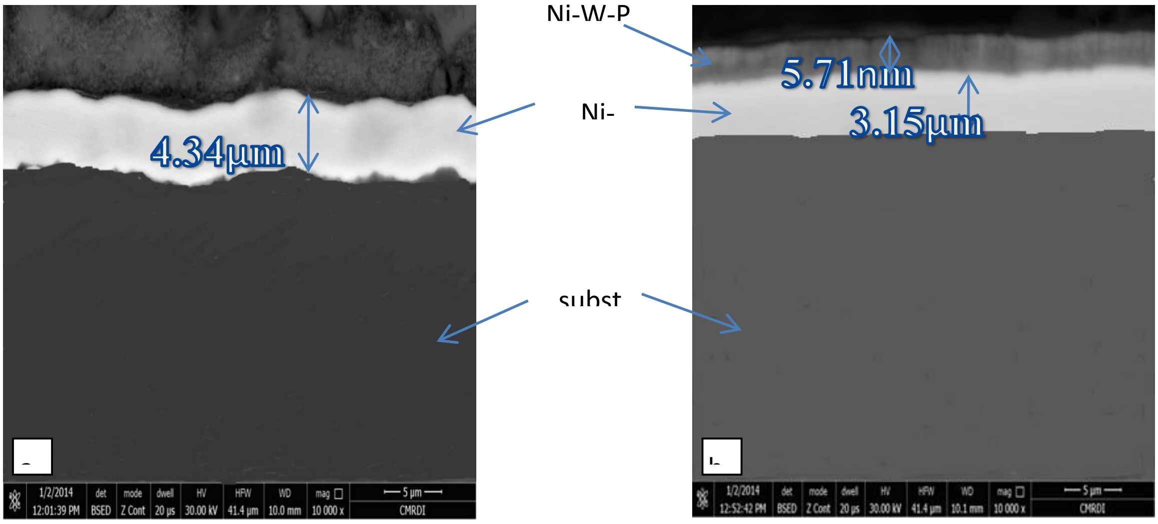
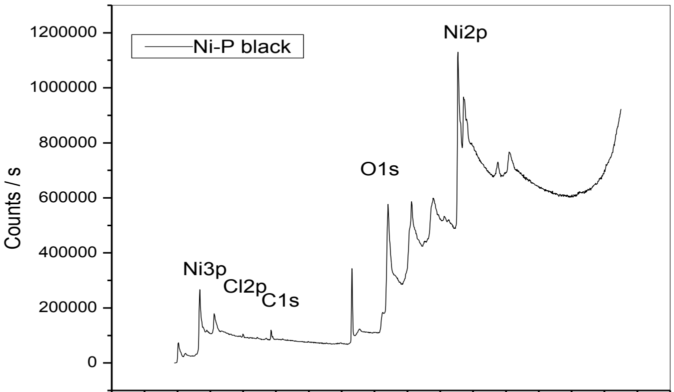


Fig.7.(a, b) Cross section of Ni-W-P and Ni-W-P black layers.



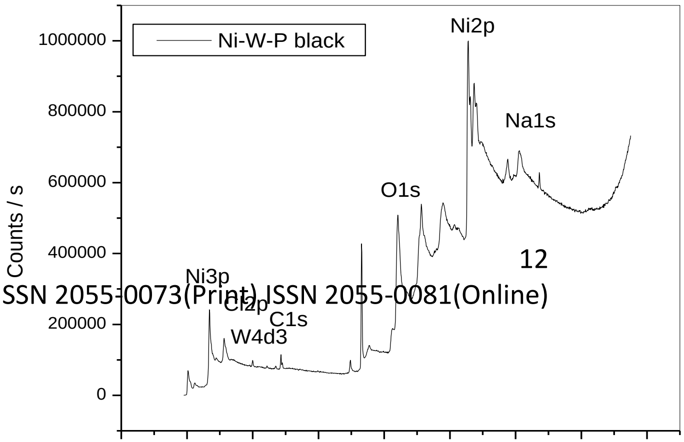


Fig.8.XPS wide scan spectrum of black Ni-P.

Fig.9.XPS wide scan spectrum of black Ni-W-P.

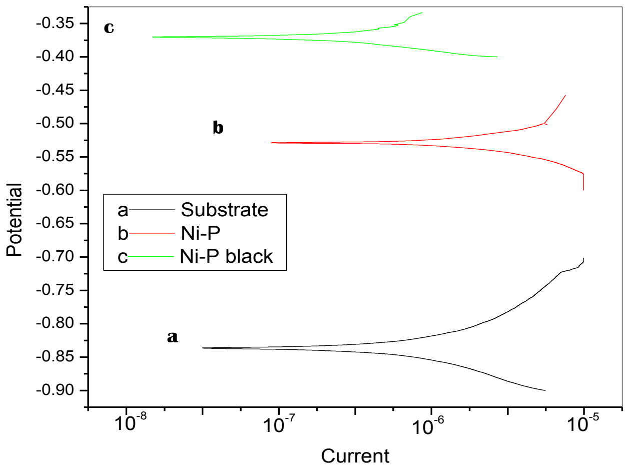


Fig.10. Potentiodynamic curves of (a) the substrate , (b) as deposited electroless Ni-P coat and (c) black coat Ni-P in 3.5% sodium chloride solution.

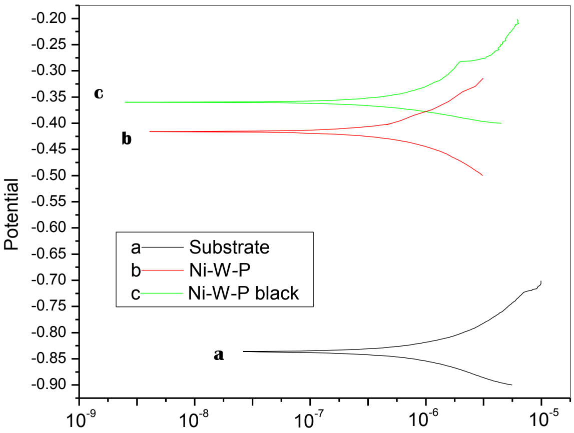


Fig.11. Potentiodynamic curves of (a) the substrate , (b) as deposited electroless Ni-W-P coat and (c) black coat Ni-W-P in 3.5% sodium chloride solution.