Preparation and Investigation composite coating (Ni-nano hydroxyapatite) on low carbon steel samples

dr. Nabaa Sattar Radhi **Zainab S. Al-Khafaji**
University of Babylon **Al-Mustaqbal University College**
E-mail: dr.nabbaa@gmail.com. Zainab_Alkafaji@mustaqbal-college.edu.iq.

Abstract:

In this work represents an attempt to introduce further improvement to the properties of Nickel coatings, by addition HA particle to electrodeposited solution. Low carbon steel samples were coated with Nickel and (Ni- HA) with different nanoscale particles size of hydroxyapatite once (20 nm) and another (40 nm). After electroplating, these samples were tested all specimen in Hank's solution to study the corrosion behavior. Then test the microhardness, surface roughness, and Topographic for Nickel coating and (Ni-HA) with (20 and 40) nm.

Keywords: Hydroxyapatite, orthopedic implant, biocompatibility, electrodeposited, nanoscale and Hank's solution.

1.1 Introduction:

Nickel is one of the most common metal that used in electroplating so as to enhance the usefulness, value and overall sales promotion for consumer goods and products manufacturing, **[1].** As well as the nickel coating is also used to enrich the physical characteristics like resistance of wear, resistance of heat, resistance of corrosion. Nickel coatings are used in many important applications due to the ability of this coating to improve the resistance of the metal against corrosion with an improving in the functional properties as well as providing a decorative shape, **[2-4].**

1.2 Bio-active Coating

Bio-active materials is a term used to refer to the materials that will be active inside the human body and it will be interact with the bones around it or with the soft tissue in some cases depending on Bioactivity Index (I_B) which introduced by (Hench) as shown in below to measure the level of bio-activity**:**

$$I_B = 100/ t\ 0.5bb$$

Whereas: t 0.5bb = the time required to get bonding interface for more than 50%. And this usually occurs during the time depending on kinetic modification of the surface, generated by implantation of the bio-active material inside the live bone. Due to the reaction between the bio-active materials which inside the live bone and the surrounding body fluids there will be an ion exchange. And this ion exchange will lead to produce of a biologically active carbonate apatite (CHA) coat on the bioactive object which is equivalent to the bone mineral phase chemically and crystallographically. And the main examples for bio-active materials are synthetic hydroxyapatite (HA), and Bio-glass **[5].**

1.3 Hydroxyapatite

Hydroxyapatite (HA), usually written as $Ca10(PO4)6(OH)2$ is a member of the apatite group of ceramics. And apatite terms refer to deceit or deception and the main origin for this term is the Greek word (a pate) and the cause of this name return to the variation of the shape and colour [6]. It was chosen many times as an artificial bone due to it nature which is similar to live bone in spite of devoid of such organic constituents as collagen and polysaccharides. The chemical similarity of HA to bone and its excellent biocompatibility and bioactivity have attracted the attention of medical professionals **[7,8].**

HA has been synthesized and used to manufacture various forms of implants (solid and porous) and as a coating on other implants **[9].**

2. Experimental part:

2.1 Electroplating Process

The samples were low carbon steel (L.C.S.) with chemical composition as shown in Table (1). The chemical analysis was performed by using a spectroscopy device for metal.

The samples that used in all the tests were prepared by using cylindrical moulds and the finals samples have disc shape with the following dimension (thickness = 2mm and diameter = 15mm) as well as the surface area for these samples are (447.667 mm^2).

On the other hands, the samples surface was prepared as following:

1. Grinding the sample surface by using Grit silicon carbide papers which carried these grade (220,240,400,600,800,1000,1200). Then the sample surface will clean by using brines and acids to be ready for Electroplating process depending on the required period for each sample.
2. Electroplating process was carried out by using basin produced from polythene and has a rectangular shape (29x21x18 cm) as shown in figure (1); and power supply which can give the current up to (6Amp) and The voltage given up to (20 Volt).

2.2 Composition of Electroplating Baths:

The Watts Nickel Plating Solution The plurality of nickel plating solutions, especially those used for decorative plating, are depending on the ‘Watts’ formulation developed by Professor Oliver P. Watts in 1916. The Watts electrolyte gather nickel sulphate, nickel chloride and boric acid. While the proportions may vary according to the application, a typical formulation together with operating parameters is given in Table (2).

2.3 Tests:

In the research, the following tests were carried out to evaluate the performance of the coating layers:

2.3.1. Thickness Test

The thickness measuring device was used to measure the thickness of Ni and Ni-HA films, in (Babylon/College of Material Engineering/University of Babylon).

2.3.2. Light Optical Microscope (LOM)

Involved identification and measurement of the phases, shape and grain size are some characteristics of grain boundaries. Each of these has distinct characteristics. The microstructure evaluated with (100x) magnification using Olympus microscope manufactured by Japan.

2.3.3. Hardness Test

Vickers Hardness (TH-717 Digital Micro Vickers Hardness Tester) was measured the hardness of Ni and Ni-HA films, at load (200N) and holding time 20 seconds in (college of Material engineering /University of Babylon).

2.3.4. surface roughness test

The surface roughness of a nickel-coated steel sample (Ni-nHAP) was measured by using the (TR-100 surface roughness tester),which is located at the University of Babylon, Faculty of Materials Engineering. The device passes on the sample surface to measure the surface roughness. The device has a sensor that records the roughness of the sample surface and takes the reading directly from the device screen. The accuracy of the device (± mμ0.01).

2.3.5. Electrochemical Test

The corrosive behavior of low carbon steel studied in Hank's solution. The chemical composition of Hank's solution is illustrated in Table (3) and pH of it at 37C° was 7.4.

2.3.5.1 Open Circuit Potential (OCP)

The experimental arrangement for the measurement of open circuit potential is described. A 500 ml capacity glass electrolytic cell is used. The tests were performed with the specimen submerged in a Hanks solution. The potential of the working electrode is measured with respect to a Saturated Calomel electrode (SCE).

2.3.5.2 Potentiostatic Polarization

Electrochemical experiments were performed in three electrode cell containing and electrolytes Hank's solution which chemical composition is shown in table (3), [10].

The test was carried out by stepping the possible using a scanning rate 0.4 mV/s from initial potential of 250 mV below the open circuit potential and the scan continued up to 250 mV above the open circuit potential. Corrosion rate measurement is got by applying the following equation [11].

Corrosion rate (mpy) = $0.13 i_{corr}(E.W.)/A.\rho$ …(1)

Where:

E. W. = equivalent weight (g/ eq)

A = area (cm^2)

ρ =density (g/ cm^3)

0.13 = metric and time conversion factor.

icorr. = current density ($\mu A / cm^2$).

The improvement percentage is calculated for coated samples, using the following equation **[11]**:

Improvement percentage $=(CR^0 - CR / CR^0) \times 100$ …(2)

Where:

CR° =the corrosion rate of master sample(without coated).

CR =the corrosion rate of coated sample (with Ni or (Ni-HAP)).

3. Results and discussion:

3.1 Thickness Results

For Ni sample the thickness is 25.7µm, while the thickness increased to (47.5, 48.7) µm for (Ni-20nHaP) samples with 10 and 20 g/L , and then the thickness reach to it is high value (49.7, 50.5) µm for (Ni-40nHaP) samples with 10 and 20 g/L. Anyhow with increasing amount and particles size of HAP, the rate of thickness increased also as shown in Table (4).

3.2 Light Optical Microscope (LOM)

The optical microscope is shown the topography behavior of coating layer for Ni and (Ni-HAP) as illustrated in figure (2(a,b,c,d,e)).

3.3. Hardness results

The hardness test was performed to determine the effect of (Ni) coating on the hardness values of low carbon steel. And finding out the effect of adding (HAP) in two different particles size on the hardness values of (Ni) coating and the low carbon steel values. Table (6) shows the results of hardness test for of the carbon steel sample, the Ni-coated steel sample, the Ni-20nHAP layers and the Ni-40nHaP layer.

The difference in hardness values observed between Ni-20nHAP and Ni-40nHAP is due to the difference in the volume of hydroxide uptake in both layers. The material hardness is clearly affected by the size of the particles, and mathematically can explain it by Hall-Petch relationship, which states, [4]:

$$HV = H_O + K/\sqrt{d}$$

whereas :

HV: Hardness of material with small granular size.

Ho: Hardness material is multi-size granular (polycrystalline grain size).

K: Constant, represents the slope of the Hv hardness when drawing against, and it depends on the type of material.

$1/\sqrt{d}$: Diameter of the particle.

Hall-Petch relationship is one theory that explains why ultra-fine microstructures have higher hardness values when compared to the coarser-grained ones and the same hardened material.

3.4 Surface roughness results

It is clear from table (6) the roughness of (Ni-40nHAP,20g) is the highest. This may be attributed to the bigger HAP particles size. This is idea is supported by the fact that (Ni) layer which is free of HAP particles possesses the lowest value of surface roughness. The surface roughness of the deposited layers are presented in table (6).

3.5 Corrosion Tests

3.5.1 Open Circuit Potential (OCP)- Time Measurements

The OCP - time was measured with respect to SCE in Hank's solution at 37°C for uncoated samples and coated samples (Ni and Ni-HA Coating). The data of OCP are shown in Table (4).

3.5.2 Potentiostatic Polarization

This test was done by using the Potentiostatic polarization test in Hank's solution) for uncoated, Ni and Ni-HA coated samples at 37 °C, as shown in table (7) and figure(3).

These results indicate stability behavior of HA coating layer. Along with an improvement of corrosion resistance, this HA coating is able to change the characteristics of the surface on the materials without affecting the characteristics of the bulk **[12,13]**. Also, the presence of HA in coatings can improve corrosion resistance of the coated implant in biological solutions which can decrease metallic release and promotes fixation via chemical bonding **[12,14].**

Conclusion:

1. The adding of hydroxyapatite to the electrolytic coating of metal (Ni) makes the coating layer has good properties.
2. Ni-20nHAP, 20 g / L) showed better results than (Ni-40nHAP, 20) due to the small size of the hydroxyapatite particles, which support the crystal structure by the interaction with the Crystalline structure.
3. The coating layer (Ni-20nHAP, 20 g / L) showed hardness and good corrosion resistance because hydroxyapatite is a chemically inert and has high hardness so as to it properties are reflected on the Ni coating layer. The results of the coating layer (Ni-20nHAP, 20 g / L) was much better than the results of the coating layer (Ni-40nHAP, 20 g / L) due to the small size of hydroxyapatite, which enter deeply in the alloy and its small size near the distance between the atoms in the crystal structure makes it as supporting particles for this Composition.

Tables:

Table (1) Chemical composition of the sample used.

C	Si	Mn	Cr	Fe
0.12	0.17	0.65	0.04	Rem

Table (2) Components of plating solution, [1].

Solution	Chemical composition	Condition of Deposition
Ni	$NiSO_4.6H_2O$=240 g/l $NiCl_2.6H_2O$=45 g/l H_3BO_3=25 g/l	pH = 3.5 Temp=55°C. Coating time= 60 min. Nickel Anodes=(99.9%) Current density=2.5 (Amp/dm^2)
Ni-nHAP	$NiSO_4.6H_2O$=240 g/l $NiCl_2.6H_2O$=45 g/l H_3BO_3=25 g/l HAP=10 g/l Nano scale , d (20) nm	pH = 3.5 Temp=55°C. Coating time= 60 min. Nickel Anodes=(99.9%) Current density=2.5 (Amp/dm^2)
Ni-nHAP	$NiSO_4.6H_2O$=240 g/l $NiCl_2.6H_2O$=45 g/l H_3BO_3=25 g/l	pH = 3.5 Temp=55°C. Coating time= 60 min.

	HAP=20 g/l Nano scale , d (20) nm	Nickel Anodes=(99.9%) Current density=2.5 (Amp/dm²)
Ni-nHAP	$NiSO_4.6H_2O$=240 g/l $NiCl_2.6H_2O$=45 g/l H_3BO_3=25 g/l HAP=10 g/l Nano scale , d (40) nm	pH = 3.5 Temp=55°C. Coating time= 60 min. Nickel Anodes=(99.9%) Current density=2.5 (Amp/dm²)
Ni-nHAP	$NiSO_4.6H_2O$=240 g/l $NiCl_2.6H_2O$=45 g/l H_3BO_3=25 g/l HAP=20 g/l Nano scale , d (40) nm	pH = 3.5 Temp=55°C. Coating time= 60 min. Nickel Anodes=(99.9%) Current density=2.5 (Amp/dm²)

Table (3): Chemical Composition of Hank's Solution **[10]**

NO.	CONSTITUENT	(mg/l)
1	NaCl	8.0
2	CaCl2	0.14
3	KCl	0.4
4	NaHCO3	0.35
5	Glucose	1.0
6	Mg Cl2.6H2O	0.1
7	Na2HPO4. 2H2O	0.06
8	KH2 PO4	0.06
9	Mg SO4. 7 H2O	0.06

Table (4): The Thickness of Ni and (Ni-HAP) Layer Coating.

Samples	**Thickness (µm)**
Ni	25.7
Ni-20nHAP,10g	47.5
Ni-20nHAP,20g	48.7
Ni-40nHAP,10g	49.7
Ni-40nHAP,20g	50.5

Table (5) The hardness value

Layer coating	**hardness value**
L.C.S	**200**
Ni	**251**
Ni-20nHAP,10g	**304**
Ni-20nHAP,20g	**344**
Ni-40nHAP,10g	**295**
Ni-40nHAP,20g	**306**

Table (6) Surface roughness value

Layer coating	**roughness value**
L.C.S	**-**
Ni	**0.153**
Ni-20nHAP,10g	**0.265**
Ni-20nHAP,20g	**0.570**
Ni-40nHAP,10g	**0.293**
Ni-40nHAP,20g	**0.775**

Table (7): Illustrate the Corrosion Potential (Ecorr.), Corrosion Current (Icorr.) and Improvement Percentage of coated Samples in Hank's solution at 37 °C

samples	Icorr. µA/cm^2	Ecorr. (-mV)	Corrosion rate (mpy)	Improvement percentage%
L.C.S	24.51	506.3	46.533	-
Ni	6.49	344.2	12.321	73.522
Ni-20nHAP,10g	1.35	255.1	2.563	94.492
Ni-20nHAP,20g	0.556	24.2	1.055	97.732
Ni-40nHAP,10g	1.47	354.8	2.790	94.004
Ni-40nHAP,20g	0.984	199.4	1.868	95.986

Figures:

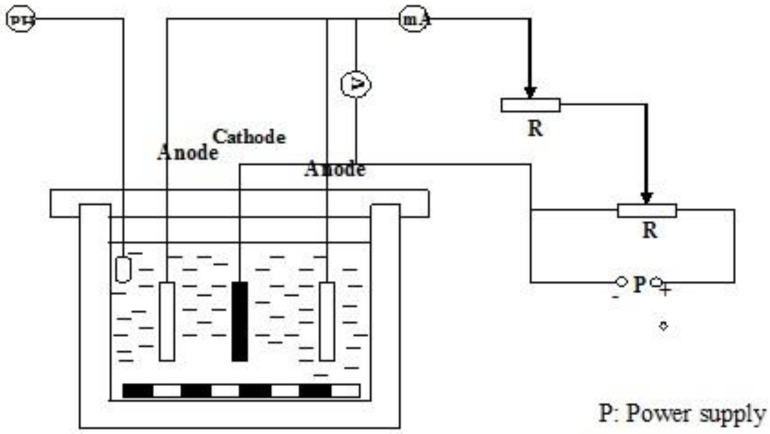
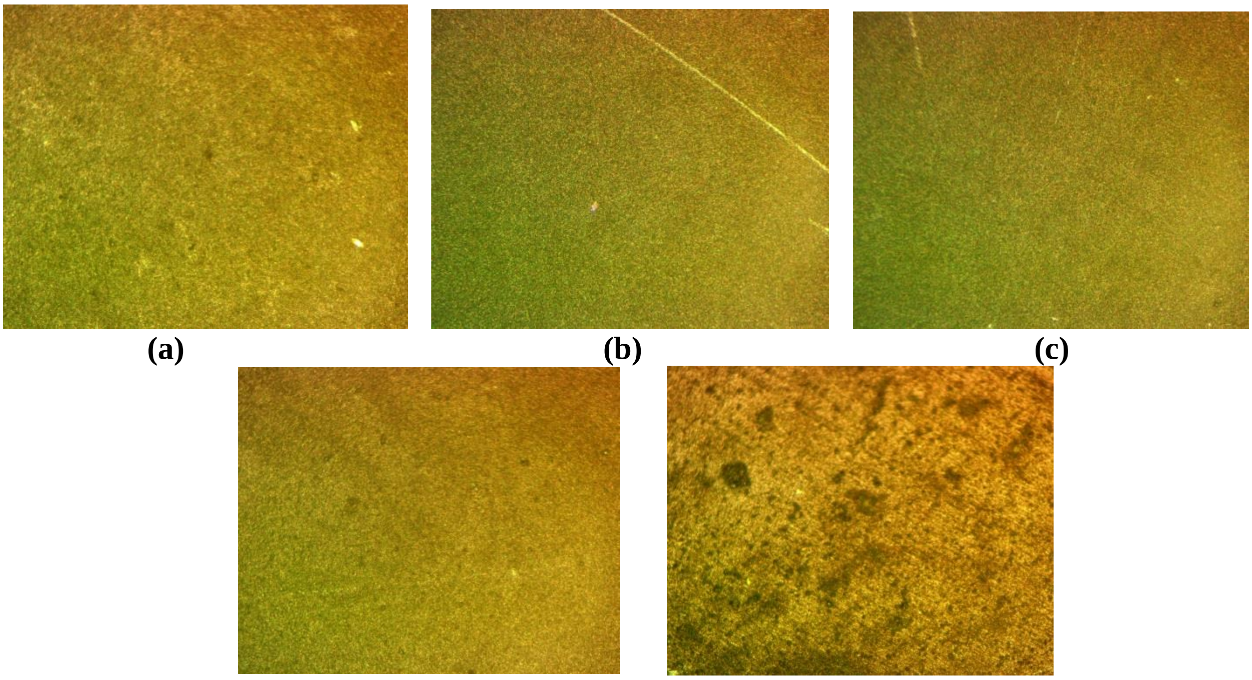


Figure (1) electroplating cell.

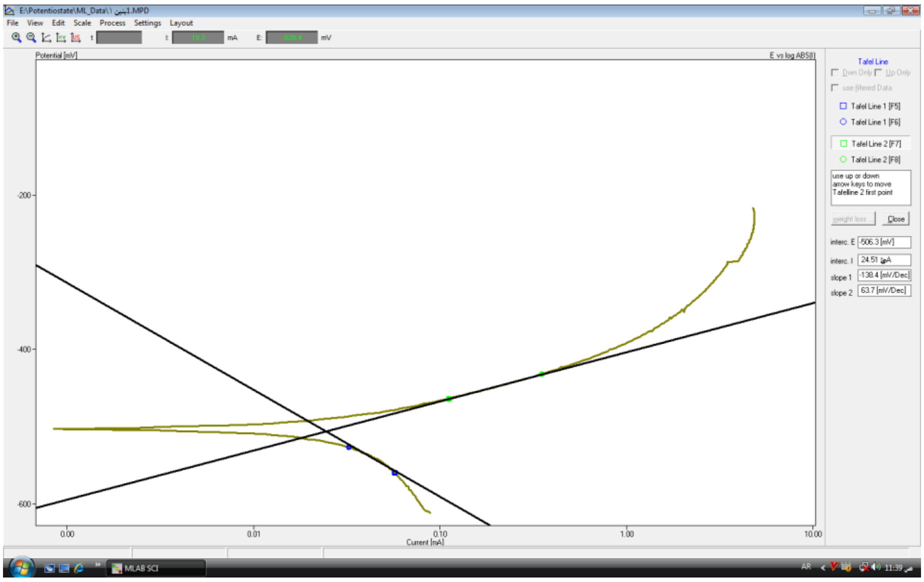


(a) (b) (c)

(d) (e)

(a): Ni coating layer, (b): Ni-20nHAP,10g coating layer, (c): Ni-20nHAP,20g, (d): Ni-40nHAP,10g, (e): Ni-40nHAP,20g

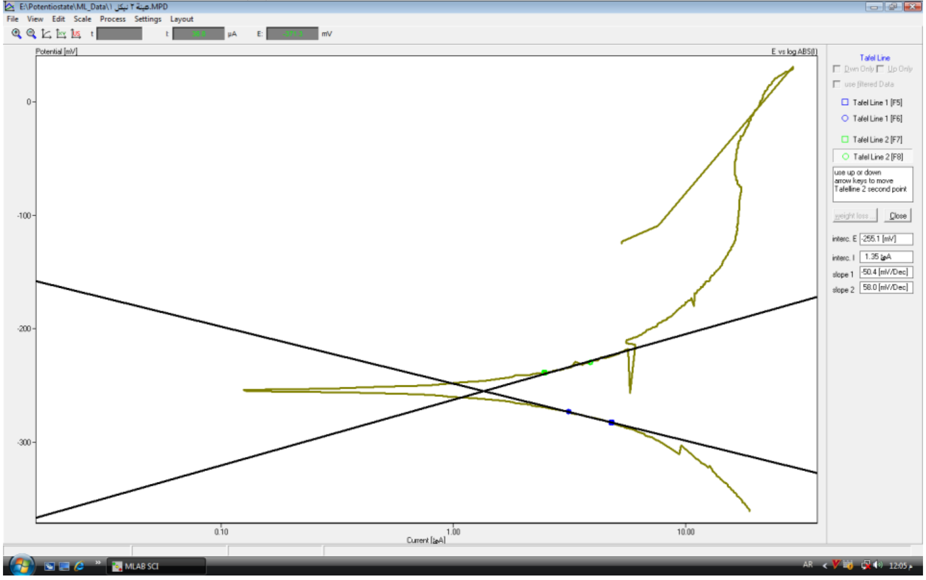
Figure (2) topographic morphology.



use up or down
arrow keys to move
Tafelline 2 first point

interc. E -506.3 [mV]
interc. I 24.51 µA
slope 1 -138.4 [mV/Dec]
slope 2 63.7 [mV/Dec]

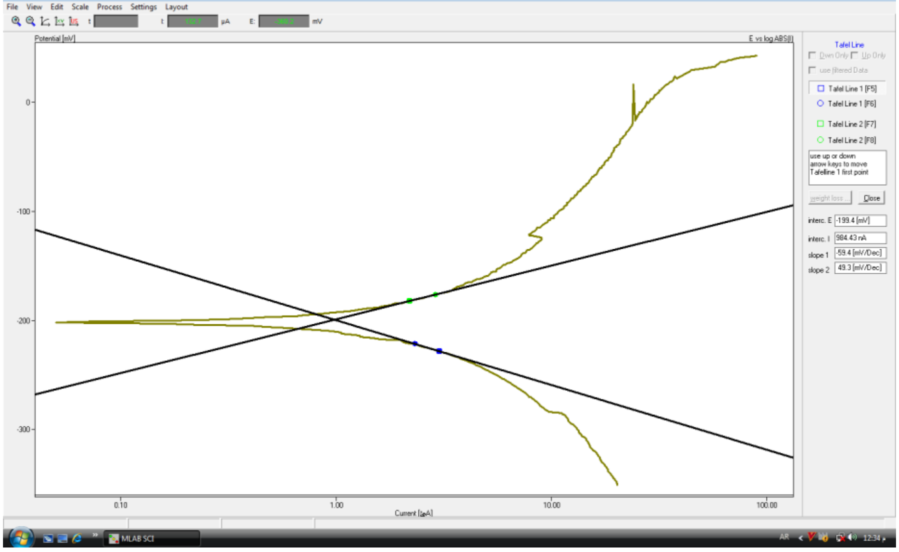
(a) Low carbon steel in Hank's solution.



use up or down
arrow keys to move
Tafelline 2 second point

interc. E -255.1 [mV]
interc. I 1.35 µA
slope 1 -50.4 [mV/Dec]
slope 2 58.0 [mV/Dec]

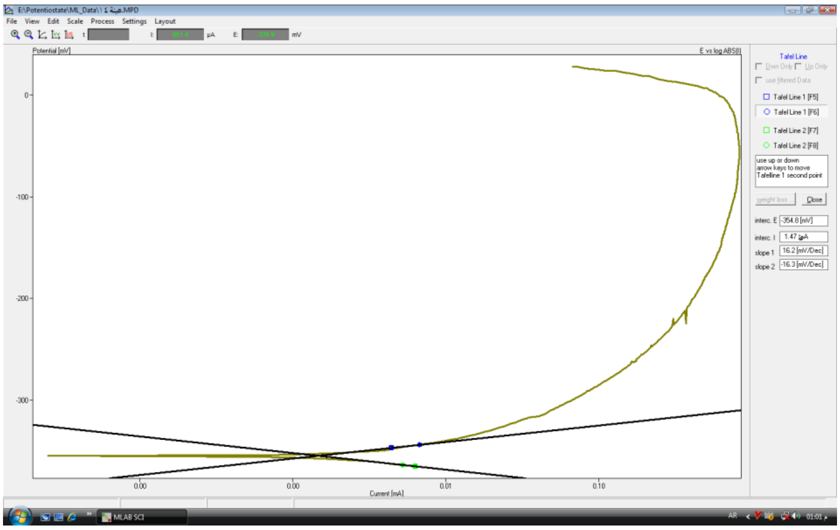
(b)Low carbon steel coating with Nickel layer in Hank's solution.



use up or down
arrow keys to move
Tafelline 1 first point

interc. E -199.4 [mV]
interc. I 984.43 nA
slope 1 -59.4 [mV/Dec]
slope 2 49.3 [mV/Dec]

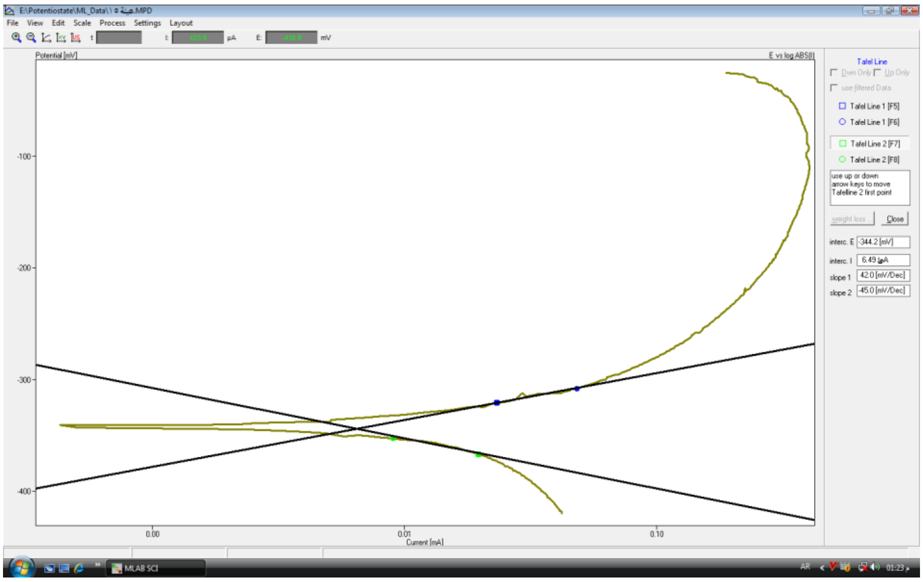
(c) Low carbon steel coating with (Ni-40nHAP,10g/L) in Hank's solution.



use up or down
arrow keys to move
Tafelline 1 second point

interc. E -354.8 [mV]
interc. I 1.47 µA
slope 1 16.2 [mV/Dec]
slope 2 -16.3 [mV/Dec]

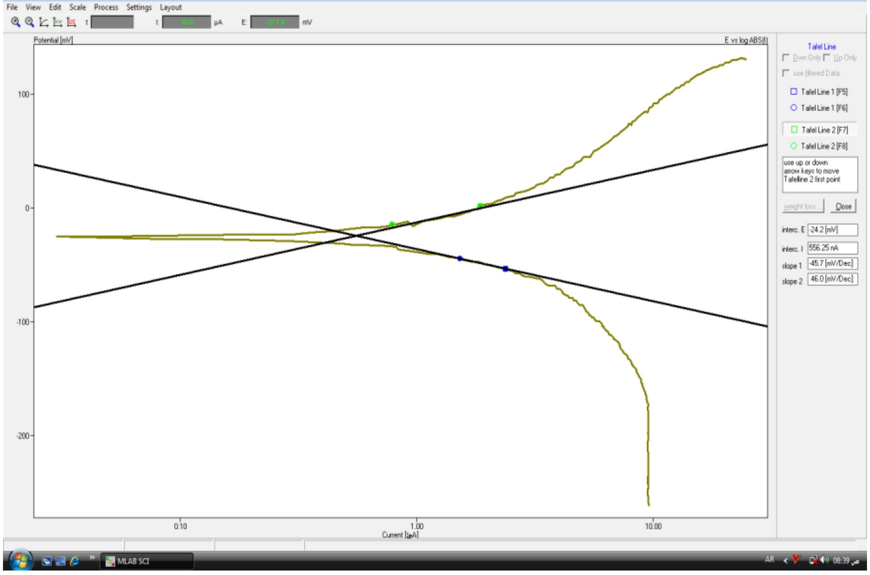
(d) Low carbon steel coating with (Ni-40nHAP,20g/L) in Hank's solution.



use up or down
arrow keys to move
Tafelline 2 first point

interc. E -344.2 [mV]
interc. I 6.49 µA
slope 1 42.0 [mV/Dec]
slope 2 -45.0 [mV/Dec]

(e) Low carbon steel coating with (Ni-20nHAP,10g/L) in Hank's solution.



use up or down
arrow keys to move
Tafelline 2 first point

interc. E -24.2 [mV]
interc. I 556.25 nA
slope 1 -45.7 [mV/Dec]
slope 2 46.0 [mV/Dec]

(f) Low carbon steel coating with (Ni-20nHAP,20g/L) in Hank's solution.

References:

1. NICKEL PLATING HANDBOOK 2014.
2. Dr.Abdalwahid K. Rajih, Dr.Jaleel K. Ahmed, Dr.Nabaa S. Radhi,"INVESTIGATION SOME PROPERTIES OF (Zn-Ni-SiC) COMPOSITES COATING ON LOW CARBON STEEL",The Iraqi Journal for Mechanical – and Materials Engineering, 2018.
3. Dr.Jaleel K. Ahmed, Dr.Nabaa S. Radh, "Protective the carbon steel from corrosion by coating (Zn-Ni) alloy", The Iraqi Journal For Mechanical And Material Engineering, Vol.11, No.1, 2011.
4. Dr.Jaleel K. Ahmed, Dr.Nabaa S. Radh, "IMPROVEMENT THE HARDNESS AND WEAR OF (ZN-NI) COATING LAYER BY ADDING SILICON CARBIDE", The Iraqi Journal For Mechanical And Material Engineering, Vol.11, No.3, 2011.
5. Yadava A.A., Masumdara E.U., Moholkar A.V., Neumann-Spallartc M., Rajpured K.Y., and Bhosaled C.H.(2011)‘ Effect of substrate temparature on the crystal growth orientation and some physical properties of SnO_2:F thin films deposited by spray pyrolysis technique’ Journal of Alloys and Compounds 448, 350–355.
6. Okner, R. G. and andler , D. M .(2011)‘ Electrochemical coating of medical implant applications electrochemistry and nanotechnology in biology and medicine’, springer science and business media ,LLC,pp.1-13.
7. Silva, M. H. , limos , A. F. and ferreira, J.(2010) ‘Mechanical characterization of porous glass reinforced Hydroxyapatite ceramic –bonelike’,Material researcher.Vol.2,pp. 98-102F.
8. Farah Sami Rasheed Abood," **Surface Modification by HA of 316 L S.S for Biomedical Applications''**, MSC thesis, University of Babylon Collage of Materials Engineering, 2018.
9. Park, J. ‘bioceramics, properties, characterization and application’, springer.
10. Wang, N .li and Rae , G.(2007)'Stress corrosion cracking of Ni Ti in artificial saliva', dental materials ,vol. 23,pp.133-137.
11. K. W.NG, H. C. Man and T.M.Yue(2011)'characterization and corrosion study of Ni Ti laser surface alloyed with Nb or Co',vol. 257,Isaue.8,32 G9.
12. Ajay, S. and Abhinandan, R.(2010) ‘Study of hydroxyapatite and hydroxyapatite-chitosan composite coatings on stainless steel by electrophoretic deposition method’, National Institute of Technology.
13. Shalabi, M. M.,Wolke, J. G. and Jansen, V. M.(2007)‘Evaluation of bone response to titanium – coated polymethacrylate resin (PMMA)implants by X-ray tomography’J. Mater sic. Mater Med, vol.18,pp.2033-2039.
14. Roether, J. A. and Deb, S. (2004) ‘The effect of surface treatment of hydroxyapatite on the properties of bioactive bone cement ’Journalof materials science ,material in medicine , vol.15,pp.413-418.