PREPARATION AND CORROSION BEHAVIOR OF NITI SHAPE MEMORY ALLOY COATED WITH BIOCOMPATABLE LAYER

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ABSTRACT :

In this paper NiTi shape memory alloy has prepared from elemental Nickel and Titanium powders by powder metallurgy Technique, the is 620 MPa compacting pressure , 850 ˚C temperature and10^{-3} torr vacuum atmosphere. The Porosity and density before and after sintering have been calculated. X-ray diffraction analysis showed that Nickel and Titanium are completely transformed into NiTi and Ni_3Ti phase. Poly Methyl Methane Acrylate and Poly Methyl Methane Acrylate / Hydroxy apatite coating are applied to the surface of the alloy. Optical microscopy technique is used to characterize the surface of each sample. The corrosion rate has been studied in vitro by using electrochemical technique by a potentiostate in Hank's Solution, Artificial saliva and 0.9% NaCl solution at 37 ºC. Atomic Absorption Spectroscopy technique is used to detect the Ni ion release from the alloy in 0.9% NaCl solution. The corrosion test results shows that the corrosion rate after Poly Methyl Methane Acrylate / Hydroxyapatite coating decreased from 12.14 mpy for bare sample into 0.132 mpy in 0.9% NaCl solution , from 4.94 mpy into 0.39 mpy Artificial saliva and from 12.66 mpy into 0.217 mpy in Hank Solution. The Ni release test shows that the amount of releasing Ni ion decreased into undetectable amount after coating with Poly Methyl Methane Acrylate and Poly Methyl Methane Acrylate / Hydroxyapatite.

Keywords: Nitinol, Shape Memory Alloys, Powder Metallurgy , Ni Ion Release, Hydroxyapatite, Poly Methyl Methane Acrylate Coating.

تحضير ودراسة سلوك التاكل لسبيكه نيكل- تيتانيوم المتذكرة للشكل مطليه بطلاء ذو توافق حيوي

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الخلاصة :-

في هذا البحث تم تحضير سبيكة نيكل-تيتانيوم المتذكره للشكل بواسطة تقنية ميتالورجيا المساحيق باستخدا ضغط كبس مساوي 620 MPa ودرجهة حراره تلبيد850 ˚C وبجو مفرغ 10^{-3} torr. تم حساب المساميه والكثافه قبل وبعد عملية التلبيد.فحص حيود الاشعه السينية اظهر ان النيكل والتيتانيوم تولا بالكامل الى NiTi وNi_3Ti. تم طلاء سطح العينات بطبقة بولي مثيل ميثان اكريليت وطبقة بولي مثيل ميثان اكريليت\هيدروكسي اباتايت ومن ثم دراسة سطح العينات بواسطة المجهر الضوئي.معدل التاكل تم حسابه بالطريقه الكهروكيمائيه باستخدام جهاز المجهاد الساكن في محلول هانك،محلول اللعاب الصناعي،ومحلول 0.9% كلوريد الصوديوم بدرجة 37 ºC.كميه ايون النيكل المتحرر تم حسابها بواسطة مطيافية الامتصاص الذري بعد الغمر بمحلول 0.9% كلوريد الصوديوم .نتائج التاكل بينت ان معدل التاكل قد انخفض بعد الطلاء ب بولي مثيل ميثان اكريليت\هيدروكسي اباتايت من 12.14 mpy قبل الطلاء الى 0.132 mpy في محلول0.9% كلوريد الصوديوم،ومن 4.94 mpy الى 0.39 mpy في محلول اللعاب الصناعي ومن 12.66 mpy الى 0.217 mpy في محلول هانك. فحص تحرر ايون النيكل اظهر ان تحرر ايون النيكل تم تقليله الى قيم لا يتحسسها جهاز مطيافيه الامتصاص الذري بعد الطلاء ب بطبقة بولي مثيل ميثان اكريليت وطبقة بولي مثيل ميثان اكريليت \ هيدروكسي اباتايت.

INTRODUCTION :-

Titanium–Nickel alloy or NITINOL is an intermetallic compound of Ti and Ni. It composed of equiatomic ratios of Ti and Ni.This alloy exhibits reversible transformation which effectively enables the alloy to recover its original shape spontaneously after being subjected to macroscopic deformation more than its elastic limit without irreversible plastic deformation intervening, by up to 16% elongation/contraction. This shape recovery may take place upon heating or after loads discharging. This phenomenon arises fascinating properties such as Shape memory effect (SME) and superelasticity (SE) these properties in combining with corrosion resistance and desirable mechanical properties for example good fatigue strength ,relatively low modulus, machinability , and formability, make NiTi shape memory alloy demanded in many medical and engineering applications[Vojtech et.al (2010),Liu and Ding (2004),Porter(1992)]. Applications of Nitinol are sundry and cover both biomedical and engineering scope. The Early commercial applications of NiTi are in non-medical fields such as Couplings for industrial oil line pipes. Water pipes and similar types of Piping have also been adopted. The first industrial application sphere was in warplanes, coupling as a replacement of welding at the closest area of fuel storage units in 1969. Now days the use of Nitinol in engineering is propagating for instance it is presented in aerospace ,robotics, and automotive industries as electrical switches, actuators and sensors, safety devices, temperature switches, and so many other devices [Mizar(2005)]. In the last two decades, NiTi has been used for medical purposes such as dentistry, orthopedics, and cardiovascular operation, And NiTi shape memory property of allow phases change at the human body temperature and these are some of Nitinol listed below[Dilibal and Adanir (2013),Yee Joan(2007)].

The NiTi alloy is one of the most popular SMAs (shape memory alloys) in bioengineering applications owing to its biocompatibility and its other remarkable properties. Titanium is well recognized to be biocompatible with long-term corrosion resistance. In contrast to Ti, Ni release from the surface of NiTi implants has been a concerning issue because the dissolution and concentration of Ni ions or wear debris above a certain amount an adverse effects like as allergenicity, toxicity and potential carcinogenic effects [Ryhanen(1999)]. **Chen**(2003) has employed a chemical treatment to form an apatite layer on NiTi shape memory alloy .The samples was treated with 32.5% HNO_3 solution ,then boiled in 1.2M NaOH in order to form TiO_2 An apatite layer was formed subsequent to immersion in BSF at 37 ° C for one day. **Alher** (2013) studied the effect of TiO_2 and TiO_2/Hydroxyapatite(HA) coatings on Ni ion released from NiTi shape memory alloy , H_2O_2-oxidation was used to produce TiO2 and the samples subsequently immersed in fivefold concentration body simulated fluid to to produce HA layer .Ni released test achieved at 37 °C in 0.9% NaCl solution .and the results indicated that the Ni releasing was decreased as compared with bare samples. **Cheng** el at. (2006) modified the of equiatomic NiTi with tantalum coating by multi arc ion plating process followed by annealing treatment. the Ni released test was applied for the samples for 49 days in 0.9%NaCl .the results indicated that Ni-released reduced by 30 times lower than the uncoated samples. **Li** et al.(2013) studied the effect of iridium oxide (IrO_2) coating on Surface characteristics and electrochemical corrosion behavior of Ti-50.6 at.% Ni, alloy .the coating layer was applied by dipping the NiTi samples into $H_2IrCl_6{\cdot}6H_2O$ solution for 0.5 hour .and then oxidation process. **Barcos** et.al (2008) investigated the effect of Nitrogen ion implantation on the corrosion resistance of equiatomic NiTi in Hank solution. This paper aims to prepare NiTi SMA by powder metallurgy technique and apply biocompatible coating, PMMA and PMMA/HA at the alloy surface and then study the corrosion behavior and Ni release for coated and uncoated samples.

EXPERIMENTAL PART :

In this work, Elemental powders of Nickel and Titanium used to prepare the NiTi shape memory alloy, cylindrical samples with dimension of 12.7 mm diameter and 8 mm thickness by powder metallurgy. The powders were mixed for two hours then compacted at 620 MPa. The compacted samples sintered for 6 hours at 850˚ C under vacuum condition. The samples surface subsequently ground, polished and then characterize with optical microscopy. The density and porosity was calculated before sintering according to **(1, 2)** equations [Abid Ali(2008)]

$$\rho_g = m_g/V_g \quad (1)$$

Where:

ρ_g :is the green density (g/cm^3) ,and m_g :mass of green compacted (g)

V_g: volume of green compacted (cm^3).

$$P_g = (1 - \rho g/\rho th) \times 100 \quad (2)$$

Where:

P_g=green porosity (%), ρ_g= green density (g/cm^3)

ρ_{tb}=theoretical density of mixed powders(g/cm^3)

and after sintering according to ASTM B328, in order to determine the porosity and density of sintered samples the following procedure was followed:

1-After drying at 100˚C for 5 hours in a vacuum furnace the sample was weighed, and the weight represent mass A.

2-the sample is completely immersed in Paraffin oil with density 0.8 g/cm^3 and an evacuating system (to decrease the pressure) for 30 minutes at room temperature.

3-the impregnated (soaked) sample has been weighed in air, and the weight was mass B.

4- Mass C was determined by weighing the impregnated sample in water.

5- The porosity and density have been calculated by the following equations (3, 4) [ASTM B – 328(2003)]:

$$P = [\frac{B-A}{(B-C)D^{\circ}} \times 100] D_W \quad (3)$$

$$D = [\frac{A}{B-C}] Dw \quad (4)$$

Where:

D°=the density of the used oil

D_w= the density of water

The samples divide into three groups the first one was left as polished the second group was dipped in a 10% Poly Methyl Methane Acrylate (PMMA) solution was prepared by adding 10 g from PMMA to a 90 mL of Acetone and stirred for 3 hours on a magnetic stirrer at room temperature. The dipping process done in dip coater the dipping and dwelling speed was 100 mm/min **.** A solution of 10% in concentration was prepared by dispersing 10 g of Hydroxy Apatite (HA) in 90 mL of Acetone and stirred for 3 hours, then this solution was added to 10% PMMA solution in 1:1 ratio and then stirred for about 12 hours at 40 ˚c and The third group was dipped in this solution in the same condition of the second group. The corrosion behavior of samples has been studied by using electrochemical technique technique in three different solutions: 0.9% NaCl, Hank's solution and artificial saliva, the composition of the later tow solution indicated in **table (1, 2)** respectively. The corrosion rate calculated according to the following equation **(5) [**ASM book 1992]:

$$\text{Corrosion Rate (mpy)} = 0.13.\,(i_{corr}).(EW)/A.\rho \qquad (5)$$

Where:

i_{corr} is corrosion current density ($\mu A/cm^2$)

EW is equivalent weight (g/eq.)

A is area (cm^2) and ρ is density (g/cm^3)

And the improvement percentage was calculated according to equation (6):

$$\text{Improvement percentage} = \frac{CR^{\circ} - CR}{CR^{\circ}} \times 100 \qquad (6)$$

Where:

CR°=corrosion rate without coating (bare sample)

CR=corrosion rate of coated sample

The Ni ion release test for each group of samples has been done in 0.9% NaCl simulated body solution, where samples were immersed in glass containers with 50 mL of 0.9% NaCl solution for four weeks and the Ni released amount was assessed by AAS.The accumulative mass of released Ni was calculated according to equation (7) [Surmenev et.al (2010)]:

$$m_{Ni} = V1.C_{Ni} / S_{surface} \qquad (7)$$

Where:

m_{Ni} =accumulated Ni released rate($\mu g/cm^2$)

V_1= solution volume (started with 0.05 L then 0.045 L, 0.04 L and 0.035 L)

C_{Ni}=Ni concentration in ppm (µg/L), $S_{surface}$= surface area of the sample (cm²)

RESULTS AND DISCUSSION :-

The porosity before sintering was 24.8 and after sintering was 21.4, and the density for greem compacted was Density of the green compact is 4.7854 g/cm^3 and after sintering is 5.0044 g/cm^3 this densification is might be attributed to the pores shrinkage or rounding and this increase densification. **Fig (1)** shows the XRD patterns of the alloy after sintering. it can be observed that the sintering temperature and time are enough to complete the phase transformation and all Ni, Ti transformed into monoclinic NiTi phase (M-NiTi) cubic NiTi phase (A- NiTi) which exhibit the shape memory properties and hexagonal Ni_3Ti phase which it is harmful phase because it hasn’t a shape memory properties and it has more tendency to corrode than the other two phases. The formation of Ni_3Ti is as a result of slow cooling of samples. Light optical microscope test are carried out for the sintered sample after being chemically etched. **Fig (2)** shows the microstructure of sintered sample microstructure of this sample shows pores with different size, present phase and grain boundaries. The pores are rounded and randomly distributed. **Figs(3)** indicate the microstructure of the coating layers , the surface images indicate a homogenious structure with a very little amont of porosity and cracks free surface layer,as well as the cross section images of these coating layer shows a good adherence with NiTisubstrate.

CORROSION RESULTS :-

The corrosion parameters of all samples are calculated from the potentiostatic polarization curves in three simulated body fluids 9% NaCl solution, artificial saliva and Hank’s solution in order to investigate the effect of the coating layer and its validity as a biocompatible layer. present the corrosion parameters (corrosion potential, current density and corrosion rate)which calculated by tafel extrapolation method and the improvement of corrosion resistance after each coating process in Hank’s solution Artificial saliva and 0.9% NaCl solution, indicated in **Tables (3-5)** respectively. It can be noticed that improvement in corrosion behavior of samples coated with PMMA and PMMA/HA samples which it is an adherent, thick and protective layer and it represents a protective layer isolates the alloy from its surrounding. The corrosion potential became more negative after the coating process, the corrosion density is shifted to less value and the corrosion resistance was decreased into a small amount as a result of the coating process. The corrosion rate is the least by coating PMMA/HA layer in the three solutions. The polarization curves of the uncoated and coated samples **Figs (4-6)** show that the corrosion current is shifted into a lower values and the corrosion potential is shifted into less noble values after coating process. These results indicate stability of coatings layer against dissolution.

Ni Release Results

Although the good corrosion resistance of NiTi, there is a problem associated with Ni high content, Ni ion can leach from Nitinol in some biological environment and this metallic ions could accumulate in the implant’s surrounding tissues or could be transported by blood. Ni is element with a potentially high toxicity for human body, however its toxicity remains difficult to assess because it seems to vary from person to person [Mantovi 2000], but the

PMMA and PMMA/HA coating decreased the Ni amount into undetectable amount because these layers acts as a barrier isolating the alloy from its surrounding and suppressing the release of Ni ions. **Table (6)** shows the results of accumulation Ni ion result that assessed by Atomic Absorption Spectroscopy (AAS) after 28 immersions in 0.9% NaCl solution.

CONCLUSIONS :

From the obtained experimental results, the following conclusions can be drawn as:

1- PMMA and PMMA/HA coatings act as a barrier and suppressed the Ni release into undetectable levels.

2- The applied coatings achieved an excellent improvement in corrosion behavior in 0.9% NaCl, Artificial saliva and Hank's solution.

Table (1) composition of artificial saliva [Giacomelli et.al (2004)]

Constituent	Concentration g/L
NaCl	6.7
KSCN	0.33
KCl	1.2
$NaHCO_3$	1.5
Na_2HPO_4	0.26
Na_2HPO_4	0.2

Table (2) Composition of Hank solution [Bao et.al (2015)]

Constituent	Concentration g/L
NaCl	8
$CaCl_2$	0.14
KCl	0.4
$NaCO_3$	0.35
Glucose	1
$MgCl_2.H_2O$	0.1
$MgSO_4.7H_2O$	0.06
$Na_2HPO_4.2H_2O$	0.06
Na_2HPO_4	0.06

Table (3) corrosion parameters of all group samples in Hank solution

Sample code	OCP (mV)	Icorr. (µA/cm²)	Ecorr. (mV)	CR (Mpy)	Improvement percentage (%)
Bare sample	-45	29.2	-76	12.66	
PMMA coated	-85	0.694	-179	0.3	97.6
PMMA/HA coated samples	-167	0.502	-158.1	0.217	98.2

Table (4) corrosion parameters of all group samples in Artificial Saliva solution

Sample code	OCP (mV)	Icorr. (µA/cm²)	Ecorr. (mV)	CR (Mpy)	Improvement percentage (%)
Master sample	-91	11.4	-121.8	4.94	
PMMA coated	-150	1.08	-240	0.46	90.6
PMMA/HA coated samples	-124	0.916	-147	0.39	92.1

Table (5) corrosion parameters of all group samples in 0.9% NaCl

Sample code	OCP (mV)	Icorr. (µA/cm²)	Ecorr. (mV)	CR (Mpy)	Improvement percentage (%)
Master sample	-135	28	-20.4	12.14	
PMMA coated	-184	0.848	-332	0.36	97
PMMA/HA coated samples	-171	0.305	-278	0.132	98.9

Table (6) the amount of accumulation Ni ion released after immersion in 9% NaCl solution for four weeks. N.D. (not detectable)

Sample code	Ni ion concentration (µg/cm²)
Master sample	0.183
PMMA coated	**N.D.**
PMMA/HA coated samples	**N.D.**

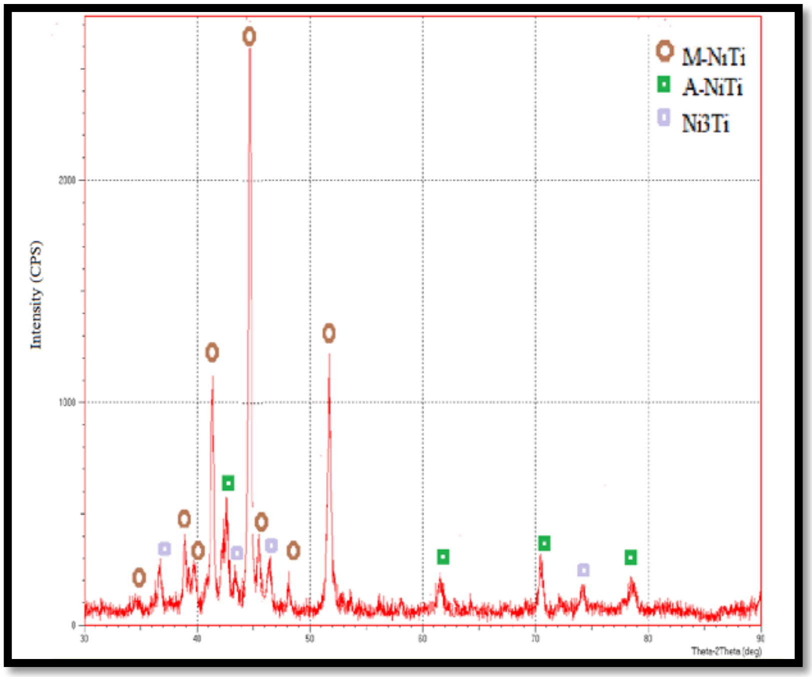
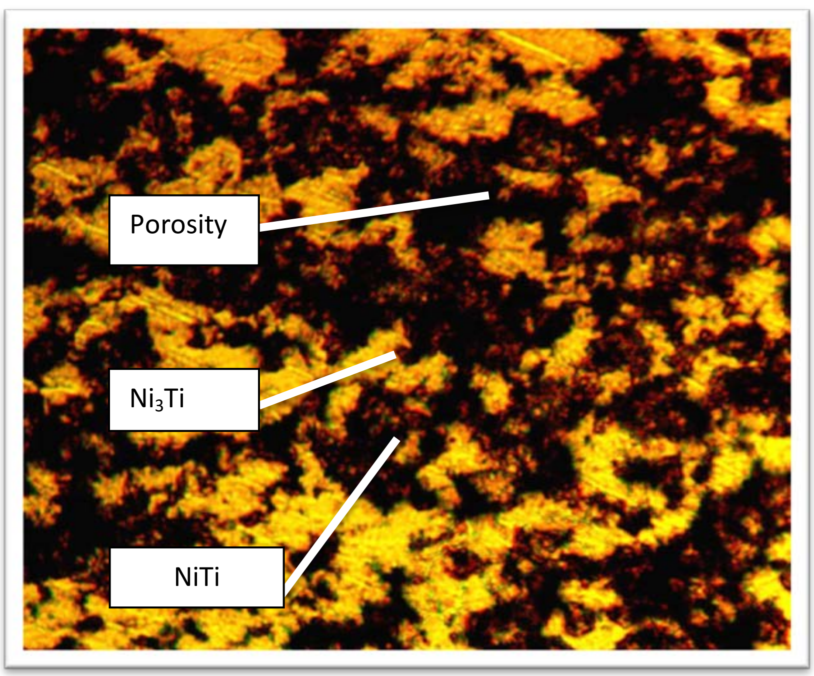
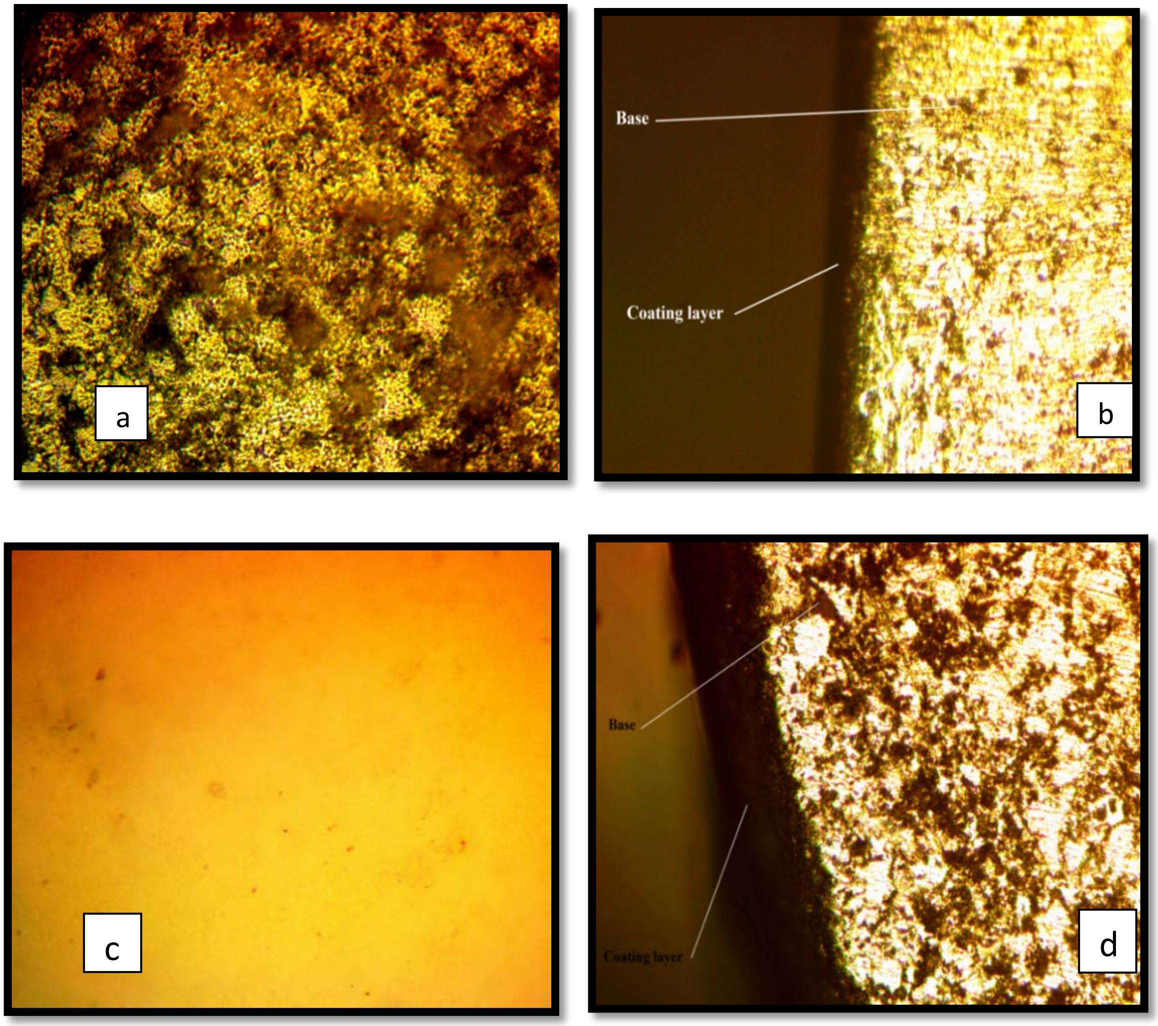


Fig (1) X-Ray diffraction of sintered sample

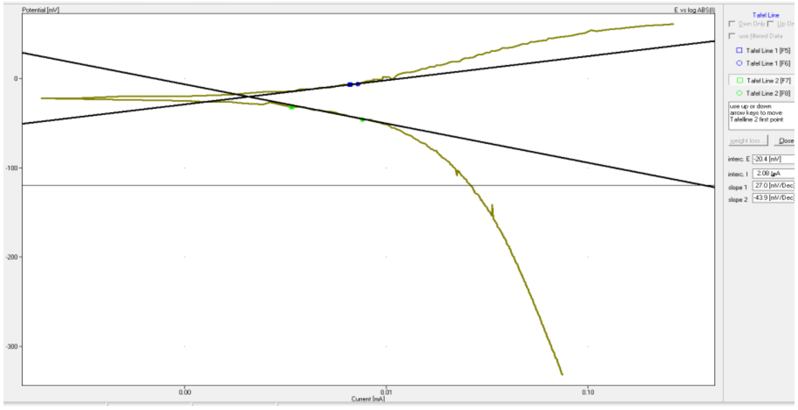


Fig(2)Microstructure of bare samples

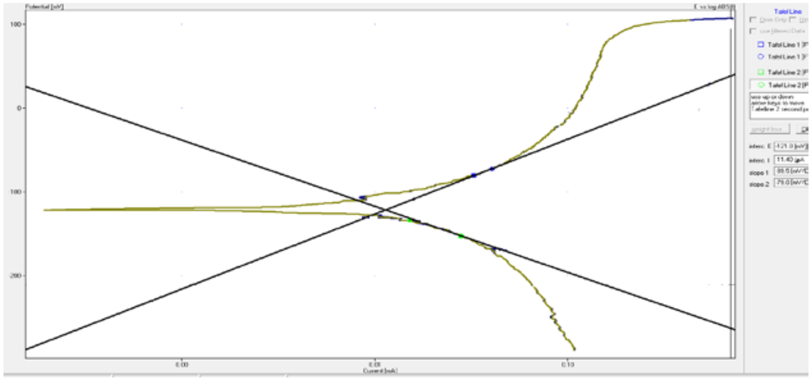


Fig(3)Microstructure of Costing layer a:PMMA surface, b:PMMA cross section

C:PMMA/HA surface, d: PMMA/HA cross section.



a



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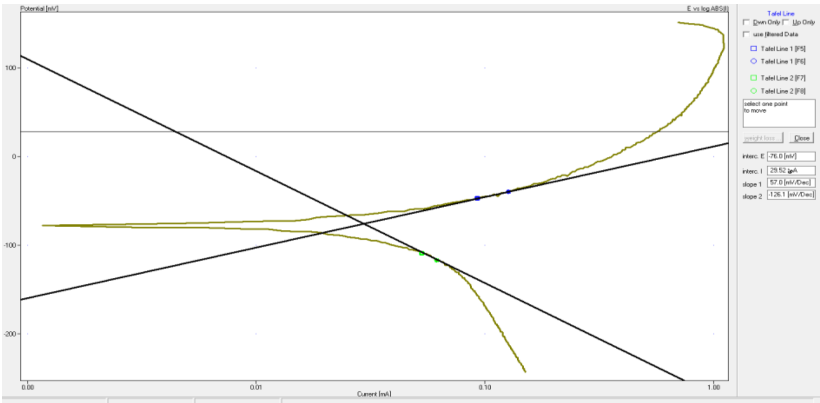

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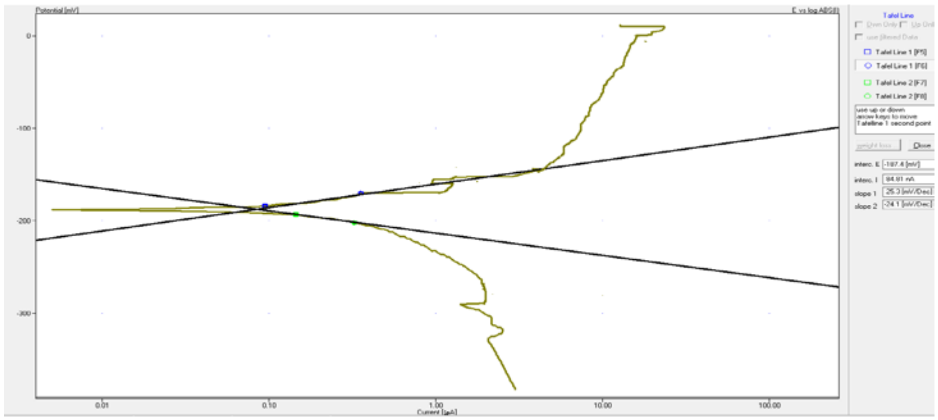
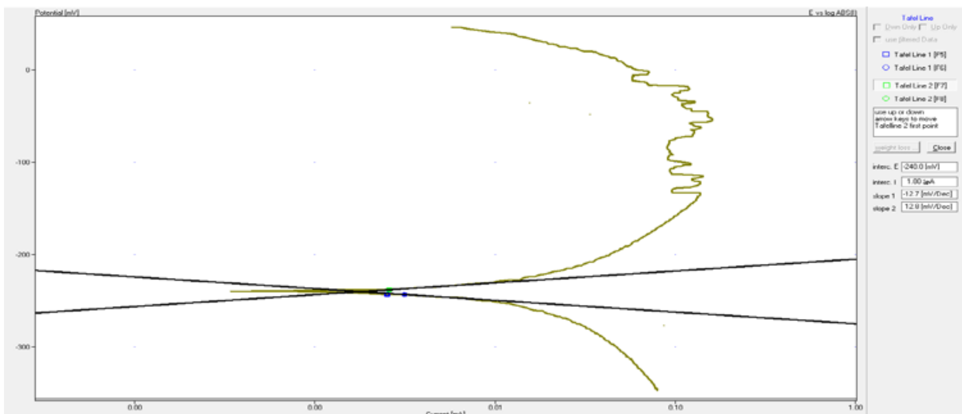
Fig(4) Polarization curves of bare samples in a: 0.9%NaCl,

b:Artificial saliva, c: Hank solution.



a



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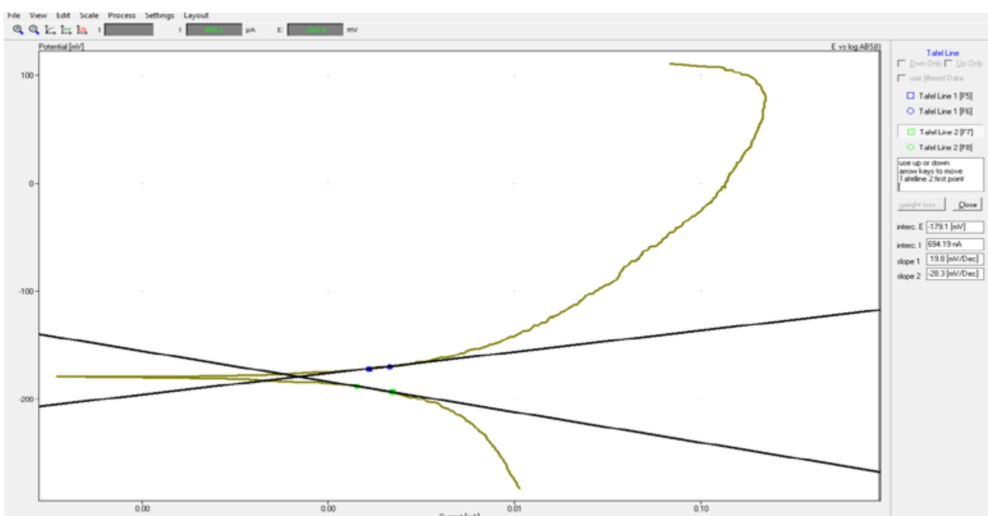

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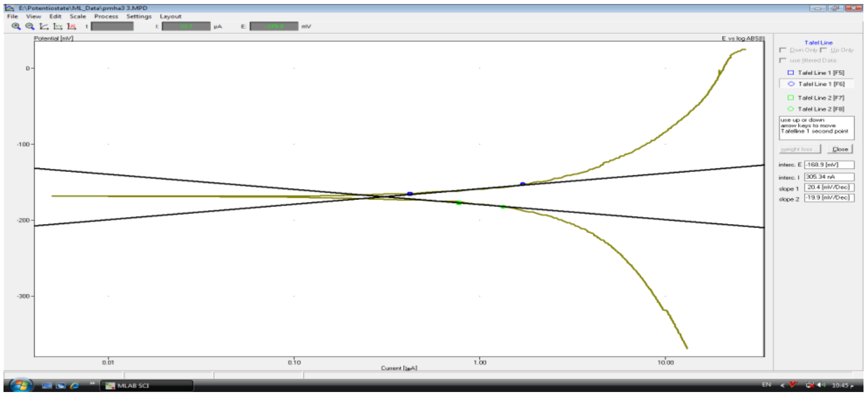
Fig(5) Polariation curves of PMMA coated samples in a: 0.9%NaCl, b:Artificial saliva, c: Hank solution.



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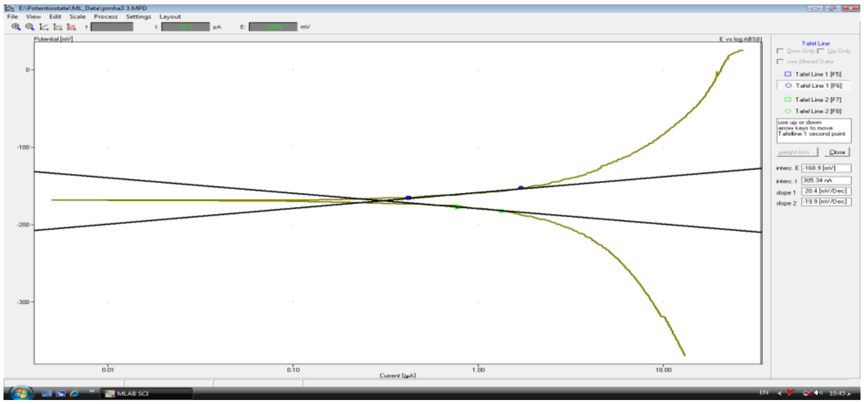

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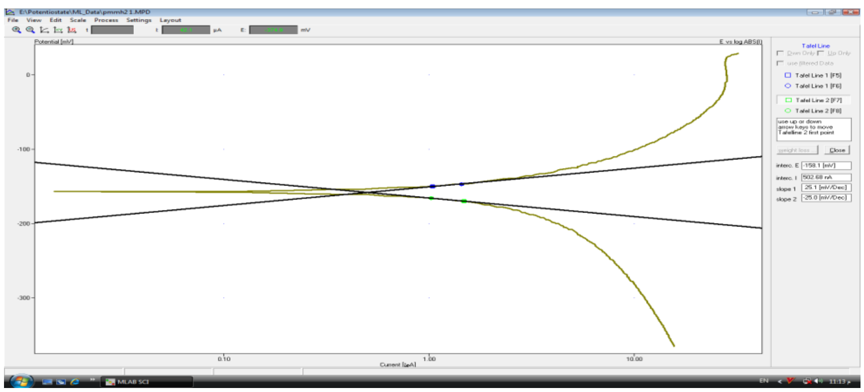

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Fig(6) Polarization curves of PMMA/HA coated samples in a: 0.9%NaCl, b:Artificial saliva, c: Hank solution.

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