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Research Article

The Electrochemical Deposition of Apatite on Titanium and It's Alloy

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Abstract: In this research we investigate the corrosion behavior of pure Ti and Ti6Al4V that coated with hydroxyapatite by electrodeposition from aqueous solution containing $\text{Ca}(\text{NO}_3)_2 \cdot \text{H}_2\text{O} = 7 \text{ gm/l}$, $(\text{NH}_4)_2\text{HPO}_4 = 3.5 \text{ gm/l}$, $\text{Na}(\text{NO}_3)_2 = 8 \text{ gm/l}$ in order to improve the bonding strength of hydroxyapatite and medical metal and alloy and increasing the biocompatibility. The suitable conditions for coating such as potential, temperature and solution pH was identified and confirmed and the coating layer morphology was investigated by XRD, Optical microscope and SEM tests, the corrosion tests was made by use synthesis simulated body fluid (SBF).

Keywords: Electrochemical deposition, hydroxyapatite coating, medical metals and alloys treatments.

INTRODUCTION

Surgical implants made from titanium and its alloy has been widely used to treat bone fractures and for dental applications because of its corrosion resistance and biocompatibility¹. Because the hydroxyapatite (HAp) has a structure $(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)$ similar to that for bone, so it has great biocompatibility and the ability to bonding with the bone from the early stages of implantation². Many methods has been used to coating hydroxyapatite on medical implants like coating by laser, plasma spray, electrophoretic deposition, dip coating³⁻⁶.

The electrochemical deposition from aqueous solutions has come a complementary series of these methods ⁷. This method has many advantages as below:

1. It's used a low-temperature degrees for coating which enables the formation hydroxapatite without any undesirable byproduct.
2. The ability to control the conditions of the coated layer easily by controlling the potential of coating and pH of solution, temperature and distance between the electrodes, these are the key factors for the electrochemical deposition, which allows formation of hydroxyapatite appropriate layer on the surfaces of surgical implants.
3. The low coast of such system unit than that of plasma sputtering and laser deposition methods.

The method of electrochemical deposition from aqueous solutions depend on the water electrolysis which produce hydroxyl ion (OH^-) which conceder the essential parameter to form hydroxyapatite in aqueous solutions beside calcium and phosphate ions ⁸. Because the surface roughness and chemical composition play a key role in bonding with the bone, so the method of electrochemical deposition provide a coating layer with high porosity and high bonding between the hydroxyapatite and the surface of the metal or alloy with appropriately thickness, which improves the corrosion resistance inside living organisms and accelerates osseointegration with living bone tissue ⁹.

To ensure the coating of hydroxyapatite free of undesirable products, the treatment of the coating layer by with a solution consist from (NaOH) as a source of extra hydroxyl ion ensure turned brushite compound ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) which is produced during the operation to hydroxyapatite ¹⁰. Therefore, the electrochemical deposition process adopted in this research is based on the use of a solution consist of 7gm/l calcium nitrate ($\text{CaNO}_3 \cdot 2\text{H}_2\text{O}$), 3.5 gm/L diaminium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) and 8.5 gm/l sodium nitrate (NaNO_3) and putting experimental program includes investigate optimal conditions for the coating, such as voltage, temperature and solution pH and the treatment of the coating resulting solution (NaOH) to ensure there are no undesirable outputs will form, and a thermal treatment after that to ensure the good crystalline for hydroxyapatite layer and good bonding with base metal.

MATERIALS AND METHODS

The samples of 20 mm diameter titanium and Ti-6Al-4V alloy was grinding with (500 – 1200 p) SiC grinding paper, chemically cleaned by a solution of $\text{HNO}_3:\text{HF}:\text{H}_2\text{O}$ with (3:1:6) volume respectively ,cleaned with acetone using ultrasonic bath (Ultrasonic cleaner KQ200E,CHINA) for 15 minutes twice and cleaned with distilled water using ultrasonic bath for 15 minutes once time. The coating solution was prepared from 7 gm/l calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 3.5 gm/l diamonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ and 8 gm/l sodium nitrate NaNO_3 dissolved in distilled water using magnetic stirrer, then the coating experiments will done with the following order:

1. Three samples from each titanium and Ti-6Al-4V alloy was coated using the solution prepared before with pH = 5.5, temperature = 25 °C, coating period 1 hr. and changing potential with (6,9,12) volt for each single sample in order to investigate the appropriate coating potential.
2. Four samples from each titanium and Ti-6Al-4V alloy was coated using the same solution but with pH = (4.5, 5.5, 6.5, 7.5) for each single sample and fixed potential at 9 volt, temperature 25 °C and coating period 1 hr. in order to investigate the appropriate solution pH.

- Three samples was coated using the same solution before but with $\text{pH}=5.5$, the coating potential was 9 volt, 1hr. period and the temperature varied as (25, 40, 60) °C for each single sample in order to investigate the appropriate temperature for coating. After coating was finished in each step the samples was immersed in 1M NaOH solution to complete the converting of brushite to hydroxyapatite and prevent formation any undesirable byproduct, then the samples was thermally treated at 400 °C for 1hr. in air atmosphere .the samples was tested by optical microscope, XRD and SEM, and the corrosion characteristics was investigated by using (Parastat 2273, USA made) for all samples.

RESULTS AND DISCUSSION

Potential Identification Experiments:

Titanium results: from polarization curve (tafel) test we see the decreasing in corrosion rate with increasing the potential of coating as shown in **Figure (1)**, that because the increasing in potential leads to increasing in coating layer thickness which reach to 180 μm with high porosity for the sample coated at 12 volt and 125 μm with low porosity for 9 volt coated sample, while the coated layer at 6 volt was not uniform and not thick as shown in **Figure (2)** which represent the optical microscopic images for coated samples at different potential.

The corrosion characteristics for samples coated at different potential shows that the lowest corrosion rate was achieved at 9 volt sample ($1.77 \times 10^{-3} \text{ mm/y}$) , i.e the corrosion rate reduce 10 times than that for uncoated sample as shown in **Table-2**.

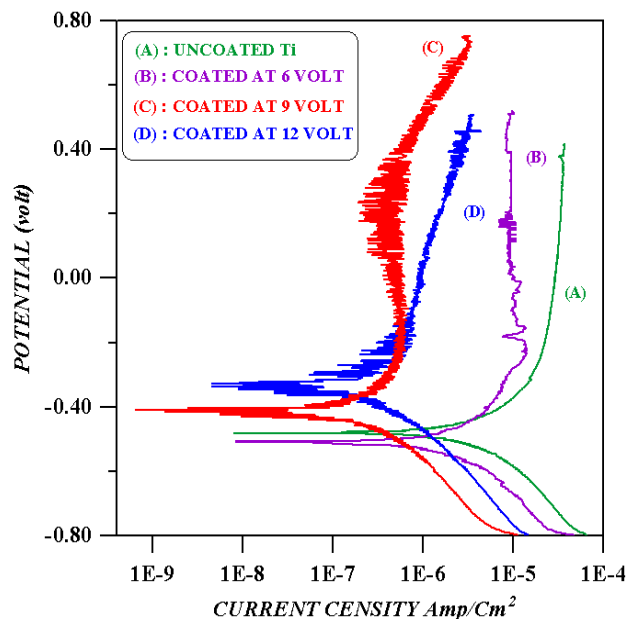


Figure 1: Polarization curve (tafel) for titanium samples coated at different potential.

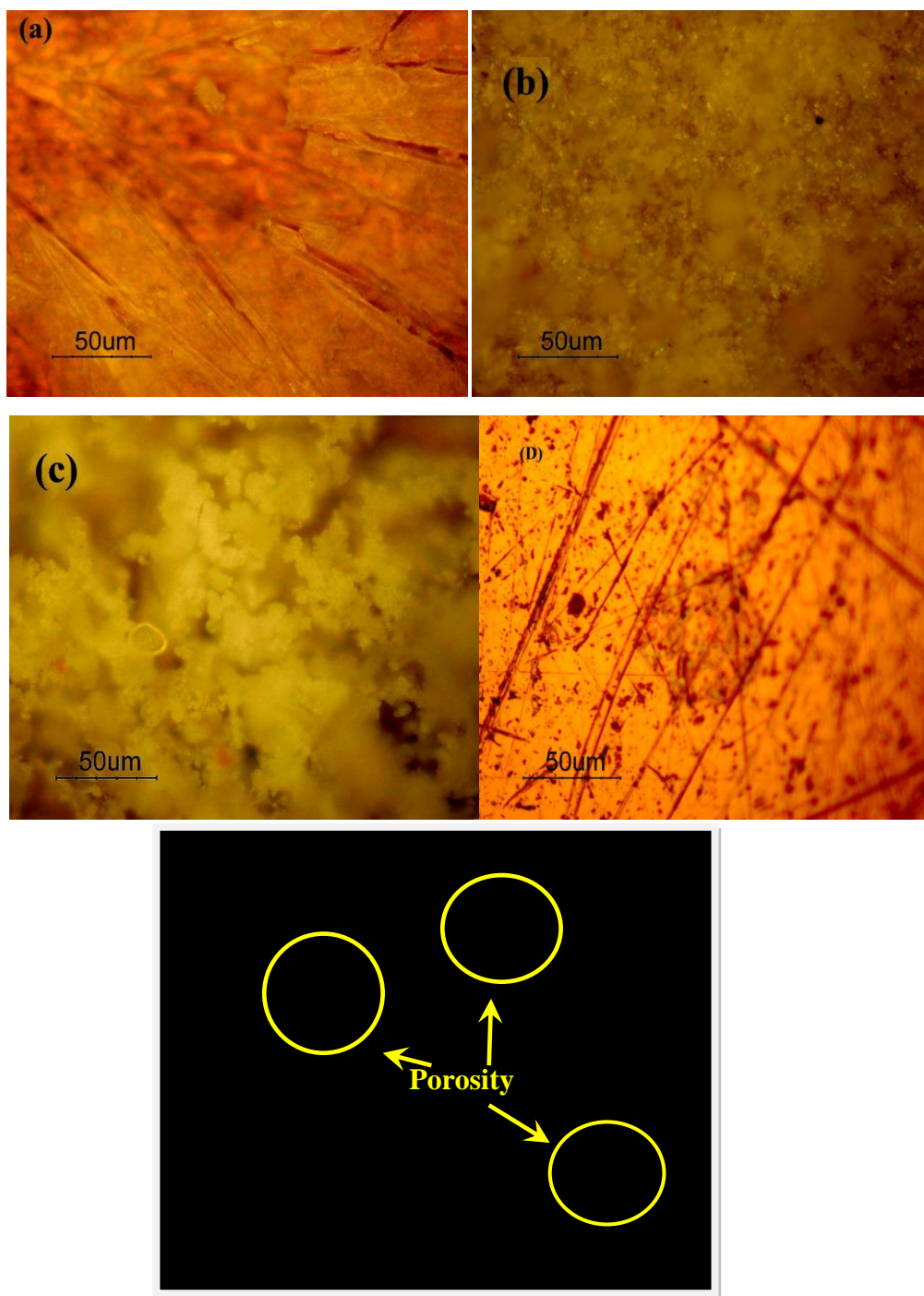
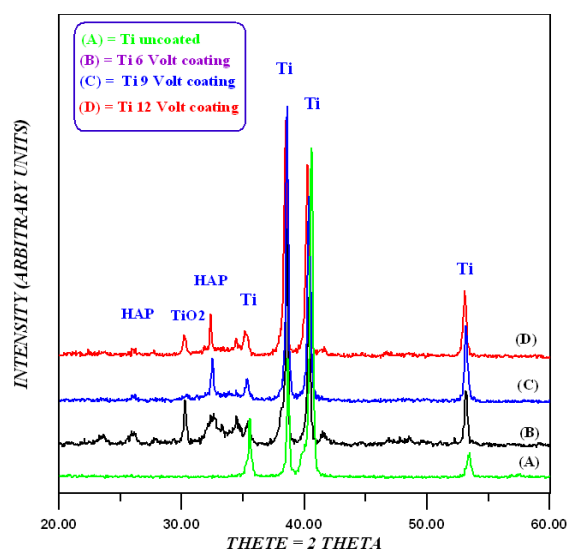
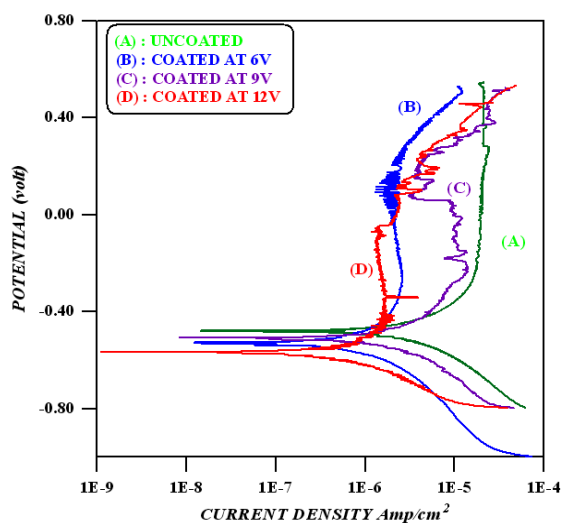


Figure (2): Microscopic images for titanium samples coated at different potential.

The XRD pattern for titanium samples coated at different potential in **Figure (3)** shows obviously the hydroxyapatite in all samples, TiO_2 peak appear in the sample coated at 6 volt because the coating was not uniform and there was many uncoated spots, the bushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) also appear in the samples coated at 6, 12 volt but not appear in sample coated at 9 volt.

Table-2: corrosion characteristics for titanium samples coated at different potential.

ITEM	Cor.rate mm/y	E.Cor. volt	I.Cor. Amp μ
uncoated	2.13×10^{-2}	-0.476	2.45
6 volt	8.0×10^{-3}	-0.512	8.96×10^{-1}
9 volt	1.77×10^{-3}	-0.428	1.9×10^{-1}
12 volt	2.25×10^{-3}	-0.395	9.53×10^{-2}

**Figure 3:** XRD pattern of titanium samples coated at different potential.**Figure (4):** Polarization curve (tafel) for Ti-6Al-4V alloy samples coated at different potential.

Ti-6Al-4V alloy results: the polarization curve for coated samples at different potential in **Figure 4** shows that less corrosion rate achieved was at sample coated at 12 volt (1.23×10^{-3} mm/y), it was reduced 10 times compared with uncoated sample (2.13×10^{-2} mm/y) as shown in **Table-2** which represent the corrosion characteristics for Ti-6Al-4V alloy samples coated at different potential.

Table-2: corrosion characteristics for Ti-6Al-4V alloy samples coated at different Potential.

ITEM	Cor.rate mm/y	E.Cor. volt	I.Cor. Ampμ
uncoated	1.023×10^{-2}	-0.482	1.128
6 volt	8.133×10^{-3}	-0.512	8.96×10^{-1}
9 volt	6.83×10^{-3}	-0.532	7.53×10^{-1}
12 volt	1.23×10^{-3}	-0.571	1.94×10^{-2}

From **Figure (5)** which represent the XRD pattern for Ti-6Al-4V alloy coated at different potential we see hydroxyapatite appear in all patterns especially in the sample coated at 12 volt, but also we see the brushite appear in samples coated at 6, 9 volt but not appear in sample coated at 12 volt.

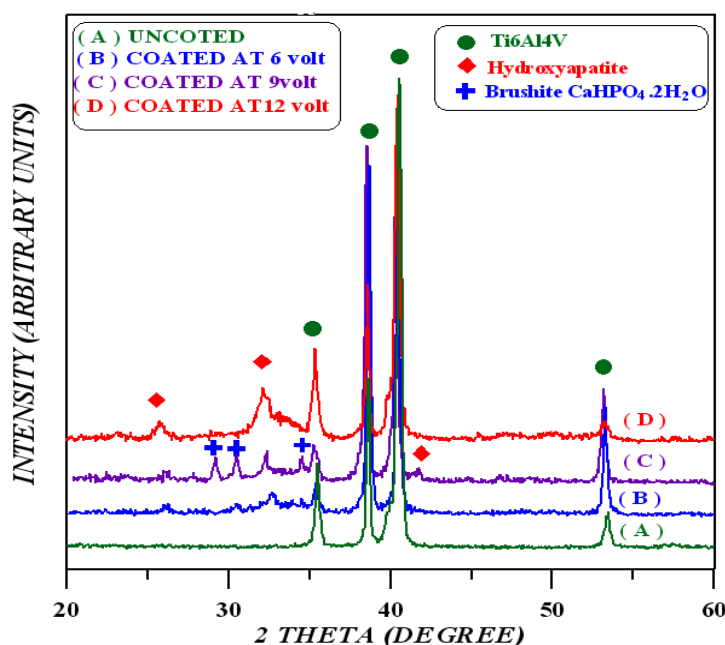


Figure (5): XRD pattern for Ti-6Al-4V alloy coated at different potential.

The hydrogen gas evolution at high potential lead to form huge porosity in the coating layer. The morphology of the hydroxyapatite formed affected by the nature of the base material, there are difference in crystals shape between the hydroxyapatite formed on titanium to that formed on Ti-Al-4V as shon in **Figure (6)** which represent the SEM images for hydroxyapatite formed on titanium and Ti-6Al-4V

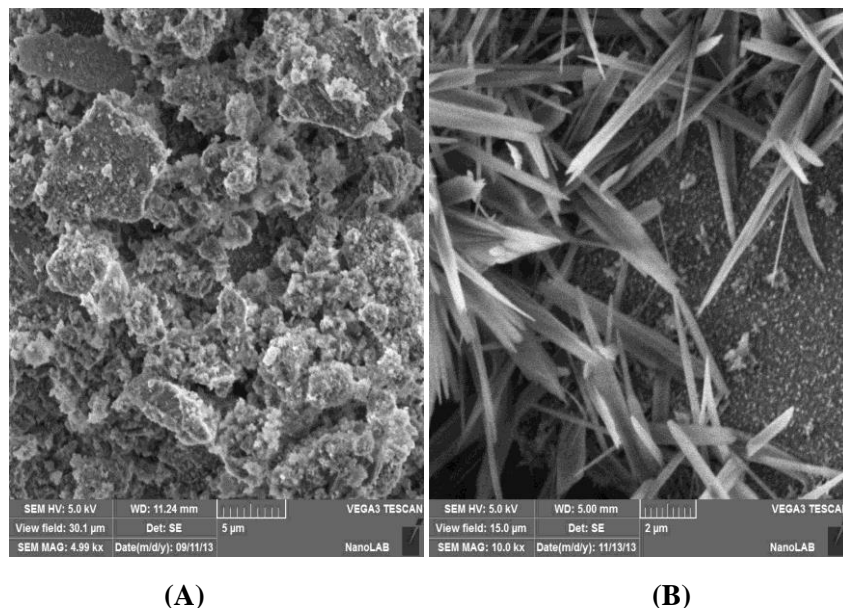


Figure (6): SEM images for hydroxyapatite formed on titanium and Ti- 6Al-4V.

Solution pH identification experiments:

Titanium Results: The polarization curve (tafel) shows that the optimum pH was 5.5 .as shown in **Figure (7)** and were the corrosion rate was $(2.89 \times 10^{-1} \text{ mm/y})$ as shown in **Table-(1)** which represent the corrosion characteristics for titanium coated at different pH.

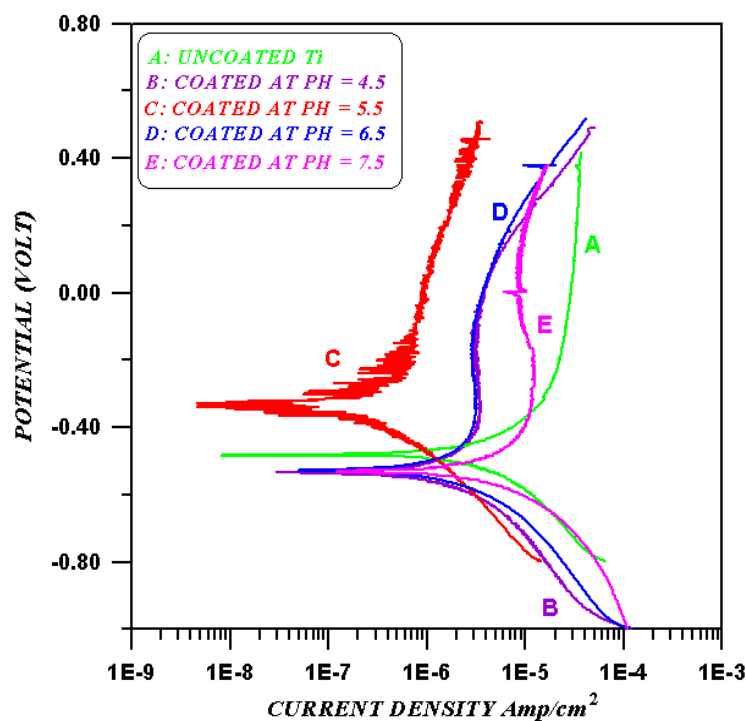
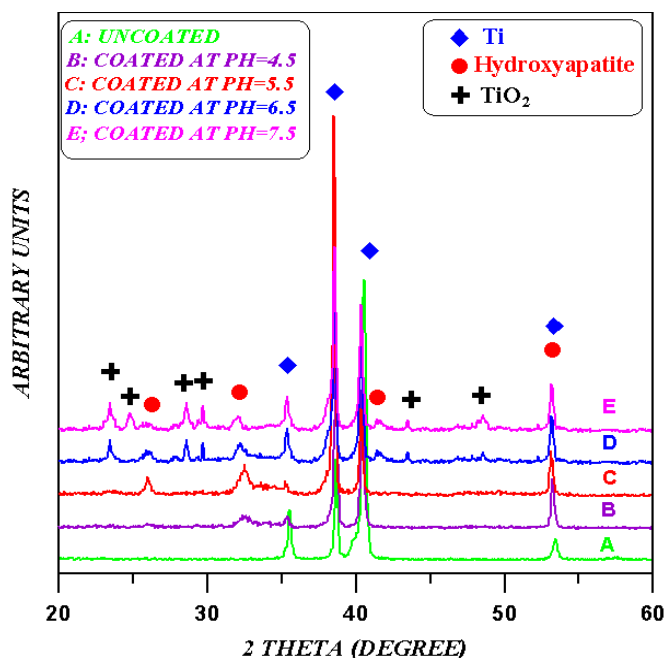


Figure (7): polarization curve (tafel) for titanium samples coated at different solution pH.

Table-3: corrosion characteristics for titanium samples coated at different pH.

ITEM	Cor. rate mm/y	E. Cor. volt	I. Cor. Amp μ
uncoated	2.13×10^{-2}	-0.476	2.45
PH=4.5	6.64×10^{-3}	-0.534	7.63×10^{-1}
PH=5.5	2.25×10^{-3}	-0.335	2.89×10^{-1}
PH=6.5	8.6×10^{-3}	-0.522	9.89×10^{-1}
PH=7.5	3.02×10^{-2}	-0.525	3.481

It's important to mention that the increasing of solution pH must not increasing the hydroxyapatite formation. We see that from XRD pattern in **Figure (8)** for titanium samples coated at different pH, we see the prushite formation in the samples coated at pH = 6.5 and 7.5 volt.

**Figure (8):** XRD pattern for titanium samples coated at different solution pH.

The optical microscope images shows that the sample coated at pH 4.5 and 7.5 are not coated uniformly, and the samples coated at pH 5.5 and 6.5 are coated uniformly but sample coated at pH 5.5 have a thicker layer from that coated at pH 6.5 as shows in **Figure (9)** which represent the optical microscope images for titanium samples coated at different pH.

Ti6Al-4V results: from polarization curve in **Figure (10)**, we that the appropriate solution pH was 5.5, when the solution pH increased the corrosion rate increased.

The corrosion characteristics of the coated samples at different solution pH listed in **Table-(3)**.

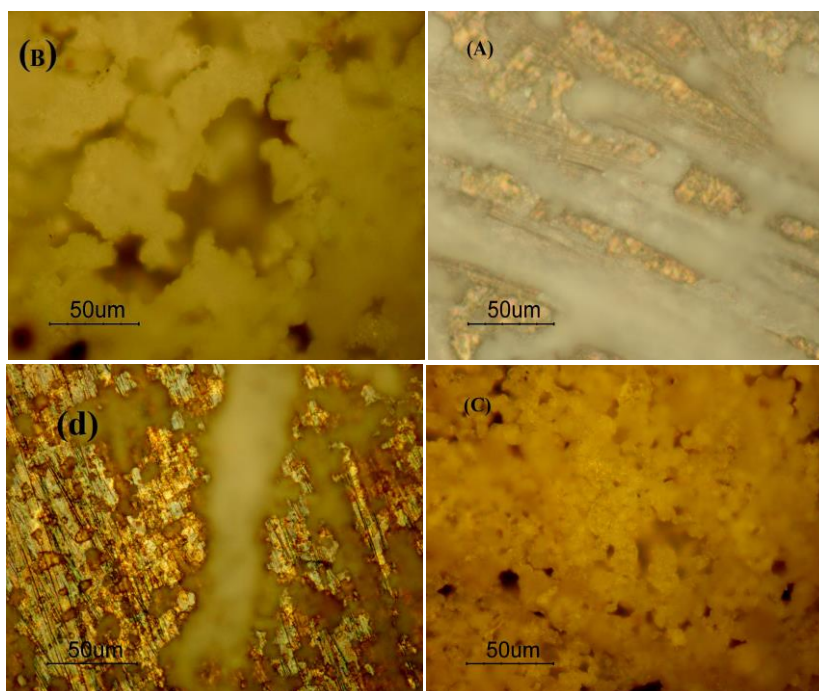


Figure (9): optical microscope images for titanium samples coated at different pH (a) 4.5, (b) 5.5, (c) 6.5, (d) 7.5.

Ti6Al-4V results: from polarization curve in **Figure (10)**, we that the appropriate solution pH was 5.5, when the solution pH increased the corrosion rate increased, the corrosion characteristics of the coated samples at different solution pH listed in **Table-3**.

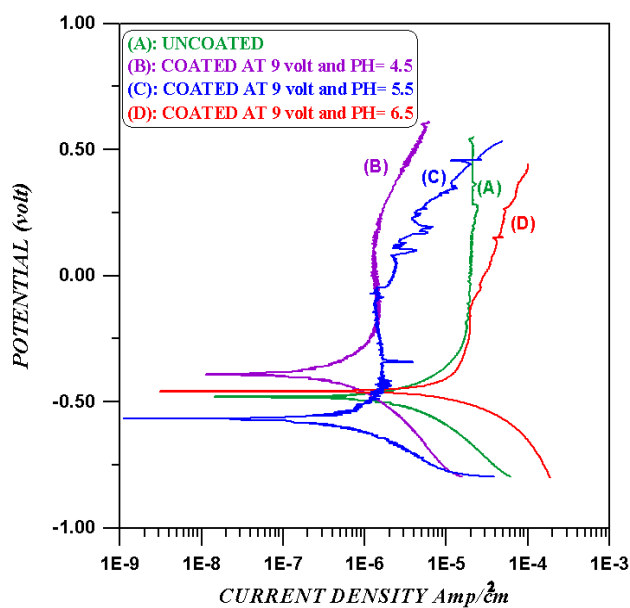


Figure (10): The polarization curve (tafel) for Ti-6Al-4V coated samples at different solution pH.

Table-4: The corrosion characteristics of the coated samples of Ti-6Al-4V at different solution Ph.

ITEM	Cor.rate mm/y	E.Cor. volt	I.Cor. Amp μ
uncoated	1.023×10^{-2}	-0.482	1.128
PH=4.5	3.971×10^{-2}	-0.391	4.378×10^{-1}
PH=5.5	1.23×10^{-3}	-0.571	1.94×10^{-2}
PH=6.5	4.279×10^{-2}	-0.451	4.717

The XRD pattern for coated samples at different pH shows the appearance of hydroxyapatite in samples coated at pH= 4.5 and 5.5 as the appropriate pH as undesirable product ,that lead to choose the ph 5.5 appropriate pH as shown in **Figure (11)** which represent the XRD pattern for samples coated at different pH.

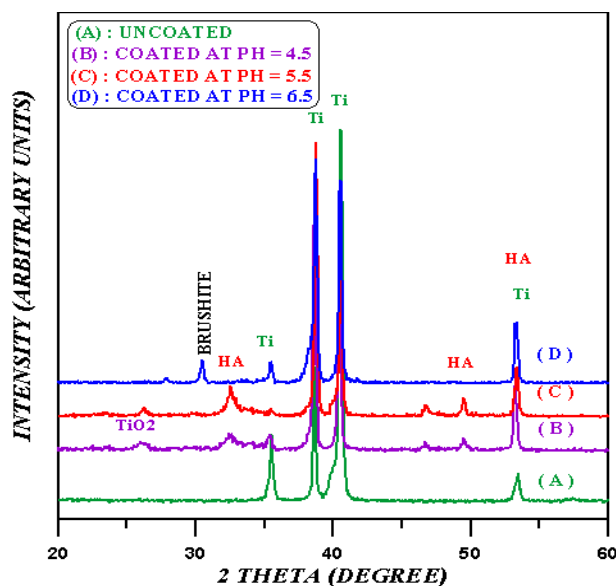


Figure (11): XRD pattern for Ti-6Al-4V samples coated at different pH.

Identification of the Appropriate Temperature:

Titanium results: From **Figure (12)** which represent the polarization curve for samples coated at different temperatures and **Table-5** the corrosion characteristics of the coated samples of titanium at different temperatures ,we see the decreasing in corrosion rate especially for sample coated at 50 °C, the corrosion rate decreased 24 times for that uncoated sample, this happen because the high temperature accelerate the reaction of hydrogen evolution and hydroxyl ion formation we need to form hydroxyapatite ,and also accelerate the reaction of formation of hydroxyapatite as catalyst as shown below ⁸:





The thickness of coated layer reach to 185 microns, but it was porous layer as shown in **Figures (13)**, **(14)** and **(15)** which represent the optical microscope image, optical camera images for coated at 60 °C.

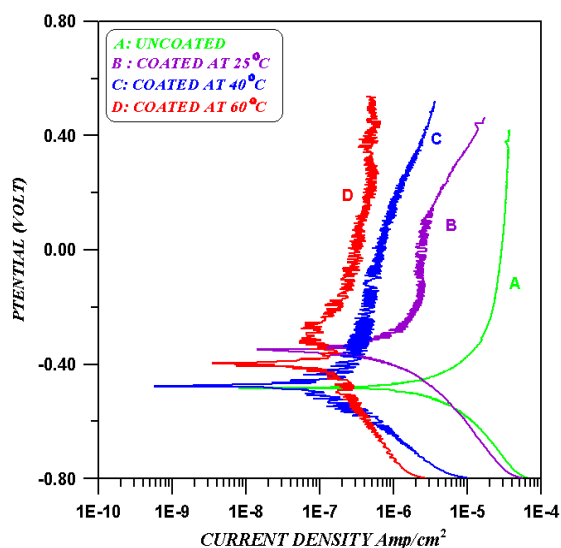


Figure (12): Polarization curve for titanium samples coated at different temperatures.

Table-5: The corrosion characteristics of the coated samples of titanium at different temperatures.

ITEM	Cor.rate mm/y	E.Cor. volt	I.Cor. Ampμ
uncoated	2.13×10^{-2}	-0.476	2.45
At 25 °C	2.255×10^{-3}	-0.335	2.89×10^{-1}
AT 45 °C	2.61×10^{-3}	-0.350	3.0×10^{-1}
AT 60 °C	9.07×10^{-4}	-0.474	1.04×10^{-1}

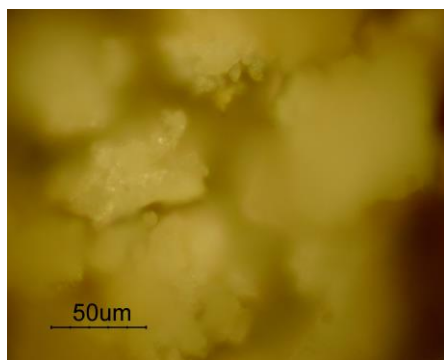


Figure (13): Optical microscope image for titanium sample coated at 60 °C.



Figure (14): Optical camera image for titanium sample coated at 60 °C.

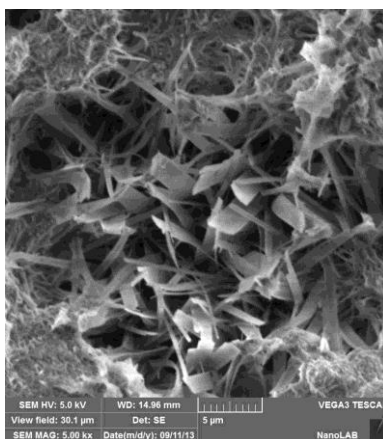


Figure (15): SEM image for titanium sample coated at 60 °C.

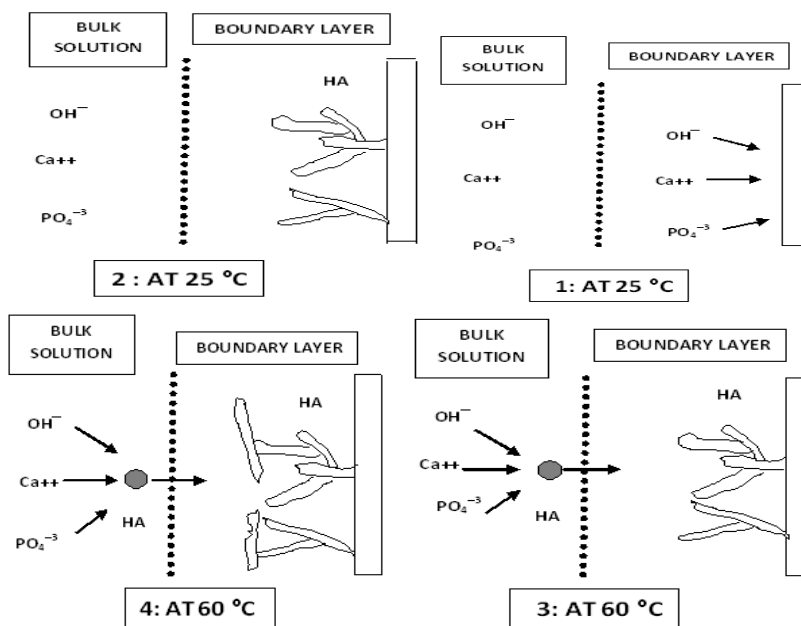


Figure (16): The mechanism of formation and coating hydroxyapatite on the titanium substrate.

The hydroxyapatite forms at boundary layer near the titanium cathode when the electrodeposition begin, and hydroxyapatite take the flake type structure, but the increasing in temperature increase the formation of hydroxyapatite in the bulk solution with time of electrodeposition processes, leads to coating with another vertical layer of hydroxyapatite over the old flake structure shape as shown in **Figure (16)** Below which represent the mechanism of formation and coating hydroxyapatite on the titanium substrate.

Ti-6Al-4V results: From **Figure (17)** and **Table-6** which represent the polarization curve and corrosion characteristics for Ti-6Al-4V alloy samples, we see the decreasing in corrosion rate especially for sample coated at 60 °C, where the corrosion rate decreased to 54 times than that for uncoated sample, and the layer was porous for the same reason we mention before in titanium results, **Figures (18)** and **(19)** which represent the optical microscope image and optical camera image shows the thick layer coated on titanium sample that coated at 60 °C.

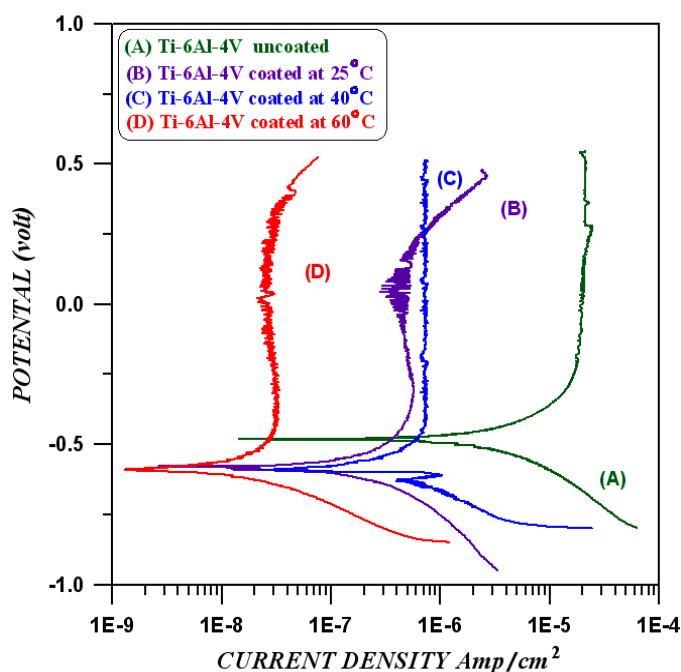


Figure (17): Polarization curve for Ti-6Al-4V alloy samples coated at different temperatures.

Table-6: Corrosion characteristics curve for Ti-6Al-4V alloy samples coated at different temperatures.

ITEM	Cor.rate mm/y	E.Cor. volt	I.Cor. Ampμ
uncoated	1.023×10^{-2}	-0.482	1.128
At 25 °C	1.23×10^{-3}	-0.571	1.94×10^{-2}
AT 45 °C	5.31×10^{-3}	-0.590	3.0×10^{-1}
AT 60 °C	1.906×10^{-4}	-0.587	2.1×10^{-2}

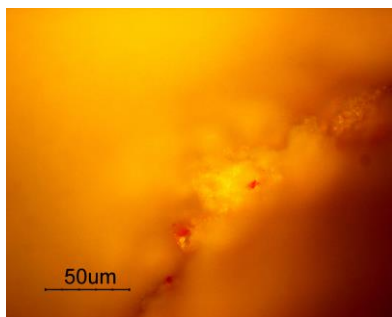


Figure (18): Optical microscope image for Ti-6Al-4V alloy samples coated at 60 °C.



Figure (19): Optical camera image for Ti-6Al-4V alloy samples coated at 60 °C.

From **Figure (20)** which represent the SEM images for Ti-6Al-4V alloy samples coated at 60 °C we see the difference in crystal shape for hydroxyapatite formed on Ti-6Al-4V substrate, and that mean the difference in substrate composition affect the morphology of the hydroxyapatite formed by electrodeposition, also see there are two layers formed on the substrate, first is the thick and had a compact form, the second has a needle structure shape and coated on first layer vertically in the titanium results section.

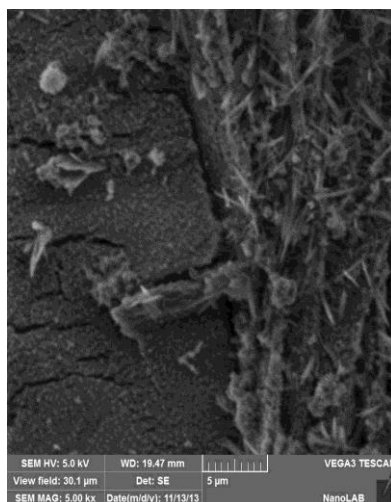


Figure (20): SEM image for Ti-6Al-4V alloy sample coated at 60 °C.

The XRD pattern for Ti-6Al-4V alloy samples coated at different temperatures in **Figure (21)** shows the appear of hydroxyapatite in all samples without the appear of any undesirable product, and the appear of TiO₂ layer from during the heat treatment for samples.

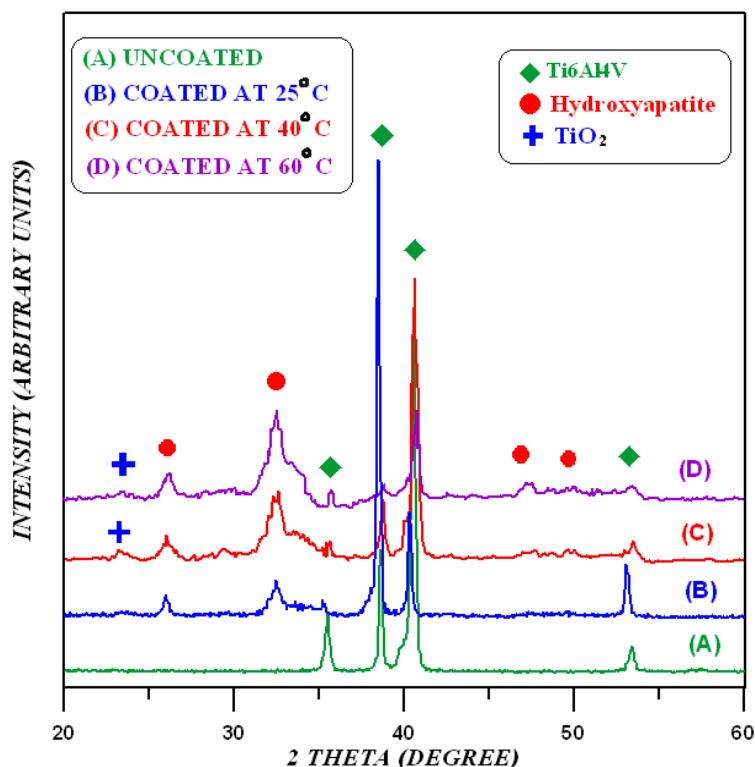


Figure (21): XRD pattern for Ti-6Al-4V alloy samples coated at different temperatures.

CONCLUSIONS

From the results before we conclude that the optimum condition for hydroxyapatite coated on titanium substrate by electrochemical deposition was at potential = 9 volt, pH = 5.5 and temperature = 60 °C were the corrosion rate reduced 24 times compared with uncoated sample, while the optimum condition for hydroxyapatite coated on Ti-6Al-4V alloy substrate by electrochemical deposition was at potential = 12 volt, pH = 5.5 and temperature = 60 °C were the corrosion rate reduced 53 times compared with uncoated sample, the morphology of hydroxyapatite was affected by the different composition of the substrates.

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