Evaluation of corrosion behavior of bioceramics coated commercially pure titanium and Ti-6Al-4V alloy

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ABSTRACT

Background: This study report the corrosion behavior of commercially pure titanium and Ti-6Al-4V alloy samples without coating and with hydroxyapatite, partial stabilized zirconia and mixture of partial stabilized zirconia and hydroxyapatite coating and comparison between them through electrochemical polarization tests in 37 ^{0} C Hank's solution.

Materials and methods: Electrophoretic deposition technique (EPD) was used to achieve the coating from each one of three types of the coating materials (HAP, PSZ and mixture of 50% HAP and 50%PSZ) on Cp Ti and Ti-6Al-4V alloy samples. The electrochemical corrosion test was performed when samples were exposed to Hank's solution prepared in the laboratory and the polarization potential, corrosion rate and the open circuit potential of the samples were measured.

Results: The results indicated that the corrosion rate is significantly higher for Ti-6Al-4V than for Cp Ti .The three types of coating significantly reduced the corrosion rate for Cp Ti while did not for Ti-6Al-4V alloy .After coating the corrosion rate for Ti-6Al-4V remained significantly higher than the coated Cp Ti samples .The open circuit potential (OCP) for both Cp Ti and Ti-6Al-4V samples was in the following sequence PSZ > HAP> mixture of HAP and PSZ >uncoated.

Conclusions: Cp Ti showed less corrosion rate than Ti-6Al-4V alloy with and without coating .Coating significantly decreased the corrosion rate of Cp Ti but did not for Ti-6Al-4V alloy.

Key words: Corrosion, pure titanium, Ti-6Al-4V alloy. (J Bagh Coll Dentistry 2014; 26(3):41-48).

الخلاصة

المقدمة: ان تحقق نجاح عملية زراعة الاسنان سريريا ليس بسبب المتانة الميكانيكية او الانسجام الحيوي المتميز لمادة الزراعة وحسب بل بسبب صفات اخرى لمادة الزراعة مثل خواص السطح وسلوك التاكل.

المواد وطريقة العمل: استعمل الترسيب بالهجرة الكهربائية للحصول على طلاء متجانس لواحد من ثلاثة انوع من طبقات الطلاء (الهايدروكسي ابيتايت ,الزركونيا المثبتة جزئيا وخليط الهايدروكسي ابيتايتاوالزركونيا المثبتة جزئيا)على النماذج المكونة من التيتانيوم النقي وسبيكة (Ti-6Al-4V).

اما بالنسبة لاختبارات التاكل الكهروكيمياوي فقد تم قياسها للنماذج في محلول الجسم المماثل المحضر مختبريا وايضا قياس جهد الاستقطاب ومعدل التاكل وجهد الدائرة المفتوحة

النتائج: تشير نتائج هذة الدراسة الى ان هناك معدل تاكل عالي لسبيكة Ti-6Al-4V عند مقارنتها مع التيتانيوم النقي .ولقد لوحظ ان معدل التاكل قل بشكل واضح لنماذج التيتانيوم النقي المطلية بالطلائات الثلاث بينما ذالك لم يظهر لسبيكة Ti-6Al-4V.وايضا بقي معدل التاكل لسبيكة Ti-6Al-4V بعد الطلاء أعلى من التيتانيوم النقي .

الاستنتاجات: معدل التاكل للتيتانيوم النقي اقل من سبيكة Ti-6Al-4V قبل الطلاء وبعد الطلاء .الطلاء قلل معدل التاكل للتيتانيوم النقي بينما ذالك لم يؤثر على سلوك سبيكة Ti-6Al-4V.

INTRODUCTION

Oral implantology provides a reliable and rather safe solution to replace missing teeth [(1)]. Clinical success of osseointegrated implant depends on many factors. Those related are mechanical properties, biocompatibility and corrosion resistant of implant material. Corrosion is defined as the action, process, or effect of corroding is a product of corroding, the loss of elemental constituents to the adjacent environment [(1)]. Resistance to corrosion is critically important for dental materials especially implant materials. Corrosion can lead to roughing of the surface, weakening of the restoration and liberation of elements from the metal or alloy, liberation of elements can produce discoloration of adjacent soft tissue; local pain or swelling in the absence of infection was attributed to corrosion products of the implant material [(2)].

Bone loss and osteolysis was attributed to the particles that are released, are reportedly phagocyted by macrophages stimulating the release of inflammatory mediators such as cytokines. These mediators are released towards bone surface contributing to its resorption by osteoblast activation [(3)].

Commercially pure titanium and titanium six aluminum four vanadium (Ti-6Al-4V) alloys are more frequently used implant materials osseointegration the implant could be coated by bioactive materials like HAP. It was found better bonding between the bones and implant material Ti-6Al-7Nb coated with HAP or partial stabilized zirconia PSZ or mixture of both than uncoated samples when implanted in rabbit tibia [(4)]. This work is designed to study the corrosion behavior of uncoated Cp Ti and Ti-6Al-4V implant material through evaluation the corrosion note and the results were compared with those of coated samples with HAP, PSZ and mixture of 50/50 HAP and PSZ.

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MATERIALS AND METHODS

Sample preparation

Commercially pure Titanium and Ti-6Al-4V alloy was used as the substrate for coating. Thirty two small rectangular pieces of (27 mm x17 mm x 2 mm) was used for Ti-6Al-4V alloy and thirty two small rectangular (17 mm x17 mm x5 mm) for Cp Ti. After polishing and ultrasonic cleaning, they were divided into four subgroups according to coating material, eight samples from each metal were kept uncoated, eight samples were coated with HAP powder, eight samples were coated with PSZ, eight samples were coated with mixture of 50/50 HAP and PSZ by Electrophoretic technique .

Electrophoretic deposition

In this study three suspensions were prepared according to the type of coating material used. The first suspension was used for hydroxyapatite coating .The suspension was prepared by adding HAP powder to the solvent which was the ethanol (100g/I liter) in a container over a stirrer without adding any dispersant agent or binder agent [(5)]. The stirring was continued until a colloidal suspension was obtained **.**The second suspension was used for PSZ coating. The suspension-was prepared by adding PSZ powder to solvent which is ethyl alcohol (200 g/1 liter) in a container over a stirrer. Phosphate ester (3 g/1 liter) dispersant agent was added. After stirring the polyvinylbutyral was added as a binder (3.5g/1 liter) [(6)]. The third suspension was prepared by adding 50:50 ratio HAP /PSZ powders to the solvent which was ethyl alcohol in a container over a stirrer, after 10 minutes phosphate ester 3 g/1liter dispersant agent was added. And after stirring, polyvinylbutyral was added as a binder (3.5g/1) [(4)].

Microscopical examination

One sample from each type of the coating was examined by using optical microscope (Nikon type 120, Japan optical microscope) to show the appearance of the coated surface layer of the sample.

X-Ray phase analysis

Phase analysis was employed on Cp Ti and Ti-6Al -4V alloy samples before and after coating with different materials using 3121 powders x-ray diffractometer using Cu Ka radiation. The 2θ angles were swept from 20-80 ^{o} in step of one degree.

Electrochemical corrosion test

Electrolyte solution preparation

The electrolyte used was Hank's solution (NaCl, KCl, CaCl, $MgSo_4.7H_2O$, $NaH_2PO_4.2H_2O$, $NaHCO_3$, Glucase, KH_2PO_4, $MgCl_2.6H_2O$) [(7)]. A constant temperature of 37±2 ^{0} C was maintained by using a water path.

Tafel Extrapolation

The potentiodynamic polarization test was used to evaluate corrosion behavior by measuring the corrosion rate. Electrochemical corrosion test system was composed from potentiostat and glass cell and its electrodes; working electrode WE, counter electrode CE and reference electrode RE .The specimen was fixed on orifice on the side of corrosion cell through 1cm diameter for one hour. The corrosion-potential E_{corr} and corrosion current density I_{corr} were determined which were used to measure the corrosion rate by mmpy by the following equation: **Corrosion rate (mmpy) =0.13 × I_{corr} × EW/d ×1000×25.4 ……(1).**

In this study the unit used to measure corrosion rate is mmpy (millimeter per year) therefore to convert the unit from mpy (mils pear year) to mmpy. The equation is multiplied by 1000 and 25.4 because the mils mean milli-inch (Inch=1000 milliinch) (Inch=25.4 millimeter).

RESULTS

X-ray diffraction of coating samples

Figure 1 show the XRD patterns of Ti-6Al-4V specimens coated with HAP by Electrophoretic deposition method and heat treated at 400^{o} C in comparison with uncoated specimen .The pattern of uncoated Ti-6Al-4V specimens shows strong line of αTi at 2θ .The XRD results of HAP coated specimens shows strong line of HAP.The XRD patterns of Ti-6Al-4V alloy coated with PSZ in comparison with uncoated specimen is shown in Figure 2. The pattern indicated that surface of specimens are well covered with PSZ layer. The specimens coated with mixture of HAP powder and PSZ showed the domination of PSZ in the coated layers shown in Figure 3.The XRD pattern of uncoated Cp Ti specimens showed strong line of α Ti, while the XRD results of HAP coated specimens showed strong line of HAP as shown in Figure 4**.**The XRD patterns of Cp Ti coated with PSZ in comparison with uncoated specimen is shown in Figure 5.The pattern indicated that surface of specimens are well covered with PSZ layer. Figure 6 is showing the XRD of specimens of Cp Ti coated with mixture of HAP powder and PSZ, the XRD pattern shows the domination of PSZ in the coated layer.

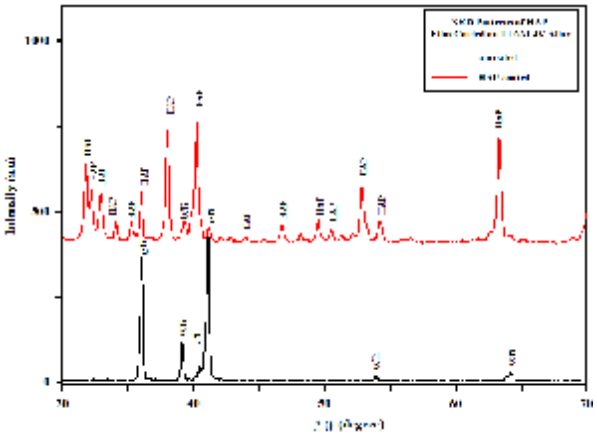


Figure 1: X-ray diffraction patterns of HAP coated Ti-6Al-4V specimens in comparison with uncoated specimen

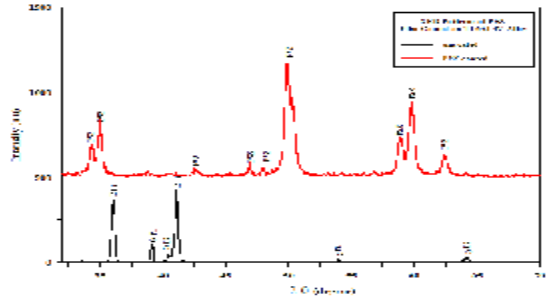


Figure 2: X-ray diffraction patterns of PSZ coated Ti-6Al-4V specimens in comparison with uncoated specimen

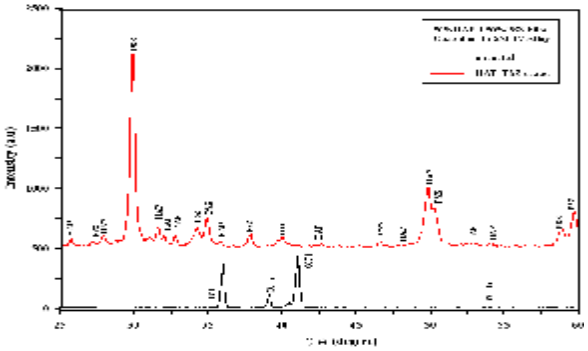


Figure 3: X-ray diffraction patterns of Ti-6Al-4V specimens coated with HAP and PSZ in comparison with uncoated specimen

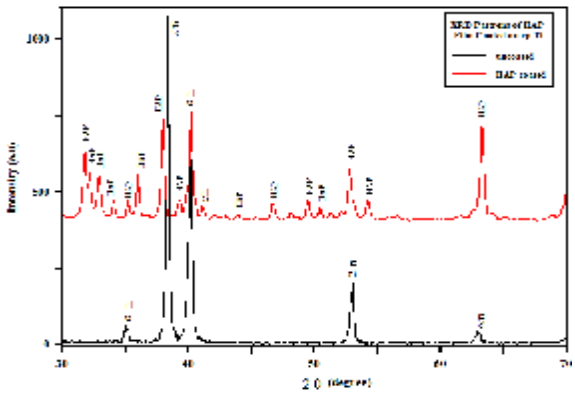


Figure 4: X-ray diffraction patterns of PSZ coated Cp Ti specimens in comparison with uncoated specimen

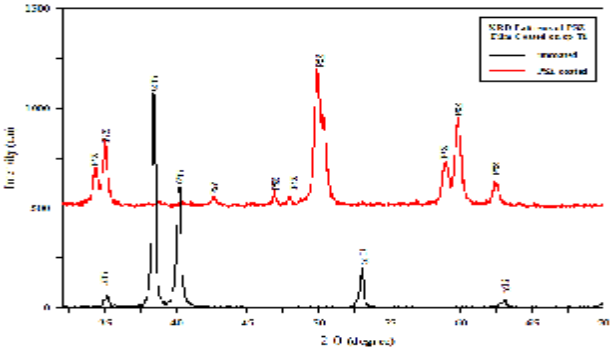


Figure 5: X-ray diffraction patterns of PSZ coated Cp Ti specimens in comparison with uncoated specimen

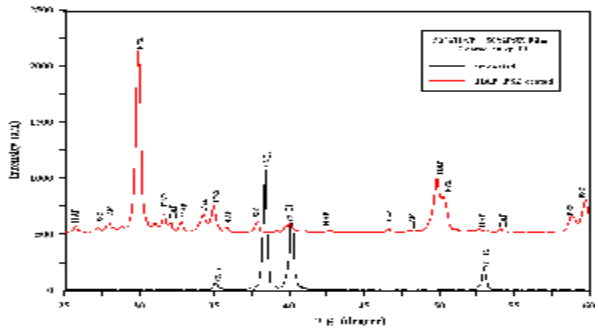
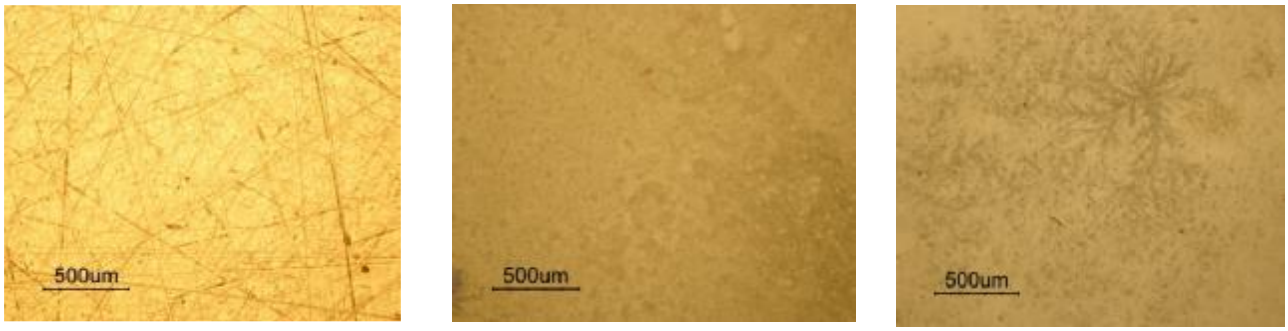


Figure 6: X-ray diffraction patterns of Cp Ti specimens coated with HAP and PSZ in comparison specimen with uncoated

Microscopical Examination

Micrographs illustrate the microstructure of uncoated, HAP, PSZ and mixture of HAP and PSZ coated Cp Ti alloy surfaces before corrosion Figure (7) and Figure (8)**.**The surface of Cp Ti samples coated with HAP shows rough surfaces; no cracks appear on the surface of any sample, Figure (7)B**.** The surface of Cp Ti samples coated with a layer of PSZ shows tree like appearance of the coated layer, Figure (7) C. The surface of Cp Ti samples coated with the mixture of HAP and PSZ shows homogenous and rough surfaces with no cracks appear on any sample, Figure (8) Micrographs illustrate the microstructure of

uncoated, HAP, PSZ and mixture of HAP and PSZ coated Ti-6Al-4V surfaces before corrosion are shown in Figure (9) and Figure (10).The surface of Ti-6Al-4V samples coated with HAP shows non homogenous surfaces with large number of porosity and small uncoated areas randomly distributed on the surfaces of all samples Figure (9)B The surface of Ti-6Al-4V samples coated with PSZ shows uniform surfaces and continuous smooth surfaces without porosity and no cracks appear on the surface of any sample, Figure (10) A. The surface of Ti-6Al-4V samples coated with the mixture of HAP and PSZ shows non homogenous and rough surfaces with no cracks appear on the surface of any sample, Figure (10) B.



A- Uncoated Cp-Ti **B- Cp Ti coated HAP** **C- Cp Ti coated with PSZ**

Figure 7: Optical micrograph view of Cp Ti, A) uncoated Cp Ti; B) Cp Ti coated with HAP; C) Cp Ti coated PSZ before corrosion

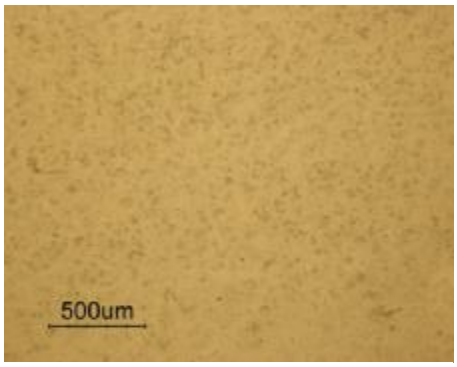
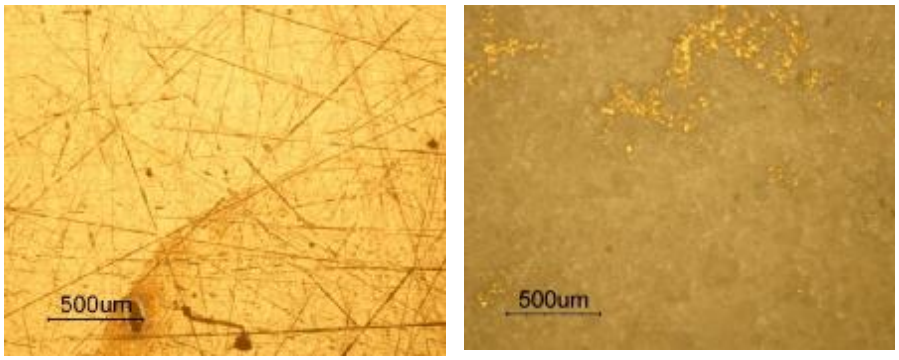
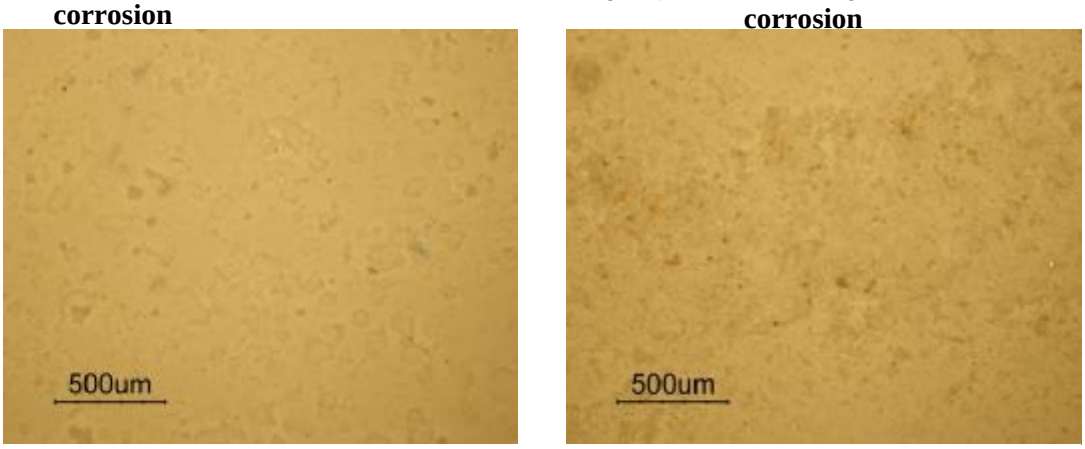


Figure 8: Optical micrograph view of Cp Ti coated with mixture of HAP and PSZ before corrosion



A- uncoated Ti-6Al-4Valloy **B- Ti-6Al-4V coated with HAP**

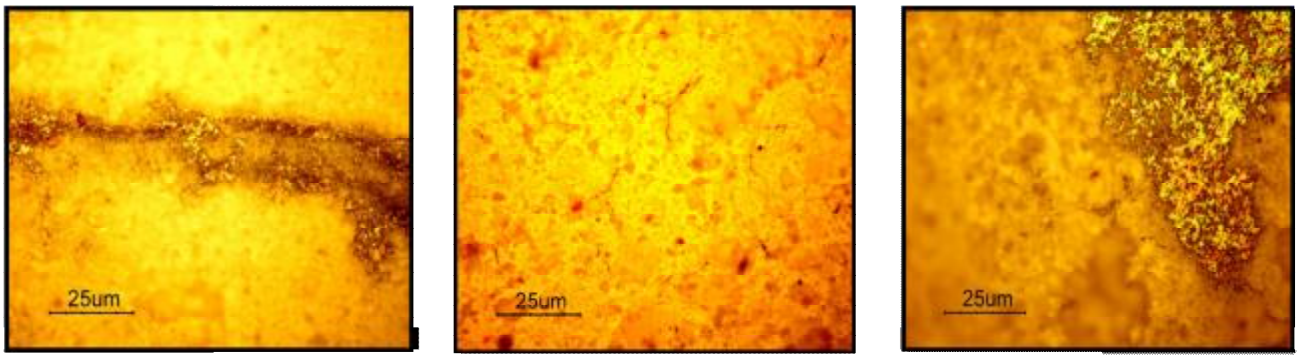
Figure 9: Optical micrograph view of Ti-6Al-4Valloy, A) uncoated Ti-6Al-4Valloy; B) Ti-6Al-4Valloy coated with HAP before corrosion



A- Ti-6Al-4V coated with PSZ **B-Ti-6Al-4V coated HAP and PSZ**

Figure 10: Optical micrograph view of Ti-6Al-4V alloy, A) Ti-6Al-4Valloy coated PSZ; B) Ti-6Al-4Valloy coated with mixture of HAP and PSZ before corrosion.

After corrosion, the microstructure of HAP, PSZ and mixture of HAP and PSZ coated Ti-6Al-4V surfaces are shown in Figure (11).The surface of Ti-6Al-4V sample coated with HAP shows large uncoated areas randomly distributed on the surfaces Figure (11) A. The surface of Ti-6Al-4V sample coated with PSZ shows crack on the surface but the surface of alloy is not seen Figure (11) B. The surface of Ti-6Al-4V sample coated with the mixture of HAP and PSZ shows large uncoated area Figure (11) C.



A-Ti-6Al-4V alloy coated with HAP. **B-Ti-6Al-4V alloy coated with PSZ.** **C-Ti-6Al-4V alloy coated with HAP and PSZ.**

Figure 11: Optical micrograph view of Ti-6Al-4V alloy, A) Ti-6Al-4Valloy coated with HAP; B) Ti-6Al-4Valloy coated with PSZ; C- Ti-6Al-4V alloy coated with mixture of HAP and PSZ at 500 um power after corrosion.

Corrosion test

Open circuit potential (OCP)

The open circuit potentials for coated and uncoated specimens by different surface coating materials are shown in **Figures (12) and (13)**. As the higher the OCP, the more resistance to corrosion, therefore the specimens were in the following sequence from most corrosion resistance to the lowest PSZ(Cp Ti= -0.212 V , Ti-6Al-4V =-0.265 V)> HAP(Cp Ti= -0.225 V , Ti-6Al-4V =-0.40 V) >mixture(Cp Ti= -0.358 V , Ti-6Al-4V =-0.550 V)>uncoated (Cp Ti= -0.383 V , Ti-6Al-4V =-0.825 V).

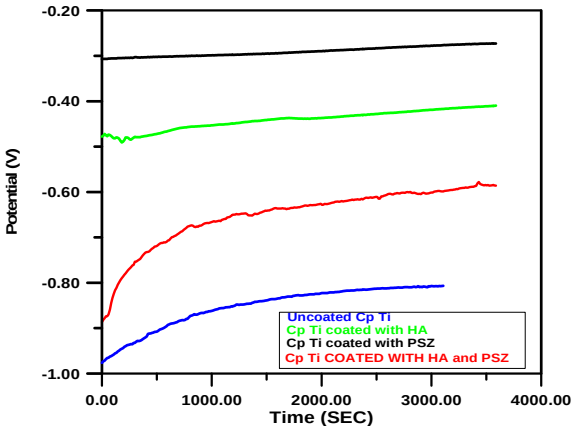


Figure 12: Open circuit potential for uncoated and coated Cp Ti with different coating materials.

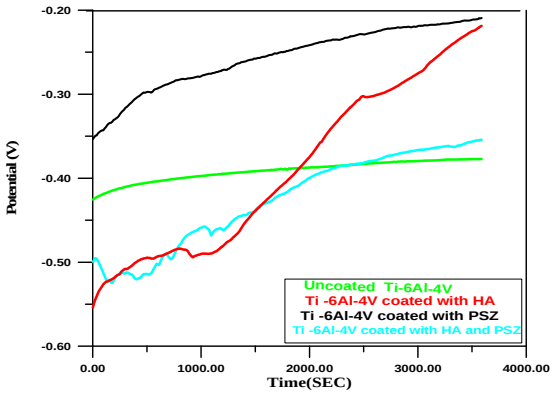


Figure 13: Open circuit potential for uncoated and coated Ti-6Al-4V alloy with different coating materials

Potentiodynamic polarization curves

Uncoated specimens

Figure (14) shows the higher polarization voltage (-0.332V) and lower current density (3.11×10^{-5} A/cm^2) of uncoated Cp Ti indicates better resistance to corrosion than uncoated Ti-6Al-4V alloy which had lower polarization voltage (-0.465 V) and higher current density (8.91×10^{-4} A/cm^2).

Coated specimens

The polarization curve of Cp Ti and Ti-6Al-4V alloy coated with HAP, PSZ and mixture of HAP and PSZ are shown in Figures (15) , (16),

(17) respectively .The polarization curve of the coated Cp Ti specimens is higher than the coated Ti-6Al-4V alloy specimens.

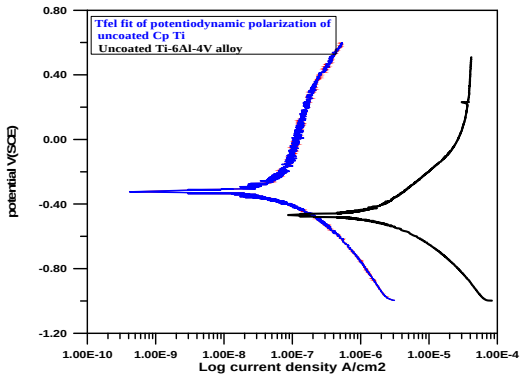


Figure 14: The polarization curves of uncoated Cp Ti and uncoated Ti-6Al-4V alloy.

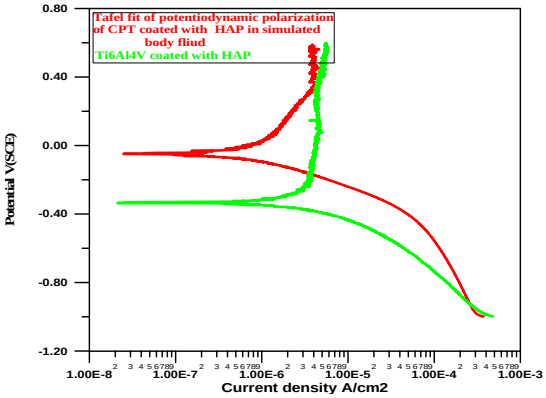


Figure 15: The polarization curves of Cp Ti and Ti-6Al-4V alloy coated with HAP.

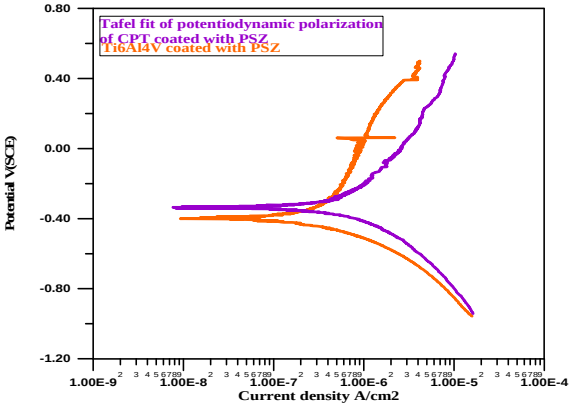


Figure 16: The polarization curves of Cp Ti and Ti-6Al-4V alloy coated with PSZ.

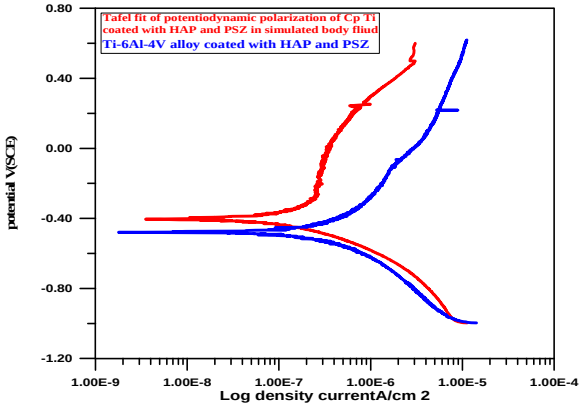


Figure 17: The polarization curves of Cp Ti and Ti-6Al-4V alloy coated with HAP and PSZ.

Corrosion rate

Corrosion rate of Cp Ti and Ti-6Al-4Valloy

The corrosion behavior of implant materials (Ti-6Al-4V alloy and Commercially Pure Titanium) was evaluated in this study by measuring the corrosion rate .Different coatings were applied (HAP, PSZ and mixture of HAP and PSZ) on both alloys and comparison was done between them. The mean and standard deviation for all study groups are listed in Table (1). All coated groups show lower corrosion rate than uncoated samples for Cp Ti and alloy. Figure 18 shows summary statistics of corrosion rate parameter for coated and uncoated for the Ti-6Al-4V alloy and commercially pure titanium in mmpy. Coincidence's tests for parameters (Variances and Means) showed highly significant difference among groups of Cp Ti and Ti-6Al-4V alloy samples as shown in the **Table(2).**

Table 1: Summary statistics (Means and standard deviation) of corrosion rate parameter for coated and uncoated for the Ti-6Al-4V alloy and commercially pure titanium (mmpy)

Groups	No.	Ti-6Al-4V		Cp Ti	
		Mean $\times 10^{-2}$	S.D. $\times 10^{-2}$	Mean $\times 10^{-2}$	S.D. $\times 10^{-2}$
Uncoated	8	2.94	± 1.430	1.420	±0.357
Coating with HAP	8	2.39	± 0.471	0.437	± 0.181
Coating with PSZ	8	2.02	± 0.852	0.363	± 0.236
Mixture of PSZ and HAP	8	2.40	± 0.330	0.998	± 0.223

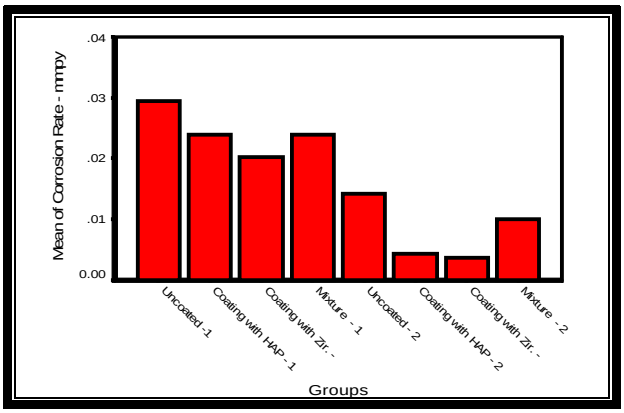


Figure 18: Bar chart plot for mean values of the corrosion rate of Ti-6Al-4V (1) alloy and Cp Ti (2) with different coatings

Table 2: Coincidence's tests for parameters (Variances and Means) between different treated materials according to the "Corr. Rate" parameter

Criteria	Test of Homogeneity of Variances (σ^2)		ANOVA- Test of equality of means (μ)	
	Levene's Statistic	Sig.	F-test	Sig.
Corrosion rate	12.333	0.000	17.711	0.000 (*)

All coated groups of Cp Ti showed significantly lower corrosion rate when compared with uncoated groups. Among the coated groups, coating with HAP did not significantly differ from coating with PSZ, while there was a highly significant difference between the rest groups. All three types of Ti-6Al-4V alloy coating did not significantly differ from the uncoated alloy. Coating of Ti-6Al-4V alloy with three coating materials showed significantly higher corrosion rate than all coated Cp Ti groups.

DISCUSSION

In this study the maximum corrosion rate was observed for Ti-6Al-4V alloy. There is a highly significant difference between corrosion of uncoated Cp Ti and uncoated Ti-6Al-4V alloy and this may be due to that the Ti-6Al-4V alloy is composed of different elements like Al and V and to the more defective nature of grown passive layers and the increased reactivity of alloy which made the alloy with high corrosion also this may be due to the development of another type of corrosion like intercrystalline corrosion or another type of corrosion which can occur more frequently in the alloy than in the pure base metal similar to the result of [8]. For coated Cp Ti groups the lowest corrosion rate is for Cp Ti samples coated with PSZ and those coated with HAP, yet there is no significant differences between them, this may be due to powerful insulting effect of both coating materials which act as a barrier between the substrate surface (Cp Ti) and the solution of body fluid. Also the effective bond between both coating and the surface of the substrate. Coating with a mixture of HAP and PSZ showed highly significant increase in corrosion rate compared to HAP and PSZ alone, this might be due to some sort of incompatibility between these two materials as they are deposited together on the same surface. Also it might be due to the difference in the coefficients of thermal expansion and contraction between HAP and PSZ. During sintering procedure and cooling period this mismatch might create microcracks exposing the substrate surface to the solution and making corrosion rate the highest.

All three types of coated Ti-6Al-4V alloy groups did not significantly differ from the uncoated alloy indicating the weak bonding of the coating to the surface of the alloy. In Electrophoretic deposition charged particles are deposited on surface and as the alloy is composed of three main different elements Ti, Al and V each with different electromotive force so this might affect on the attraction of charged particles and the movement toward the alloy surface and then on bonding of the coating materials with the alloy therefore influence the thickness of the coating .The coating might be easily detached thus exposing the surface to the electrolyte solution. Coating of Ti-6Al-4V alloy with three coating materials showed significantly higher corrosion rate than all coated Cp Ti groups which may be due to the weak bond established between the coating materials and the alloy surface .Also due to the reduced thickness of the coating layer on the alloy than on the Cp Ti .Coating the alloy with

PSZ reduced the corrosion rate; that made non significant differences between it and uncoated Cp Ti which may be due to the better adhesion of PSZ on the alloy compared to HAP and the mixture.

The open circuit potential for both Cp Ti and Ti-6Al-4V groups was in the following sequence from most corrosion resistance to the lowest PSZ(Cp Ti= -0.212 V , Ti-6Al-4V =-0.265 V)> HAP(Cp Ti= -0.225 V , Ti-6Al-4V =-0.40 V) >mixture(Cp Ti= -0.358 V, Ti-6Al-4V =-0.550 V)>uncoated (Cp Ti= -0.383 V , Ti-6Al-4V =-0.825 V). The parameter obtained for uncoated Cp Ti is higher than uncoated Ti-6Al-4V alloy and after coating. The corrosion rate of uncoated Cp Ti was less than uncoated Ti-6Al-4V alloy and after coating. The corrosion rate of Cp Ti was significantly reduced by coating with coating materials HAP, PSZ, and mixture.The lowest corrosion rate was for Cp Ti coated with PSZ. The corrosion rate of Ti-6Al-4V alloy was insignificantly reduced by coating with each coating material and lowest corrosion rate was for Ti-6Al-4V coated with PSZ.

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