Corrosion Performance of (Ha-Psz) Bio Ceramic Coated Ti-20Co Alloy in Simulated Physiological Media

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Abstract

The present investigation provides experimental results of corrosion performance in simulated body fluid of Ti-20Co medical alloy coated with hydroxyapatite (HA) and Partially Stabilized Zirconia (PSZ) composite layer by electrphoretic deposition (EPD) technique. A three mixing ratios of HA and PSZ powders (namely 90%HA+10%PSZ, 66%HA+34%PSZ and 25%HA+75%PSZ) were electrophoretically deposited on the surface of a Ti-20Co substrates. Post heat treatment at 800C^{o} in inert environment was performed to improve the adhesion strength of the coated layers. The coated samples were subjected to electrochemical study in artificial saliva (Modified Carter's solution) and simulated blood plasma in order to determine the optimum coating conditions that can give corrosion resistance in simulated body fluid condition. The influence of mixing ratios and deposition thickness on the corrosion performance of the alloy are discussed in details based on the Open Circuit Potential (OCP), corrosion potential and corrosion rate using potentiodynamic polarization. Results showed that the coating efficiency is highly depending on parameters like composition, coating thickness, layer porosity and adhesion to substrate. The corrosion aspects resulting from various deposition thicknesses are discussed in details.

Keywords: Corrosion, Hydroxyapatite, Partially Stabilized Zirconia, Electrophoretic Deposition, Ti alloy.

Introduction

Titanium and titanium alloys are widely used today in both dentistry and orthopedic surgery because of their favorable biocompatibility, high corrosion resistance, light weight, and various mechanical properties. In spite of the many advantages, the high melting temperature and strong tendency to oxidize and chemically react with mould material make pure and low alloy titanium difficult to fabricate by casting [1]. Among the various alloys, the Ti-Co system has been of particular interest, not only because the melting temperature can be largely lowered, but also because cobalt is a widely accepted biocompatible element [2]. Corrosion resistance of metallic biomaterials such titanium alloys is one of the basic criteria determining their performance, however, usually deteriorated when large amounts of alloying additions were added [3]. According to Chern Lin et al [4], within their polarization scan limit (600 mV SCE), breakdown did not occur in either the Ti-Ni alloys with 20 wt% Ni or less, or Ti-Co alloys with 30 wt% Co or less in Ringer's solution. As cobalt or nickel content reached 30 wt%, the breakdown potential went down sharply. Chern et al [5] found that breakdown potentials of Ti-Co alloys with 25-30 % Co were all higher than 900 mV and the critical anodic current densities were all lower than 8μA/cm2 in artificial saliva. Electrphoretic deposition is a relatively new technique in ceramic processing that enables the formation of thick ceramic films. Several investigations have been undertaken on the electrophoretic deposition (EPD) of hydroxyapatite (HA) and Partially Stabilized Zirconium (PSZ) e films on Ti and its alloys for biomedical applications [6-8]. Both, HA and PSZ are well-known as valuable implant materials. However, the interest in their composites which could combine the unique biocompatibility and bioactivity of HA ceramics with very good mechanical properties of the materials based on partially stabilized zirconia has started quite recently [6,9]. Preparation of a two-phase (HA +ZrO_2)

composite material gives rise to some questions, which have not been fully clarified in previous studies. In particular, these questions concern the influence of ZrO_2 on phase stability of HA [9]. Thermal behaviors of HA in the presence of ZrO_2 as the admixture depends on a number of factors which may, but not necessarily have to, cause its degradation. This problem is of crucial importance from both scientific and application points of view since HA degradation results in changes in its physic-chemical properties. This determines the behavior of an implant material in a living system by altering its solubility, biocompatibility and restorability. Most of the studies which have been carried out in recent years dealt with the preparation of HA–ZrO_2 composites in the form of dense sinters [10, 11]. Only a few reports described the HA–ZrO_2 composite coatings obtained on other materials [12]. In our recent work we have found that mixing of a bonier ceramic material (PSZ) with bioactive one (HA) led to high integration between bone and implant by increasing the bioactivity of the product and to promote mechanical properties of the implanted screws and enhanced osseointegration during the healing period [6]. Therefore this work is aimed to evaluate the effect of phase composition, homogeneity, porosity and adhesion of HA–PSZ composite layer prepared by EPD technique on the corrosion behavior of Ti-20Co alloy in simulated body fluids (artificial saliva).

Experimental Procedure

Electrophoretic Deposition

Electrophoretic deposition EPD suspension was produced by breaking down the agglomerates and uniformly distributing a dispersing agent on the surfaces of the ceramic particles. Suspension of different mixing ratios of HA and PSZ (93.8ZrO_2+HfO_2, 5.4Y_2O_3, 0.1SiO_2, 0.12TiO_2, 0.25Al_2O_3, 0.003Ce_2O_3, 0.02Na_2O and 0.05CaO wt%) powders (namely 90%HA+10%PSZ, 66%HA + 34%PSZ and 25%HA + 75%PSZ) were prepared by adding appropriate ratio of the powders to the solvent (100 gL^{-1} isobropanol) in a container under continuous stirring for 10 minutes, then dispersant agent (3.5 gL^{-1} phosphate ester) was added. The binder (3g gL^{-1}polyvinyl butyral) was added after stirring for 10 minutes or continued until a colloidal suspension was obtained. The square specimens with dimension of 10×10×2 mm were cut from Ti-20Co alloy and grinded up to 1000 grit before the deposition process was carried out. The Ti-20Co specimen was used as cathode electrode and a plate of 316L stainless steel was used as anode electrode and 10 mm distance between the electrodes was maintained. A current density of 0.3 mA/cm^2 was applied between the two electrodes in the electrophoretic cell (applied voltage 30 volts). The HA+PSZ coatings were obtained on Ti-20Co specimens for different period of time (namely 1, 2, 3, and 4 minutes). The coated specimens were then sintered at 800ºC for one hour under inert atmosphere. The thickness of the deposited layer was measured using ERICHSEN MINI test 3000 micro process coating thickness tester. The phases present in the as received was investigated using high resolution optical microscope (Nikon Eclipse ME 600L/441002, Japan), whereas the coated specimens of Ti-20Co alloy were characterized using XRD. Shimadzu LabX XRD-6000 powder X-ray diffractometer using Cu Ka radiation was used for this study. XRD patterns were collected for different 2θ values ranging from 25 to 60° with a 0.05^o step and counting time of 5 s per step.

Electrochemical Measurements

Open Circuit Potential:

The electrochemical measurements were carried out using potentiostat / galvanostat (Weking Mlab200, Bank Elektronic, Germany) provided with electrochemical interface controlled by commercial software-SCI 2007. The electrochemical cell used in this study was fabricated according to the ASTM standards G5-87 (Annual Book of ASTM Standards, vol. 03.02, 1987). The aim of the OCP-time measurements is to understand the corrosion behavior ch/s (characteristic) of the electrophoretically HA+PSZ coated Ti-20Co specimens under equilibrated conditions in the body environment. The open circuit potential versus time measurement is considered as an important parameter for evaluating the stability of the passive film of the alloys. The

specimens were immersed into the electrolyte and immediately the initial potential of the specimens was noted and monitored as a function of time up to 60 min.

Potentiodynamic Polarization:

Potentiodynamic polarization was carried out for coated and uncoated Ti-20Co specimens in artificial saliva (Modified Carters solution NaCl: 0.7, $K_2H\ PO_4$:0.2, KCl: 1.2, $NaHCO_3$:1.5, Na_2HPO_4:0.26, KSN: 0.33, Urea: 0.13gL^{-1} respectively) and simulated blood plasma (NaCl: 6.8, $MgSO_4$:0.1, KCl: 0.4, $NaHCO_3$:2.2, Na2HPO4:0.126, CaCl2: 0.2, NaH_2PO_4 : 0.26 gL^{-1} respectively), the solutions were adjusted at pH of 7.4 and temperature of 37.4±1^oC. Nitrogen gas was continuously purged into the electrolyte throughout the study to eliminate the dissolved oxygen. All the potential measurements were made with reference to a saturated calomel electrode (SCE) and platinum mesh was used as auxiliary electrode. When the specimen attained a constant potential, polarization was started from an initial potential of 250 mV below the open circuit potential. The specimen was scanned in the positive direction reaching a potential of 2.0 V at a sweep rate of 1mV/sec, and the current was monitored with respect to the potential. The critical parameters like corrosion potential (E_{corr}), Corrosion current I_{corr} and corrosion rate were evaluated from the polarization curves.

Results and Discussions

Microstructural Analysis

Optical micrographs in Fig.(1) show the microstructure of the as received Ti-20Co alloy contain the pre-eutectiod Ti_2Co (white dendrites) precipitate was formed predominately at original ßTi (bcc) grain boundaries. Also it can be seen from the higher magnification micrograph that in the binary Ti-20Co alloy, relatively few needle-shaped αTi (hcp) crystals were observed within the ßTi dominate matrix. Chern Lin et al [5] conformed that in Ti-25Co and Ti-20Co-5Ni systems, the large amount of Ti2Co or Ti2(Co, Ni) precipitate appeared as a continuous phase, whereas the retained ß-Ti (in Ti-25Co) or α-Ti plus Ti,(Co, Ni) in (Ti-20Co-5Ni) appeared in the form of isolated islands surrounded by pre-eutectoid Ti2Co or Ti2(Co, Ni) particles.

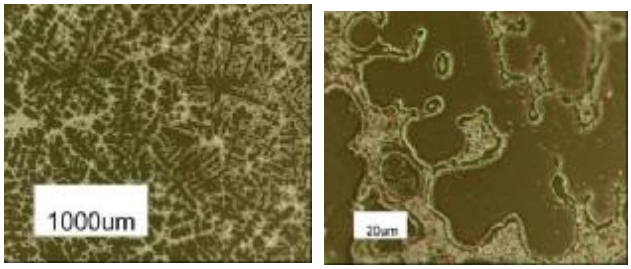

Fig.(1) Optical micrographs of the microstructure of Ti-20Co alloy, etched with 10 ml Hf, 75 ml HNo_3 and 15ml deionized distilled water.

X-ray Diffraction

Fig.(2) shows the XRD patterns of the Ti-20Co specimens before and after EPD coating with (66%HA+34%PSZ) and (75%PSZ+25%HA). The patterns indicated that the surface of the specimen are well covered with PSZ and HA layer. The strongest lines in the pattern of the coated specimens are (111) and (022) at 2θ 30.081 and 49.900 respectively which is responsible for ZrO_2 (JCPDS-ICDD files # 17-0923 & 37-1413) and (002),(102), (211),(300) and (222) at 2θ 25.870, 28.050, 31.769, 32.902 and 46.650 which are responsible for the hexagonal $Ca_5(PO_4)_3(OH)$ (JCPDS-ICDD file # 00-090-423). The patterns show also the line (220) at 2θ 34.35 which is responsible of $Ca_3(PO_4)_2$ phase (JCPDS-ICDD file # 09-0169).

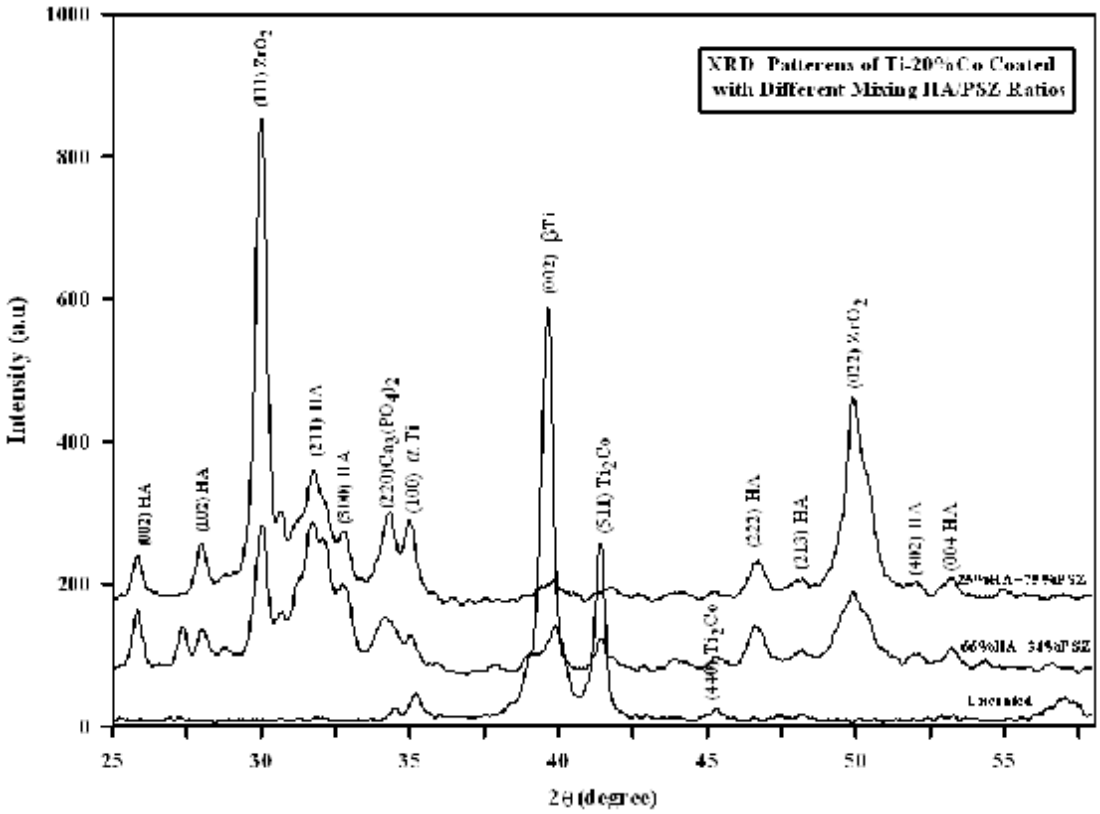

Fig.(2) Patterns of the Ti-20Co specimens before and after EPD coating.

Open Circuit Potential-Time

Passivity in body fluids is the major characteristics of surgical alloys. The stability of passive condition of the coated Ti-20Co alloy at different deposition period is illustrated by the potential-time curves in Figs.(3a and b). The OCP of the uncoated and coated specimens were found to be in the active region and shows stable potential with time. The OCP's of both HA/PSZ mixing ratios measured for the specimen deposited for 4 minutes were found to be lower than that of the steady state of uncoated specimen (-794 and -734 mV and -834 mV respectively).

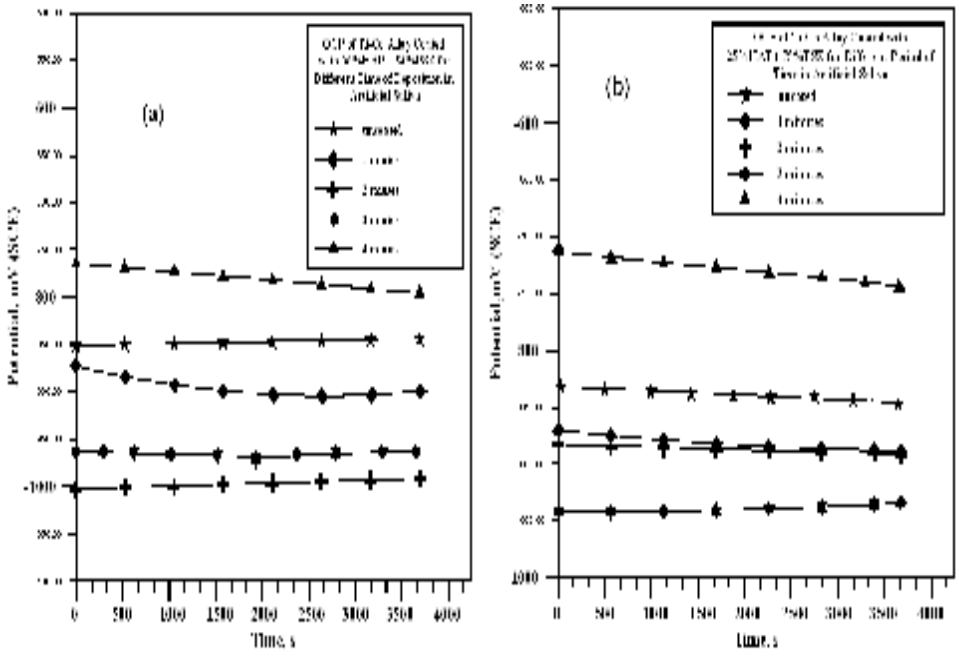

Fig.(3) Open circuit potential (OCP) versus time measurements for Ti-20Co alloy uncoated and electrophoretically HA/PSZ coated in artificial saliva;
a: 66%HA+34%PSZ, b: 25%HA+75%PSZ.

Potentiodynamic Polarization

Corrosion behavior of the present alloys was evaluated using potentiodynamic polarization technique. The electrochemical parameters obtained from the Tafel fit of the polarization profiles for the specimens EPD coated with (25%HA+75%PSZ) in the modified artificial solution are shown in Tables (1). The results prove that HA/PSZ coating by EPD modified the electrochemical behavior of Ti-Co alloy. All specimen coated with 25%HA+75PSZ show high reduction in the corrosion rate value, which was even lower than that for the reference uncoated specimen. The lower corrosion rate was recorded specimen coated for 1 minute (3.7×10^{-3} mm/y) comparing to that of the uncoated specimen (13.02×10^{-3} mm/y). As the deposition time was progressed the corrosion rate increases and this may be attributed to the coating porosity which was found to increase as the deposition time increases.

Table (1)
Corrosion parameters of specimen EPD coated with (25%HA+75%PSZ) for different deposition time in artificial saliva.

Deposition Time (minutes)	***Coating thickness (μm)***	***Corrosion Potential E_{corr},mV_{SCE}***	***Corrosioncurrent densityi_{corr}, μA***	***Corrosion rate (mm/y) × 10^{-3}***
Un coated	Un coated	–905	1.37	13.02
18.9	–826		0.39	3.70
28.7	–883		0.49	4.65
31.4	–926		0.5	4.75
4	46	–800	0.52	4.94

The corrosion parameters in Table (2) show the same scenario, the corrosion rate of the specimens coated with (66%HA+34%PSZ) was increases as the deposition time increases indicating that as the coating thickness increases the coating layer becomes more porous, and also the lower corrosion rate was recorded for the specimen deposited for one minute (4.75×10^{-3} mm/y) which mean that this time of deposition can provide dense coating layer. Meng et al [13] confirmed that EPD with a low voltage of 20 V can create a coating of fine, dense HA particles (Ra<150–200 nm). However, a constant higher voltage created a porous surface composed of large HA particles (~400 nm). For this reason we have found that as the HA addition to the composite layer increases the porosity and decreases the adhesion strength of the coated layer for the three trialed mixing ratios 90%HA+10%PSZ, 66%HA+34%PSZ and 25%HA+75%PSZ (20, 60 and 120 N/cm^2 respectively).

Table (2)
Corrosion parameters of specimen EPD coated with (66%HA+34%PSZ) for different deposition time in artificial saliva

Deposition Time (minutes)	***Coating thickness (μm)***	***Corrosion Potential E_{corr},mV_{SCE}***	***Corrosion current densityi_{corr}, μA***	***Corrosion rate, (mm/y) × 10^{-3}***
Uncoated	Uncoated	–905	1.37	13.02
9.9	–955	–955	0.27	2.56
13.9	–973	–973	0.5	4.75
30.4	–970	–970	0.72	6.84
33.7	–806	–806	0.8	7.60

The pours nature of the coating layer may be also due to the decomposing of the HA phase to tricalcium phosphate $Ca_3(PO_4)_2$ (Fig.(2)) during the heat treatment of the coated specimens which has porous nature. Also we have noticed that the pore adhesion of the 90%HA+10% PSZ layer produced on the specimen resulted in failure in the coated layer immediately after immersed in the artificial saliva. The micrographs in Fig.(3) show a clear evidence of the pours nature of this HA/PSZ coated layer with high HA content. The failure may be due to the crakes occurs after heat treatment. The increase in the I_{corr} as the thickness increases is due to the corrosion process that occurs as results of the microporous of the coating. It is through this porous the electrolyte attacks the base metals. Zhao et al [14] found that the most challenging problems facing the elctrophoretic deposition of composites like Al_2O_3/Ce-$ZrO_2$and Y-ZrO_2/Ce-ZrO_2 are the cracking of the deposit during drying and the cracking of the sintered body during heating.

Among all the coated specimens, one coated at applied voltage of 30 volt for 1 minute (thickness 9.9 μm) shows best corrosion behavior.

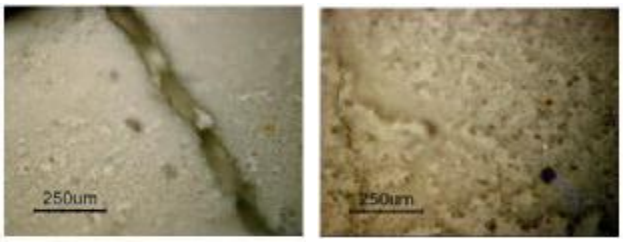

Fig. (4) Micrographs of 90%HA+10%PSZ layer produced by EPD on Ti-20Co alloy.

Kwok et al [15] found that specimens EPD coated with HA had a thickness of about 10 μm and free of cracks, with corrosion resistance higher than that of the substrate. Fig.(5) shows the effect of variation of coating thickness on the corrosion rate of Ti-20Co alloy. The figure shows that increasing the layer thickness and HA content in the composite layer result in increase in the corrosion rate.

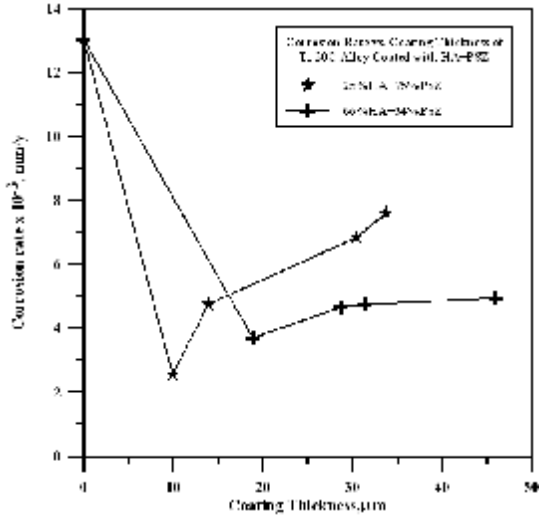

Fig.(5) The variation in corrosion rate with coating thickness for Ti-20Co in artificial saliva.

Table (3) demonstrated the electro-chemical parameters obtained from the polarization curves of the specimens EPD coated with 66%HAP+34%PSZ and 25%HAP+75%PSZ at deposition time of 1 minute in simulated blood plasma. The results confirm our results obtained from the polarization curves in artificial saliva, that using deposition time of one minute for this type of composite coating can enhance the corrosion properties of Ti-20Co alloy in different body fluids environments.

Table (3)
Corrosion parameters of specimen EPD coated with 66%HA+34%PSZ and 25%HA+75%PSZ for 1 minute in simulated blood plasma.

Sample condition	***Coating thickness (μm)***	***Corrosion Potential E_{corr},mV$_{SCE}$***	***Corrosion current densityi_{corr}, μA***	***Corrosion rate, (mm/y) × 10^{-3}***
Uncoated	–	−335	0.81	7.69
66%HAP+34 %PSZ	9.9	−338	0.16	1.58
25%HAP+75 %PSZ	18.9	−206	0.22	2.09

Conconclusions

Electrophoretic deposition of HA+PSZ on samples of Ti-20Co with varying thickness showed marked changes in the corrosion resistance; optimum thickness was found to be 9.9 µm. This can be attributed to dense nature of the coated layer formed on the samples which will resist the mobility of the active ions like Cl- and other ions through the film. The coating layer may block the path-way for a Ti4+ migration from the metals to the solution which normally occurs during anodic polarization. The corrosion parameters show that increasing the PSZ content in the EPD of composite HA+PSZ coated layer enhance the corrosion behavior of Ti-20Co alloy in different body fluids environments.

Acknowledgment

The authors would like to acknowledge the research funding from Directorate of Materials Science (MSD), Ministry of Science & Technology (MOST), Iraq.

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الخلاصة

تم في هذا البحث دراسة نتائج فحوصات التآكل في محاليل الجسم لسبيكة Ti-2oCo ذات الاستخدام الطبي والمطلية بمادة الهيدروكسي ابتايت (HA) ومركب الزركونيا المثبتة جزيئاً (PSZ)باستخدام تقنية الترسيب بالهجرة للدقائق العالقة(EPD).

حضرت ثلاثة نماذج من (Ha) و (PSZ) هي (90%HA+ 10%PSZ, 66%HA+34%PSZ, 5%HA+75%PSZ) والتي تم ترسيبها على سبيكة Ti-2oCo في محيط غاز فاصل وبدرجة 800^0c لغرض الحصول على افضل التصاق بين السبيكة والمواد المرسبة.

تم دراسة النماذج من خلال الاختبارات الكهروكيميائية من خلال غمرها في محلول اللعاب الصناعي وبلازما الدم والتي تم تحضيرها مختبرياً للحصول على السلوك العام للتآكل عند تعرض هذه المواد لمثل هذه الضروف.

النسب المعتمدة والاسماك المهيئة للعينات المستخدمة تم قياس جهد التآكل لها ومعدل التأكل من خلال غمرها في المحلول ومن ثم قياس جهد الدائرة المفتوحة للغرض باستخدام قياس جهد الاستقطاب (OCP) اظهرت النتائج ان كفاءة معدل التآكل يعتمد على عدة عوامل منها النسب المستخدمة لمواد الطلاء وسمك الطلاء والفجوات الحاملة في طبقات الطلاء اضافة الى قوة الالتصاق على السبيكة المستخدمة. وقد تم مناقشة تأثير كل من نسب التركيب وسمك الطلاء خلال تفاصيل البحث.