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Effect of Hydroxyapatite layer Coating on Corrosion Behavior for Ti-20%Co alloy.

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ABSTRACT

Electrochemical corrosion of Ti-20%Co alloy coated with hydroxyapatite (HAP) performance depends on various parameters like applied potential, time, thickness and sintering temperature thus, the optimum parameters required for development of stable HAP coating was found by using electrophortic deposition (EPD) technique. This study discusses the result obtained from XRD and potentiodynamic polarisation, the measured corrosion potential in the synthetic blood plasma for the HAP coated specimens are more noble than the uncoated specimens. The specimen coated for (3) minutes was found to be the best corrosion resistance in comparison with the un coated specimens.

Introduction

Biomaterials have received much interest and intensive research during the last few decades, due to their obvious use as replacements of various body parts or even organs. Their use and the improvement of their reliability and life span would undoubtedly improve the quality of human life in more than one aspect. The prosthetic devices commonly used to replace human bone are currently obtained from biocompatible metals and alloys, such as stainless steel, Ti and its alloys with Al, Fe and V, gold, platinum, CoCr and so on.

These metals are used mainly due to their mechanical properties (mechanical resistance, Young's modulus, corrosion resistance), however they do not exhibit any biointegration properties, meaning that the human organism accepts these implants only by isolating them, and sometimes rejection reactions occur. [1,2]

The use of bulk ceramic biocompatible materials, such as zirconia, calcium phosphates and mainly hydroxyapatite (Ca5(PO4)3OH) is limited to very small implants, without being subjected to high loads, due to the low values of their mechanical properties, especially fracture toughness and elasticity modulus (too high) [3,4] The next step in improving the bone implants properties is the coating of metallic implants, having good mechanical properties, with thin biocompatible ceramic films, in order to improve the osteointegration of these implants. The main problem of these coatings is raised by their poor adhesion to the metallic substrates, due to the sometimes large difference between their thermal coefficients, causing the appearance of tensile stresses at the interface. This causes the coatings obtained by high-temperature processes to fail either during the mounting procedure, or during service in the human body. The commercial processes of obtaining these ceramic coatings are: the dip coating method, the sol-gel process, pulsed laser deposition and, most of all, the plasma spraying process, used for a wide range of materials. One of the

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most interesting alternatives of obtaining these biocompatible coatings is by electrodeposition. This process is developed at room temperature, and has many advantages over other, more commercial deposition processes, such as: uniformity of the deposited layer, availability of various substrate shapes other than plates, good control of the deposition thickness and quality, low energy consumption and also the fact that it is an environmentally friendly process [5].

Experimental work

Materials

Type Ti-20%Co alloy electrodes of(10×10×2) mm size samples were mechanically polished from 120 to 600 grit SiC papers followed by using a 0.5µm diamond paste to get a mirror finish [6]. The electrodes were washed thoroughly with running distilled water, rinsed and ultrasonically degreased with acetone and dried. The electrophoretic deposition process is carried out at room temperature the suspension was prepared by adding (HAP) powders to the solvent which was isobropanol (100g/1liter) in a container over a stirrer, after 10 minutes a dispersant agent phosphate ester 3.5g/1liter was added. After stirring for 10 minutes poly vinyl butyral was added as a binder (3g/1liter). The stirring was continued until a colloidal suspension was obtained.

Constant-current or constant-voltage regimes could be used for EPD. The electric field drives ceramic particles toward the electrode & exerts a pressure on the deposited layer. It is desirable to maintain a high potential difference between the anode & the cathode. In EPD process application of a DC field causes the charged particles to move forward and deposit on the oppositely charged electrode. The HAP powders acquired a positive charge and under went cataphoresis (deposition on the cathode). Therefore a highly conductive charge surface area anode was used for charging the particles The Ti-20%Co specimen was put on the cathode electrode and a piece of 316L alloy was used as an anode electrode. Both electrodes were connected to the power supply and the meter. The distance between the electrodes was 10mm and the power supply was used with applied voltage to produce enough current according to the size of the sample [5] The polished specimens were weighted before and after coating using an electronic analytical balance (Scaltel, SPB31, Germany, Readability= 0.0001g). Sintering of the coated specimens was carried out using Carbolite furnace type MTF 1200, England. The treatment was done under inert gas (argon), to prevent oxidation of the specimen. The (HAP) coating was obtained after 1 min. In order to understanding the effect of time on the coating thickness, the same procedure was repeated for a period of time 2, 3, 4, 5 and 6 min. X-ray diffraction patterns were recorded with a Shimadzu LabX XRD-6000 diffractometer to study the phase changes and depth profiling of the coating microprobe. By (ERICHSEN MINI) Test 3000 Microprocessor Coating Thickness Gauge The potentiodynamic polarisation studies of the alloy uncoated and coated with (HAP) were conducted using a Weking Mlab200, 2007 from Bank Elektronic,Germany). potentiostat/galvanostat electrochemical interface controlled by commercial software-SCI 2007 .

Potentiodynamic polarization and electrochemical studies.

Potentiodynamic cyclic polarization of the Ti-20%Co alloy uncoated and coated samples was carried out under simulated body fluid synthetic blood plasma (Chemical Composition is explained in Table (1) with adjusted pH7.4.

Table (1) The chemical composition of synthetic blood plasma [7].

No	Constituent	Weight (gm/l)
1	NaCl	6.800
2	KCl	0.400
3	$CaCl_2$	0.200
4	$NaHCO_3$	2.200
5	$Na_2 HPO_4$	0.126
6	NaH_2PO_4	0.026
7	$MgSO_4$	0.100

A saturated calomel electrode (SCE) and a platinised platinum black were used as the reference and auxiliary electrodes respectively. The area of the coated surface exposed to corrosion study was 1 cm2. The other sides of the electrode and its edges were masked with lacquer and were dried in air. The electrodes were further dipped into the electrolytic solution to study the corrosion process. Similar procedure was followed for uncoated type Ti-20%Co alloy also. The electrochemical measurements carried out on the coated samples is cyclic polarisation measurements, the critical parameters like corrosion potential (Ecorr), were evaluated from the polarisation curves. The samples were immersed in blood plasma and the OCP (Ecorr) was monitored for half hour. During cyclic polarisation study, the potential was increased from 0.200 V below the OCP towards the noble direction at a rate of (10 mV/min) until 0.200 V above the OCP The sweep direction

Results and discussions

Effect of sintering temperature

Sintering temperatures have a deleterious effect on the properties of coating and the metal substrate. Low sintering temperatures can lead to weakly bond low- density coating. High sintering temperatures result in phase changes of the metal substrate catalyzing the decomposition of HAP to anhydrous calcium phosphates [8].

Thus the regime of sintering temperature was varied in the present to dissolution and posse's high bond strength .The bond strength of the coating is achieved by sintering.

Thus the regime of sintering temperatures was varied in this study at (800 and 900) o C

For one hour.

XRD studies

Figure (1) shows the XRD patterns of Ti-20Co uncoated. Though there is no JCPDS-ICDD standard for this material and the known data from the literature are sufficiently numerous for detailed comparison. We have fitted our results to those reported for the hexagonal α Ti (JCPDS-ICDD file # 44-1294), cubic β Ti (JCPDS-ICDD file # 44-1288), cubic Ti2Co (JCPDS-ICDD file # 07-0141) and cubic TiCo2 (JCPDS-ICDD file # 17-0031). The XRD pattern of Ti-20Co alloy shows the domination of β-Ti phase (2θ= 39.629). It's clear from the pattern the coexisting of alpha titanium (□-Ti) and Ti2Co precipitate.

Figure (2) shows the XRD pattern of the HAP coated Ti-20%Co alloy obtained by electrophoretic deposition at a constant potential of 30 V and (3) min deposition. The presence of diffraction peaks with minimal line broadening and high intensities, which indicate a well crystallised material. The strongest lines in this XRD pattern corresponds to reflections The strongest lines in the XRD pattern are (002), (211),(300), (202) and (312) at 2θ 25.870, 31.769, 32.902, 34.059, and 48.083 respectively, appeared markedly higher than other HA peaks. The strongest (211) peak corresponding to crystalline hydroxyapatite (P63/m) belonging to the hexagonal symmetry. Of HAP after indexing with the JCPDS file no.9-432. The patterns showed no structural transformation either in crystallinity or stoichiometry and confirm the stable nature of the HAP coatings formed after thermal treatment with no extraneous peaks, thus indicating the presence of stoichiometric HAP with a Ca/P ratio of

1.67 at sintering temperatures 800oC. When HA powder was sintered at 900oC, HA gradually reconstructed into TCP, and one can easily observe a prominent peak at 2θ values of 31.040 compared to the patterns of the powder sintered at temperatures 800oC. Which is responsible for 100% intensity of the (210) plane TCP. After indexing with the JCPDS file no. 32-0176

Coating thickness

The coating thickness has been increased when applied potential or time increased[9] .Showed that a thicker coating will give a brittle material prone to cracking under bending or shearing force. the increased in coating weight of HAP thus lead to loss of thicker coating from the metal surface due to de cohesion between the surface and the coating[8] .The surface of the coating becomes rougher with increase in coating time [10].

Potentiodynamic polarization

From polarization results the uncoated Ti-20%Co alloy specimens exhibit a higher corrosion rate compared with that of HAP coated specimens as shown in Table (2)and Fig(3,4,5and6).Uncoated specimens are susceptible to corrosion in the presence of chloride ions. The ability of uncoated specimens to repassivation in biological environments is also considerably lower compared to coated specimens. Generally, the corrosion behavior for uncoated and HAP coated specimens for different coating time intervals indicates that the corrosion potentials for HAP coated specimens are more noble The electrochemical parameters obtained from potentiodynamic polarization curves for the uncoated and HAP coated Ti-20%Co alloy, for various coating time intervals from 1 to 3 minuets at constant potential of 30V. With further increase in coating time, the surface coated layer becomes porous with irregular film. This can be due to the increase in corrosion rate with coating time more than 3minunts.

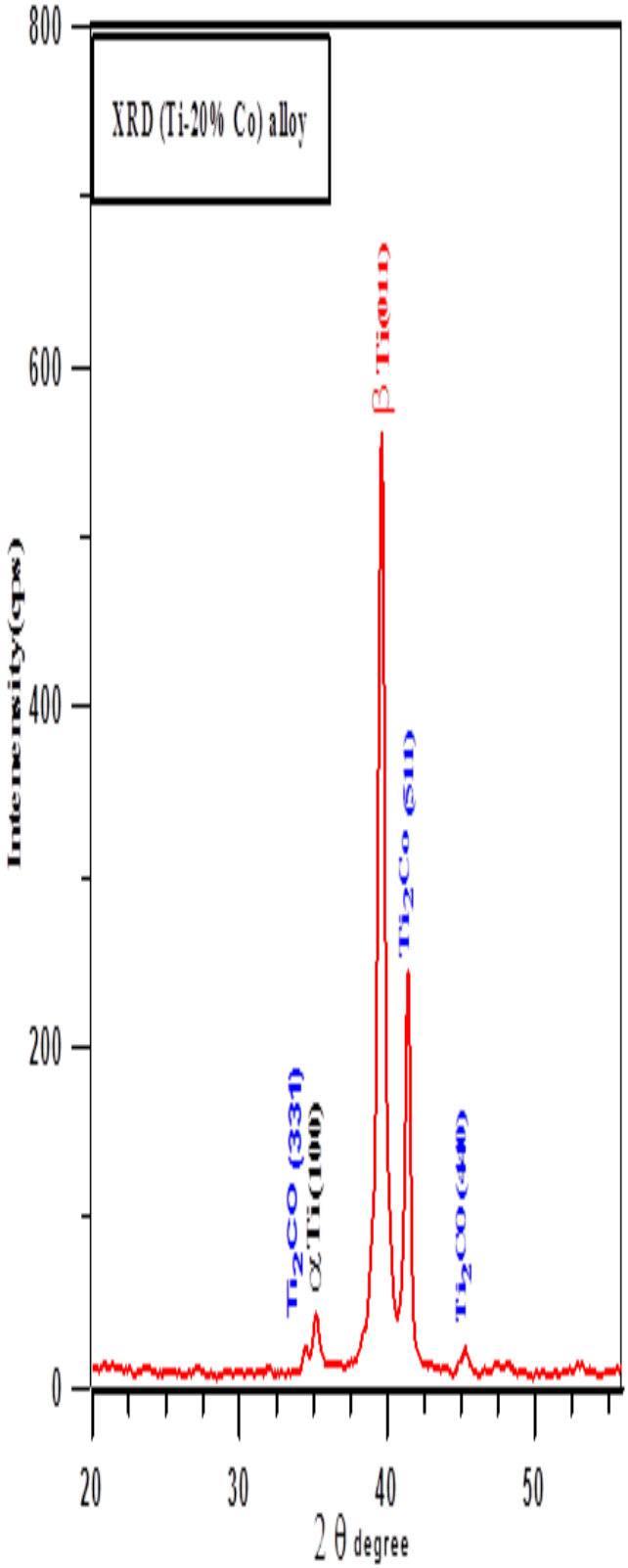

Fig.1: XRD patterns Ti-20%Co alloy uncoated.

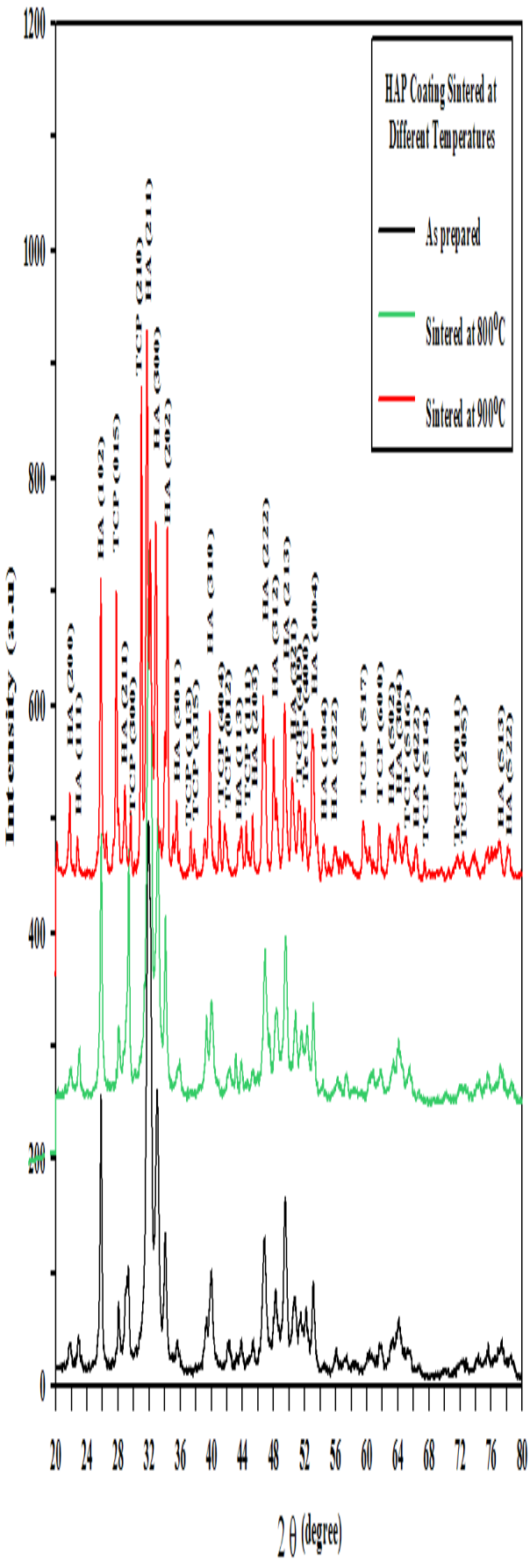

Fig.2: XRD patterns of HAP coated Ti-20%Co alloy after sintering in inert gas (argon) at 800oC and 900oC

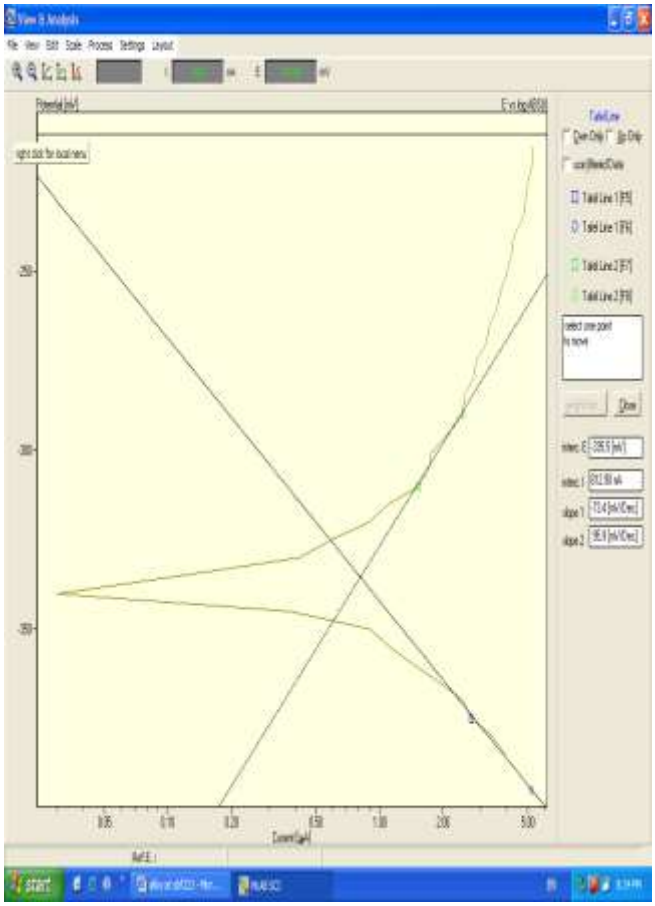

Figure: 3. Potentiodynamic polarization behavior for uncoated Ti-20%Co alloy in synthetic blood plasma Solution.

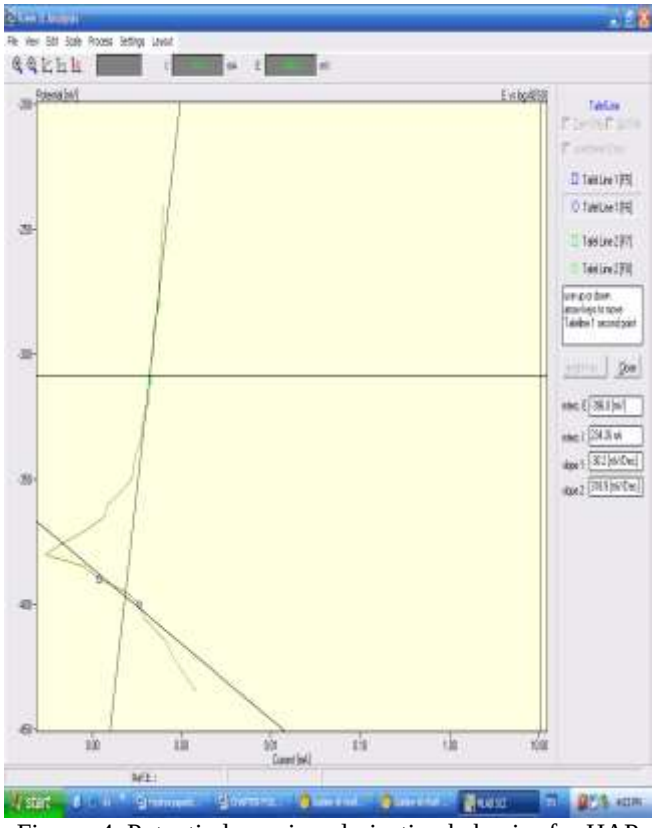

Figure: 4. Potentiodynamic polarization behavior for HAP coated for1 minute Ti-20%Co alloy in synthetic blood plasma.

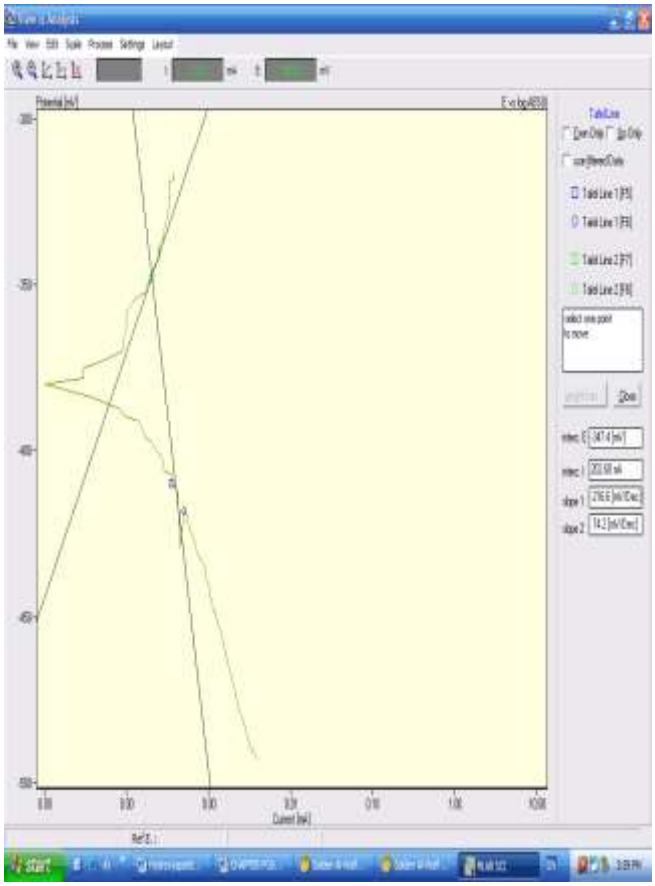

Figure: 5. Potentiodynamic polarization behavior for HAP coated for 2 minute Ti-20%Co alloy in synthetic blood plasma.

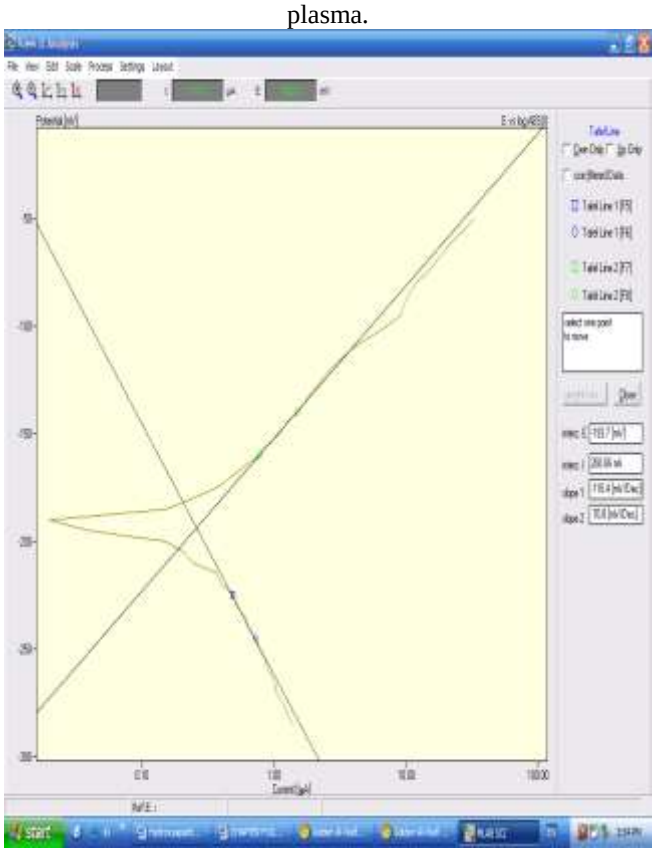

Figure: 6. Potentiodynamic polarization behavior for HAP coated for 3 minute Ti-20%Co alloy in synthetic blood plasma.

Table (2) corrosion current value fore all Sample coated with HAP at different Thickness Coating.

i_{corr} (A/cm^2)	Thickness of coating (µm)	Time of deposition (min)
2.05×10^{-6}	Un coated 0	Un coated 0
260.66×10^{-9}	5	1
234.26×10^{-9}	10	2
202.60×10^{-9}	15	3

The conclusions drawn from the research work are as follows:

1. In electrophoretic deposition of bioactive ceramic coating material, the thickness of the coating increases with an increase in time of the deposition.
2. The specimen coated for 3 minutes exhibits better corrosion resistance behavior than that of the other coated specimens.
3. Hydroxyapatite coating obtained by electrophoretic deposition proves as available alternative for improving the corrosion resistance of Ti-20%Co alloy for enhancing the biocompatibility of the implant devices.
4. The electrochemical behavior of uncoated and hydroxyapatite coated Ti-20%Co alloy was investigated in simulated body fluid solution (synthetic blood plasma)at 37˚C,corrosion potential for all coated specimens is more noble than that of the uncoated specimens.
5. The XRD patterns show that the stoichiometric HAP coating remains stable without formation of decomposition products at sintering temperature 800oC. The XRD results show that HAP coating was composed of two crystalline phases of tetracalcium phosphate (TeCP) and α-tricalcium phosphate (αTCP). There were no other calcium phosphate phases to be traced when HAP coating was sintered at 900oC.

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تأثير طبقة الطلاء بمادة الهايدروكسي ابتايت على سلوك التآكل لسبيكة Ti-20%Co

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الخلاصة

التآكل الكهروكيمياوي لسبيكة Ti-20%Co المطلية بمادة الهايدروكسي ابتايت يَعتمدُ على معلمات الطلاء المُختَلِفةِ مثل الفولتية المسلطة، والزمن، والسُمك ودرجةَ حرارة التلبيد. إذ تعد هذه أفضل المعلمات المطلّوبة لتطويرِ الطلاء بمادة الهايدروكسي ابتايت المستقرِّ كما أنها قد وُجِدتْ باستعمال تقنية الترسيب بالهجرة للدقائق العالقة المشحونة.تُناقشُ هذه الدراسةِ النتائج التي حَصل عليها مِنْ منحيات الاستقطاب، إذ تمت قياسات ألتآكل في محلول بلازما الدمِّ الصناعيِ إذ أظهرت النماذجَ المطلية بمادة الهايدروكسي ابتايت سلوك أكثر نبلاً مِنْ النماذجِ غير المطلية. كما وجد أن الأنموذج المطلي بزمن3 دقائقِ له أفضلية من حيث المقاومةِ للتآكلِ بالمقارنة بالنماذجِ غير المطلية.