

EFFECT OF BIOCERAMIC COATINGS ON CORROSION BEHAVIOR FOR MEDICAL ALLOYS USED IN ORTHOPEDICS AND DENTAL APPLICATIONS

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ABSTRACT

In this study, electrophoretic deposition (EPD) method was used for hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) coating on medical substrates in order to enhance their biocompatibilities. Chemically synthesized ultra fine powders of HAP were prepared by the addition of orthophosphoric acid (0.6M) to calcium nitrate solution (1M) by strongly controlled the all parameters affected the producing of a bioactive material like the standard of natural bone ceramic. A solution of 2.5 wt% HAP in isopropyl alcohol mixed with a surfactant sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$) to reinforce the adherence of particles on the surface. The results showed that at a constant voltage the coating deposition increases with an increase in coating time whereas when the coating time was kept constant, the fineness of the coating increases with an increase in the voltage. The optimum coating conditions obtained were (60 volt for 4 minute, sintering at 800°C for 2 h in open atmosphere) gives stable and homogeneous coating layer. Corrosion rates were measured after immersed in Ringers solution for coated and uncoated specimens by potentiodynamic polarization technique which revealed the highly corrosion resistance for coated specimens compared with uncoated specimens. XRD analysis showed some visible peaks of HAP in the coated substrate along with peaks of stainless steel, this could be to the lesser intensity peaks of pure HAP. It was observed from the images structure analysis that HAP deposited on stainless steel substrate at 15 minute showed smooth and good adherence whereas for deposition more than 16 minute showed discontinuous and weak adherence deposition leading to crack formation.

Key words: hydroxyapatite, biocompatibility, electrophoretic deposition, potentiodynamic polarization

تأثير الطلاء بمركب السيراميك الأحيائي على سلوك التآكل للسبائك الطبية المستخدمة في حقل جراحة العظام والاسنان

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الخلاصة

في هذا البحث ، تم طلاء مادة الهيدروكسي اباتيت ($HAP, Ca_{10}(PO_4)_6(OH)_2$) باستخدام طريقة هجرة الدقائق المشحونة (EPD) من اجل تعزيز التوافقية البايولوجية مع أنسجة الجسم. الطريقة الكيميائية الرطبة استخدمت لتحضير مركب الهيدروكسي اباتيت بتفاعل محلول 1مولاري نترات الكالسيوم مع محلول 0,6 مولاري اورثو- حامض الفسفوريك ومن خلال السيطرة الدقيقة على جميع العوامل المؤثرة على إنتاج مركب مطابق للمواصفات القياسية لمادة سيراميك العظام والاسنان. محلول الطلاء يحضر بنسبة 2,5 % وزنا من مسحوق الهيدروكسي اباتيت في سائل الايزوبروبيل الكحول المخروط مع مادة ($SDS, C_{12}H_{25}SO_4Na$) لتعزيز خواص الالتصاقية ، وقد بينت النتائج انه عند إجراء عملية الطلاء بفولتية ثابتة مع تغيير الوقت فان مادة الطلاء تترسب على سطح السبيكة وبمسك اكبر بمرور الزمن بينما لوحظ عند تثبيت زمن الطلاء وتغيير الفولتية فيمكن الحصول على طبقة طلاء صافية ومتجانسة وأكثر التصاقية . إن أفضل النتائج كانت عند العمل بالمتغيرات (60 فولت وزمن 45 دقيقة ودرجة حرارة تلييد 800م° ولساعتين) حيث أظهرت تجانس طبقة الطلاء وقوة ثباتيتها.

اجريت فحوصات التآكل باستخدام تقنية الاستقطاب الديناميكي لحساب معدل التآكل للسبيكة المغمورة في مشابهاة محاليل الجسم (محلول رنكر) للعينات المطلوبة بالابتابت ومقارنتها بالسبائك غير المطلوبة حيث أظهرت السبائك المطلوبة مقاومة شديدة للتآكل مما يعزز توافقيتها البايولوجية مع أنسجة الجسم . فحوصات حيود الأشعة السينية (XRD) أظهرت تكون طبقة طلاء الهيدروكسي اباتيت على سطح سبيكة الستنلس ستيل ولكن وجود بعض الحيود في قيمة (peak) للابتابت المطلبي عن الابتابت النقي بسبب تداخل بعض بيكات السبيكة مع مركب الابتابت. نتائج فحص الصور المجهرية تبين أهمية الالتزام بوقت الطلاء لان زيادة الوقت تؤدي إلى تكوين طبقة طلاء سميكة يمكن إن تؤدي إلى حدوث تشققات في طبقة الطلاء.

INTRODUCTION

Hydroxyapatite is a salt of calcium and phosphorus having the Ca/P ratio as 1.67. It is one of the major mineral components of the bone due to which it shows excellent biocompatibility. Because of its poor mechanical properties hydroxyapatite cannot be used directly in load bearing structures. An alternative approach to utilize the biocompatibility of hydroxyapatite is by using it as a coating material. A suitable material for this purpose is medical grade stainless steel, which has been used to make prosthesis, bone fixation screws, guide wires etc. Bioactive ceramics (calcium phosphates hydroxyapatite HAP) are used for placement of coatings over metallic substrates. The mechanism of tissue attachment is directly related to the type of tissue response at the implant interface [Hae et al 2004 and Abdulsalam et al 2008].

Many techniques are available to modify the surface of materials, the criteria for the choice of a suitable surface modification technique is that the coating should not impair the properties of the bulk material, the deposition process must be capable of handling the component in terms of both size and shape. Electrophoretic deposition is a procedure of mild nature not involving extreme temperatures and has the advantage of producing a stoichiometric, uniform coating of the desired thicknesses (Prashant et al 2005, Thair et al 2008 and Nagarajan et al 2009).

The relative levels of reaction of the implant influence the thickness of the interfacial zone or layer between the material and tissues. The concept behind micro porous bioceramic was the in growth of tissue into the pores on the surface throughout the implant as described by [Marcelo et al 2003].

The electro deposition of Ca-P depends on the degree of HAP supersaturating in the solution, pH of the electrolyte, applied voltage, ionic strength of the electrolyte, its temperature and state of the cathode surface [Wel et al 2001 and Gross & Berndt 2002].

The statements of this work deal with the difficulties that which hydroxyapatite cannot be used directly in load bearing structures because of its poor mechanical properties; moreover its lack of interfacial stability is one of the causes behind the need for revision surgery of metallic implants. An alternative approach to utilize the biocompatibility of hydroxyapatite is by using it as a coating material.

The present investigation was undertaken with the aim of studying the corrosion behavior of HAP coated 316L SS alloy under *in vitro* conditions and to predict the possible implications on the biocompatibility of such material.

MATERIALS AND METHODS

HAP Synthesis

Hydroxyapatite (HAP) was prepared using the conventional polycrystalline method. Solutions of $\text{Ca}(\text{NO}_3)_2$ 1 M and H_3PO_4 0.6 M in distilled water were prepared. The pH was adjusted to above 10 with concentrated NH_4OH solution. The $\text{Ca}(\text{NO}_3)_2$ solution was vigorously stirred at room temperature and the phosphate solution was added drop wise to it in about 30 min to produce a milky and somewhat gelatinous precipitate which was then stirred and heated for 24 h. It was then filtered in a Buchner funnel with application of a mild suction. After filtration the compact, sticky, filter cake was dried at 90°C for 2 h. Sintering was carried out at 900°C for 1 h to produce polycrystalline HAP.

Electrophoretic Deposition

Uncalcinated and calcinated HAP powders obtained were used as coating materials. 0.5 g of powders was added into 80 ml isopropyl alcohol. After magnetically stirring for 15 minutes, suspensions were dispersed ultrasonically for 30 minutes and then suspensions were left for 30 minutes to eliminate by sedimentation the bigger and/or agglomerated particles. Finally suspensions were ultrasonically dispersed again for 30 minutes to ensure a good dispersion of the particles. 316 L SS substrates of 11×11×2 mm sized were polished from 240 to 1000 grid SiC papers followed by using a 1 µm diamond paste to get a mirror finish. The substrates were thoroughly washed before deposition with detergent in ultrasonic bath for 30 minutes followed by washing in acetone for another 20 minutes. The electrodes were placed parallel to each other in the suspension, with a separation of 10 mm approximately, and connected to a DC power supply. The EPD coating was performed under a constant voltage of 50 V for 1 minute. After deposition, the green form coatings were dried at room temperature in air, and then sintered in the tube furnace at 800°C for 2 hours in atmosphere at a heating rate of 10°C/min and left to cool in the furnace.

Corrosion Tests

Ringer's solution with adjusted pH 7.4 was used as the electrolyte whose composition in wt% (gm/l) is: NaCl (9.00), KCl (0.43), CaCl_2 (0.24) and NaHCO_3 (0.20). Surface condition of the alloy has been produced for Electrophoretic Deposition process (EPD). The polarization test cell and the probe used were similar to the one conventionally used. A 500 ml capacity cell equipped with a platinised platinum electrode as auxiliary electrode, and standard calomel electrode which serves as reference electrode were used. A Luggin capillary

was kept in such a way that the working electrode and its tip remain at a distance of about 2 mm in between to avoid ohmic drop, a constant stirring condition was maintained throughout the experiments. The experiments were conducted with the cell housed in a single compartment placed in Faraday cage.

The uncoated and coated samples were immersed in the electrolyte for an hour in order to establish a steady state between the electrolyte and the specimen. The change in potential with respect to time was monitored until the potential reaches a steady state. The potential of the working electrode with respect to reference electrode after stabilization period is termed as open circuit potential OCP or corrosion potential E_{corr} . The potentiodynamic polarization studies of the uncoated and HAP coated type 316L SS were conducted as per [ASTM G30, 1996]. The critical parameters such as E_{corr} , E_p (pitting/breakdown potential) and E_r (repassivation potential) were determined to evaluate the corrosion resistance.

The pitting susceptibility of the implant materials is often determined by measuring the critical pitting potential i.e. the pit repassivation potential. After the samples attained a constant potential OCP, anodic cyclic polarization scan was started at a potential 0.2V below OCP, at a scan rate of 0.15mV/min.

RESULTS AND DISCUSSIONS:

The phase constitution and chemical homogeneity of the sample were examined by quantitative chemical analysis via EDTA titration, gravimetry and AAS. The Ca/P molar ratio was found to be 1.67, which indicates the formation of pure HAP. Figure 1 shows FT-IR spectra of hydroxyapatite sintered at temperature of 900°C. The spectral data indicate that carbonate ion is present in the prepared HAP samples. The carbonate ion substitution is identified by characteristic doublet peak of the carbonate ions around 1420 and 1480 cm^{-1} and a singlet peak at 875 cm^{-1} which is attributed to the vibrational modes of the carbonate ions, substituted at the phosphate site. A typical XRD profile of HAP powder synthesized by wet chemical method has been shown in figure 2. The XRD phase analysis has been performed using JCPDS card number 09-0432

Figure 3 shows the OCP curves for the uncoated and HAP coated substrates developed at different applied potentials ranging from 30 to 90V at a constant time of 3 minute. A nobler shift was observed for all the coated metal samples when compared to the uncoated samples, which indicates its better corrosion resistance. A continuous decrease in OCP towards active potential with time was noticed for the uncoated sample, before it

attained the steady state potential [Mudali et al 2003].

The uncoated sample initially showed an OCP of -0.130V and constantly shifted towards active direction and then reached a potential of -0.290V after 60 minutes. The OCP- time curves of the coated HAP specimens shifted towards noble direction (more positive potential) and reached a steady state potential in a short duration of time. This indicates the protective nature of the coatings on 316LSS. It also indicates that no free metal surface area is available for the attack of aggressive ions. The noble behavior of the ceramic HAP coatings could be due to the insulating nature of the surface. Thus the OCP-time behavior of HAP coatings developed at different potentials showed variations in the noble behavior. The coatings obtained at a potential of 60V performed better. It showed an initial OCP of -0.061V, reached a steady state and gradually increased to +0.031V.

The curve obtained for the coatings with deposition potential more than 70V, showed variations in OCP. This may due to the existence of a large diffusion path within such thick coatings, capable of causing large potential drops. From the OCP was shifted to a nobler region and the time taken to attain constant OCP was faster and more significant when compared with samples uncoated. This may be due to the modifications at the alloy surface and also due to the presence of HAP coating, which acts as barrier.

The electrochemical parameters obtained from the cyclic polarization curves of the HAP coated substrates are given in figure 4. Higher E_b and E_p values were obtained for all the coated samples compared to the uncoated samples. At a coating voltage of 60V, The E_b for the samples coated at 60V was found to be +0.508V and with a repassivation potential of +0.033V, whereas for the uncoated samples the E_b and E_p were +0.323V and -0.221V respectively. The coated samples after polarization were observed under the optical microscope, no pits were observed on the surface of the coating. Rapid increase in current density was observed for the uncoated specimen, which could be due to the growth of pits caused by the presence of chloride ions in solution. Chloride being a relatively small anion with high diffusivity interferes with the passive film and then penetrates to cause damage hence a large hysteresis loop was obtained. The hysteresis loop with considerable area observed for 316LSS indicate the extensive operation of pit propagation mechanism. This also confirmed by [Kannan et al 2002 and Mudali et al 2003], this indicates that the pit propagation kinetics is higher, in other words, repassivation tendency of the material is hindered. The current density curves are smaller for the coated samples, which indicate the

easier repassivation tendency due to the presence of HAP, which can act as a barrier in arresting the growth of the pits. The decrease in the value of breakdown potential E_b with the increase in coating voltage can be attributed to the thickness of coating and subsequent weakening of substrate coating bond strength.

Coatings obtained at 20V resulted in incoherent coatings but the difference in E_b and E_p values are higher in comparison with the uncoated samples.

As mentioned earlier during electrophoretic deposition, hydrogen evolution increases with increase in coating voltage and time, which results in an increase in porosity and pore size of the coating, this is well in agreement with the reports [Sridhar et al 2001] that as the pore size increase, the breakdown potential decrease and hence, its corrosion resistance decreases.

The above results suggest that 30 to 70V is the effective coating range for obtaining stable HAP coatings. In this stage, the optimal applied potential for electrophoretic deposition of HAP on type 316L SS is 60V and 4 minutes.

It is evident from the results that HAP coated samples exhibit enhanced E_b and E_p values, suggesting an improvement in the pitting corrosion resistance in Ringer's solution.

HAP CHARACTERIZATIONS

XRD Analysis

The XRD pattern obtained for the coated samples after immersion for 30 days and subjected to electrochemical measurements is given in figure 5. The patterns showed no structural transformation either in crystallinity or stoichiometric, this indicates that the HAP structure is virtually unaffected as no extraneous peaks of calcium phosphate phases and other contaminants are observed in comparison with the synthesized stoichiometric HAP powder and HAP coated type 316L SS at the optimum coating parameters after sintering [Prashant et al 2005].

The strongest lines in the XRD pattern corresponds to reflections at 002, 211, 112, 300, 202 and 310 planes of HAP after indexing with the JCPDS file no. 9-432 [Joint committee 198].

EDXRF Analysis

The EDXRF spectrum given in figure 6 indicates the presence of intense peaks for Ca, and Fe, which was similar to that of the coated samples obtained at the optimal coating parameters (figure 6). Small peaks corresponding to Cr and Ni present in the alloy were also detected; the intense peaks for Ca and P suggest the presence of strong HAP coating over the surface. These studies confirm that the HAP structure was not altered and iron peaks were detected on the surface.

Figure 7 showed the optical micrograph for ultra fine hydroxyapatite powder which was prepared and then sintered at 900°C for 1 hour, while figure 8 showed the micrographs of HAP coated type 316L SS after immersed in Ringers solution to evaluate the corrosion rate of alloy specimens, it was showed the smooth and homogenous coating layer on the alloy surface.

CONCLUSIONS

HAP powder synthesized are crystalline, stoichiometry and absence of other Ca-P phases after coating.

The results from electrochemical corrosion studies suggest that HAP coating exhibit highly corrosion resistance than the uncoated specimens, further HAP coating developed on 316L SS by electrophoretic deposition are not lost by dissolution and the coatings formed by this process are adherent and intact.

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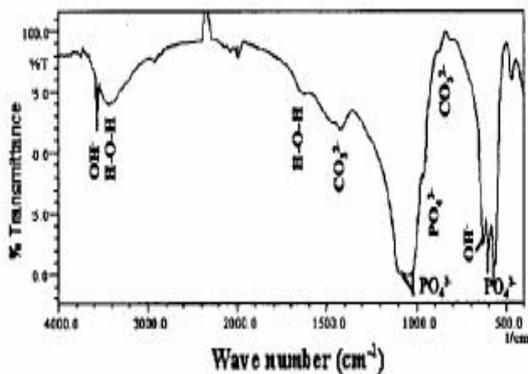


Fig 1: FT-IR spectra of HAP sintered at 900 °C.

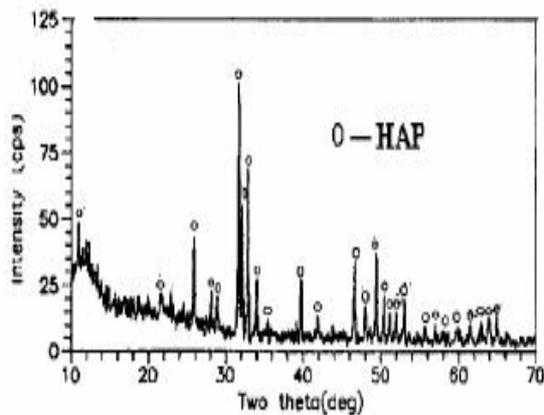


Fig 2: XRD pattern of HAP sintered at 900 °C.

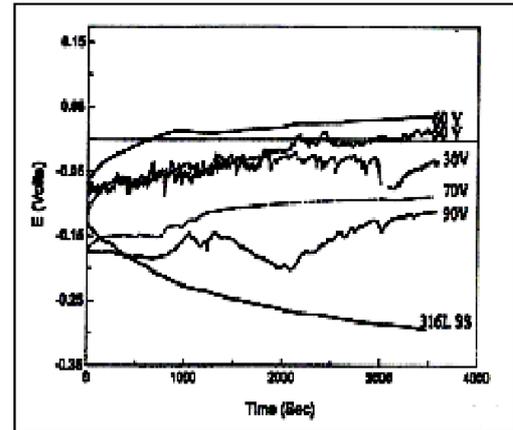


Fig. 3: OCP-time measurement of uncoated and HAP coated samples

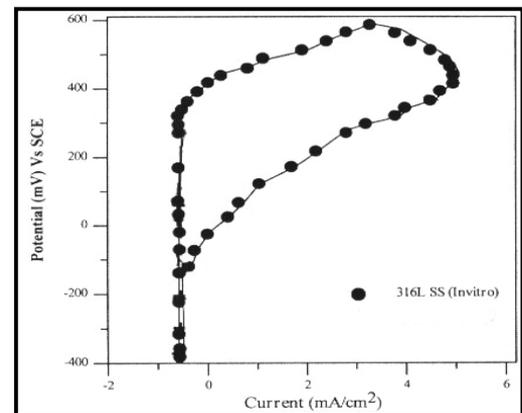


Fig. 4: Cyclic polarization curves of type 316L SS under invitro study.

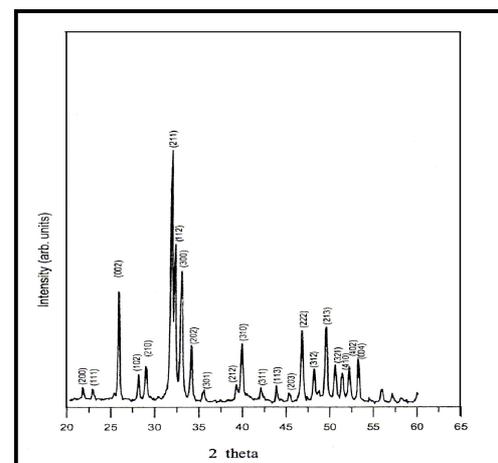


Fig 5: XRD patterns of HAP coated 316L SS

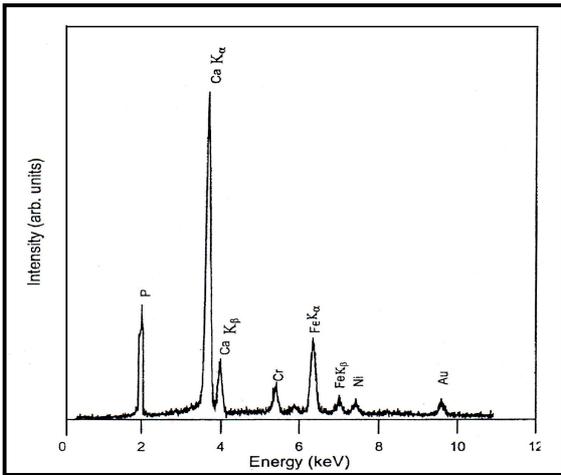


Fig. 6: EDXRF spectra of coated HAP at the optimum coating parameters

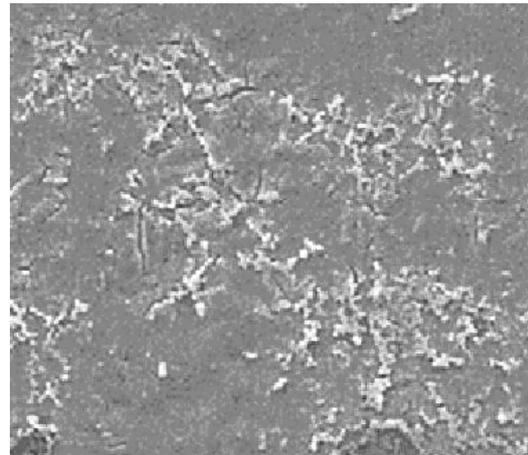


Fig. 7: Optical micrographs of sintered HAP powder

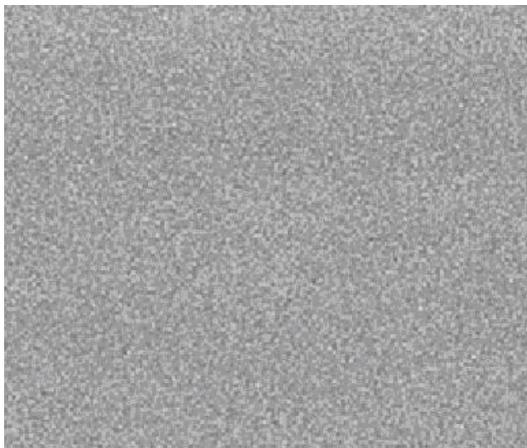


Fig. 8: Optical micrographs of coated HAP on 316L SS alloy.