Effect of Hydroxyapatite Coatings on Corrosion Behavior for Biotype 316L SS Used in Orthopaedic Applications

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Abstract:

Electrochemical corrosion of hydroxyapatite (HAP) coated performance depends on various parameters like applied potential, time, thickness and sintering temperature. Thus, the optimum parameters required for the development of stable HAP coatings was found by using electrophoretic deposition (EPD) technique.

This study discusses the results obtained from open circuit potential-time measurements (OCP-time), potentiodynamic polarisation and immersion tests for all alloy samples done under varying experimental conditions, so that the optimum coating parameters can be established. The ageing studies of the coated samples were carried out by immersing them in Ringer’s solution for a period of 30 days indicates the importance of stable HAP coatings to prevent corrosion on the substrate material, so that enhancement to the biocompatibility will be increased.

Key words: electrophoretic deposition, biocompatibility, simulated body fluid, corrosion

Introduction:

Many techniques are available to modify the surface of materials, the criteria for the choice of 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 and there should be minimum dimensional changes of the finished products) [1].

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 [2].

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 microporouse bioceramics is the in growth of tissue into the pores on the surface throughout the implant as described by [3]

The electro deposition of CaP depends on the degree of supersaturating, pH of the electrolyte, applied voltage, ionic strength of the electrolyte, its temperature and state of the cathode surface, degree of agitation and the types of ions present in the electrolyte [4].

A number of novel methods of HAP coating formations have been proposed offering the potential for better control of film structure. In many instances the coating thickness are limited to micron dimension presenting a concern whether long term coating be a requirement. Better control of coating structure and chemistry might enable greater film

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stability but in vivo studies are also required [5].

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.

Material and Methods:

Electrolyte

Ringer’s solution with adjusted pH 7.4 was used as the electrolyte whose composition is given in table 1.

Table1: Chemical composition of Ringer’s solution [6].

NO.	CONSTITUENT	WEIGHT (gm/l)
1	NaCl	9.00
2	KCl	0.43
3	$CaCl_2$	0.24
4	$NaHCO_3$	0.20

Sample Preparation

Surface condition of the alloy plays major role in the development of HAP coating and its corrosion resistance. Type 316L SS alloy in as received mill annealed condition was cut in to 11x11x2 mm size piece. All sides of the specimens were polished up to 1000 grit SiC paper to bring it to uniform surface condition, then polished specimens were washed with detergent solution, degreased with acetone and thoroughly washed with distilled water, this was followed by ultrasonic cleaning in acetone for 10 minutes and then the samples was rinsed in deionizer water, dried and used for Electrophoretic Deposition (EPD) process.

Cell Assembly

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.

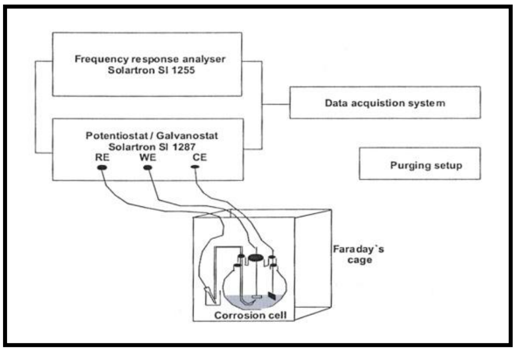

Fig. 1: Schematic representation of potentiostatic circuit diagram.

Open Circuit Potential (OCP)

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}.

Cyclic Polarization Study

The potentiodynamic polarization studies of the uncoated and HAP coated type 316L SS were conducted as per [ASTM G30, 1996] [7] methods using a Solatron SI 1287 potentiostat/ galvanostat electrochemical interface controlled by commercial software-CorrWare, version 2.1a © 1990-1998, Scribner associates Inc. And the data was analysed with CorrView software version 1.5c, © 1996, Scribner Associates Inc. the critical parameters such as E_{corr}, E_b (pitting/breakdown potential) and E_p (repassivation potential) were determined to evaluate the corrosion resistance.

Determination of pitting potential

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.

Typical cyclic anodic polarization behavior of 316L SS in Ringer's solution is given in figure 2. The parameters of interest from the polarization curve are the corrosion potential E_{corr}, the critical pitting potential Eb, and repassivation potential E_P [8].

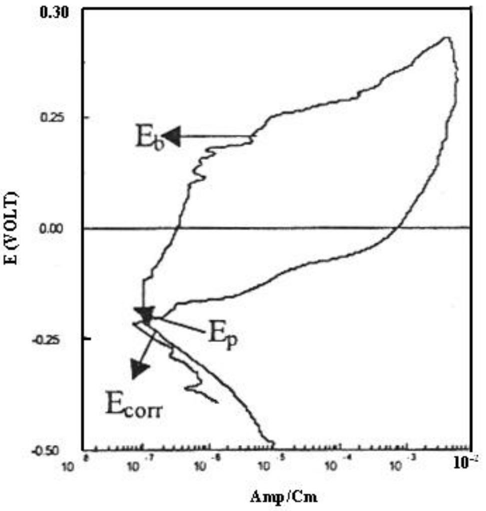

Fig. 2: Typical cyclic anodic polarization behavior of type 316L SS in Ringer's solution.

Ageing studies

The ageing studies were conducted by keeping the specimens immersed in a 250 ml glass beaker containing Ringer's solution with adjusted pH 7.4 for 30 days and kept in a thermostatic bath at 37C°. Four sets of HAP coated (obtained at the optimum coating parameters) and uncoated samples were selected. These samples on which electrochemical studies were also carried out were removed after the immersion period and dried; they were then characterized by XRD. The morphological characteristic of the samples after immersion were observed with optical microscope, the surface profile with EDXA (Twin-Oxford Co., England).

Results and Discussions:

Open circuit potential- time measurements (OCP-T)

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 [8].

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

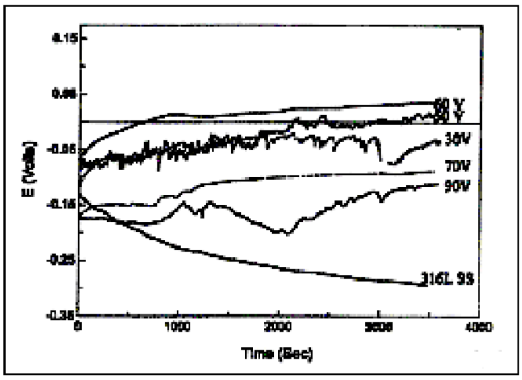

Fig. 3: OCP-time measurement of uncoated and HAP coated samples.

Cyclic polarization studies

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 (table 2), 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 area of hysteresis loop is a direct measure of the pit propagation kinetics. The hysteresis loop with considerable area observed for 316LSS indicate the extensive operation of pit propagation mechanism. This also confirmed by [8, 9], 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 evaluation 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 that as the pore size increase, the breakdown potential decrease and hence, its corrosion resistance decreases [10].

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 3 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.

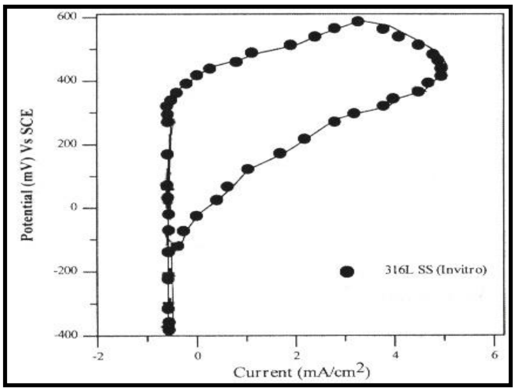

Fig. 4: Cyclic polarization curves of type 316L SS under invitro study.

Table 2: Electrochemical corrosion behavior of uncoated and HAP coated type 316L SS in Ringer’s solution.

Sample no.	Coating time(min)	Ringer’s solution		
		E_{cor}(V)	E_b(V)	E_p(V)
1	Uncoated	-0.241	+0.323	-0.221
2	2	-0.015	+0.475	-0.010
3	3	+0.031	+0.508	+0.033
4	4	+0.012	+0.491	+0.005
5	5	-0.056	+0.435	-0.071

Characterization of HAP Coated Samples

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 by using (Philips 3121 powder X-ray diffractometer using Cu Kα radiation). The patterns showed no structural transformation either in crystallinity or stiochiometric, 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 synthesised stiochiometric HAP powder and HAP coated type 316L SS at the optimum coating parameters after sintering [1].

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 [11].

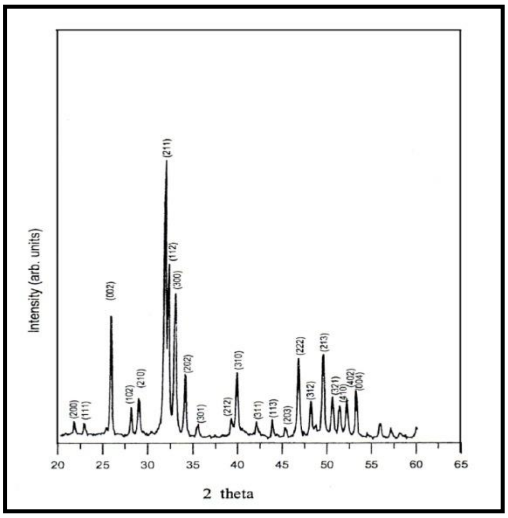

Fig. 5: XRD patterns of HAP coated 316L SS after immersion period.

EDXA analysis

The EDXA spectrum given in figure 6 indicates the presence of intense peaks for Ca, P and Fe, which was similar to that of the coated samples obtained at the optimal coating parameters figure 7. 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 are detected on the surface.

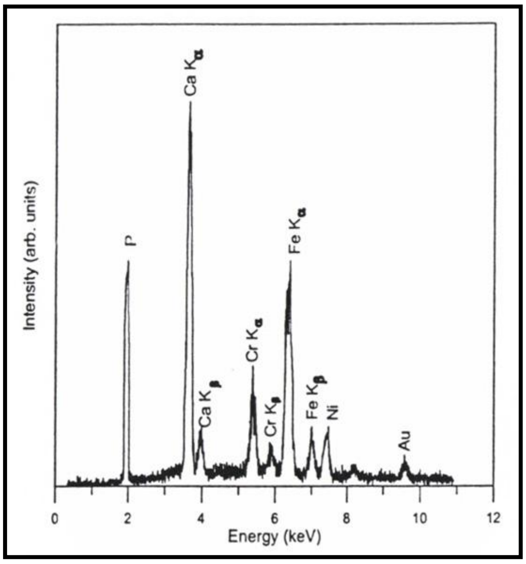

Fig. 6: EDXA Spectra of HAP coated type 316L SS.

Morphological study

The optical micrographs for uncoated 316L SS as shown in (figure 8) immersed in Ringer's solution for 30 days indicated the formation of pits. A number of pits were scattered and a few deep pits were also observed. This suggests that the 316L SS is highly susceptible towards pitting attack in simulated body fluid condition, while figure 9 showed the micrographs of HAP coated type316L SS after immersion for the same period, this fact was also confirmed by [11].

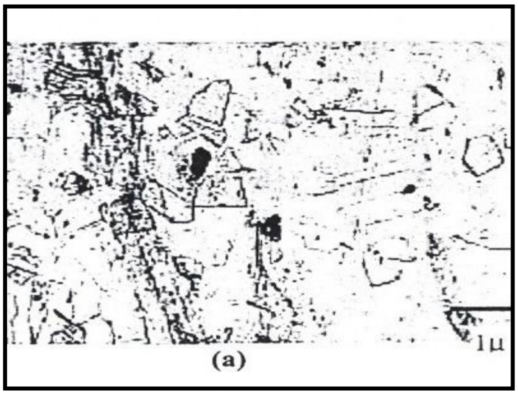

Fig. 8: Optical micrographs of uncoated type316L SS after immersion studies.

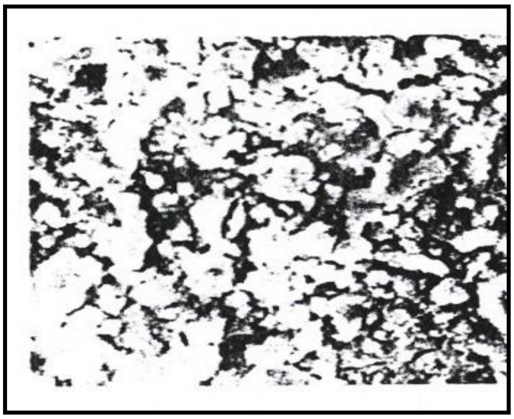

Fig. 9: Optical micrographs of HAP coated type316L SS after immersion studies.

Conclusions:

The results from electrochemical corrosion studies suggest that HAP coating prevent the corrosion process and hence, the release of metal ions by acting as barrier to their transfer from the underlying substrate. This further strengthen the fact that 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. These data also prove the fact that the coating and HAP powder synthesized are crystalline in nature and the absence of other CaP phases after coating.

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تاثير الطلاء بمركب الاحيا- سيراميك على سلوك التاكل لسبيكة الفولاذ المستخدمة في حقل جراحة ا لعظام

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الخلاصة:

العمليات الكهروكيميائية التي تختص بدراسة مقاومة التاكل في مشبهات محاليل الجسم تعتمد على العوامل الحاكمة والمؤثرة اثناء عملية الطلاء (الفولتية المجهزة، سمك طبقة الطلاء ودرجة حرارة التلبيد) .

ان طريقة الطلاء بترسيب الدقائق المشحونة العالقة وجدت كافضل تقنية للحصول على طبقة طلاء منتظم ومستقر لمركب الهيدروكسي ابتايت (هاب) على سطح السبيكة.

في هذا البحث تمت مناقشة نتائج المتغيرات التي تعتمد عليها دراسات التاكل (قياسات الدائرة المفتوحة مع الوقت، الاستقطاب الديناميكي وعمليات الغمر في مشبهات محاليل الجسم) لجميع العينات المطلية بمادة هاب وكذلك غير المطلية لاجل المقارنة بينهما.

لقد اظهرت نتائج غمر النماذج المطلية لمدة 30 يوم في المحلول المحضر و من خلال دراسة صور المايكروسكوب عدم حصول تاكل لتلك العينات وهذا يفسر اهمية الطلاء بمادة هاب لكونها تمنع حصول عملية التاكل اضافة الى التوافقية البايولوجية التي تمتاز بها.