Hydroxyapatite Coating Improved Corrosion Resistance of 316L Stainless Steel Used For Surgical Implants Applications

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Received on: 26/9/2007
Accepted on: 3/1/2008

Abstract

Incidences of failure of stainless steel implant devices reveal the occurrence of significant localized corroding pitting and crevice corrosion. To reduce corrosion and achieve better biocompatibility, the alloy of stainless steel was coated by hydroxapatite (HAP) by electrphoretic depositing method.

The study involves modified surface of 316L stainless steel by coating it with hydroxyapatite by electrophoretic deposition. The method was carried out in various time intervals (from 1 to 5 minutes) at constant potential of 60 V. The electrochemical behavior of 316L stainless steel (uncoated and HAP coated specimens) was studied in simulated human body environment. Synthetic blood plasma was utilized for simulated body fluid conditions.

The corrosion parameters obtained from open circuit potential and potentiadynamic polarization for the specimens indicate nobler shift in the polarization parameters, OCP-time, corrosion potential (E_{rr}) and corrosion current density (I_{corr}), for all coated specimens in comparison with the uncoated specimen. The final corrosion results for the alloy indicated that the specimen coated for 3 minutes was found to be more noble and have optimum corrosion properties compared with the other coated specimens.

الخلاصة

إن حدوثُ الفشل في الزوارع الجراحية المصنعة من الصلب المقاوم للصدأ هو بفعل التآكل. من اجل تحسين خواص التآكل وللحصول على ملائمة بيولوجية أفضل , تم طلاء سبيكة الصلب المقاوم للصدأ بمادة الهايدروكسي ابتايت $(HAP/Ca_{10}(PO_4)_6(OH)_2)$ بطريقة الترسيب (Electrophoretic deposition).

تتضمن الدراسة تحسين سطح الصلب المقاوم للصدأ 316L بطلائه بمـادة الهايدروكسـي ابتايـت (HAP) بطريقة الترسيب (EPD). تم إجراء عملية الطلاء بأزمان طلاء مختلفة (من 1الى5 دقيقة) بثبوت الجهد المسلط 60 فولت. الاختبارات الكهروكيمياوية للصلب مقاوم للصدأ 316L (النماذج المطلية والغيـر مطلية) درِستَ بمحلول بلازما الدم المحضر للحصول على السلوك العام وقيـاس معـاملات الاسـتقطاب للنماذج. تشير نتائج دراسات التآكل التي تضمنت قياس جهد التآكل في الدائرة المفتوحة وقياس الاستقطاب الكاثودي والانودي إلى أن هناك تغير بالاتجاه النبيل لكل من جهد التآكل ومعاملات الاستقطاب لكل العينات المطلية مقارنة بالعينات الغير مطلية. وبينت نتائج التآكل النهائية للسبيكة إن العينة المطلية لفترة زمنيـة 3 دقيقة أكثر نبلا ولها خواص تأكل جيدة مقارنة مع العينات المطلية الأخرى.

1-Introduction

The austenitic stainless steels, especially types 316 and 316L re most widely used for implant fabrication.

Stainless steel that has a low content of impurities and a passivated finish is entirely suitable for implantation in the human body [1].

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https://doi.org/10.30684/ etj.26.8.6
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Many reports of failures due to corrosion of stainless steel implants have been reported. Clinical experiences have shown that they are susceptible to crevice and pitting form of attack in the human body causing release of metallic ions into the tissue surrounding the implants [2]. This may cause local irritation or systemic effects and in some cases removal of implant is necessary moreover in certain instances, allergens reactions do occur. In many countries, it is used both as temporary implant as well as permanent prostheses due to affordable cost and availability when compared to other implant materials [3]. The alternate ways to reduce corrosion of orthopedic are materials selection and surface modification by protective coatings. Surface protective biocompatible coatings are the only way left out to improve the corrosion resistance of the currently used implant materials [4].It is well known that the composition of human bones an inorganic/organic hybrid consisting of 70% apatitic calcium phosphate and 3% organic (largely collagen) constituents by weight. The apatitic calcium phosphate of bone mineral consists of carbonate, small amount of sodium, magnesium and other trace elements.

The submicroscopic crystal of calcium phosphate in bone resembles the crystal structure of synthetic hydroxyl apatite [5].

Bioactive ceramics are dense calcium phosphate based ceramics with a composition and structure similar to that of inorganic components of bone. Of the various calcium phosphate ceramics, hydroxyapatite $Ca10.(PO4)_6$ $(OH)_2$ (HAP) is the vital constituent present in bones and teeth [6]. HAP is the most versatile material used for implantation purposes owing to its similarity with natural bone mineral and its ability to bond to bone. HAP is also known to have a simulating effect on bone formation, which is known as Osseo-induction. It enhances the osseo-intergration, and there are indications that chemical bonding may occur between HAP and bone [7]. These attractive features of HAP are offset by the lack of strength necessary for load bearing applications. Therefore to combine the bioactivity of HAP and the strength of the materials used in orthopedic implants, it can be applied as coatings. Among the various modifications, the coating technologies have emerged as a viable process and have opened up a new possibility for implant and prosthetic devices [8].

Ceramic coated metal implants for prosthetic applications provide the necessary porosity for bone ingrowths, while the underlying metal substrate bear the load and the full weight bearing capacity is ensured soon after surgery. Thus, bioceramics play a twin (dual) role both in preventing the release of metal ions (rendering it more corrosion resistant) and also in making the metal surface bioactive [9]. The performance of bioceramic coatings on metals and alloys are influenced by biocompatibility, thickness, crystallinity, porosity, biodegradation, adhesion, strength, corrosion, wear and fatigue properties. Coating of metals and alloys is accomplished by a host of coating techniques and processes for producing thin, bio-compatible films of calcium phosphate (Ca–P) materials on implant devices, has been the subject of investigation for the past several years. However, the high temperature involved during the coating process or the subsequent heat treatments after deposition causes alteration of the starting material by the creation of considerable amorphous material, the loss of OH from

the HAP structure, and the formation of small amounts of other crystalline phases The bond strength is also somewhat less than that desired in cases where high shear or torsional loading may occur. Bonding is almost exclusively by mechanical interlocking and thus is highly dependent on surface roughness of the substrate [10,11].

2-Experimental Parts

2-1 Materials

The material used in this work was austenitic stainless steel (type 316L). Chemical analysis of this material was carried out using (ARL Spectrometer 3460).

2-2 Specimen preparation

The specimens were cut out in dimensions of (1*1) cm for electrochemical studies. These specimens were ground with SiC emery papers in sequence on 120, 180, 220, 320, 500, 800, 1000, and 1200 grit to get flat and scratch- free surface. The specimens were polished using polish cloth and alpha alumina 0.3µm and washed with tap water followed with distilled water. These specimens were used for microstructure evolution and electrochemical investigation.

2-3 coating

The specimens were cut into small rectangular samples (10*10*2 mm). The specimens were metalographically gritted until 1000 grit using a SiC emery paper and cleaned in water and acetone. The samples were soaked in 5N NaOH solution at 90 °C for 30 minute [12]. The such as tricalcium phosphate.

treated samples were washed with deionized water and dried. The schematic diagram of electrode arrangement in the electophoretic cell, which was used for coating samples, has been reported elsewhere [13]. A500 ml beaker was used as the deposition cell. A regulated D.C. power supply source was used to supply the necessary electric power.

The pH of suspension was determined by a pH meter. The electophoretic deposition coating was carried out for various time intervals (1, 2, 3, 4, 5 minutes) at a constant potential of 60V.

After electophoretic deposition, the cathode sample on which deposition was made was carefully removed and washed carefully in distilled water to remove any adhered suspension. The green deposition was slowly dried in air, followed by heating the samples at 120 °C.

2-4 Electrochemical studies

2-4-1 Solutions

Solutions used in this work were synthetic blood plasma (Chemical Composition is shown in Table 1 with adjusted pH.7.4.

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_2HPO_4	0.126
6	NaH_2PO_4	0.026
7	$MgSO_4$	0.100

Table 1 the chemical composition of synthetic blood plasma [14].

Table 2 A nominal [15] and analytical chemical composition of 316L stainless steel

Element / Alloy	C	Cr	Ni	Mn	Si	P	S	Mo	N	Fe
ASTM	**0.03 Max**	**16-18**	**10-14**	**2.00 Max**	**0.75 Max**	**0.045 Max**	**0.03 Max**	**2-3**	**0.10 Max**	**Balance**
Analytical	**0.027**	**16.18**	**11.81**	**1.61**	**0.67**	**0.02**	**0.01**	**2.2**	**0.08**	**Balance**

Table 3 The thickness of layer HAP coating with various time intervals.

Coating	1	2	3	4	5
Thickness layer (μ)	50	61	73	85	98

Table 4 Electrochemical parameters of uncoated and HAP coated type 316L stainless steel obtained for various time intervals at constant potential of 60V.

Coating time (minute)	E_{corr}, mV SCE	I_{corr} mA/cm^2	C.R mpy
1	-20	$1.8*10^{-9}$	$7.5*10^{-10}$
2	-12	$1.6*10^{-9}$	$6*10^{-10}$
3	+37.5	$1*10^{-9}$	$4.1*10^{-10}$
4	+15	$1.6*10^{-9}$	$6.7*10^{-10}$
5	-58	$1.4*10^{-9}$	$5.8*10^{-10}$
uncoated	-280	$700*10^{-9}$	$30000*10^{-10}$

immediately the initial potential of the specimens was noted and monitored as a function of time up to 100 min.

2-4-3 Potentiodynamic polarization test

Potential dynamic polarization was carried out in synthetic blood plasma at pH adjusted to 7.4 and temperature 37°C±1°C for both as uncoated and hydroxyapatite coated for various time intervals. All the potential measurements' were made with reference to a standard calomel electrode (SCE). A platinum foil was used as counter electrode and potentiostate (potentiostate type PRT 10-0.5-TACUSSEL, ELECTRNIQU Co. France) was used for conducting the polarization experiment. When the specimen attained a constant potential, potentiodynamic polarization was started from an initial potential of 250 mV below the open circuit potential and the scan was continued up to +600mV.

The specimen was scanned in the positive direction at a sweep rate of (1mV/sec) and the current was recorded with respect to the potential.

2-4-2 Open circuit potential (OCP)

The aim of the OCP-time measurement is to understand the corrosion behavior of the coated and uncoated specimens under equilibrated conditions in the simulated body environment. The OCP-time measurement is considered as an important parameter for evaluating the stability of the passive film of the specimens. The specimens were immersed into the electrolyte and

3- Results and Discussion

3-1 Elemental Analysis

Table 2 shows the nominal and the analytical chemical compositions of 316L stainless steel used in this Study.

3-2 Characterization of hydroxyapatite coating

The surface of the coating becomes rougher with increase in coating time. The use of high time intervals (Above 5 min) results in significant hydrogen evolution at the cathode, which in turn increases the porosity of the deposit [16].

Loss of thicker coating from the metal surface was observed due to adhesion that occurs between the surface and the coating.

Figures (1 a) and (2 b) show the coating specimen and cross-section specimen respectively. The coating layer obtained in various time intervals (1-5 minutes) resulted in high purity, stability on specimens, uniform distribution, high layer adhesion, no significant hydrogen evolution was observed. The surface roughness and sintering temperature affect the stability of HAP coating layer on specimens. The surface finish of resulting coating depends on pH of the bath composition. At pH 7.2, the bath coating of surface with thickness to be about 50-100 ±2 µm depends on the duration of coating. At the coating of 6 minutes, the thickness increases to about (105µ) but

hydrogen evolution is observed. The different thicknesses with various time coatings are showed in Table 3.

3-3 Electrochemical studies

3-3-1 Open circuit potential (OCP)

The variations in the open circuit potential (OCP) of the uncoated type 316L stainless steel and hydroxyapatite (HAP) coated specimens at different time intervals are illustrated by the potential time curves in Figures (2,3,4,5,6,7).

Figure (2) shows the OCP' s measured for uncoated 316L stainless steel, the potential generally changes from an initial negative value -460mV (SCE) to the positive direction -288mV (SCE) within about 50 minute and the Potential remains stable at this value for more than 50 minute. The increase in potential in the positive direction in this case may be due to stable passive film. 316L stainless steel contains enough chromium to confer corrosion resistance by passivity [17]. The OCP' s measured for specimens coated for 3 minute and 4 minute (Figures 5 & 6) were found to shift towards passive direction continuously with the time and very low positive OCP values were recorded (+31mV (SCE) and +12mV (SCE) respectively) indicating strong surface passivation. This ensures the high purity of HAP layers form desired thickness and high layer adhesion to substrate, rendering it more corrosion resistant [18]. Remarkable shift in the OCP – time towards the noble direction was observed in comparison to uncoated 316L stainless steel.

3-3-2 Potentiodynamic polarization

It is very important to evaluate the susceptibility to localized corrosion of the material under study, which can be determined by means of potentiodynamic polarization curves. The main parameters that can be obtained from these curves are the corrosion potential (E_{corr}), and the corrosion current density (I_{corr}). The potentiodynamic polarization for uncoated and hydroxyapatite coated specimens are presented in Figures (8 to 13).All figures show cathodic and anodic polarization curves of uncoated and hydroxyapatite coated specimens in synthetic blood plasma solution. These figures indicate that corrosion potential has less negative value than that for uncoated specimens; this means that the corrosion potentials of coated specimens are more noble than that for uncoated specimens. The nature of polarization curve indicates that the anodic dissolution current of uncoated specimens is larger than that for HAP coated specimens and the barrier films on the HAP coated specimens are formed quickly in comparison with the type of 316L stainless steel due to uniform coating layer and decohesion between the surface and the coating. The curves of HAP coated specimens show a similar corrosion behavior except the differences in the corrosion potential and other parameters. The minimum corrosion rate is observed on coating specimen at 3minutes coating time. This may be related to surface uniform HAP coating layer.

4- Conclusion

The electrochemical behavior of uncoated and hydroxyapatite coated 316L stainless steel 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.

The anodic polarization and immersion studies clearly reveal that various time intervals in HAP coated play important role in corrosion behavior of type 316L stainless steel. The specimen coated for 3 minutes exhibits superior corrosion behavior.Hydroxyapatite coating obtained by electrophoretic deposition proves as available alternative for improving the corrosion resistance of type 316L stainless steel for enhancing the biocompatibility of the implant devices.

Hydroxyapatite ceramics obviously show attractive properties, such as lack of toxicity, absence of intervening fibrous tissue, the possibility of forming a direct contact with bone and the possibility to simulate bone growth.

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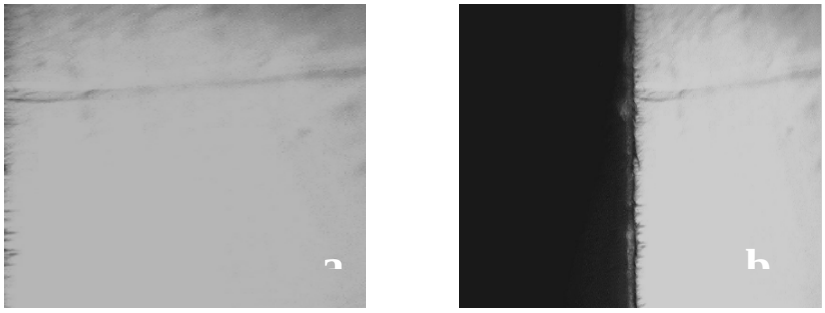

Figure 1 The hydroxyapatite coating;(a) Surface coated specimen (b) Cross- section of coated specimen

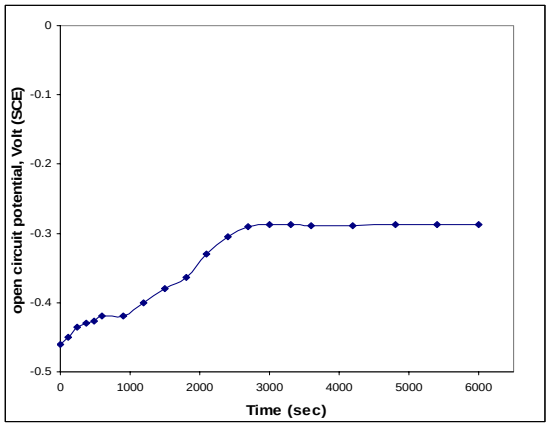

Figure (2) Open circuit potential (OCP) versus time in synthetic blood Plasma solution for uncoated 316L stainless steel.

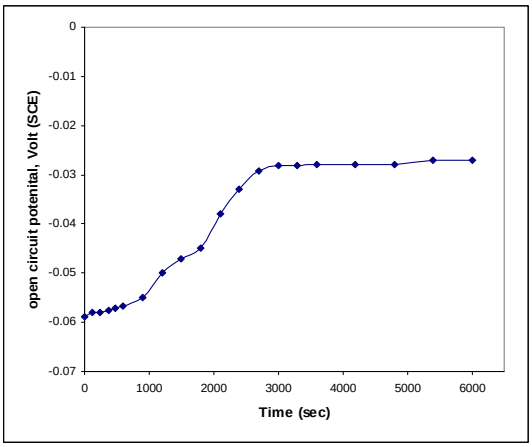

Figure 3 Open circuit potential (OCP) versus time in synthetic blood Plasma solution for HAP coated 316L stainless steel at 1 minute immersion

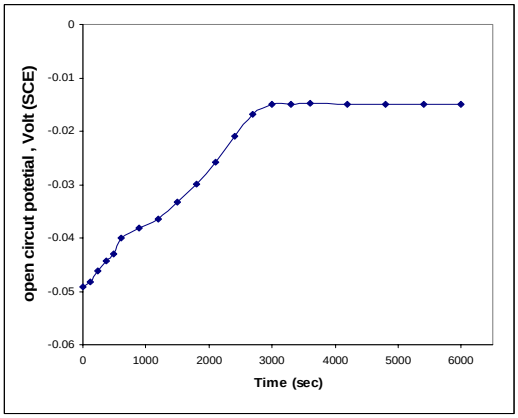

Figure 4 Open circuit potential (OCP) versus time in synthetic blood

Plasma solution for HAP coated 316L stainless steel at2 minute mumersion.

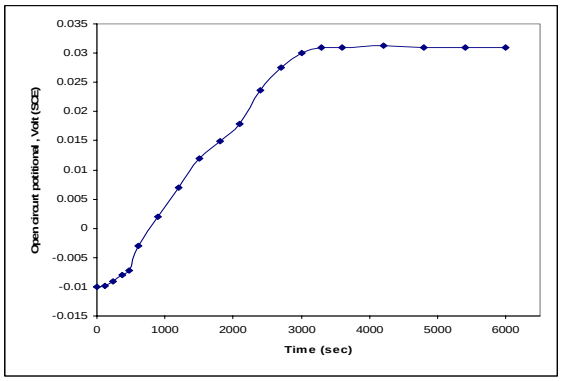

Figure 5 Open circuit potential (OCP) versus time in synthetic blood Plasma solution for HAP coated 316L stainless steel at 3 minute immersion.

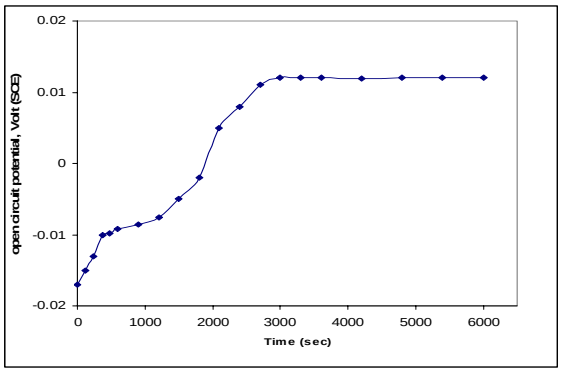

Figure 6 Open circuit potential (OCP) versus time in synthetic blood Plasma solution for HAP coated 316L stainless steel at4 minute immersion.

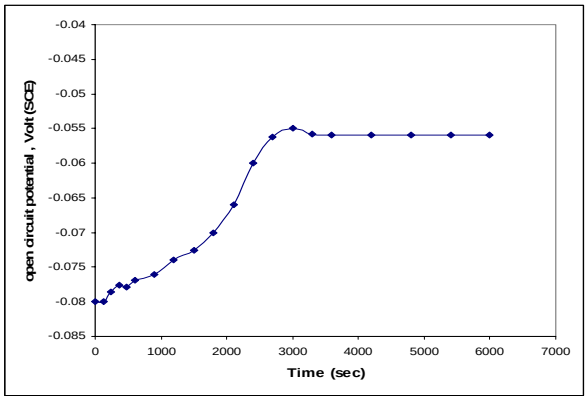

Figure 7 Open circuit potential (OCP) versus time in synthetic blood Plasma solution for HAP coated 316L stainless steel at5 minute immersion.

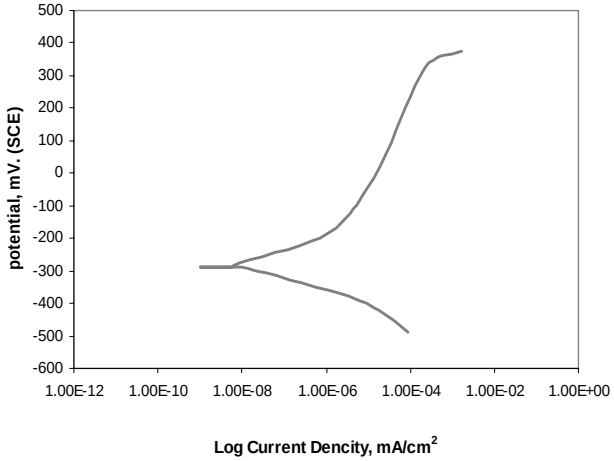

Figure 8 Potentiodynamic polarization behavior for uncoated Type 316L stainless steel in synthetic blood plasma Solution at sweep rate of 1mV/sec.

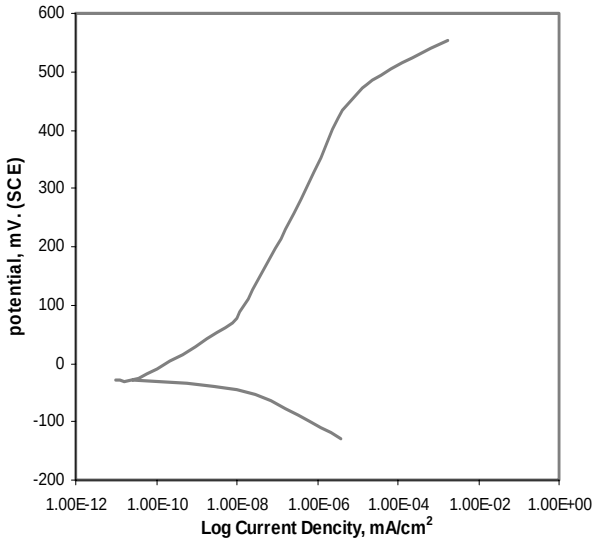

Figure 9 Potentiodynamic polarization behavior for HAP coated for 1 minute type 316L stainless steel in synthetic blood plasma Solution at sweep rate of 1mV/sec.

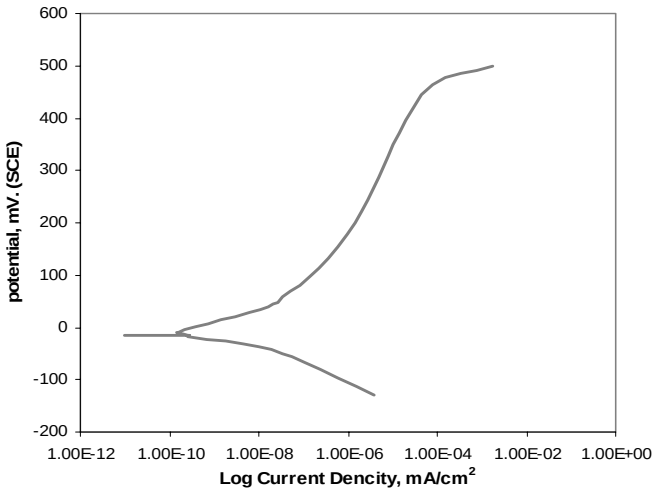

Figure 10 Potentiodynamic polarization behavior for HAP coated for 2 minute type 316L stainless steel in synthetic blood plasma Solution at sweep rate of 1mV/sec.

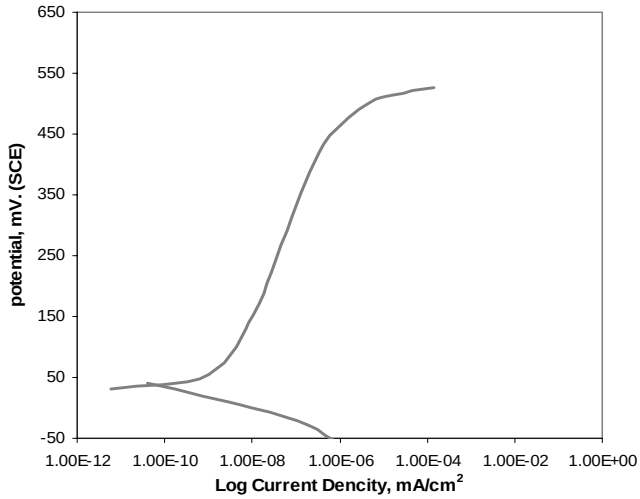

Figure 11 Potentiodynamic polarization behavior for HAP coated for 3 minute type 316L stainless steel in synthetic blood plasma Solution at sweep rate of 1mV/sec.

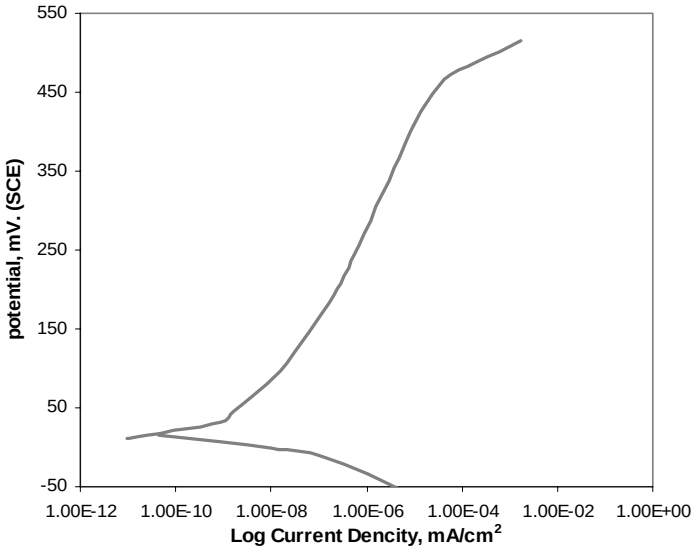

Figure 12 Potentiodynamic polarization behavior for HAP coated for 4 minute type 316L stainless steel in synthetic blood plasma Solution at sweep rate of 1mV/sec.

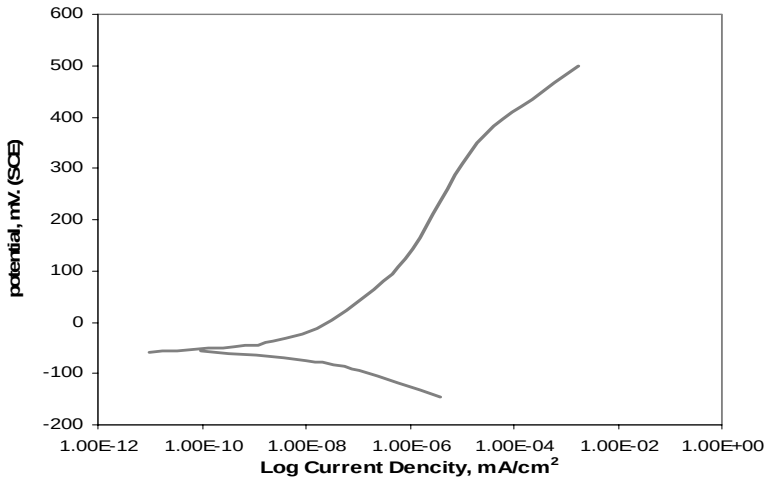

Figure 13 Potentiodynamic polarization behavior for HAP coated for 5 minute type 316L stainless steel in synthetic blood plasma Solution at sweep rate of 1mV/sec.