Corrosion Behavior and Biocompatibility of Hydroxyapatite Coating on H₂SO₄ Passivated 316L SS for Human Body Implant

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The aim of this studies at simultaneous improvement of the corrosion behavior and biocompatibility of metallic implant and bone Osseointegration simultaneously. Stainless steel 316L (SS) was used as metallic substrate and after surface treatment with 15 vol.% sulfuric acid, it was coated with hydroxyapatite coating employing plasma – spraying process. Structure characterization techniques including XRD, SEM and EDX were also utilized to investigate the microstructure, morphology, and crystallinity of the coating. Electrochemical potentiodynamic tests were performed in two types of physiological solutions in order to determine and compare the corrosion resistance behavior of the coated and uncoated specimens as an indication of biocompatibility.

The results indicate that the surface treatment and hydroxyapatite coating improve the corrosion resistance behavior of SS. The corrosion current density of the surface treated and the hydroxyapatite coated SS also decrease. These also show that surface treated and hydroxyapatite coated SS can be used as human body implants with the goals of corrosion resistance improvement (biocompatibility) and bone osseointegration.

KEY WORDS: Surface treatment; Hydroxyapatite coating; Corrosion behavior; Plasma spray; Stainless steel 316L; Human body implant

1. Introduction

Biocompatibility is ability of materials to perform with an appropriate host response in a specification application^[1–3]. Since the human body is particularly favorable for the biodegradation of metals due to its ionic, microbiological and enzymatic properties, it can be presumed that the patient is exposed to a certain extent to products of the corrosion process^[4]. Also chloride ions are the most aggressive species existing in the body^[5,6].

The most common materials suitable for metallic implants are austenitic stainless steel, cobalt-chromium alloys and titanium and its alloys^[7]. The austenitic stainless steel is most popular materials because of their relatively low cost, ease of fabrication

and reasonable corrosion resistance and the good mechanical properties in the cold worked condition and availability at low cost, but clinical experience has shown that they are susceptible to localized corrosion in the human body causing the release of metal ions into the tissues surrounding the implants^[1,8]. The corrosion products include iron, chromium, nickel and molybdenum ions^[4]. Leach chromium and especially nickel ion toxic species and powerful, allergens have been shown to be carcinogenic in rats^[6]. This release of ions depends on the corrosion rate of the alloy and the solubility of the first formed corrosion products^[7]. Thus corrosion is aspect in the evaluation of biocompatibility^[9]. Biocompatibility of the alloys mainly has a relationship with corrosion. An alloy that have higher corrosion, release more metallic elements and corrosion products in body and increase the unwanted hazardous reactions with tissue^[6–8]. Intensive investigations have been carried out on biomaterials in order to study their corrosion behavior,

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Table 1 Chemical composition of AISI 316L SS type (wt.%)

Cr	Ni	Mo	Mn	P	C	Si	S	Fe
17.55	13.65	3.1	1.2	≤0.040	0.03	≤0.80	≤0.030	Bal.

ion release and its effects, toxicity and immunity of alloys^[6–11].

Nowadays, surface engineering technology by making suitable coatings on the metal surface or performing surface modification treatment can improve corrosion behavior and raise the biocompatibility of the metals and consuming alloys in medicine and dentistry^[12]. Advanced techniques have been used for determining toxicity and tissue reaction around metal implants^[13,14]. In vitro evaluation of corrosion behavior of metals in body simulation conditions can obtain a good predication of their biocompatibility^[15]. Ion release rates in vitro can be used to determine the proportionality of release in vivo but long-term in vivo studies have been made and results indicate that metal ion release increases with the exposure time^[16,17].

Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA) is a biocompatible and bioactive ceramic. However, it cannot be directly used for making implant devices because of its brittleness and strength limitations and hence a great seal of research concentrates on the development of Hydroxyapatite coatings (HAC) and composites^[18]. One reason for used of HAC is to cause earlier stabilization of the implant where the healing time is reduced^[18,19]. HA has reached a significant level of clinical application as a coating for fixation of implants^[19,20]. HAC have been used on dental implants and orthopedic prostheses for more than a decade. They have provided a rapid and stronger fixation to surrounding bone. In the metallic implants, the osteoconductive effect of HA has produced enhanced bone growth and could be a key factor in increasing implant fixation^[21]. The HA coatings provide stable fixation of the implant to bone and minimize adverse reaction by provision of biocompatible phase and enhance bone in growth into the pores. Moreover, the HAC decrease the release of metal ions from the implant to the body and shield the metal surface from environmental attack^[22].

Many techniques have been investigated for coating of HA on metallic surfaces, including flame, plasma and high velocity oxyfuel spraying, ion beam sputtering, chemical vapor deposition, electrochemical and electrophoresis deposition^[20–22]. Among these techniques plasma spraying is the most popular method for coating implants with HA. Despite the successful application of plasma-sprayed coatings in the biomedical field, there has still been a great interest among material scientists and orthopedists to develop these coatings to meet the increasing demands of patients^[18–24].

The aim of the present study is to design a multi-purpose coating (surface treatment and HA coating)

on metallic implants in order to optimize the corrosion behavior as an indication of biocompatibility and improvement in histological response, tissue reaction and bone osteointegration, simultaneously.

2. Experimental

2.1 Materials and samples preparation

Type 316L SS was used as the metal substrate and the elemental composition is given in Table 1. Type 316L SS alloy was cut into 20 mm × 15 mm × 2 mm pieces. Prior to study, the 316L SS samples were polished using silicon carbide papers of 120–1200 grit. Final polishing was done using silicon carbide papers 2500, 4000 grit in order to produce scratch-free mirror-finish surface. The polished specimens were examined under optical microscope for the presence of pits or scratches on the surface. The polished specimens were degreased with acetone and thoroughly washed with distilled water. The specimens used for passivating in H_2SO_4 was followed by cleaning in acetone for 10 min and finally the sample was rinsed in distilled water, dried and used for further studies.

2.2 Surface treatment process by H_2SO_4 acid

The entire sample surface was subjected to surface treatments of complete immersion in 15 vol.% sulfuric acid (H_2SO_4) for 1 h. it is important to note that all immersions were carried out at room temperature. After surface treatment by acid, the samples were washed with running distilled water and dried by heater for 30 min. Energy dispersive analysis of X-rays (EDX) technique were utilized to investigate the condition of treated surface. The Surface treated samples were characterized by EDX technique to evaluate the situation of passive layer on surface.

2.3 Hydroxyapatite coating

After surface treatment with 15 vol.% sulfuric acid, crystalline hydroxyapatite coating with 40–60 μm was produced using plasma-spraying technique on AISI 316L stainless steel.

2.4 Experimental procedure

X-ray diffraction (XRD) technique (Philips X'pert –MPD System with a CuK_α wavelength of 0.15418 nm) was used to analyze the structure and phases presented in the hydroxyapatite coating. This technique was also used to estimate the percentage

Table 2 Mean values (standard deviation) of the corrosion current densities (i_{corr}) and corrosion potentials (E_{corr}) in normal saline solution at 37 °C

Material	E_{corr} (mV)	i_{corr} (nA/cm ²)	
		Tafel	Linear
Pristine 316L SS	-174 ± 20	265 (16)	194(16)
15 vol.% H ₂ SO ₄ treated 316L SS	-100 ± 25	57 (5)	49(3)

Table 3 Mean values (standard deviation) of the corrosion current densities and corrosion potentials in Ringer's solution at 37 °C

Material	E_{corr} (mV)	i_{corr} (nA/cm ²)	
		Tafel	Linear
Pristine 316L SS	-195 ± 20	218 (17)	181 (20)
15 vol.% H ₂ SO ₄ treated 316L SS	-75 ± 25	38 (6)	27 (3)

of crystalline of the HA coating. Scanning electron microscopy (SEM) (Philips XL 30) was used to investigate the microstructure and morphology of the coating. EDX analysis was utilized to estimate the ratio of Ca to P of HA coating and the composition of the coating.

In order to perform potentiodynamic polarization electrochemical experiments, pristine 316L SS specimens and surface treated and hydroxyapatite coated 316L SS specimens were subjected to physiological solution in the temperature of 37 °C in order to obtain desired equilibrium. Prior to each test, the surface dimensions of specimens in contact with the electrolyte were measured. An electrochemical corrosion polarization test cell was used for in vitro potentiodynamic corrosion tests in physiological solutions. Graphite electrode was used as the counter electrode and saturated calomel electrode (SCE) as a reference electrode. Physiological normal saline (0.9 wt.% NaCl) and Ringer's solution (NaCl 8.6 g/L, CaCl₂·2H₂O 0.66 g/L and KCl 0.6 g/L) were solutions that were used as electrolytes. Dynamic polarization curves were recorded at a potential scanning rate of 0.5 mV/s initiated at -250 mV below the open circuit potential and atmosphere was open to air. In order to evaluate and compare the corrosion behavior of surface treated specimens, coated and uncoated specimens were dynamically polarized in two different types of physiological solutions. Potentiodynamic polarization curves were determined at (37±1)°C (controlled by Eyelathermistor Temppet T-80) using an EG&G model 263A Potentiostat/galvanostat interfaced with a computer and a recorder. The tests were started after a steady open-circuit potential was attained (not more than ±5 mV drift in 5 min). The anodic and cathodic polarization curves were obtained for each specimen and corrosion current densities were determined by Tafel extrapolation and linear polarization methods. The mean value and standard deviation of the results were calculated.

3. Results

3.1 Evaluation H₂SO₄ treatments

Potentiodynamic polarization curves of the surface

treated and pristine specimens in normal saline solution and Ringer's solution have been shown in Fig. 1 and Fig. 2, respectively. The mean values (standard deviation) of corrosion current densities and corrosion potentials in normal saline and Ringer's solution are given in Table 2 and Table 3, respectively. Comparing the corrosion behavior of the specimens shows that current corrosion density of type 316L SS in the normal saline solution without surface treatment (i_{corr} =265 nA/cm²) is more than the specimens treated. In the other hand, pristine 316L SS in the normal saline solution has the lowest corrosion resistance and the samples treated in H₂SO₄ have more corrosion resistance in the similar solution. In Ringer's solution corrosion behavior of specimens is similar to normal saline solution. Consequently, type of the solution or electrolyte does not affect on classification of substrate corrosion resistance. Surface treatment has a considerable effect on corrosion behavior of type 316L SS. Corrosion potential of the surface treated stainless steel (E_{corr} =-100 mV, i_{corr} =57 nA/cm²) in normal saline solution is more noble in comparison with the pristine 316L SS (E_{corr} =-174 mV). Corrosion current density

Fig. 1 Potentiodynamic polarization curves of the pristine 316L SS (a) and surface treated 316L SS (by 15 vol.% H₂SO₄, immersion period of 1 h) (b) in the normal saline solution (0.9 wt.% NaCl) at 37 °C

Table 4 Electrochemical parameters of surface treated 316L SS in normal saline solution

Material	Break down potential	Repassivation potential
	E_b (mV)	E_p (mV)
Pristine 316L SS	+341	−171
15 vol.% H ₂ SO ₄ treated 316L SS	+637	+139

Fig. 2 Potentiodynamic polarization curves of the pristine 316L SS (a) and surface treated 316L SS (b) (by 15 vol.% H₂SO₄, immersion period of 1 h) (b) in the Ringer's solution at 37 °C **Fig. 3** Cyclic polarization curves of the pristine 316L SS (a) and surface treated 316L SS (by 15 vol.% H₂SO₄, immersion period of 1 h) (b) in the normal saline solution (0.9 wt.% NaCl) at 37 °C

of surface treated type 316L SS which was treated in H₂SO₄ (i_{corr} =57 nA/cm²) and in normal saline solution decreased considerably in comparison with the pristine 316L SS (i_{corr} =256 nA/cm²). The same behavior in Ringer's solution is considered.

3.2 Cyclic polarization experiment

Table 4 shows the electrochemical parameters of types of surface treated 316L SS in comparison with the pristine 316L SS. It is clear that surface treatment in H₂SO₄ improve the E_b and E_p in comparison with the pristine type 316L SS. Cyclic polarization curves of the surface treated and pristine 316L SS are shown in Fig. 3. The result shows that the surface treated type 316L SS ability to close the pits is improved this behavior is due to stable chloride complex formation that leads to reduction of chloride ion concentration in the pit and repassivation of the pit.

3.3 Structural characterization of HA coatings

Molybdenum is an alloy element with a strong beneficial influence on the pitting resistance of the stainless steel. Molybdenum chloride salts have a low solubility in aqueous solution, whereas chromium and iron chlorides are soluble. The formation of stable chloride complexes may lower the concentration of free chloride ions within the pit enough to allow repassivation^[25]. Pure molybdenum cannot form three-dimensional passive film, but is used as an alloying element in stainless steel to participate in the

passive film formation. Six-valence molybdenum exists on the concentrated surface. Two type of six-valence molybdenum are MoO₃ that solves in acidic electrolytes and MoO₄^{2−} with more stability^[26]. The formation of passive films on 316L SS due to the surface treatment of H₂SO₄ appears to follow the bipolar duplex membrane. The bipolar model proposed that CrO₄^{2−} and the more abundant MoO₄^{2−} anions may convert the intrinsically anion selective hydrated oxides to cation selective phases. The deprotonation reaction may follow course^[24–26].

The XRD patterns of the plasma-sprayed HA coating on surface treated stainless steel is shown in Fig. 4. There are numerous sharp peaks and low background indication of highly crystalline HA coating. The SEM micrograph showing a typical plasma-sprayed HA coating on a surface treated 316L SS substrate is shown in Fig. 5. The structure appears to be partially melted and porous and micro cracks can be observed scattered throughout the structure, probably as a result of a very rapid cooling rate during the deposition process. The SEM micrograph showing the cross section of the surface treated and HA coated on a 316L SS substrate is shown in Fig. 6. The result of EDX analysis of HA coating surface is shown in Fig. 7 and Table 5. The stoichiometric molar ratio of calcium to phosphorus (Ca/P) in HA is 1.67; however, it varies from 1.2 to almost 2 in HA. The Ca/P=2.01 is a desirable ratio, because HA is pure and has a

Table 5 Relative concentration (wt.%) for elements of 316L SS due to H₂SO₄ surface treatment process that is obtained by EDX analysis technique

Material	Fe	Cr	Ni	Mo	O
Pristine 316L SS	66.21	17.74	9.38	1.71	4.95
15 vol.% H ₂ SO ₄ treated 316L SS	65.92	17.86	8.44	2.51	5.27

Fig. 4 XRD pattern of the HA coating on surface treated 316L SS **Fig. 5** SEM micrograph of a typical HA coating on surface treated 316L SS substrate shows partially melted with some porosity and micro cracks **Fig. 6** SEM micrograph of cross section of HA coating on surface treated 316L SS shows HA layer on the substrate

crystal structure. In fact, it does not contain other elements such as carbon, iron and nitrogen which may be formed during plasma spray procedure for coating HA on metal surface^[27].

Fig. 7 EDX analysis of HA coating on surface treated 316L SS (desirable Ca/P is obtained) **Fig. 8** Potentiodynamic polarization curves of the pristine 316L SS (a) and HA coating on surface treated 316L SS (b) in the normal saline solution (0.9 wt.% NaCl) at 37 °C

3.4 Corrosion behavior

The potentiodynamic polarization curves of the uncoated 316L SS and surface treated and HA coated 316L SS in normal saline solution are shown in Fig. 8. The similar curves that are obtained in Ringer's solution are plotted in Fig. 9. These curves are selected because their extracted data were the most nearest to the mean values of the current densities of each group of specimens.

The mean values (standard deviation) of the corrosion current densities and corrosion potentials in normal saline and Ringer's solution are given in Table 6 and Table 7, respectively.

According to Table 6 and Fig. 8, the uncoated 316L SS possesses lower corrosion resistance and thus higher corrosion current density ($E_{\text{corr}} = -174$ mV,

Table 6 Mean values (standard deviation) of corrosion current densities and corrosion potentials in normal saline solution at 37 °C

Material	E_{corr} (mV)	i_{corr} (nA/cm ²)	
		Tafel	Linear
Pristine 316L	−174±20	265 (16)	194 (16)
15 vol.% H ₂ SO ₄ treated 316L SS with HA coating	−115±15	56 (4)	37 (3)

Table 7 Mean values (standard deviation) of corrosion current densities and corrosion potentials in Ringer's solution at 37 °C

Material	E_{corr} (mV)	i_{corr} (nA/cm ²)	
		Tafel	Linear
Pristine 316L	−195±20	218 (16)	181 (16)
15 vol.% H ₂ SO ₄ treated 316L SS with HA coating	−117±10	45(3)	33 (2)

Fig. 9 Potentiodynamic polarization curves of the pristine 316L SS (a) and surface treated 316L SS with HA coating (b) in the Ringer's solution at 37 °C

$i_{\text{corr}}=256$ nA/cm²) in normal saline solution in comparison with the coated substrate. The similar trend could be observed in Ringer's solution ($E_{\text{corr}}=-195$ mV, $i_{\text{corr}}=218$ nA/cm²). The surface treated and HA coated had a significant effect on corrosion behavior of 316L SS so that the corrosion density of the surface treated and HA coated 316L SS decreased ($i_{\text{corr}}=56$ nA/cm²) in normal saline solution. Surface treatment could decrease the corrosion current density of the surface treated 316L SS in both type of the physiological solutions (Table 6 and Table 7).

4. Discussion

Previous studies by other researchers showed that austenitic stainless steels normally have excellent corrosion resistance in oxidizing media, but they are very prone to corrosion in acids like H₂SO₄. It is well known that the corrosion resistance of virtually all stainless steels against non-oxidizing acids can be remarkably increased depending on the alloying elements of composition. Type 316L SS samples without

any additions are passive when expose to H₂SO₄. Selective dissolution of Fe and surface enrichment of Cr and Mo was found on exposure to 1 mol/L H₂SO₄. The surface treatment can be used for improving corrosion behavior and biocompatibility of 316L SS^[28].

Also previous in vitro studies by other present authors showed single HA coating could decrease the corrosion current density of the stainless steel substrate in physiological solutions ($E_{\text{corr}}=-105$ mV, $i_{\text{corr}}=68$ nA/cm²). But this effect was not adequately complete. This was due to the fact that the structure and surface morphology of the single HA coating consists of porous surface and some micro crakes (Fig. 5) and could not act as a barrier to release of metal ions from metallic implant to physiological solutions and corrosive environment. The HA coating acted simply as a semi-mechanical barrier. Although the substrate contacts with the solution in the micro cracks and pores of the HA coating, the corrosion rate was drastically reduced^[29].

Many attempts have been made for improvement and optimization of the implant surface conditions by creating a bioceramic coating on implant surface^[30,31]. In this case the surface treatment and bioceramic coatings have been recently considered by a number of research works for improvement of biomedical applications and offering potential clinical benefits in orthopedic and dental surgery^[28–32].

The in vitro electrochemical polarization corrosion tests results indicate that the surface treated and HA coated have a beneficial and desired effect on corrosion behavior of 316L SS. This can improve the corrosion resistance (Fig. 5 and Fig. 6) and subsequently can be decrease the release of metallic ions and consequently prevention of tissue damages, inflammation and irritation and obtain desirable histopathological response. The second improvement is in terms of bone osteointegration and bone bonding with the coated implant. The polarization curve (b) in Fig. 8 of the surface treated and HA coated 316L SS was shifted to the left upper area, compared with curve (a), which is the uncoated 316L SS spec-

imen. It means that the surface treated and HA coated 316L SS ($E_{\text{corr}}=-115$ mV, $i_{\text{corr}}=56$ nA/cm²) were more corrosion resistance than uncoated 316L SS ($E_{\text{corr}}=-174$ mV, $i_{\text{corr}}=256$ nA/cm²) and were near to single HA coated commercially pure Ti ($i_{\text{corr}}=44$ nA/cm²) with attention to pervious in vitro study by other present authors^[32–34].

5. Conclusions

Surface treated and HA coated 316L SS can be used as a human body implants and two goals including improvement of corrosion resistance and bone osteointegration can be obtained simultaneously that lead to earlier stabilization of the implant in surrounding bone and reducing the healing time.

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