The Effect of Surface Treatment on Corrosion behavior of Surgical 316L Stainless Steel Implant

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Abstract

The AISI 316 L Stainless Steel (SS) specimens were exposed to passivation surface through two different processes including; holding in 40-vol% HNO_3 at temperature of 60 °C for 30min and 15-vol%H_2SO_4 at ambient temperature for 1 hour. The corrosion behavior of specimens was evaluated in physiological solutions by electrochemical in vitro tests through linear and Tafel polarization tests. Cyclic polarization tests were performed for investigating of the specimen's resistance against pitting. Finally, the corrosion resistance of untreated and modified specimens was compared. The results show that the corrosion resistance of 316L SS metallic implant is increased due to passivation surface treatment.

Keywords: Surgical Implant, 316L Stainless Steel, Corrosion Behavior, Surface Treatment, Biocompatibility.

1. Introduction

Metals and alloys have a wide application in dentistry, medicine, orthopaedic and bone fractures as a component of an artificial implant or restored materials. Nowadays, alloys with the ability of passive layers formation on the surface are used for biomaterial applications [1]. Austenitic stainless steel (SS) are the alloys of great interest in technological applications where materials with high corrosion resistance are required. The stability of passive film formed on austenitic stainless steels depends mainly on the alloy composition, temperature, passive time and working environment [1-2]. It is highly probable that electronical structure of oxide films also play a major role when their protective character is considered. Oxide film on the surface of stainless steel consists of two regions; first the inner region that mainly chromium oxide forms it and the outer region that mostly consists of iron oxide and nickel oxide. Stoichiometry of inner layer is approximately constant (Cr_2O_3). Surface engineering technology by making suitable coatings on the metal surface or performing surface modification treatment can improve corrosion behavior and increase the biocompatibility of metals and consuming alloys in medicine and dentistry. Common consuming metals that are being used in implants may expose to corrosion in the body and this leads to poisonous effects. In order to use metals and alloys, it is necessary to study and investigate their biocompatibility. The most fundamental characteristic of biomaterials that are being used as an implant in the body is the biocompatibility characteristic. Biocompatibility is the ability of a material to perform with an appropriate host response in a specific application [1-2]. In fact, biocompatibility means that the tissue of the patient that comes into contact with the materials doesn't suffer from any toxic, irritating, inflammatory, allergic, mutagenic or carcinogenic action [1-2]. Biocompatibility of alloys mainly has a relationship with corrosion. An alloy that have higher corrosion, release more metallic elements and corrosion products in the body and increase the unwanted hazardous reactions with tissue. However, every metallic element that is released in tissue dose not cause important and considerable problems, but nickel and chromium can cause allergy and local problems due to their toxic effects. For this reason, metallic implant corrosion evaluation, particularly stainless steel that is used in the body has been admitted over years [2]. Various methods and techniques of experimental and clinical tests have been used to evaluate corrosion and effects of different environments on stainless steel implants and corrosion in alive existing body and the consequences. Electrochemical experiments such as potentiodynamic polarization in physiological solutions have been commonly used. Nowadays, metallic alloys that are being used in surgical implants are austenitic stainless steel, titanium alloys and chromium-cobalt alloys. Advantages of stainless steels compare with other materials are low cost, mechanical properties related to bone mineral, acceptable corrosion resistance and ease of fabrication [2-3].

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Austenitic stainless steels are prone to localized corrosion in longtime applications because of harsh biological effects. In fact, chromium oxide passive film on the surface of the metal is unstable because of harsh environment. Therefore, corrosion products that consist of iron, chromium, nickel and molybdenum release in the body. Ions can be gathered in tissue around the implants or covey to the other parts of the body. A lot of reports have been suggested about the passivation of metallic alloys in oxidizing environment such as NaOH and HNO_3 in order to increase corrosion resistance and prevent corrosion, but a few have reported on the possibility of passivation in non-oxidising media. The environmental behaviour of 316L SS containing noble alloying elements was reported previously [3]. It was found that the noble alloying elements enhance the self-passivation process and enable passivation even in the samples with some degree of porosity. Type 316L SS type without any additions are passive when expose to H_2SO_4 [4]. Selective dissolution of Fe and surface enrichment of Cr was found on exposure to 1M H_2SO_4.It is well known that the corrosion resistance of virtually all stainless steels against non-oxidising acids can be remarkably increased depending on the alloying elements in composition.In this research, the tendency of type 316L SS in nitric acid and sulfuric acid to form passive film and the nature of passive film on the surface of type 316L stainless steel were explored. Electrochemical studies were employed in order to assess corrosion behaviour of type 316L SS in physiological solutions that are similar to body fluid [4-7].

2. Method and Materials
2.1. Sample preparation

Type 316L SS was used as the metal substrate in the form of plate and its elemental composition is given in Table 1. Type 316L SS alloy was cut into pieces 20 mm × 15 mm × 2 mm size. The samples were polished using silicon carbide papers of 120, 220, 320, 600, 1200 grit. Final polishing was done using silicon carbide papers of 2500, 4000 grit in order to produce scratch- free and mirror- finished surface. The polished specimens were investigated by the optical microscope for insurance of the absence of pits or scratches on the surface. The polished specimens were degreased with acetone and thoroughly washed with distilled water. The specimens used for passivation in H_2SO_4 were followed by cleaning in acetone for 10 min.Finally the samples were rinsed in distilled water, dried and used for further studies.

2.2. Surface treatment process by H_2SO_4 solution

The entire sample surface was subjected to surface treatments by complete immersion in 15%vol of sulphuric acid (H_2SO_4) for 1 h. It is important to mention that all immersion of samples was carried out at room temperature. After surface treatment by acid, the samples were washed with running distilled water and dried by heater for 30 minutes. Energy dispersive x-rays analysis (EDX) technique was utilized to evaluate the situation of passive layer on the surface [8].

2.3. Surface treatment process by HNO_3 solution

The surface of samples was subjected to surface treatments of complete immersion in 40% vol of HNO_3 in the temperature of 60 °C for 30 minutes. After surface treatment, the samples were washed with running distilled water and dried in the air. All the stages were performed according to ASTM standard F86 [7-8].

2.4. Corrosion behaviour evaluation

In order to perform electrochemical potentiodynamic polarization experiments, 316L SS specimens without surface treatment and surface treated 316L SS specimens were subjected to physiological solution at the temperature of 37 °C in order to obtain desired equilibrium. Prior to each test, the surface dimensions of each mounted specimen in contact with the electrolyte were measured. An electrochemical corrosion polarization test cell was used for in vitro potentiodynamic polarization tests in physiological solutions. Graphite electrode was used as the counter electrode and saturated calomel electrode (SCE) was used as a reference electrode. Physiological normal saline (0.9 wt% NaCl) and Ringer's solution (NaCl 8.6 g/l, $CaCl_2.2H_2O$ 0.66 g/l and KCl 0.6 g/l) were physiological solutions that were used as electrolytes. In order to evaluate and compare the corrosion behaviour of specimens with and without surface treatment, 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 a EG & G model 263A Potentiostat/galvanostat interfaced with a computer and a recorder. The tests were started after 30 min that a steady open-circuit potential was attained after 10 min (not more than ±5 mV drift in 5 min) and the scan rate was 0.5mV/sec The anodic and cathodic polarization curves were

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

Element	Cr	Ni	Mo	Mn	P	C	Si	S	Fe
%	17.55	13.65	3.1	1.2	≤0.040	0.03	≤0.080	≤0.030	Balance

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 and Discussion
3.1. Corrosion behavior evaluation .

Potentiodynamic polarization curves of surface treated specimens and untreated specimens in normal saline solution and Ringer's solution shows in Figures 1 and 2 respectively.
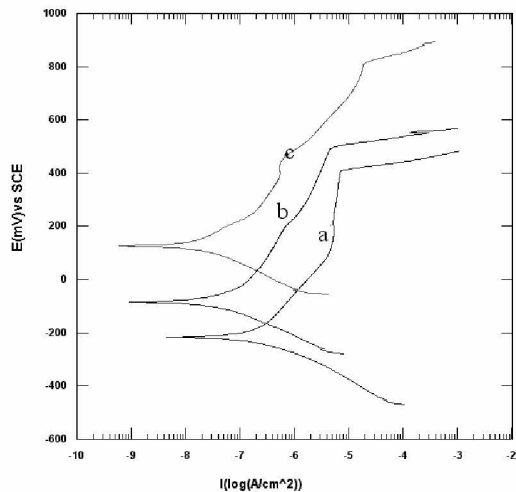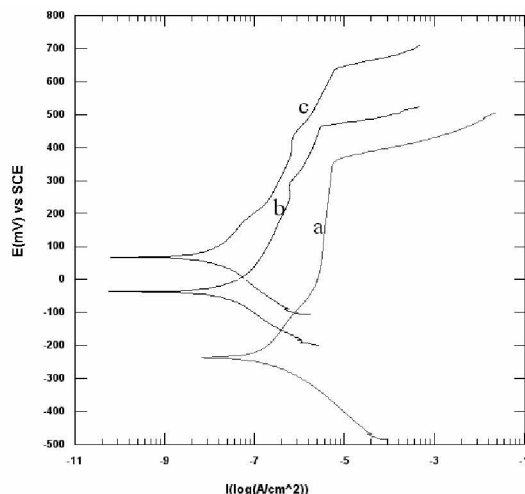

Fig. 1. Potentiodynamic polarization curves of: (a) The untreated 316L SS; (b), (b) Surface treated 316L SS (by 15% vol H_2SO_4, immersion period of 1 h), (c) Surface treated 316L (by 40% vol HNO_3 and immersion period of 30 min), in the normal saline solution (0.9 wt% NaCl) at 37°C.

Fig. 2. Potentiodynamic polarization curves of: (a) The untreated 316L SS; (b); (b) Surface treated 316L SS (by 15% vol H_2SO_4, immersion period of 1 h); (c) Surface treated 316L SS (by 40 % vol HNO_3, immersion period of 30 min), in the Ringer's solution at 37°C.

The mean values and standard deviation of corrosion current densities and corrosion potentials in normal saline and Ringer's solution are given in Table 2 and 3, respectively. The results show that corrosion current density of 316L SS in the normal saline solution (icorr = 265 nA/cm^2) is more than the surface treated specimens (57, 31 nA/cm^2 for H_2SO_4 and HNO_3 treated stainless steel respectively). 316L SS without surface treatment has the lowest corrosion resistance in the normal saline solution media and the samples that were surface treated in H_2SO_4 acid or HNO_3 acid have more corrosion resistance in the same media. Corrosion behavior of the specimens in Ringer's solution is similar to normal saline solution and the same trend can be observed. Consequently, the type of the solution or physiological media does not affect on the trend of samples corrosion resistance. Surface treatment, particularly by nitric acid has a considerable effect on corrosion behaviour of 316L SS. Corrosion potential of surface treated stainless steel (E_{corr} = -100 ± 25 mV, i_{corr} = 57 nA) and (E_{corr} = 100 ± 25 mV, icorr = 31 nA) in normal saline solution is more noble in comparison with the untreated 316L ss (Ecorr = 174 ± 20 mV). Corrosion current density of surface treated 316L ss which was treated in H_2SO_4 (icorr = 57 nA/cm^2) and was treated in HNO_3 acid (icorr = 31 nA/cm^2) in normal saline solution decreased considerably in comparison with the untreated 316L SS (icorr = 256 nA/cm^2). The same trend was observed in Ringer's solution too.

3.2. EDX analysis

Stoichiometry of outer layer is various iron oxides. Inner layer mainly gives a protective nature to passive layer against environmental agents. Nickel oxide in the form of NiO has been identified in outer layer accompanied with iron oxide. Nickel concentration in passive film is lower than main alloy and in inner and outer layers are 5 and 10 percent respectively. Inner and outer layers exhibit different types of semiconductivity [10-11]. Molybdenum improves the pitting resistance of stainless steel in environments consist of chloride [12-13]. Studies show that molybdenum affects on selective dissolution and passivation.

Table 4 illustrates the elemental composition (wt %) of surface treated 316L SS in H_2SO_4 and pristine 316L SS. It may be assured from the table values that the enrichment of Mo has occurred in H_2SO_4 surface treated 316L SS. It seems that increasing the molybdenum oxide concentration and decreasing the iron concentration in the surface, are responsible for corrosion resistance of 316L stainless steel in normal saline solution.

Molybdenum is an alloy element with a strong beneficial influence on the pitting resistance of 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 [14]. 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 MoO_3 that solves in acidic electrolytes and MoO_4^{2-} with more stability [4].

Table 2. Mean values and 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
Untreated 316L	-220 (20)	265 (16)	194 (16)
15-vol% H_2SO_4 316L SS	-100 (25)	57 (5)	49 (3)
40-vol % HNO_3 316L SS	100 (25)	31 (6)	26 (6)

Table 3. 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
Untreated 316L	-195 (20)	218 (17)	181 (20)
15% vol H_2SO_4 316L SS	-75 (25)	38 (6)	27 (3)
40% vol HNO_3 316L SS	66 (25)	27 (2)	25 (3)

Table 4. Relative concentration (wt %) of the elements of 316L SS due to H_2SO_4 surface treatment process that is obtained by EDAX analysis technique

Materials	Fe	Cr	Ni	Mo	O
Untreated 316L SS	66.21	17.74	9.38	1.71	4.95
Surface treated 316L SS (15% vol H_2SO_4)	65.92	17.86	8.44	2.51	5.27

Table 5. Electrochemical parameters of surface treated 316L SS in normal saline solution

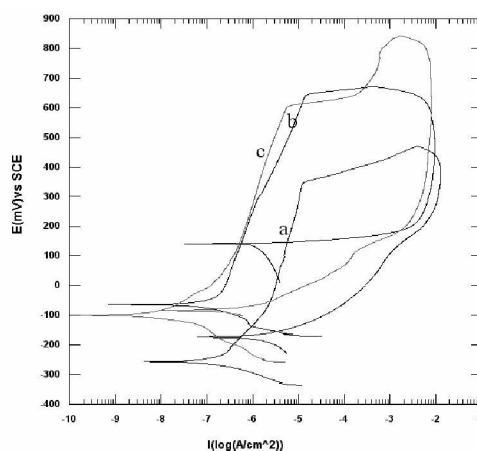| Materials	Electrochemical parameters	
	Break down potential. E_b (mV)	Repassivation potential, E_p (mV)
Untreated 316L SS	+341	-171
Surface treated 316L SS (15% vol H_2SO_4)	+637	+139
Surface treated 316L SS(40% vol HNO_3)	+605	-86

Fig. 3. Cyclic polarization curves of: (a) the untreated 316L SS, (b) Surface treated 316L SS (by 15% vol H2SO4, immersion period of 1 h), (c) Surface treated 316L (by 40% vol HNO3, immersion period of 30 min), in the Ringer's solution at 37°C.

3.2. Cyclic polarization experiment

Table 5 shows the electrochemical parameters of surface treated 316L SS in comparison with the untreated 316L SS. It is clear that surface treatment process in H_2SO_4 has improved the E_b in comparison with the pristine 316L SS. Cyclic polarization curves of surface treated 316L SS and pristine 316L SS in normal saline solution are shown in Figure 3. It is concluded that the ability of surface treated type 316L SS to close the pits is improved. This behaviour is due to stable chloride complex formation that leads to reduction of chloride ion concentration in the pit and repassivation of the pit.

Conclusion

Surface treatment of 316L SS with H_2SO_4 solution is more effective than HNO_3 solution in increasing corrosion resistance. Electrochemical tests showed that surface treatment of 316L SS with H_2SO_4 enrich the Mo concentration on the surface and increase the pitting corrosion resistance of it in Ringer and physiological solutions.

Acknowledgements

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