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The Effect of pH Value on the Corrosion Behaviour of Ti-6Al-4V and 316L SS Alloys under Physiological Environment

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The corrosion behaviour for stainless steel 316L and Ti-6Al-4V at pH 5.2 and 7.4 under simulated biological conditions either with or without the presence of proteins were investigated using electrochemical methods. The electrochemical tests were performed with and without the addition of bovine serum albumin (BSA) with concentration of 10 g L^{-1} to the phosphate buffer solution (PBS) with two different phases of pH, which are acidic (pH 5.2) and neutral phase (pH 7.4) at 37 ˚C. The electrochemical methods used in this study were open circuit potential (OCP) and potentiodynamics polarization. The results of electrochemical tests showed that the corrosion potential (E_{corr}) values of stainless steel at both pH values are slightly higher than Ti-6Al-4V in absence of BSA. The chromium (III) oxide (Cr_2O_3) film formed on stainless steel is more stable in neutral and also in acidic one without the presence of proteins. Meanwhile, the E_{corr} of Ti-6Al-4V increases at acidic (−611.0 mV) and neutral pH (−585.0 mV) of human body in phosphate buffer solution (PBS) with addition of BSA, compared to test medium without the addition of proteins. This shows the interaction between proteins and surface of the Ti-6Al-4V have no significant effect onto its corrosion behaviour. However, the E_{corr} of Ti-6Al-4V at condition acidic pH with the absence of proteins, which is −740.0 mV showed the lowest corrosion resistance than stainless steel (E_{corr} = −652.0 mV). In terms of corrosion rate values, stainless steel alloy showed the best corrosion rate in neutral pH, which is 3.048×10^{-3} without addition of BSA in solution. But both alloys show greater corrosion rate at normal phase condition compared to acidic phase condition.

1. Introduction

316L stainless steel (316L SS) is a common bio-implant material used in orthopedic, orthodontic, and cardiovascular implants. This is due to their characteristics that meet the requirement in terms of biocompatibility, great mechanical properties, and good corrosion resistance, as well as cost effectiveness (Salahinejad et al., 2013). The type of titanium and its alloys that is commonly used as bio-implants materials are Ti-6Al-4V and Ti-6Al-7Nb. This material gives great attraction for biomaterials application as they perform well under physiological environment (Nava-Dino et al., 2012). The main concern for using metal in implantation is their tendency to corrode in human body environment (Sin, 2015). Most metals and alloys that are not suitable for implantation is because they are too reactive in the human body (Mishnaevsky et al., 2014). The pH value of human body is normally 7, and it may change from 3 to 9 due to several causes such as accidents, diseases, infections and other factors (Manivasagam et al., 2010). After surgery, the pH value of hard tissue near the implant area can change approximately to 5.2 and then recovers back to 7.4 (normal pH body) within two weeks (Al-Mobarak et al., 2011). Therefore, the change of pH value in human body may affect the corrosion behavior of a material. The aim of this work is to study the effect of pH value on the corrosion rate of Ti-6Al-4V and 316L SS alloys under physiological environment. Electrochemical methods, like open-circuit potential measurements and potentiodynamic polarization, were carried out in order to study the corrosion behavior of metals.

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2. Literature review

2.1 Metallic biomaterials used in biomedical

Metallic material such as stainless steel has a self-protecting layer by spontaneous formation of a thin oxide film. The layer formed on stainless steel is enriched in Cr_2O_3 oxide. The content of chromium in stainless steel is a major factor of corrosion resistance (Brooks et al., 2017). As chromium content increases from 17 % to 20 %, the stability of passive film also greatly increases (Santonen et al., 2010). The inner metal-oxide interface of Ti–6Al–4V contains TiO_2, TiO and Ti_2O_3 while the outer oxide-solution interface is enriched with Al_2O_3 (Fekry and Ameer, 2011). This TiO_2 oxide film provides titanium the resistance to corrosion in aggressive environments as long as the integrity of the film is maintained (Nady et al., 2017). Metallic materials have become attractive materials especially in medical application due to their improvement of implant performance and longevity; however, the rejection or implant failures cannot be avoided (Mishnaevsky et al., 2014). This phenomenon has been the reason for choosing bio-implant material of great biocompatibility in implant application and to enhance the life span of the implants and the longevity of the patients as well (Kulkarni et al., 2015).

2.2 The pH value and proteins in human body fluids

The reason why human body is considered as corrosive environment is because of the high concentration of chloride ions (Cl^-) and the range of human body temperature (36.7-37.2 ˚C) (Zieliński and Sobieszczyk, 2008). Two potential effects occur when the metallic implants corrode. First, they may weaken and tend to fail to function, which requires a revision surgery. Second, the large amount release of metal ions from the material can lead to allergic biological reaction in human body (Azar et al., 2010). The total protein content of plasma in albumin is about 50-60 % (Boldt, 2010), which the most abundant plasma protein; yet the best-known binder of biological fluids. According to previous study, protein-containing solutions could accelerate the release of elements from alloys. Wataha et al. (2001) found that more elements are released from alloys in solution that contains BSA. Pangi et al. (2016) also reported a maximum release of elements from Ni-Cr and Co-Cr alloys in BSA. No toxic effects occurred from the elements released. However, the presence of protein has been reported to either decrease or increase the corrosion rate, or have no effect which created a conflict (Yu et al., 2015).

3. Methodology

3.1 Material and sample preparation

A titanium aluminum vanadium alloy (ESPI Metals, Ashland) or Ti-6Al-4V and 316L stainless steel (AK Steel Corporation) served as the working electrode in the form of rods, with dimensions of 10 mm and 6 mm in diameter. The composition of the alloys is shown in Table 1 according to ASTM F-136-84 and ASTM A 240. The samples were sanded with 320 up to 600 grit finish, cleaned and rinsed with distilled water, dried with compressed air and left in open air for 5 min and then transferred quickly to the electrolytic cell. The Ti-6Al-4V and 316L SS samples were glued to the wire using conductive glue leaving a surface area of 4.5 cm^2 and 2.5 cm^2 for exposure to the solution.

Table 1: Ti-6Al-4V and SS 316L alloys composition

Metal	Elements	Composition (%)
Ti-6Al-4V	Ti	88-90
	Al	5.5-6.75
	V	3.5-4.5
SS 316L	Fe	< 1
	C	0.03 max
	Mn	2.00 max
	P	0.045 max
	S	0.03 max
	Si	0.75 max
	Cr	16.00-18.00
	Ni	10.00-14.00
	Mo	2.00-3.00
	N	0.10 max
	Fe	Bal

3.2 Characterization of materials

The composition of sample was measured via RIGAKU ULTIMA IV FD 3668N, X-ray diffraction (XRD) analysis. The scan region ranges from 30˚ to 90˚ operated at a scan rate of 2˚ min^{-1} with radiation of Cu Kα (40kV, 40 mA). XRD was performed to verify the chemical characterizations of all samples.

3.3 Electrochemical measurements

Electrochemical test was conducted at temperature of 37 °C (human body temperature) and maintained at pH 5.2 (pH of body fluids at implant surgery area) and 7.4 (normal physiological condition). All electrochemical tests were performed using a freshly polished sample and fresh solution in each case. All electrochemical measurements were carried out with a Gamry model G300 potentiostat/galvanostat, which was controlled by software provided by Gamry Instruments Company. All potentials in this work were measured versus SCE. The potentiodynamic polarization test was performed when the OCPs became relatively stable after immersion for 1 h. Then, the potentiodynamic polarization scan was commenced from -0.5 V below E_{oc} up to +0.5 V using a scan rate of 5 mV s^{-1}. The chemical composition of PBS is NaCl (8.19 g/L), KCl (0.2235 g/L), Na_2HPO_4 (1.42 g/L) and KH_2PO_4 (0.272 g/L).

4. Results and discussion

4.1 Characterization of materials

X-ray diffraction patterns of the Ti-6Al-4V and SS 316L alloys are presented in Figure 1. It can be clearly seen that α-Ti is the dominant structure for the Ti-6Al-4V..The peaks of α-Ti originated from (100) to (202) planes appeared. The chemical composition of SS 316L is measured according to the type 304 stainless steel, mainly composed by austenite, 304-stainless steel.

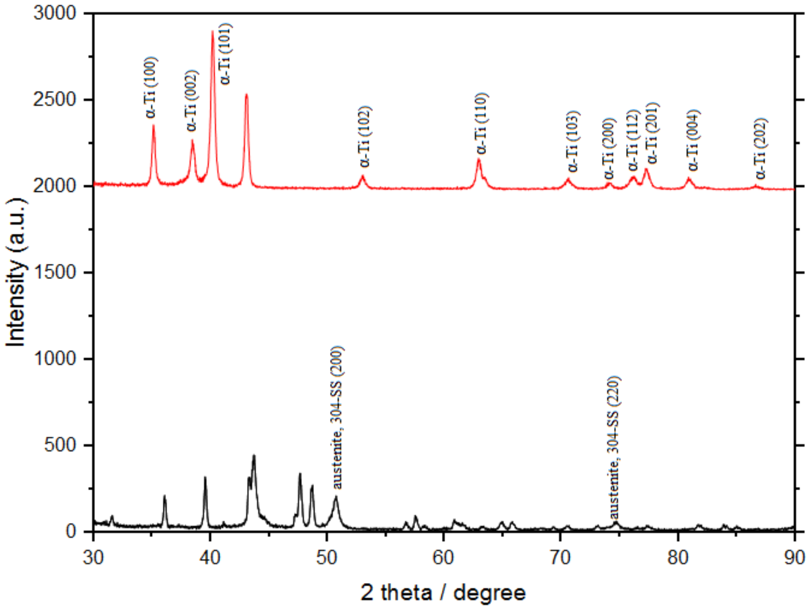

Figure 1: XRD patterns of the Ti-6Al-4V and SS 316L samples

4.2 Electrochemical measurements

Collected values of polarization resistance were used for determination one of the most important corrosion parameters—corrosion rate(Burnat et al., 2014). In order to evaluate the effect of pH on the corrosion resistance of the stainless steel and Ti-6Al-4V, polarization curves were obtained in the PBS solution, either with or without BSA in two different pH values and the results are presented in Figures 2 and 3. According to Sin (2015), the polarization curves could be divided in four zones: at potentials below the corrosion potential (E_{corr}), the current density was controlled by the cathodic reaction; at potentials around the E_{corr} there was a transition from cathodic to anodic currents; when the potential was increased above the E_{corr}, the materials were passive where a stable oxide layer was formed on their surface; finally, when the potential was further increased the passive film was fractured and the current slowly increased.

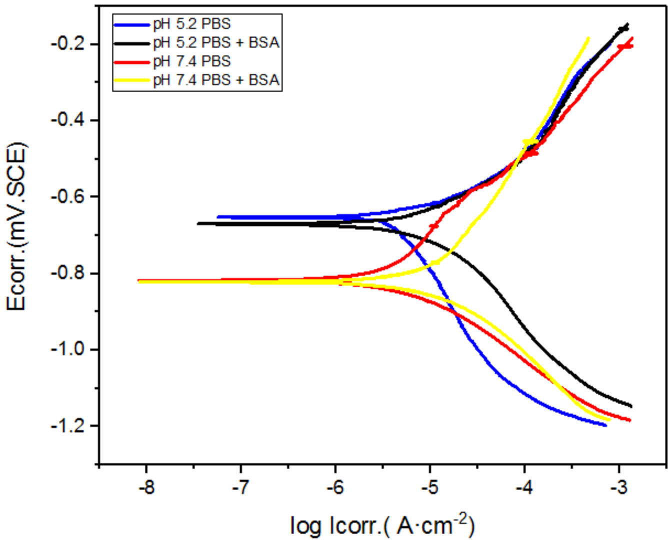

Figure 2: Potentiodynamic polarization curve of 316L SS tested in a PBS and PBS+BSA in pH 5.2 and 7.4 at 37 °C.

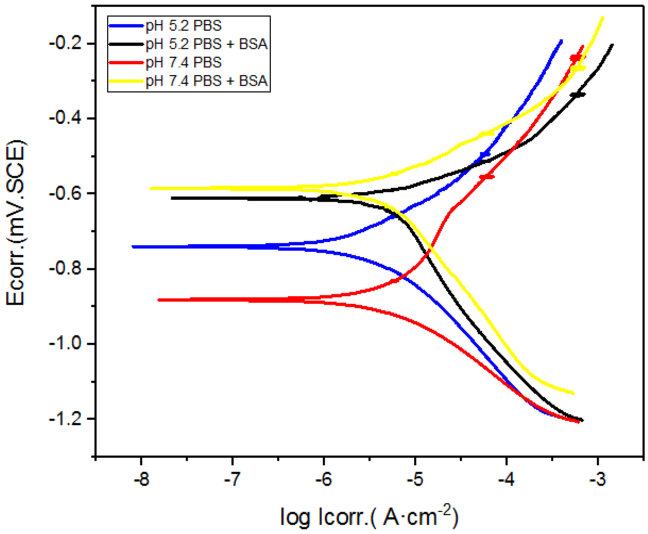

Figure 3: Potentiodynamic polarization curve of Ti-6Al-4V tested in a PBS and PBS+BSA in pH 5.2 and 7.4 at 37 °C

Tables 2 and 3 show the electrochemical parameters determined from the potentiodynamic polarization curves measured for stainless steel and Ti-6Al-4V in solutions at pH 5.2 and 7.4. The polarization curves showed a breakdown potential associated to the stainless steel at pH 5.2, in the solution with BSA. E_{corr} values of stainless steel at both pH values slightly higher than Ti-6Al-4V in absence of BSA. However, unlike the Ti-6Al-4V, corrosion potential increase at both pH values in the solution PBS + BSA.

By analyzing Figure 2, it is shown that the oxide layer, which is Cr2O3, has a stable character for stainless steel immersed in PBS at both pH values. As can be seen, the breakdown potential is increased as the current density increased in absence of proteins, which is slightly higher than solution with BSA. Meanwhile, the TiO2 layers present on the sample of Ti-6Al-4V perform well in the test medium of PBS + BSA at pH 5.2 and 7.4. This suggests at acidic phase of solutions does not caused lowering the corrosion resistance of both alloys. In Figures 2 and 3, the pattern of the graph for PBS + BSA at pH 5.2 is literally similar for both alloys. Also, stainless steel showed slightly same curves of the graph to Ti-6Al-4V at test medium of PBS with pH value of 7.4. However, at condition pH value of 7.4 with addition of proteins in solution, both alloys showed different results. For stainless steel, the potential kept constant at – 0.8 mV as the current density increased, meanwhile Ti-6Al-4V constantly at potential of – 0.6 mV. The E_{corr} of Ti-6Al-4V rapidly increased at higher current density compared to stainless steel. In this test condition showed that corrosion reaction of stainless steel affected with the presence of BSA either in pH 5.2 or pH 7.4, which caused the electrolyte reaching to metal substrate. From the polarization curves in Figure 1, it can be seen that the sample showed passive behaviour in test medium of PBS either with or without the addition of BSA at pH 7.4 because there is no significant change of E_{corr} was observed at – 0.8 mV vs. SCE approximately until two corrosion potentials seem to appear when the current density (I_{corr}) increase. However, the increase in the current at a certain anodic potential does not always have to be a breakdown of the protective oxide layer. Instead an oxidation reaction (e.g., oxygen evolution) can occur, which may result in an increased oxide thickness and more protective oxide layer towards anodic polarization (Sin, 2015).

In pH 5.2, the corrosion rate of both alloys slightly higher when compared to pH 7.4, except for Ti-6Al-4V in PBS due to formed film is stable in neutral medium than in acidic one. The interactions of phosphate and calcium ions present in the simulated body fluid with oxide films, which is responsible for both their corrosion resistance and their biocompatibility. From Tables 3 and 4, the highest corrosion rate is Ti-6Al-4V in solution with BSA at pH 5.2. It can be clearly seen that the change of pH values does not give a large different in terms of corrosion rate, however the presence of proteins in the solution does.

Table 2: Electrochemical parameters determined from the potentiodynamic polarization curves measured for 316L SS and Ti-6Al-4V in solutions at pH 5.2.

	316L SS		Ti-6Al-4V	
	PBS	PBS + BSA	PBS	PBS + BSA
E_{corr}. (mV.SCE)	-652.0	-670.0	-740.0	-611.0
I_{corr}. (A·cm^{-2})	6.350×10^{-6}	15.00×10^{-6}	3.240×10^{-6}	5.620×10^{-6}
Corrosion rate (mm/year)	4.975×10^{-3}	12.40×10^{-3}	8.832×10^{-3}	13.07×10^{-3}

Table 3: Electrochemical parameters determined from the potentiodynamic polarization curves measured for 316L SS and Ti-6Al-4V in solutions at pH 7.4.

	316L SS		Ti-6Al-4V	
	PBS	PBS + BSA	PBS	PBS + BSA
E_{corr}.(mV.SCE)	-818.0	-822.0	-881.0	-585.0
I_{corr}.(A·cm^{-2})	3.700×10^{-6}	13.60×10^{-6}	5.170×10^{-6}	4.540×10^{-6}
Corrosion rate (mm/year)	3.048×10^{-3}	11.25×10^{-3}	11.78×10^{-3}	10.56×10^{-3}

5. Conclusions

The corrosion of Ti-6Al-4V and 316L SS was investigated in this study using physiological fluids solutions either with or without the addition of BSA at pH 5.2 and 7.4. The E_{corr} values of stainless steel at both pH values slightly higher than Ti-6Al-4V in absence of BSA which show greater corrosion resistance of stainless steel in the solution without proteins. Meanwhile, the corrosion potential of Ti-6Al-4V increase at both pH values in the solution PBS + BSA compared to test medium without the addition of proteins. For Ti-6Al-4V, the addition of proteins can accelerate the E_{corr} either in acidic or neutral pH of human body but not for stainless steel.

The change of pH values in human body environment literally does not cause extensive effect to corrosion resistance of both alloys. But both alloys show greater corrosion rate at normal phase condition compared to acidic phase condition. Alloy with greater corrosion rate is stainless steel in PBS at pH value of 7.4. On the other hand, lower corrosion rate was found in Ti-6Al-4V at pH 5.2 in PBS + BSA. However, care should be taken to implanted area using stainless steel and Ti-6Al-4V as implant devices.

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