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Research paper

Electrochemical Behaviour of Titanium Alloys And Stainless Steel In Different Simulated Body Fluid

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Abstract

Biomaterials, such as titanium and 316L stainless steel, are widely used as an implant material for many health problems such as cardio stents, orthopedic and dental implant. The main concern about these biomaterials is corrosion. The biomaterials can easily corrode when exposed in human body fluid. The objective of the study is to compare the corrosion rate of titanium and 316L stainless steel in three different simulated body fluid solutions (SBF). Three different SBF that being used are Phosphate Buffered Saline (PBS) Solution, Hank's Solution and Ringer Solution. The SBF will act as an electrolyte in the three-electrochemical cell. The Gamry potentiostat machine was used to run the Open Circuit Potential (OCP) and Potentiodynamic Polarization (PDP) to obtain the corrosion rate of the samples. The phase identification and microstructure of the samples were studied using the XRD and optical microscope, respectively. Based on the results obtained it can be concluded that even though 316L SS has shown a very good corrosion resistant, however titanium is more viable option as a bioimplant material in terms of its durability and efficiency.

Keywords: *corrosion, bioimplant, titanium, stainless steel, simulated body fluid*

1. Introduction

Corrosion is the degrading process of a material that occurs gradually by an electrochemical attack. Implant of a material in a human body is also a subject matter in this issue. The human body fluid will act as an electrolyte in the electrochemical process to determine the corrosion behaviour. The body fluid contains several constituents such as water, sodium, chlorine, proteins, plasma, amino acids and along with mucin in the case of saliva [1]. The presence of protein is normally to act as a binder to metal ions and bring them away from the implant surfaces and thus accelerate corrosion process. Many studies and research work have been carried out to understand more about the corrosion behaviour focusing on which factors that contribute the most to the corrosion rate of the implants in the human body.

Corrosion of biomaterials in the human body is basically an electrochemical process. This electrochemical process is a process where ions from the metal surface will be transferred to another suitable acceptor surface. In this case, the ions from the implant surface will be transferred to another surface with the human body solution acting as an electrolyte in this process. Many types of corrosion can occur in the human body. Different types of corrosion can occur depending on the different factors. M.A Khan *et al*. studied about the conjoint corrosion and wear in titanium alloys [2]. In their paper, they investigated the effect of corrosion and wear in a corrosive environment using phosphate buffered solution with the addition of a bovine albumin solution. They concluded that in the presence of wear, the corrosion is much higher as compared to without wear. Another research had been conducted where the authors investigated the corrosion behaviour of biomaterials with different surface preparation [3]. When implants are inserted with a better and smooth surface, they can develop a new surface faster. Therefore, the tissue integration with the implants is much easier and efficient.

Bioimplants or biomaterials are materials that are used to replace the bone or tissue in a human body. Implants can help to replace the organs function that is operating below the acceptable level [4]. To select the most viable material for implant, the acceptance or compatibility of the material within the human body must be considered. Adverse effect can occur if this characteristic is neglected upon selecting the material.

C. Fonseca and M. A Barbosa in their paper stated that titanium has excellent mechanical properties and corrosion resistance [5]. The surface of titanium has about 5 nm of thick layer that is amorphous or poorly crystalline and a slightly oxygen-deficient titanium oxide. This layer is compact and is a chemically stable oxide film that can cover the metals surface. The physiochemical and electrochemical of this passive oxide layer will help to provide the surface of titanium with its long-term stability in biological environment such as the human body.

Stainless steel is a well-known good corrosion resistance material used by various industries besides titanium. Basically, stainless steel is an iron-based alloy with significant amount of chromium, approximately >11% wt. Stainless steel also has high resistance to corrosion because of the formation of chromium (III) passive surface oxide. Besides the properties of resistance to corrosion, stainless steel is still investigated for its use as a biomaterial due to its lower cost as compared to titanium [6]. Despite having less superior properties and behavior as compared to titanium as an implant material, some still find stainless steel as a viable option for oral cavity and orthopedic applications.

Electrochemical methods are suitable to be use to study and measure the corrosion rate since the basis of corrosion involves the electrochemical oxidation and reduction reactions. For corrosion testing, polarization of specimens is used using the Potentiodynamic polarization (PDP) test. The potential of the electrodes will be varied at different rates by applying current through the electrolyte. Currently, scientists and researchers are using bio-liquids as a substitute to actual human body fluids. These liquids can simulate the condition that a human body possesses. In the electrochemical method, these liquids will be acting as the electrolyte. In 2006, Tadashi Kokubo and Hiroaki Takadama published their study about the use of SBF in predicting the in vivo bone bioactivity [7]. Their findings showed that the apatite layer that formed on implanted materials in actual human also can be formed on implant materials in vivo that are exposed to SBF.

Despite many investigation regarding the corrosion of bioimplants, similar study regarding the comparison of titanium alloys and stainless steel as implants were not found. The best implant material could be decided and used in future applications to ensure better functionality.

2. Methodology

2.1. Preparation of substrate

The biomaterials used in this study are Ti-6Al-4V and 316L SS which is supplied from ESPI Metals. The composition of the biomaterial is provided and listed in Table 1.

Table 1: Chemical composition of (a) titanium and (b) stainless steel

(a) Titanium, Ti-6Al-4V	
Element	Percentage (%)
Titanium	88-90
Aluminium	5.5-6.75
Vanadium	3.5-4.5
Iron	<1
(b) 316L Stainless Steel	
Element	Percentage (%)
Carbon	0.03
Manganese	2.00
Phosphorus	0.045
Sulphur	0.03
Silicon	0.75
Chromium	16.00-18.00
Nickel	10.00-14.00
Molybdenum	2.00-3.00
Nitrogen	0.10

The samples were prepared by cutting them into smaller sizes using the Abrasive Cutter Machine. The dimension of the samples was 6 x 10 x 6 cm. The cutting machine was designed to cut the samples with optimal quality and consistency. By using the cutting liquid or liquid coolant, the samples could be cut precisely. Titanium is a very strong material, so without the coolant, the samples could not be cut properly. In addition, the microstructure of the samples could be protected from heat in the presence of the liquid coolant.

2.2 Simulated Body Fluid (SBF)

2.2.1 Phosphate Buffered Saline Solution

The PBS solution was prepared by adding the chemicals listed in Table 2 into 800 ml of distilled water. Hydrochloric acid was used to adjust the pH level up to 7.4. Distilled water was then added into the solution until it reaches a pH of 1l.

Table 2: PBS solution ingredients

Chemicals	Weight (g)
Sodium Dihydrogen, NaCl	8
Potassium Chloride, KCl	0.2
Sodium Dihydrogen phosphate, $Na_2H_2PO_4$	1.44
Potassium Dihydrogen phosphate, KH_2PO_4	0.24

2.2.2. Ringer Solution

Ringer solution was prepared by adding one tablet of Ringer solution into 500 ml of distilled water. The solution was then stirred using an autoclave.

2.2.3 Hank's Solution

The solution was purchased from R&M Chemicals and ready to be use. Therefore, no preparation was needed.

2.3 Potentiodynamic Polarization Test

The three-electrode electrochemical cell was carried out using the GAMRY potentiostat computer. A graphite rod was used as the counter electrode and saturated calomel electrode (SCE) was used as the reference electrode. The samples acted as the working electrode in the electrochemical cell. Open circuit potential measurements were carried out for 40 minutes in order to see the behaviour of the samples in SBF and to obtain a stable condition before initiating the polarization test. The OCP must be carried out before running any other test. The time to obtain stabalization depended on the type of material [8]. Unstable samples will not yield accurate result in the next process. The corrosion rate of the samples was determined by potentiodynamic polarization (PDP). The scan rate was set to 5mV/s and a sample period of 0.1s. After the polarization curves were produced, the tafel extrapolating method was performed to determine the corrosion rate of the samples.

2.4 X-Ray Diffraction

ULTIMA IV FD 3668, X-Ray Diffraction (XRD) were used to determine the phases and composition of the samples after the corrosion test. The radiation used was Cu Kα (40 kV, 40 mA) at a scan rate of 2o/min ranging from 30o to 90o. Then the data obtained was compared and verified with the standard data from the standard XRD database.

2.3 Metallography

The microstructure of the samples was observed using an optical microscope, OLYMPUS BX60 that has a magnification of 50, 100, 200, 500 and 1000 times. The microstructure was observed to see if there were any changes or differences that occurred at the samples surface after the corrosion test. To observe the microstructure, the samples must be prepared beforehand through mounting, grinding, polishing and etching process to enhance the microstructure of the samples.

3. Results and Discussion

3.1 Potentiodynamic Polarization

The polarization test of Ti-6Al-4V and 316L SS were carried out in three different body fluid solutions (SBF). Figure 1 and 2 shows the polarization curves obtain from titanium and stainless steel, respectively. Both materials showed almost similar polarization movements, potentially moving from the cathodic region towards anodic region. The behaviour of the biomaterials basically has the same passive-transpassive movement. For titanium alloys, the results barely show any changes in all three simulated body fluid. The passivation of titanium started around -1.2V that is almost the same for all three solutions. Passivation is the process where an oxide film starts to form on the surface of the sample. When the oxide film starts to grow, the active dissolution process will end. The starting point for passivation is normally characterized by two main values, the primary passive potential (E_{pp}) and the critical anodic current density (i_c).

The value of E_{corr} for the polarization curve is also near to the primary passive potential (E_{pp}) value, indicating that the titanium has tendency to passivate in the simulated body fluid. In the passive region as can be seen from the figure, the current density is decreasing rapidly. The polarization curves of titanium show that titanium in Ringer solution has lower current density as compared to titanium in the other two solutions. The lower current density in the passive region indicates that the sample have high passivation. This shows higher corrosion resistance behaviour.

Transpassivity is a process that happens when the passive film starts to oxidize towards the soluble ions. The transpassive region is considered to start upon the anodic current that is increasing. This process occurs due to the anodic current interruption and causes the passive film to decay. The passive film is considered to have great stability when the transpassive region is at the positive region. The graph indicates that the titanium does not possess a stable passive film in all of the solutions used. Per Gareth Hinds [9] reported that at the very negative potential, the formation of a protective oxide film for titanium already takes place. Even with the presence of chloride ions, the film can still resist reactions. The film rapidly decayed until it reaches almost the same value of critical anodic current density.

From the polarization curve obtained, the E_{corr} for titanium in Ringer solution shifted towards noble (positive) value compared as compared to the other two solution tests. This shows that the anodic and cathodic curves for that curve shifted to higher current density. For 316L stainless steel, the polarization curves showed the differences between the solutions as presented in Figure 2. Passivation in Hank's solution started at -1.336 V, meanwhile for both PBS and Ringer, passivation started around -1.35 V. This showed that stainless steel in Hank's solution could resist the reaction better due to the early formation of protective film.
The results also indicated that stainless steel has a lower current density in Hank's solution. Hence, it has high passivation in the solution. Stainless steel also does not have a stable passive film. E_{corr} in the Ringer solution shifted towards noble (positive) values as compared to the other two curves. From the polarization curves, the Tafel plot could be plotted and used to determine the corrosion rate of the materials in each test. The results are shown in Table 3. Based on the results obtained, it was found that for titanium the corrosion rate is much higher in the PBS solution followed by Hank's solution and lastly in the Ringer solution. This shows that titanium can resist corrosion better when the surface has high passivation.

Meanwhile, for stainless steel, the corrosion rate in Ringer solution is the highest followed by PBS and Hank's solution. This results is also supported by the lower current density obtained for stainless steel in Hank's solution through the polarization test. Higher passivation shows higher resistance to corrosion. Between the two materials, titanium has a higher corrosion rate in PBS and Hank's solution but lower in Ringer solution. According to previous researches, the effect of different simulated body fluids on anti-corrosion of biomaterials may be due to the difference in the solution composition [10]. PBS solution and Hank's solution contain additives (Na_2HPO_4 and KH_2PO_4) that a Ringer solution does not have. The results indicate that titanium and stainless steel react differently in different simulated body fluids depending on the composition of the solutions used.

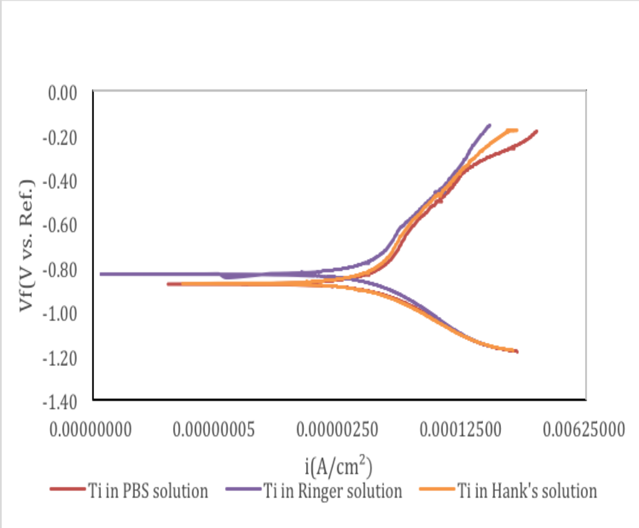


Fig. 1: Polarization curves for Ti-6Al-4V in SBF

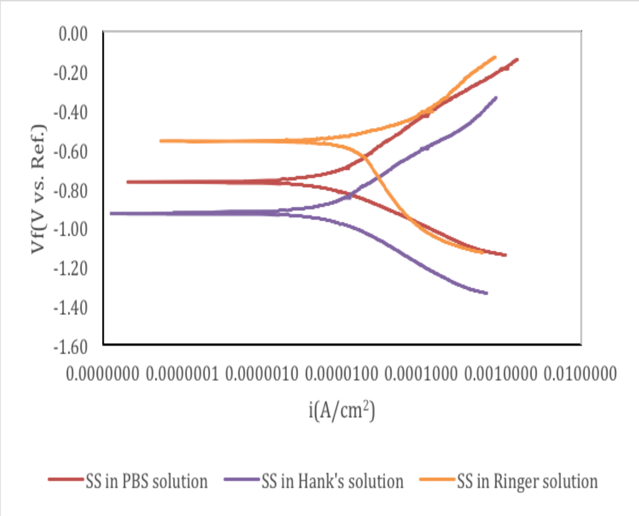


Fig. 2: Polarization curves for 316L SS in SBF

Table 3: The corrosion rate of titanium and stainless steel in SBF

Solution	Material	Corrosion Rate (Mmpy)
Pbs	Titanium	15.110×10^{-3}
	Stainless Steel	5.460×10^{-3}
Ringer	Titanium	7.670×10^{-3}
	Stainless Steel	16.470×10^{-3}
Hank	Titanium	14.370×10^{-3}
	Stainless Steel	3.740×10^{-3}

3.2 X-Ray Diffraction

X-Ray Diffraction pattern of all the samples was tested using Cu Kα radiation at a scan rate of 2˚/min. The scan was set from 2θ angle ranging from 30˚ to 90˚. The data for titanium and stainless steel in different SBF is illustrated in Figure 3 and 4, respectively. From the XRD analysis of titanium, all three highest peaks showed the existence of titanium oxide (Ti_3O) and few peaks of titanium (Ti). This indicated that the material already was oxidized during the corrosion test. Meanwhile, XRD analysis of stainless steel shows the existence of austenite, 304-stainless steel and hematite (Fe_2O_3). Presence of hematite confirmed that the samples underwent some oxidation process during corrosion test. For austenite, the database does not have any data for 316L SS. Therefore, austenite 304-stainless steel was used to compare the XRD data pattern. Since the highest peak still consist of the main composition like Ti for titanium, and austenite 304 stainless steel for 316L SS, it can be confirmed that the samples did not undergo any significant changes. This result is almost identical to a study done by

Avinash Kumar and Prasad Conda where it was found that the changes of stainless steel is insignificant on surface deposit after incubation [11]. For titanium alloys, the peaks showed the same deposit of Ti_3O about 80^0 with similar crystal structure of (0 0 8). Around 37^0, all samples exhibited the highest peak corresponding to Ti_3O (0 0 4). Ti and Ti_3O are recognized to have the same Hexagonal Closed Packed (HCP) crystal structure. Meanwhile for stainless steel, the three significant peaks indicated the hematite content and also a peak that corresponds to austenite. All highest peaks revealed at 80^0 for all samples corresponded to hematite (0 0 8). Austenite (1 1 1) was seen around 43^0 and is the same in all samples. Both samples titanium and stainless steel showed that they did not undergo any significant changes in term of its composition.

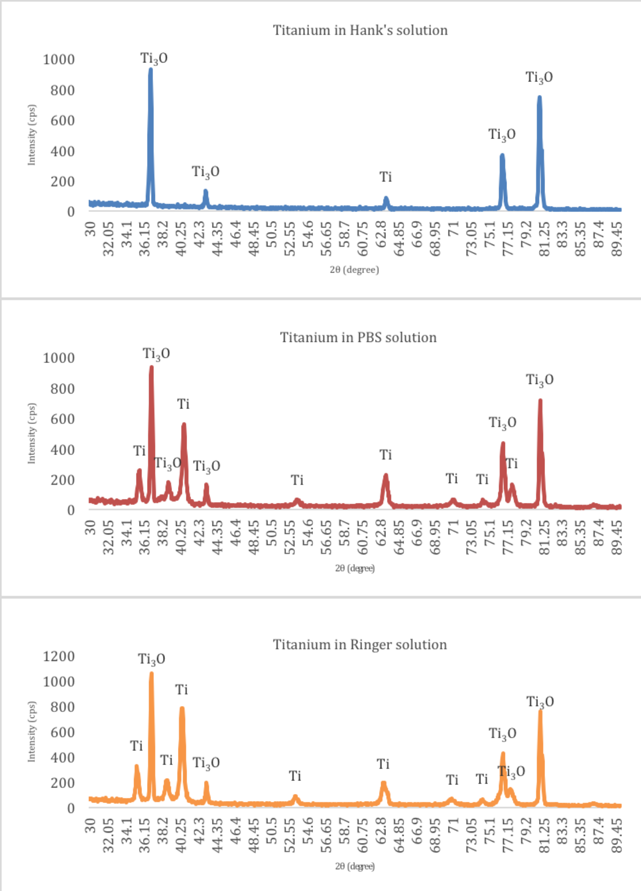
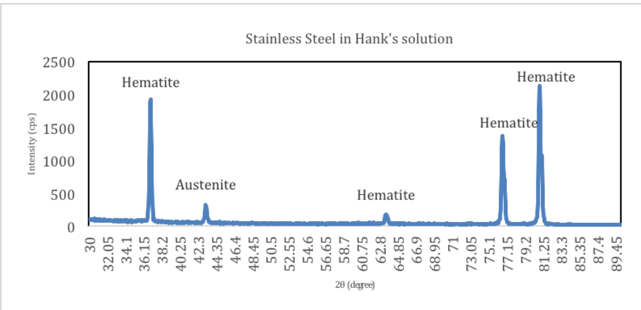


Fig. 3: XRD for Ti-6Al-4V in SBF



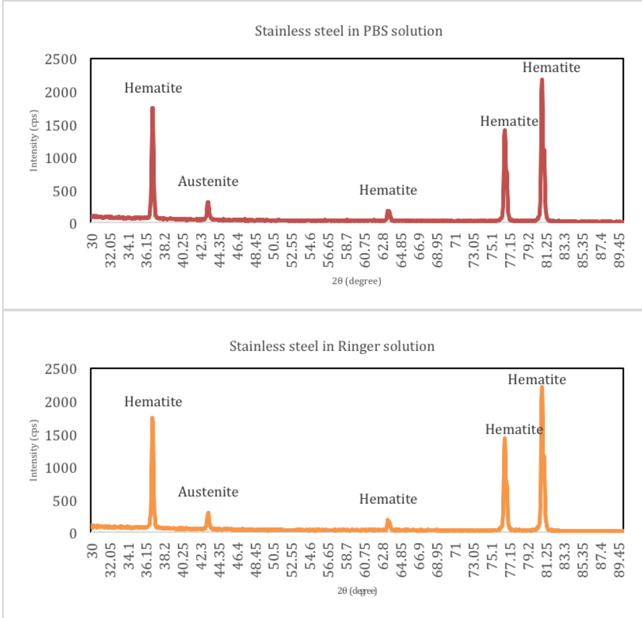


Fig. 4: XRD for 316L SS in SBF

3.3 Metallography

The metallography samples were observed using the optical microscope to see if there were any changes in terms of microstructure. The result is shown in Figure 5. Based on the observation, the microstructure of titanium in the Ringer solution is more significant while the microstructure of titanium in PBS solution is least significant. This may be related to the corrosion rate where the biomaterial in PBS solution is more prone to corrosion. The microstructure showed different reaction towards the simulated body fluid that is being used. However, the difference in each microstructure is hard to distinguish. Comparison between the titanium and stainless steel microstructure can be seen. In Hank's solution, the surface microstructure of titanium is more corroded than stainless steel by looking at the black pores present. The same observation can be made in the Ringer solution. It can be seen that the stainless steel microstructure exhibits more pores as compared to titanium. Pores can expose materials to corrosion and reduce the mechanical properties of the material. Based on this, titanium is better than stainless steel is terms of their corrosion behaviour. Therefore, titanium could resist corrosion better as compared to 316L stainless steel.

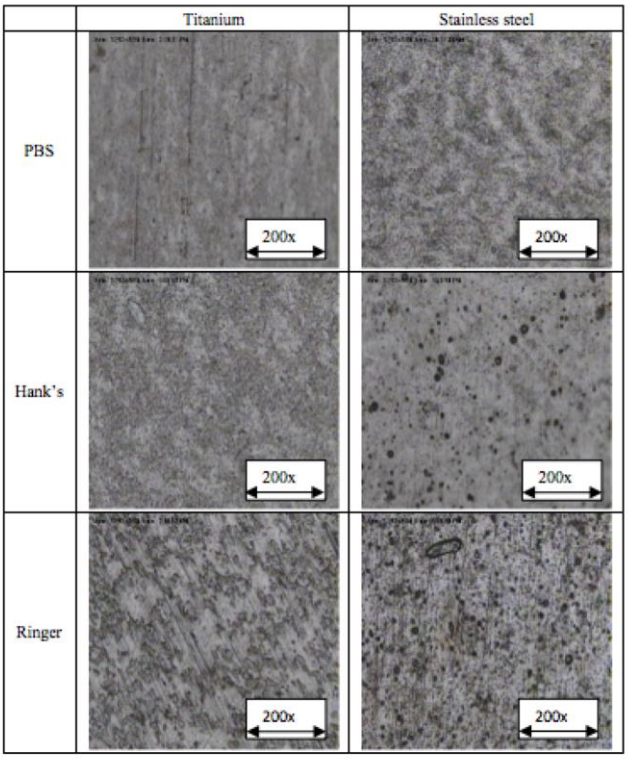


Fig. 5: Microstructure of Ti-6Al-4V and 316 SS in SBF

4. Conclusion

The corrosion study between titanium and stainless steel in three different simulated body fluids was successful performed using the potentiodynamic polarization test. In the Ringer and PBS solution, stainless steel showed greater resistance to corrosion as compared to titanium. The different ions contained in the simulated body fluid may cause the difference in the electrochemical behaviour. However, the corrosion resistance for both materials is still considered great and acceptable. The composition and microstructure of both biomaterials changes after the corrosion test but the differences are insignificant to affect the properties of the materials. Based on all of the results obtained it can be concluded that even though 316L SS has shown good corrosion resistant, titanium is still the most viable option to be used as a bio implant in terms of its durability and efficiency.

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