SCIENTIFIC RESEARCH JOURNAL,
VOL 18, No 1 (2021) 1 - 13
https://doi.org/10.24191/srj.v18i1.11389

The Effect of pH on the Corrosion Rate of 316L Stainless Steel, Nitinol, and Titanium-6%Aluminum-4%Vanadium in Hank's Solution

Nik Rozlin Nik Masdek[1*] Nor'Aini Wahab[1] Natasha Ahmad Nawawi[1] Aznul Tajudin[1]

[1]Faculty of Mechanical Engineering, Universiti Teknologi MARA
40450 Shah Alam, Selangor Darul Ehsan

**Corresponding author's e-mail: nikrozlin@uitm.edu.my*

Received: 3 December 2020
Accepted: 8 December 2020
Online First: 28 February 2021

ABSTRACT

Nowadays, the application of 316L Stainless Steel, Nitinol and Ti-6Al-4V alloys as biomaterials have become popular due to their implant performance and durability. In this research work, the effect of pH on the corrosion rate of 316L Stainless Steel, Nitinol and Ti-6Al-4V alloys have been investigated. An electrochemical method was applied to investigate the corrosion behaviour of these biomaterials under simulated biological condition. The potentiodynamic polarisation were performed in a Hank's solution with a pH value of 7.4 (neutral) and 5.2 (acidic). SEM, XRD, microhardness and surface roughness were also carried out to characterise the corroded surface. The potentiodynamic polarisation results showed that both Ti-6Al-4V and 316L stainless steel had high corrosion rate at pH 5.2 (acidic) as compared to pH 7.4 (neutral). The corrosion rate for Ti-6Al-4V alloys was 22.80×10^{-3} mmpy at pH 7.4 and increased to 23.65×10^{-3} mmpy at pH 5.2. Similar behaviour was observed for 316L stainless steel where the corrosion rate increasing from 2.387×10^{-3} mmpy at pH 7.4 to 5.325×10^{-3} mmpy at pH 5.2. However, different corrosion behaviour was observed for Nitinol as the corrosion rate decreasing from 17.65×10^{-3}mmpy to16.04×10^{-3} mmpy at pH 7.4 and pH 5.2, respectively. Hence, the decrease in pH value was found to not cause any significant effect on the corrosion resistance of Nitinol as compared to 316L SS and Ti-6Al-4V alloys.

Keywords: *titanium, Nitinol, stainless steel, corrosion rate, pH value*

INTRODUCTION

Biomaterials for biomedical implants have been used since the 19th century [1]. A good biomaterial must have good biocompatibility, high corrosion resistance as well as good mechanical properties [2] before it can be implanted in the human body. The phenomenon on the rejection of implant has been rationale for selecting bio-implant materials with excellent biocompatibility in implant utilisation [3]. Biocompatibility is described as the behaviour of a material in the human body fluid which is nontoxic and does not cause any harmful effect to the patients [4]. The interaction would occur between implants and the biological environment in the human body when it is implanted [5]. In the human body the body fluid contains protein, amino acids and organic compounds which make the human body fluid a complex environment.

It is mainly known that implants are generally made from biomaterials such as Ti-6Al-4V alloys, 316L stainless steel and Nitinol. This is due to their superior properties. The titanium's mechanical properties and corrosion resistance is magnificent which is ensured by a compact and chemically stable oxide film that spontaneously shields the metal surface [6]. The state of passivity of titanium-based biomaterial shows amazing resistance to pitting corrosion in physiological solutions which makes this titanium material have low corrosion rate, with a correspondingly slow release of corrosion product [7]. Meanwhile, 316L SS has great biocompatibility and corrosion resistance, as well as great mechanical properties such as strong formability, high yield strength and high modulus of elasticity [8]. On the other hand, nitinol is a material that has special properties in biomedical application due to its shape memory and super-elastic properties that is able to undergo huge elastic deformation [9-10].

A previous study has reported that the corrosion of implants which are implanted in the human body can lead to mechanical failure and thus causes changes in the material integrity [11]. Several studies have also been reported to study the corrosion of biomaterials in simulated body solutions [12-14]. The corrosion resistance of each metallic biomaterial is related to

the presence of a stable passive oxide film on its surface [15]. Different parts of the human body have different pH value where the corrosion resistance verifies the lasting achievement of biomaterial implant. The corrosion of biomaterial implants is influenced by the variation of pH value of the human body [3,16]. The normal pH value of human body fluid is usually 7.4 which is neutral. However, it can drop until it becomes acidic which is 5.2 to 5.5 near the implant during the initial period of implantation or after surgery [2,17].

Corrosion on metallic implants has been reported to cause several potential effects [3]. However, the corrosion behaviour of Ti-6Al-4V alloys, 316L stainless steel and Nitinol used as bio-implants is still not fully understood. As it has been reported [2,17] that the pH value can vary from being neutral to becoming acidic in the human body, it is therefore important to investigate the reaction of these biomaterials in a similar condition. Thus, the purpose of this work was to study the effect of pH value on the corrosion rate of 316L SS, Nitinol and Ti-6Al-4V alloys in a Hank's solution.

METHODOLOGY

Sample Preparation

The samples were prepared from solid rods of Ti-6Al-4V (ESPI Metals, Ashland), 316L SS (AK Steel Corporation) and Nitinol (Stanford Advanced Materials) with diameter 10 mm. Ti-6Al-4V, 316L SS, and Nitinol alloys with dimensions of 10mm × 10mm were cut from a 100mm rod of Ti-6Al-4V, 316L SS, and Nitinol using an abrasive cutter. The sample was grinded with a 300 up to 600 grade sand paper, cleaned and rinsed with distilled water, and dried with compressed air.

Corrosion Test

The electrochemical method used to obtain the corrosion rate of 316L Stainless Steel, Nitinol and Ti-6Al-4V was the potentiodynamic polarisation technique (PDP). The PDP test was carried out to find the eRect of pH on the corrosion rate. Prior to the PDP test, the electrochemical measurement was done for 1 hour in Hank's solution to achieve a stable open circuit potential

(OCP). The Hank's solution was mixed with hydrochloride acid (HCl) to decrease the pH value to 7.4 and 5.2. To obtain the corrosion rate, the Tafel extrapolation was plotted based on the result of the PDP test.

Scanning Electron Microscope

The specimens were observed under a scanning electron microscope (SEM) Hitachi SU3500 model. SEM was conducted before and after corrosion test to observe the morphology of all samples. The magnification used was 3kX, 7kX and 10kX.

X-Ray Diffraction (XRD)

X-ray diffraction (XRD) test was performed using Rigaku Ultima IV FD 3668N. The scan section ranges from 30˚ to 90˚ at a scan rate of 2˚/ min with radiation of Cu Ka (40kV, 40 mA). XRD was done to check the chemical characterizations of all samples. The data obtained was compared and verified with the XRD database.

Vickers Hardness

MVK-H1 model was used to perform Vickers microhardness test. The hardness values are measured before and after corrosion. Two different pH values were used which were 7.4 and 5.2. The test was conducted by applying a 1kg load for ten seconds on the sample. After ten seconds, the diamond shape indentation was formed and analyzed based on its length. The hardness was taken at three selected points on the sample's surface. The average value was calculated based on three points of the hardness value at the specimen surface.

Surface Roughness Test

Alicona was used according to its suitability to calculate the roughness of the specimen for all types of materials in this test. Three readings for each sample were taken to obtain the average values. This test was also conducted before and after the corrosion test to observe the eRect of surface roughness at the sample's surface.

RESULTS AND DISCUSSION

Potentiodynamic Polarisation Test

The polarisation curve for all samples is presented in Figures 1,2 and 3. Meanwhile, Table 1 shows the electrochemical parameters obtained from the potentiodynamic polarisation curves plotted for 316L SS, Ti-6Al-4V alloys and Nitinol in Hank's solution at pH 7.4 (neutral) and pH 5.2 (acidic). According to the result, the corrosion potential (Ecorr)for 316L SS at pH 7.4 was lower than pH 5.2. Similar corrosion behaviour was also obtained for Ti-6Al-4V alloy. This is because deformation of Ti oxide (TiO) passive layer enhances the corrosion resistance and diminished ion release in corrosion medium [18]. Meanwhile, corrosion potential (Ecorr) for Nitinol at pH 7.4 was higher before it decreased at pH 5.2. In an acidic environment, the corrosion rate of all materials was slightly higher when compared to the neutral condition, except for Nitinol in which the corrosion rate at pH 7.4 was higher than in pH 5.2. This is due to the oxide layer that is formed on the Nitinol's surface which increases the corrosion resistance in harsh environment condition [19].

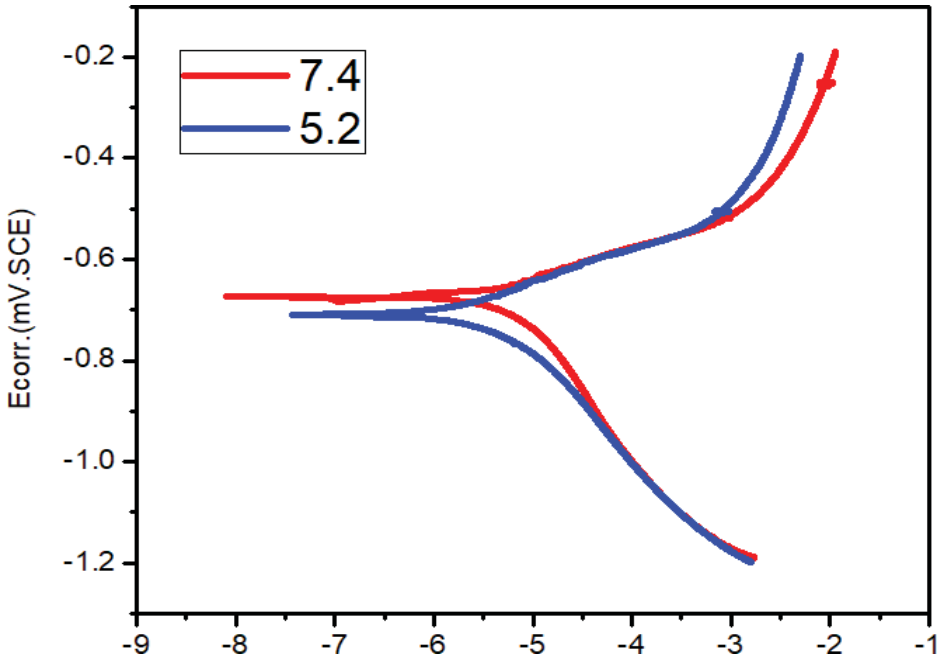

Figure 1: Potentiodynamic Polarisation Curve of 316L SS Tested in a Hank's Solution in pH 5.2 and 7.4

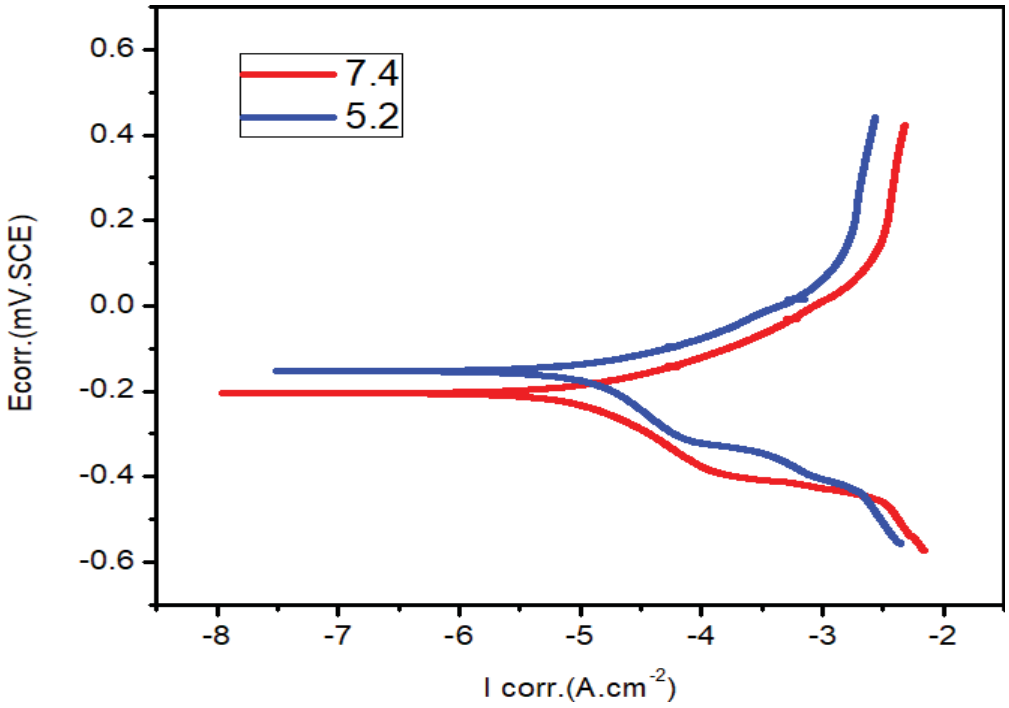

Figure 2: Potentiodynamic Polarisation Curve of Ti-6Al-4V Alloys Tested in Hank's Solution in pH 5.2 and 7.4

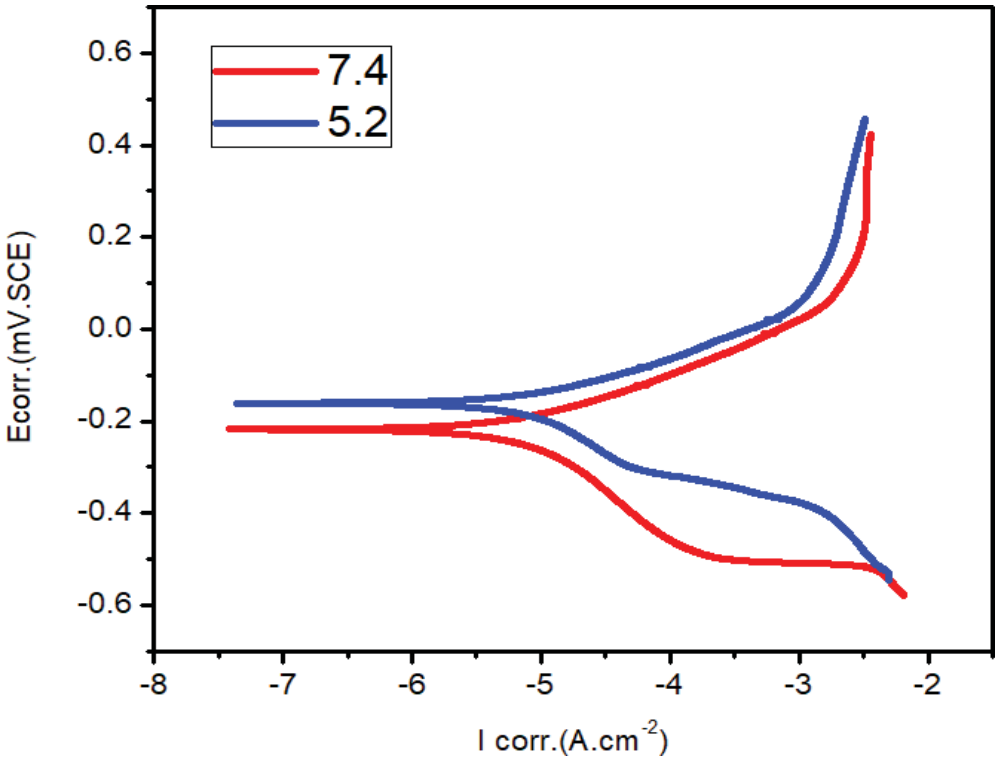

Figure 3: Potentiodynamic Polarisation Curve of Nitinol Tested in a Hank's Solution in pH 5.2 and 7.4

Table 1: Corrosion Rate for 316L SS, Ti-6Al-4V Alloys and Nitinol in pH 5.2 and 7.4

Biomaterial	pH value	$E_{corr,}$ (mV)	$I_{corr,}$ (Alcm^2)	Corrosion rate,(mmpy)
316L SS	7.4	-674.0	$1.960X10^{-6}$	$2.687X10^{-3}$
	5.2	-710.0	$3.250X10^{-6}$	$5.325X10^{-3}$
Nitinol	7.4	-218.0	$7.190X10^{-6}$	$17.65X10^{-3}$
	5.2	-161.0	$7.210X10^{-6}$	$16.04X10^{-3}$
Ti-6Al-4V	7.4	-705.0	$9.710X10^{-6}$	$22.80X10^{-3}$
	5.2	-753.0	$8.390X10^{-6}$	$23.65X10^{-3}$

Morphology

The surface morphology of the biomaterials before and after the electrochemical test at various magnifications is shown in Figure 4 and 5.

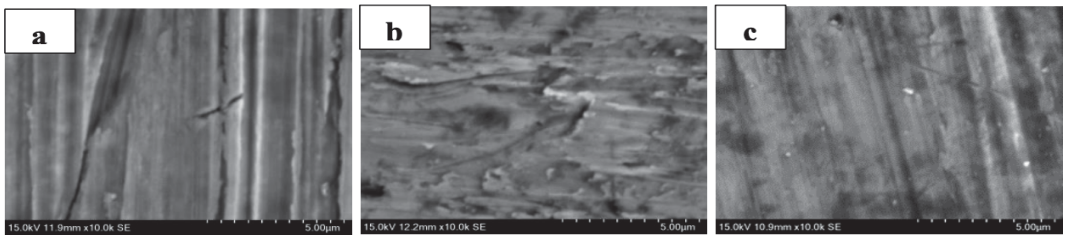

Figure 4: Microstructure of (a)316L Stainless Steel, (b) Nitinol (c)Ti-6Al-4V Before PDP in Hank' Solution

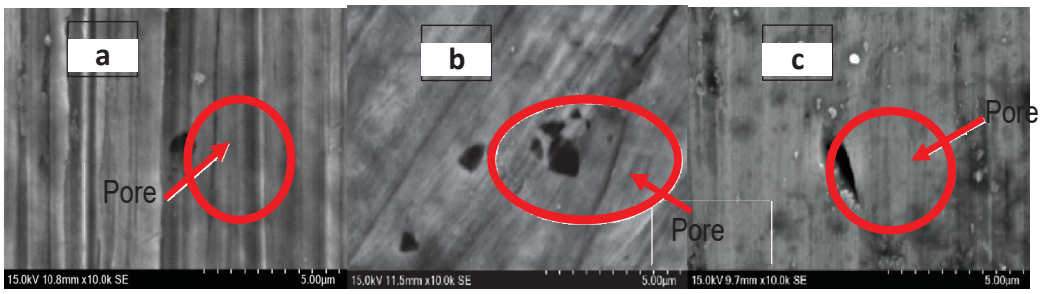

Figure 5: Microstructure After PDP in Hank's Solution for (a) Nitinol and (b) 316L SS (c) Ti-6Al-4V

It can be seen from Figure 4 that the surface of all biomaterials is smoother without any significant sign of corrosion. The materials surface began to corrode and form pores at certain spots on the biomaterials surface after the potentiodynamic polarisation test as shown in Figure 5 (a-c).

Pores would expose samples to corrosion and reduce their mechanical properties. Both 316L stainless steel, and Ti-6Al-4V also showed similar surface morphology as Nitinol where pores were present on the surface. This situation indicates the occurrence of corrosion; thus, increases the corrosion rate of the biomaterials. Small structural defects (microcracks and micropores) will lead to the failure of oxidised surfaces.

X-Ray Diffraction

Figures 6, 7, and 8 presented X-Ray diffraction structure of 316L SS, Ti-6Al-4V alloys and Nitinol, respectively. In Figure 6, the highest peaks showed the primary existence of austenite 304 stainless steel because the chemical composition of 316L SS is referred following to the type of 304 stainless steel. Figure 7 shows clearly shows combination of titanium, Vanadium and Aluminium peaks that form Ti-6Al-4V alloys. Meanwhile, in Figure 8, the XRD analysis showed the existence of NiTi as the dominant structure for the Nitinol. As can be seen from the figure, Nitinol did not have any significant change in terms of composition in both pH conditions.

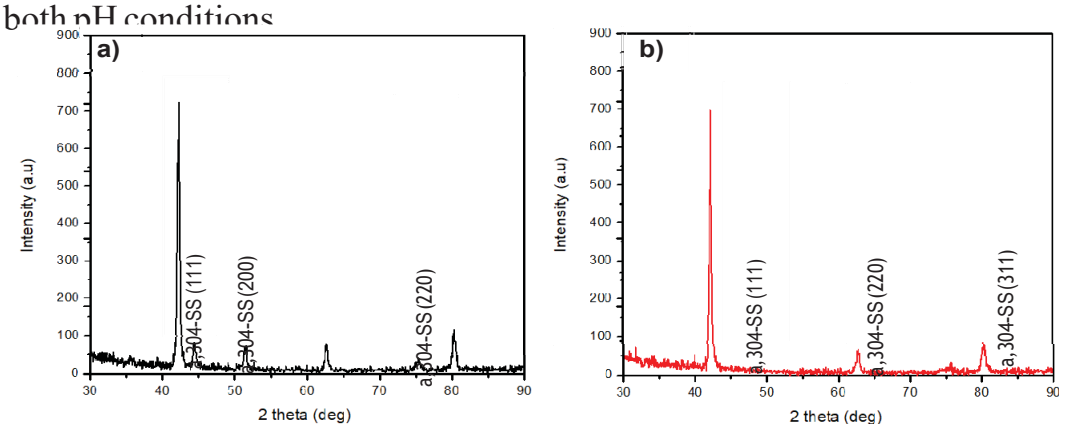

Figure 6: XRD Patterns for 316L SS at pH Value (a) 7.4 and (b) 5.2

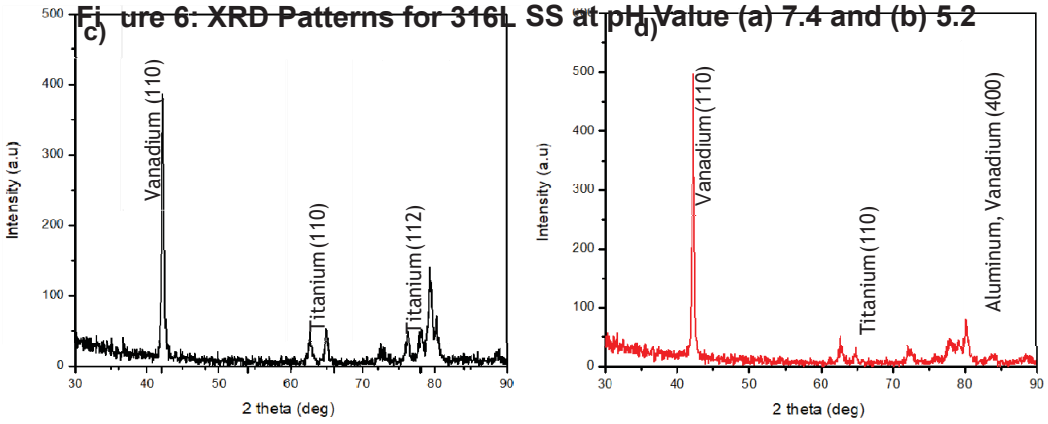

Figure 7: XRD Patterns for Ti-6Al-4V Alloys at pH Value (c) 7.4 and (d) 5.2

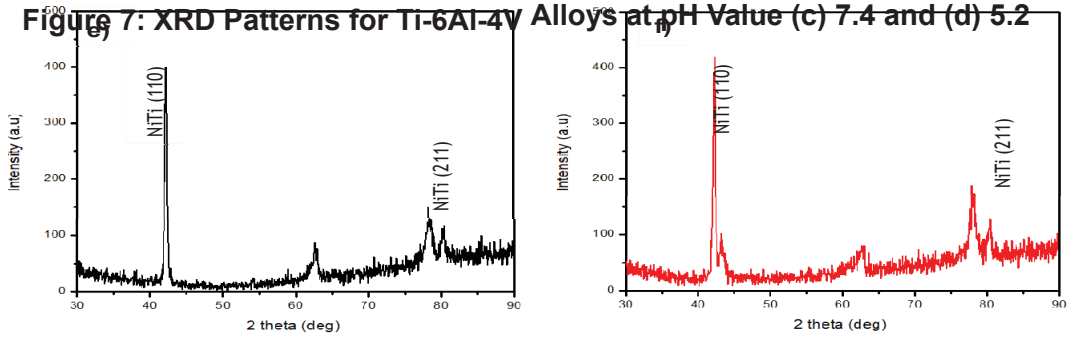

Figure 8: XRD Patterns for Nitinol at pH Value (e) 7.4 and (f) 5.2

Microhardness

Figure 9 presents the microhardness of 316L stainless steel, Nitinol and Ti-6Al-4V in different pH environment. It can be seen that the microhardness for 316L stainless steel, Nitinol and Ti-6Al-4V alloys decreased after performing corrosion test in both pH values.

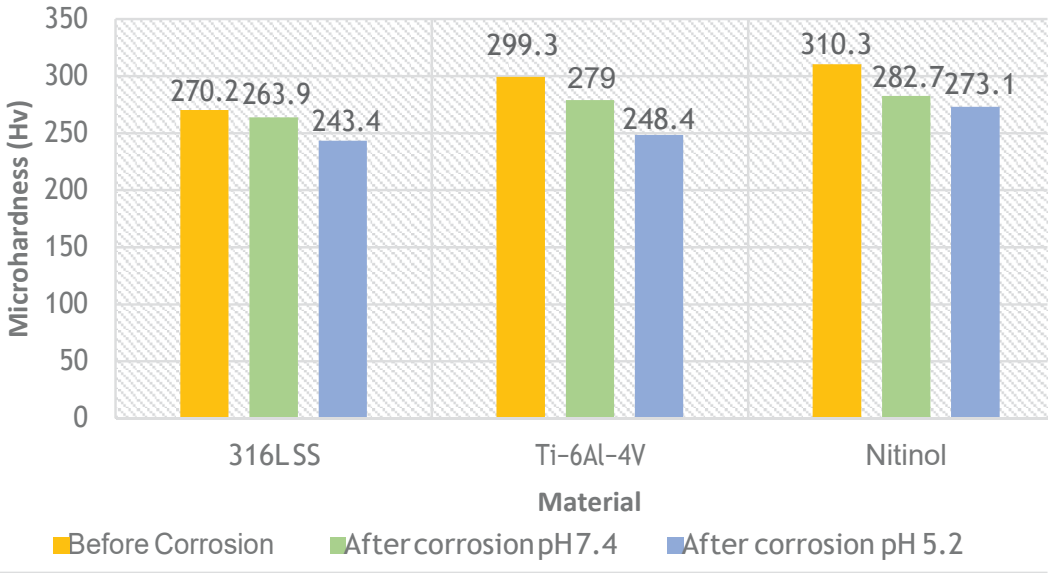

Figure 9: The Bar Chart of Microhardness under the Condition Before and After Corrosion

The microhardness obtained before the corrosion test for 316L stainless steel was 270.2 HV. However, after the PDP test at pH 7.4, it showed the value of hardness decreased 2.33% which was 263.9 HV and the hardness

value continued to drop 9.92% to become 243.4 HV at pH 5.2. Meanwhile, the microhardness for Nitinol before performing PDP was 310.3 HV. After immersion in Hank's solution at pH 7.4, the hardness of Nitinol became 282.7 HV which was equivalent to 6.78% of reduction and the percentage of hardness reduction increased until 17% at pH 5.2 which was 273.1 HV. The value of microhardness for Ti-6Al-4V after PDP at pH 7.4 was 279 HV with a reduction of 8.89% for 299.3 HV, but at 5.2, it was 248.4 HV with a reduction of 12%. This clearly shows that the corrosion in an acidic environment significantly reduces the microhardness of the biomaterials.

Surface Roughness

Table 2: Surface Roughness Before and After PDP Test in Different pH Condition

Material	pH value	Ra (μm)	
		Before	After
316L SS	7.4	1.2317	1.5633
Ti-6Al-4V		1.3803	1.8949
Nitinol		1.2993	1.9713
316L SS	5.2	1.5864	1.6192
Ti-6Al-4V		2.2518	2.6830
Nitinol		1.8977	1.9808

Table 2 shows the surface roughness of 316L stainless steel, Ti-6Al-4V and Nitinol after the potentiodynamic test in different pH conditions. The surface roughness values for all biomaterials increased after performing the corrosion test in Hank's solution with pH 7.4 and 5.2. The corroded surface increases the materials surface roughness. According to [5] the rough-textured surface on the materials assist to gain the biomaterial-tissue engagement and encourage osteoblast differentiation. Thus, treated samples would show good biocompatibility than polished material [20].

CONCLUSION

The electrochemical performance between 316L SS, Ti-6Al-4V alloys and Nitinol in Hank's solution at pH 7.4 (neutral) and pH 5.2 (acidic) was

successfully performed using the potentiodynamic polarisation test. As E_{corr} values of Ti-6Al-4V in Hank's solution showed only a slight difference for pH 7.4 and 5.2, hence change of pH does not cause a significant effect on the corrosion resistance of Ti-6Al-4V as compared to 316L SS and NiTi alloys. 316L SS displayed higher corrosion rate at pH 7.4. Meanwhile, Ti-6Al-4V and Nitinol exhibited better corrosion rate at pH 5.2 as compared to pH 7.4. Moreover, the microhardness of all biomaterials decreased while the surface roughness increased after performing the PDP test in both acidic and neutral pH conditions. Furthermore, SEM analysis showed formation of pores on the surfaces of all biomaterials after the PDP test. This promotes the occurrence of corrosion hence affected the corrosion rate of these biomaterials.

REFERENCES

[1] R.I.M. Asri, W.S.W. Harun, M. Samykano, N.A.C. Lah, S.A.C. Ghani, F. Tarlochan, M.R. Raza, 2017. Corrosion and surface modification on biocompatible metals: A review. *Mater Sci Eng C Mater Biol Appl., 77*, pp. 1261-1274. DOI: 10.1016/j.msec.2017.04.102

[2] Y. Torres, P. Trueba, J.J. Pavón, E. Chicardi, P. Kamm, F. García-moreno, & J. A. Rodríguez- ortiz, 2016. Design, processing and characterization of titanium with radial graded porosity for bone implants. *Materials & Design, 110*, pp. 179–187. https://doi.org/10.1016/j.matdes.2016.07.135

[3] A.A. Rozali, N.R.N. Masdek, M.C. Murad, & Z. Salleh, 2018. The effect of pH value on the corrosion behaviour of Ti-6Al-4V and 316L SS alloys under physiological environment. *Chemical Engineering Transactions, 63*, pp. 769–774. https://doi.org/10.3303/CET1863129

[4] M.Z. Ibrahim, A.A.D. Sarhan, F. Yusuf, & M. Hamdi, 2017. Biomedical materials and techniques to improve the tribological, mechanical and biomedical properties of orthopedic implants – A review article. *J. Alloys Compd., 714,* pp. 636–667. https://doi.org/10.1016/j.jallcom.2017.04.231

[5] G. Wang, Y. Wan, T. Wang, & Z. Liu, 2017. Corrosion Behaviour of Titanium Implant with different Surface Morphologies. *Procedia*

Manuf., 10, pp. 363–370. https://doi.org/10.1016/j.promfg.2017.07.006

[6] C. Fonseca & M.A. Barbosa, 2001. Corrosion behaviour of titanium in biofluids containing H2O2 studied by electrochemical impedance spectroscopy," *Corros. Sci., 43*, pp. 547–559. DOI:10.1016/s0010-938x(00)00107-4

[7] G.T. Burstein, C. Liu & R.M. Souto, 2005. The effect of temperature on the nucleation of corrosion pits on titanium in Ringer's physiological solution. *Biomaterials, 26*(3), pp. 245–256. DOI: 10.1016/j. biomaterials.2004.02.023

[8] N.R.N. Masdek, A. A. Rozali, M. C. Murad, and Z. Salleh, 2018. Effect of Protein Concentration on Corrosion of Ti-6Al-4V and 316L SS Alloys. *ISIJ International, 58*, pp. 1519–1523. DOI: 10.2355/ isijinternational.isijint-2018-183

[9] I. Milošev, and B. Kapun, 2012. The corrosion resistance of Nitinol alloy in simulated physiological solutions: Part 1: The effect of surface preparation. *Mater. Sci. Eng. C, 32*(5), pp. 1087–1096. https://doi. org/10.1016/j.msec.2011.11.007

[10] S. W. Robertson and R. O Ritchie, 2007. In vitro fatigue-crack growth and fracture toughness behaviour of thin-walled superelastic Nitinol tube for endovascular stents: A basis for defining the eRect of crack-like defects. *Biomaterials, 28*(4), pp. 700–709. DOI: 10.1016/j. biomaterials.2006.09.034

[11] S. Karimi, T. Nickchi, and A. Alfantazi, 2011. Effects of bovine serum albumin on the corrosion behaviour of AISI 316L, Co-28Cr-6Mo, and Ti-6Al-4V alloys in phosphate buRered saline solutions. *Corros. Sci., 53*(10), pp. 3262–3272. https://doi.org/10.1016/j.corsci.2011.06.009

[12] B. R. Milan, Z. T. Žaklina, A. T. Simonovis, M.B. P. Mihajlovis, and M. A. Antonijevis, 2020. Corrosion behaviour of titanium in simulated body solutions with the addition of biomolecules. *ACS Omega, 5* (22), pp. 12768-12776. https://doi.org/10.1021/acsomega.0c00390

[13] A. Acquesta and T. Monetta, 2020. As-built EBM and DMLS Ti-6Al-4V parts: topography–corrosion resistance relationship in a simulated body fluid. *Metals, 10*, 1015. https://doi.org/10.3390/met10081015

[14] A. Nasr, S.A. Gawad, & A.M. Fekry, 2020. A sensor for monitoring the corrosion behaviour of orthopedic drug calcium hydrogen phosphate on a surgical 316L stainless steel alloy as implant. *J Bio Tribo Corros, 6*, 36. https://doi.org/10.1007/s40735-020-0334-5

[15] B.G. Pound, 2014. Passive films on metallic biomaterials under simulated physiological conditions. *J. Biomed. Mater. Res. - Part A, 102*(5), pp. 1595–1604. https://doi.org/10.1002/jbm.a.34798

[16] N.S. Manam, W.S.W. Harun, D.N.A. Shri, S.A.C. Ghani, T. Kurniawan, M.H. Ismail, M.H.I. Ibrahim, 2017. Study of corrosion in biocompatible metals for implants: A review. *J. Alloys Compd., 701*, pp. 698–715. https://doi.org/10.1016/j.jallcom.2017.01.196

[17] W.F. Ng, K.Y. Chiu, F.T. Cheng, 2010. Effect of pH on the in vitro corrosion rate of magnesium degradable implant material. *Mater. Sci. Eng. C, 30*(6), pp. 898–903. DOI: 10.1016/j.msec.2010.04.003

[18] J. Lu, Y. Zhang, W. Huo, W. Zhang, Y. Zhao, and Y. Zhang, 2018. Electrochemical corrosion characteristics and biocompatibility of nanostructured titanium for implants. *Appl. Surf. Sci., 434*, pp. 63–72. DOI: 10.1016/j.apsusc.2017.10.168

[19] C. Trépanier and A. Pelton, 2006. Effect of temperature and pH on the corrosion resistance of passivated nitinol and stainless steel. *Proceedings of the International Conference on Shape Memory and Superelastic Technologies*, Kurhaus Baden-Baden, Baden-Baden, Germany, October 3–7, 2004.

[20] H. Güleryüz and H. Çimenoğlu, 2004. Effect of thermal oxidation on corrosion and corrosion-wear behaviour of a Ti-6Al-4V alloy. *Biomaterials, 25*(16), pp. 3325–3333. DOI: 10.1016/j.biomaterials.2003.10.009