International Journal on Advanced Science Engineering Information Technology

Vol.9 (2019) No. 5
ISSN: 2088-5334

Corrosion Behaviour of Titanium β Type Ti-12Cr in 3% NaCl Solution

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Abstract— Titanium alloy, especially titanium type Ti-12Cr for biomedical application has been a concern of many researchers recently. This titanium has excellent biocompatibility and controllable mechanical properties. Generally, titanium β type contains many alloying elements that lead to a high price. Therefore, it is interesting to develop β type with only one cheap alloying element such as Ti-12Cr that is designed as a low-cost implant material. Initially, Ti-12Cr has been developed, in particular for spinal fixation. Nowadays, the research of Ti-12Cr emphasizes only on mechanical properties. The corrosion behavior of this alloy has not been understood well yet. Therefore, corrosion characteristics of this alloy in any circumstances are necessary to investigate. This paper reports the corrosion behavior of Ti-12Cr in a salted environment using the weight loss method. Ti-12Cr samples were immersed in a 3% NaCl solution for 2, 4, and 6 weeks. Samples consist of Ti-12Cr (as-received), Ti-12Cr (ST) and Ti-12Cr (AT 30 ks). Weight of samples was measured before and after the immersing process using the digital balance. Microstructure and composition of the sample surfaces were examined by using SEM and EDX, respectively. The lowest corrosion rate after exposure for 6 weeks while the highest one is Ti-12Cr (as-received) is Ti-12Cr (AT 30 ks) that is 0,003 mmpy. The microstructure all of the samples shows black spots in the surfaces indicating corrosion has been started to occur on the samples. It was found that the corrosion is due to destruction of the chrome-oxide layer in some weak point as a result of a chemical reaction between the metal (Cr) with Cl- ions. Some oxides are formed on the surface of titanium, as indicated by a significant increment of oxygen content is the corrosive sample surface. This study indicates the corrosion resistance of Ti-12Cr (AT 30 ks) is much better than other materials in this research.

Keywords— biomedical; titanium; Ti-12Cr; corrosion behavior; 3% NaCl.

I. INTRODUCTION

Titanium alloys have been used widely for biomedical applications such as implants due to their biocompatibility, so it is safe for the human body as compared to other metal implants [1], also because of their excellent of corrosion resistance, tensile strength, and low of modulus elasticity value [2,3]. Titanium alloys that have been used for implants are β type titanium alloy with 2 or more alloying elements. Such kind of titanium has corrosion resistance and low modulus elasticity [1,3]. The example of β type titanium is Ti-13Nb-13Zr with modulus elasticity about 44–88 GPa. Nowdays, there are also Ti-12Mo-6Zr-2Fe, Ti-15Mo, Ti-16Nb-10Hf, Ti-15Mo-5Zr-3Al, Ti-15Mo-2,8Nb-0,2Si, Ti-Nb-Zr-Ta-Si-Fr etc [1,4,5]. Ti-13Nb-13Zr, Ti-12Mo-6Zr-2Fe and Ti-15Mo registered in ASTM (American Society Testing and Materials) standard, Ti-15Mo-5Zr-3Al registered in JIS (Japanese Industries Standard) with no. T 7401-6 [1]. Ti-35Nb-7Zr-5Ta (TNZT) and Ti-29Nb-13Ta-4,6Zr (TNTZ) had been developing until now [1,4]. TNTZ alloy has better tensile strength and fatigue failure as compared to Ti-6Al-4V ELI that has been used previously in biomedical applications [4]. TNTZ can be used in the human body with less negative reactions than Ti-6Al-4V ELI [6]. TNTZ have modulus elasticity under 60 GPa [1,4]. Nowadays, TNTZ alloy has been proposed for the orthopedic implant in tibia [1].

On the other hand, most of the developed β type titanium has high price due to the high amount and high price of the alloying elements [7]. Furthermore, the current titanium alloys have a composition that is difficult for recycling and needs more time to make it homogeneous. So, it is necessary to develop a titanium alloy with low price alloying element like Fe and Cr [8]. One of the alloys, Ti-12Cr, had been developing for backbone implant that has strong and springs back characteristics. Now, researches of Ti-12Cr focus on mechanical testing such as bending testing to determine modulus elasticity of alloys (Young's Modulus). High modulus elasticity and the strength of Ti-12Cr are required for spine support [9]. Further work on Ti-12Cr is to compare strength and modulus elasticity of this material with TNTZ for spine support application [10]. The result showed that Ti-12Cr is more recommended as compared to TNTZ for spine application, but aging details of these materials are still unknown. How long this material may be used and survive on the human body until getting corrosion. It is well known that the human body consists of some solution that has an effect on Ti-12Cr, like salt, blood, and sweat. This solution contains corrosive substances, in particular, chloride ion.

Actually, the corrosion behavior of metal depends on the environment and temperature [11, 12] Corrosion behavior of Ti-12Cr in chloride environment has not been well understood yet. One of the main requirements of metallic implants is to have high corrosion resistance in the human body environment. So, it is necessary to obtain corrosion resistance of Ti-12Cr through treatment with one of human body solution like NaCl. NaCl concentration level in human body is about 0,9%, this research use 3% NaCl solution. 3% NaCl solutions in this research have purposed to consider another component or substance like blood and sweat. It means that a 3% NaCl solution may refer to maximum levels in the human body. Furthermore, this solution is to accelerate the corrosion process, where the percentage increase of NaCl concentration in a solution will increase the corrosion rate [13, 14]. The corrosion resistance of Ti-12Cr is expected to predict the potential of this material for biomedical applications.

Corrosion resistance has been already studied in titanium material like using modified saliva solution at pH 5. The result showed that the corrosion rate of Ti12Cr is lower than CpTi, Ti6Al4 ELI, TNTZ-ST dan TNTZ-AT [15]. Furthermore, the corrosion behavior of titanium β type, Ti–13Mo–7Zr–3Fe (TMZF) and Ti–35Nb–7Zr–5Ta (TiOsteum), Ti6Al4V in 0,9% NaCl dan 5M HCl solution. The result showed that the corrosion resistance of TiOsteum is higher than others [16]. Corrosion resistance testing of Ti-Mo in 0,9% NaCl solution [17] indicated that oxidation tendency of Ti-Mo is lower than other materials in following order cp-Ti > Ti–6.5Mo> Ti–8.5Mo> Ti–10Mo. Some solutions have been used in corrosion behavior. Furthermore, it is necessary to investigate the corrosion behavior of Ti-12Cr in high contain chloride ion.

II. MATERIALS AND METHOD

A. Sample Preparation

Samples were some titanium β type, Ti-12Cr (as-received), and Ti-12Cr ST (Solution treatment), and Ti-12Cr STA (aging for 30 ks) with size 13x12 mm. Resin (matrix) as samples binder also used to grind and polish. Samples with small size need to mount with resin. Ethyl Ketone Peroxide (Mekpo) was also used to accelerate the hardness process of resin and alumina powder to polish samples surface. Saline solution that used in this research was 3% NaCl. It was from 3 gr NaCl in 100 ml distilled water. Then, samples were immersed in the solution for 2, 4, and 6 weeks.

B. Observation of Microstructure and Hardness Testing of Samples

Microstructure and chemical composition of samples were observed with SEM (Scanning Electron Microscope) and energy dispersive X-ray (EDX) [18]. The hardness of Ti-12Cr was measured based on ASTM 384; *Standard Test Methods for Knoop and Vickers Hardness Materials* [18] with *Vicker Hardness Tester*. Indentor that used in this testing was a diamond pyramid with angle was 136 ^{0}C. Load value was 9,8 N, and indentation time was 15 minutes.

C. Corrosion Test in 3% NaCl Solution

Size of samples was measured using caliper *Prohex, Germany*. The result was tabulated in table 1. Furthermore, samples were immersed in 3% NaCl during 2, 4, and 6 weeks. Weight of samples before and after treatment was weighed with OHAUS Pioneer^{TM} digital. The corrosion rate was calculated using the following formula 1 [15]:

$$CR = \frac{(W \times K)}{(D \times A \times T)} \quad (1)$$

where,
CR= corrosion rate (mmpy or millimeter per year)
W= lost of weight (gram)
K= constant factor of rate corrosion
= 8,76 x 10^4
D= specimen density (g/cm^3)
A= surface area of specimen (cm^2)
T= time for immersion (hours)

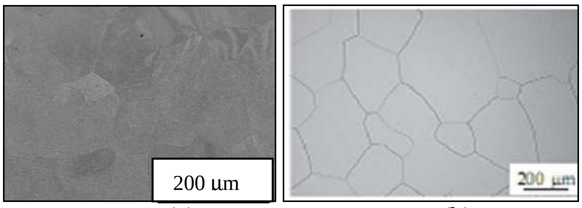
TABLE I
SIZE OF EACH CORROSION TEST SAMPLES IN 3% NACL

Samples	Immersion time (weeks)	Dimension (mm)		Surface area (cm^2)
		Thickness	Diameter	
Ti-12 Cr (as-received)	2	1,40	15	4,32
	4	1,30	14	4,09
	6	1,36	15	4,05
Ti-12 Cr (ST)	2	3,50	15	5,18
	4	3,40	15	5,13
	6	3,00	15	4,95
Ti-12 Cr (AT 30 KS)	2	3,20	15	5,04
	4	3,20	15	5,04
	6	3,20	15	5,04

III. Results and Discussion

A. Characterization of Ti-12Cr Before Immersion

The microstructure of Ti-12Cr has a similar structure with the result of another researcher [10] as shown in Figure 1. Percentage of chemical composition is tabulated in Table 2. It can be seen that the percentage of Ti and Cr (mass weight) are 89,97% and 12,03%. This result gives evidence that material is Ti-12Cr because of the value approach to Ti-12Cr.



(a) (b)

Fig. 1. (a) SEM photograph of Ti-12Cr before corrosion testing. (b) the optical microscope result from another researcher [6].

TABLE II
Composition of Ti-12Cr based on SEM-EDX examination

Elements	Weight of mass(%)
Ti	87,97
Cr	12,03
Total	100,00

B. Corrosion Behaviour

1) Mass Reduction

Result of mass reduction is shown in Table 3 and Figure 2 for all samples. Based on the graphic showed that mass reduction of Ti-12Cr is due to additional time for immersion. The higher mass reduction is for Ti-12Cr (ST) that is 9 mg, and the lowest is Ti-12Cr (AT 30 ks) that is about 1 mg in 6 weeks. Alloys have been corrosive for all immersion time in 3% NaCl. It means that Ti-12Cr (AT 30 ks) is better than others proposed alloys to biomedical application and may reduce the biological effect.

Comparing with another study, the result of mass reduction of Ti-12Cr with modified saliva solution (12 mg) [15] was higher than with 3% NaCl (mg). It is also caused by a various component of modified saliva solution than 3% NaCl, which has an effect on corrosion behavior.

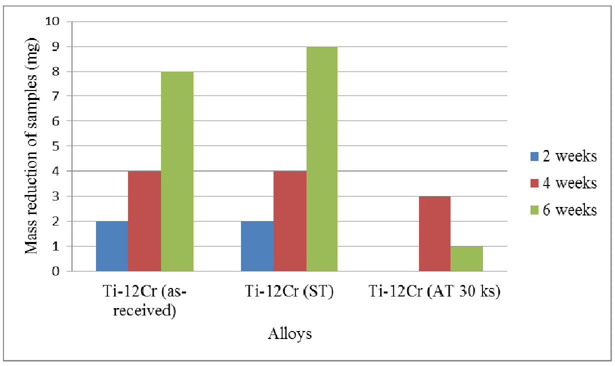


Fig. 2.Mass reduction of samples

2) Corrosion Rate

The corrosion rate of Ti-12Cr in 3% NaCl is tabulated in Table 4. Corrosion rate tends to increase along with additional of immersion time. The higher corrosion rate is Ti-12Cr (as-received). In 2 weeks immersion test, the corrosion rate is 0,0267 mmpy, 4 weeks is 0,0283 mmpy and in 6 weeks is 0,0380 mmpy. Corrosion rate takes place after 6 weeks in Figure 3. The result from observation of microstructure has shown some scratches like the abrasion process, except for Figure 4(c) that shows corrosion behavior, which is uniform for 6 weeks immersion in 3% NaCl solution. Furthermore, the chemical composition of Ti-12Cr (as-received) sample was observed for 6 weeks immersion time.

Weight of mass Ti-12Cr reduced to 70,18%. Cr element also reduced from 12% to 1,87%. It means that corrosion takes place in samples and make a scratch in the passive layer of Ti-12Cr. P and Cu element were inclusion on Ti-12Cr. Observation for chemical composition, as shown in Figure 4 and Table 5.

TABLE III
Specimen mass before and after immersion

Samples	Immersion time (weeks)	Mass before immersion (gram)	Mass after immersion (gram)
Ti-12Cr	2	0,921	0,919
	4	1,534	1,53
	6	1,492	1,484
Ti-12Cr (ST)	2	2,778	2,776
	4	2,623	2,619
	6	2,726	2,717
Ti-12Cr (AT 30 ks)	2	1,953	1,953
	4	2,485	2,482
	6	2,480	2,479

TABLE IV
Corrosion rates of the sample after immersed in 3% NaCl for 2, 4, and 6 weeks

Samples	Immersion time (weeks)	Surface area (cm^2)	Corrosion rate (mmpy)
Ti-12 Cr (as-received)	2	4,32	0,02675545
	4	4,09	0,02828874
	6	4,05	0,03804608
Ti-12Cr (ST)	2	5,18	0,02231540
	4	5,13	0,02252013
	6	4,95	0,03506706
Ti-12Cr (AT 30 ks)	2	5,04	0,00000000
	4	5,04	0,01720580
	6	5,04	0,00382351

TABLE V
RESULT OF THE CHEMICAL COMPOSITION OF TI-12CR AFTER IMMERSED FOR 6 WEEKS WITH ED

Elements	Weight of mass (%)
Ti	70,18
O	19,32
P	7,75
Cr	1,87
Cu	0,88
Total	100,00

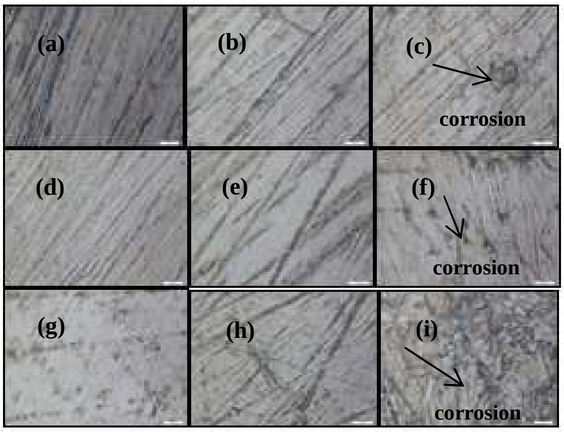


Fig. 3. Microstructure of Ti-12Cr ((a), (b), (c)), Ti-12Cr (ST) ((d), (e), (f)) and Ti-12Cr (AT 30 ks) ((g), (h), (i)) based on Optic microscop examination (magnification about 100x) during immersion time 2 weeks ((a), (d), (g)), 4 weeks ((b), (e), (h)) and 6 weeks ((c), (f), (i)) in 3% NaCl solution.

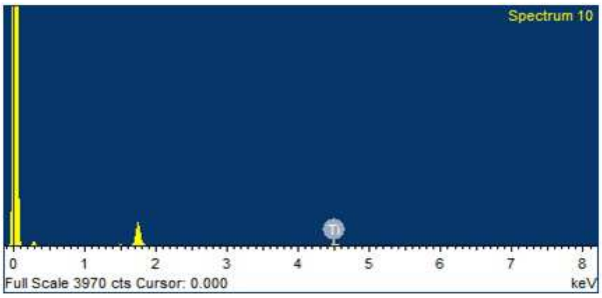


Fig. 4. Spectrum observation on chemistry composition of Ti-12Cr in 3% NaCl solution for 6 weeks with EDX.

C. Hardness

The hardness value of Ti-12Cr samples has shown in Table 6. The highest hardness value is Ti-12Cr (AT 30 ks) that is about 406 HVN, and the lowest is Ti-12Cr (ST) that is about 326 HVN for 6 weeks immersion. Enhancement of hardness value is caused by enhancing oxide layer that made on Ti alloy surface after immersion in 3% NaCl solution such as TiO_2 and Cr_2O_3. This oxide layer has high hardness value.

Corrosion may be interpreted as releasing of ion from alloy because of the tendency of element back to its original form [20]. There are two reactions which result in corrosion, namely oxidation, and reduction. In the oxidation process, the electron will be released by material with anodic features, while the reduction process takes place because of using electron by material with cathodic features. If it reacts with water, it will form titanium oxide and hydrogen [17]. The corrosion of Ti consists of the consumption of cathodic oxygen and the dissolution of anodic metal [21, 22].

TABLE VI
HARDNESS VALUE OF TI-12CR SPECIMEN BETWEEN BEFORE (0 WEEKS) AND AFTER IMMERSION WITH 3% NACL SOLUTION DURING 2,4 AND 6 WEEKS.

Samples	Immersion test (HVN)			
	0 week	2 weeks	4 weeks	6 weeks
Ti-12Cr	286	340	370	366
Ti-12 Cr (ST)	309	385	386	326
Ti-12Cr (AT 30 ks)	390	395	501	406

$$Ti(s) + 2H_2O\ (g) \rightarrow TiO_2\ (s) + 2H_2\ (g) \quad (2)$$

Rey [23] explained that the release of Ni and Cr ions in orthodontic excessively or corrosion causes negative effect to implant and braces. Ni and Cr are classified into heavy metal and may be allergic or carcinogenic effect to the body. Cr could make a protective oxide surface due to there is oxygen in its surface [24]. When Cr ion contact to oxygen in electrolyte media, it will be deposited to the surface becomes chromium oxide (Cr_2O_3).

Another research declared the corrosion behaviours of biomedical titanium alloys include Ti-12Cr. Ti-12Cr has been investigated in NaCl and HCl solutions. These solutions simulate biomedical implants environment that might be experienced in service. In NaCl solutions, the materials exhibit increasing OCP (open circuit potentials), the similarity of polarization curves, and passive behavior of materials. The resemble researches were also reported by Cai *et al.* [25] in aerated artificial saliva solution for CP Ti, Ti–6Al–4V, Ti–6Al–7Nb, and Ti–13Nb–13Zr. Oliveira and Guastaldi [26] viewed similar OCP behaviour in aerated Ringer's solution for Ti (pure), Ti–6Mo, and Ti–10Mo. On the other hand, deaerated conditions are used recently. Yu and Scully [25] investigated that similar OCP trends in deaerated Ringer's solution for Ti–6Al–4V Grade 5, Ti–35Zr–10Nb, Ti–15Mo– 3Nb–3Al and Ti–55Ni alloys, so the difference of material behaviours could be expected. Moreover, based on the E-pH diagram of Ti at 37°C [27], the more acidic pH could shift change the reaction of oxygen evolution becoming higher potentials, the open circuit potentials of all three alloys in 3% NaCl were within the stable region of TiO_2, indicating that spontaneous passivity is predicted thermodynamically.

Atapour *et al.*, (2011) [16] also showed the major corrosion behavior in the metastable ß condition could be related to the presence of Cr and its single-phase microstructure. According to his research, [28, 29] and also Codaro *et al.*, (2003) [30], corrosion in a/ß Ti alloys often gets started at α/ß interfaces. Furthermore, Shoesmith *et al.* explained that the different values of film formation on the α and ß phases also might cause film fracture at α/ß interfaces so initiating the corrosion attack [31]. We may state that The single-phase metastable ß microstructure was more corrosion resistant than the two-phase α+ß. In another hand, previous studies have shown that thermal oxidation produces a multi-layered structure atop of the bulk titanium, comprising a hardened oxygen diffusion zone (ODZ) and a rutile oxide layer (TiO2) at the surface [32-35]. The oxide layer has a tendency to delaminate from the substrate due to the high internal stresses built up in the layer during thermal oxidation. This is especially true when thicker layers are generated by oxidation at high temperatures or for prolonged times [36-38]. It has been observed that an oxidation temperature between 600^0C and 650^0C offers the best combination between oxide layer thickness and adhesion [36, 38, 39].

The result showed that there are Cr ions released to the solution based on Table 4. It indicates a mass reduction of samples, and it could give a negative effect. Configuration values of data to human body fluid are still unknown, so it is still unclear whether Cr ion released having negative effect seriously or not. It still needs more observes and data. Interactions between body fluids and the surface oxide layer (TiO_2) may cause adverse biological reactions and ion release, which could eventually lead to the failure of metallic bio-implants. Ion release of an implant can disturb cell behaviour and cellular metabolism by changing the pH and oxygen partial pressure [40].

IV. CONCLUSIONS

The following conclusions are reached: Corrosion rate depends on the time of immersion, where the highest corrosion rate is 0,038 mmpy in Ti-12Cr (ST) sample, and the lowest corrosion rate is 0,003 mmpy in Ti-12Cr (AT 30ks) samples in 6 weeks immersion time. The hardness value of Ti-12Cr surface increased exponentially with a time of immersion, where the highest hardness value is 406 HVN for Ti-12Cr (AT 30 ks) sample, and the lowest is Ti-12Cr (ST) sample that is 326 HVN in 6 weeks immersion time. Ti-12Cr (AT 30ks) is better than others for biomedical application based on corrosion resistance value.

ACKNOWLEDGMENT

First and second authors thank Ministry of Research, Technology, and Higher Education of the Republic of Indonesia for PMDSU scholarship and PMDSU research grant with the contract number 25/UN.16.17.PP.PMDSU /LPPM/2017. However, this work is mainly supported by research grant cluster GB Andalas University with the contract number 67/UN.16.17/PP.HGB/LPPM/2017.

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