Corrosion Resistance of $\beta$ type titanium (TNTZ) in 3%NaCl solution

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Abstract. Corrosion resistance of TNTZ in a salted environment has been done using a weight loss method. All samples were immersed in 3% NaCl solution for 2, 4, and 6 weeks. Samples consist of TNTZ (AT), TNTZ (ST), Ti6Al4V ELI, and CP-Ti. The weight of samples was measured before and after the immersion process using digital balance. Microstructure and composition of the sample surfaces were examined by using the optic microscope and EDX, respectively. The lowest corrosion rate after exposure for 6 weeks is CP-Ti while the highest one is TNTZ (AT) that is 0,003 mmpy. All microstructure of samples shows pitting, and crevice corrosion in the surfaces indicating corrosion has been started to occur on the samples. It was found that the corrosion is due to the destruction of the oxide layer in some weak point as a result of chemical reaction between the metal ions with Cl- ions. Some oxides are formed in 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 TNTZ (ST) ($\beta$ type Titanium) is much better than other materials in this research.

1. Introduction

Nowadays, titanium (Ti) and titanium alloy (Ti alloy) are the most purposed widely biomaterial in medical fields especially in orthopedic. There are several requirements that biomaterials have to
possess as implants like excellent physical, mechanical, chemical and biological properties. Strengths and Young's modulus would be closed to the human bones that are necessary to bear loads and doing various biofunctions [1]. Corrosion resistance of material should exist by preventing any debris or degradation in human body fluids and also biocompatibility knowing by no toxicity, allergic or inflammatory reaction that are important prerequisites for biomedical application. As we know that material response to the physiological environment is influenced by the surface properties of the material, so we need to assure material properties are excellent [2]. It relates to the long-term success of material as a medical implant. Furthermore, despite their mechanical and physiological relevance, microstructural investigation of the cyclic deformation behavior of implant alloys also have to be considered.

Some studies have been done to identify corrosion resistance and biocompatibility of pure Ti. Data showed that corrosion resistance of pure Ti was 40% in simulated biological solution exceed Ti6Al4V alloy [3]. Titanium and its alloys show excellent corrosion resistance. Another research found that Ti and Ti alloys under in vivo test, cut in a line of the passive layer has never been observed [2]. Pitting and crevice corrosion did not find on implants of Ti alloy also cobalt base alloys [4,5] under in vivo condition. Under in vitro test using isotonic saline solution, showed a weak susceptibility of the latter material class [5]. Cp titanium showed minimum current densities than Ti6Al4V and several β-alloys [6]. Atapour [7] has identified corrosion behavior of Ti–13Mo–7Zr–3Fe (TMZF), Ti–35Nb–7Zr–5Ta (TiOsteum), and Ti6Al4V in 0.9% NaCl and 5 M HCl solutions. All of three alloys indicated spontaneous passivity and very low corrosion rate in 0.9% NaCl, but in 5 M HCl, TiOsteum and TMZF in the metastable β condition have shown spontaneous passivity. It indicated that α/β phase boundaries were preferential sites for corrosion than the β phase.

Ti29Nb13Ta4.6 Zr (TNTZ), one of Ti alloys has been reported closer to modulus elasticity of cortical bone [8]. Other researches found that Niobium element could increase the corrosion resistance of the material. tantalum element [9] could be better in corrosion resistance because its oxidation stability highly [10,11] and its superior corrosion resistance also the biocompatibility of tantalum have been extensively evaluated [11]. Zirconium element (Zr) showed acceptable mechanical strength [12], and an in vivo study reports that zirconium implant exhibits good osteointegration [13]. This data showed that TNTZ is an excellent material as a medical implant. Zr is a neutral element of Ti that has a higher solubility for α Ti and β Ti. The alloy contains Zr can enhance strength dan improve plasticity of alloys so that the great processing properties could be guaranteed. Mo, Ta, Nb named as β phase stabilized elements which can completely solid-solubilized in βphase, lowers the βtransus temperature. They cause a strengthening effect on Ti and improve their properties [14].

Corrosion test of the implant is generally performed in simulated body fluid like physiological saline, Hank's solution or Ringer's solution even they do not show exactly body fluid responses that also contain some proteins, enzymes, and blood. But these simulated body solutions are near to in vivo conditions remaining the ion strength and possibly, the inorganic salts content [2]. Influence of proteins and enzymes is considered lower in a minimum number of investigations. So this research has used NaCl 3% to identify corrosion resistance of TNTZ compared with Ti6Al4V and CP-Ti.
2. Materials and Methods

2.1. Sample Preparation

Samples in this research were some titanium as TNTZ (AT), TNTZ (ST), Ti6Al4V and CP-Ti. 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.

2.2. Observation of Microstructure and Hardness Testing of Samples

Microstructure and chemical composition of samples were observed with Optic microscope and energy dispersive X-ray (EDX). 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°C. Load value was 9,8 N and indentation time was 15 minutes.

2.3. 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. The weight of samples (before and after treatment) was weighed with OHAUS PioneerTM digital. Corrosion rate was calculated using the following formula 1 [14]:

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

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 a specimen (cm^2)
T= time for immersion (hours)
3. Results and Discussion

![Microstructure images](image)

**Figure 1.** Microstructure of TNTZ AT (a,b,c), TNTZ ST (d,e,f), Ti6Al4V (g,h,i) and CP-Ti (j,k,l) after immersion test in 2, 4, and 6 weeks (left to right) in NaCl 3% solution with optic microscope (magnification about 100x).

Figure 1 shows samples surface condition. Along with the time, the surface has scraped and caused corrosion process happened. In other hands, the sample surface also makes protection by creating an oxide layer to minimize the corrosion process. This layer protects material to reduce corrosion behavior. The corrosion form is general, crevice and fretting corrosion (Figure 1) where these corrosion types could operate in combination [15]. General corrosion is experienced by metallic biomaterial, include titanium alloy (TNTZ) because of releasing metal ion after exposure time in physiological fluid. Metal ions release dissolution of passive oxide film dan ion transport passes the
film. Another research found that exposure Ti-6Al-4V in human serum formed Ti complexes with serum protein [16]. This phenomenon has been experienced in this research too.

![Chemical composition spectrum of TNTZ (AT) with EDX](image)

**Figure 2.** Chemical composition spectrum of TNTZ (AT) with EDX

| Element | The weight of mass (%) |
|---------|------------------------|
| Ti      | 41.38                  |
| Nb      | 28.22                  |
| O       | 15.79                  |
| Ta      | 9.07                   |
| Zr      | 3.39                   |
| Si      | 2.15                   |
| Total   | 100.00                 |

Table 1. The chemical composition of TNTZ (AT)

Corrosion form of TNTZ (AT) is uniform overall and increased by the immersion time. Based on EDX result (Figure 2 and Table 1) percentage of each element has changed and has been found element O. It proved that oxide layer existed there to protect material (TNTZ) and the concentration increased following corrosion process.

Mass reductions tend to increase along with immersion time, respectively. The highest value of mass reduction belongs to uncoated TNTZ (AT) for 6 weeks immersion time that is 0.012 gram (Figure 3). Reducing of mass affects the corrosion rate where increasing of reducing mass makes the corrosion rate becomes higher (Table 2 and Figure 4). Overall, the corrosion resistance of titanium TNTZ (ST) is better compared to other titanium alloys (Ti6Al4V) or pure titanium.
Figure 3. Mass reduction after immersion test in NaCl 3% 

Table 2. The corrosion rate of samples after 2,4,6 weeks was immersed in NaCl 3%

| No | Type of Titanium | Immersion time (weeks) | Surface area (cm^2) | Mass reduction (gram) | Corrosion rate |
|----|------------------|------------------------|---------------------|-----------------------|----------------|
| 1  | TNTZ (AT)        | 2                      | 4.47                | 0.002                 | 0.0258         |
|    |                  | 4                      | 5.04                | 0.009                 | 0.0516         |
|    |                  | 6                      | 5.09                | 0.012                 | 0.0454         |
| 2  | TNTZ (ST)        | 2                      | 4.95                | 0.000                 | 0.0000         |
|    |                  | 4                      | 5.11                | 0.000                 | 0.0000         |
|    |                  | 6                      | 4.95                | 0.001                 | 0.0116         |
| 3  | Ti6Al4V ELI      | 2                      | 5.04                | 0.001                 | 0.0114         |
|    |                  | 4                      | 4.52                | 0.002                 | 0.01278        |
|    |                  | 6                      | 4.47                | 0.005                 | 0.02153        |
| 4  | CP-Ti            | 2                      | 4.52                | 0.001                 | 0.01278        |
|    |                  | 4                      | 4.53                | 0.001                 | 0.00637        |
|    |                  | 6                      | 4.47                | 0.000                 | 0.00000        |
The corrosion rate of TNTZ (ST) is lower than other alloys because it formed passive film from two layers, an inner barrier layer for corrosion resistance and an outer porous layer, necessary for osseointegration [17, 18]. After chemical and heat treatment, it became bioactive [18]. Along by the time, corrosion happens, because passive film and oxides will hydrolize caused pH changing and accelerate the corrosion process on some zone of the implant [19].

Corrosion test also affects the hardness of samples. Based on the graph (Figure 3), TNTZ (AT) has the highest hardness value than other samples. Hardness measurement is a tool to estimate the effect of aging treatment like TNTZ (AT) on mechanical properties and to investigate the phase change of an alloy [20]. It has been shown on TNTZ (AT). Zhou [20] found that aging treatment causes hardness becomes high because the presence of $\omega$ phase beside oxide layer is forming.
4. Conclusions

The following conclusions are reached:

1. Corrosion rate depends on the time of immersion, where the highest corrosion rate is 0.0116 mmpy in TNTZ (ST) sample, and the lowest corrosion rate is 0.0454 mmpy in TNTZ (AT) samples in 6 weeks immersion time.
2. The hardness value of samples surface increased exponentially with the time of immersion, where the highest hardness value is 437 HVN for TNTZ (AT), and the lowest is CP-Ti, 178 HVN in 6 weeks immersion time.
3. TNTZ (ST) is better than others for biomedical application based on corrosion resistance value.

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