Corrosion Behavior Of New Type Titanium Alloy As Candidate For Dental Wires In Artificial Saliva On Fluctuating Temperatures

Jon Affi1, Fadhli Ihsan1, Hidayatul Fajri2, Gunawarman1*
1Mechanical Engineering Department, Faculty of Engineering, Andalas University, Padang, Indonesia
2Biomedical Science, Faculty of Medicine, Andalas University, Padang, Indonesia
*Corresponding author (E-mail): gunawarman@eng.unand.ac.id

Abstract. Titanium alloys are widely used for implant material due to high biocompatibility properties. It is well known that the corrosion resistance of titanium alloys is better than other metallic materials. However, if the alloys are applied for unknown condition such as wire in orthodontic application, the fluctuating temperature is important to be considered as parameter which influences on corrosion rate. In this study, the effect of fluctuating temperature on corrosion behavior of TNTZ was investigated. Two conditions of TNTZ were used in this study, i.e., Ti-29Nb-13Ta-4.6Zr aging treatment (AT) and TNTZ solution treatment (ST). For comparison, the commercial Ti6Al4V ELI was also used in this study. The corrosion rates of the samples were characterized in artificial saliva on fluctuating temperatures range between 10°C and 50°C by immersion testing. The results showed that the lowest corrosion rate for each variation of temperature was TNTZ ST. The corrosion process seems to decrease the hardness of TNTZ up to 26 VHN. The result also showed that the corrosion rate of TNTZ is much lower than that of Ti6Al4V in all cycles. Moreover, the hardness of Ti6Al4V decreases more significantly i.e., up to 77.2 VHN. The artificial saliva with fluctuating temperature induces corrosion process and decreases the hardness of the alloys.

Keywords: TNTZ, fluctuating temperatures, artificial saliva, corrosion rate, hardness.

I. Introduction

Titanium alloy has been used widely in the medical application such as orthodontic and orthopedic.[1]–[3] Compared with other traditionally metallic biomaterials, such as stainless steel and cobalt-chromium, the alloys have superior biocompatibility, lower modulus young, and enhanced corrosion resistance.[1] The attempting to upgrade the biocompatibility of titanium alloys in research is growing due to low biomedical performance of titanium still founds in some cases such as corrosion product attached at the tissue, implant breaks after long period’s implantation, and etc. Several Ti alloys have been developed, such as Ti-6Al-4V and Ti-6Al-7Nb for their enhancement wear resistance and improvement mechanical strength[2], [3], Ti15Zr4Nb4Ta and Ti29Nb13Ta4.6Zr with better corrosion resistance and mechanical properties, [4], Ti25Ta25Nb and Ti25Ta25Nb3Sn related to their on cytotoxic property [5].
The corrosion rate of biomedical metal is more often quantified using simulated (artificial) physiological solutions which model the human body fluid. Generally, the simulated solutions consist of salts which are almost similar to actual physiological solution content. Therefore, the using of simulated solution for evaluation of corrosion performance is accepted. Corrosion resistance of the metals is generated by continues oxides which is covered surface against oxygen. However, the contact of actual physiological solution with metals causes wear at surface and lead localized breakdown. Utilizing of Ti alloys as biomaterial implants has shown tendencies to break after long term using in replacing the hard tissue. [6]. In the cavity of the mouth, the using of metal for dental material exhibiting higher degradation degree if the environment with fluctuating temperature, pH varieties, high humidity, stress, and microorganism [7]. The effect of metals corrosion behavior contact with fluids may be different between them. The temperature variation may also effect on the corrosion rate of metals. In order to verify the corrosion rate of the biomedical implant at fluctuating temperature, the metals were immersed in the artificial saliva for certain temperature in hot and cold alternately by different time scheme.

II. Material and Methods

Two types titanium alloy were used in this experiment namely TNTZ and commercial Ti6Al4V ELI. TNTZ was provided by condition as solution treatment (ST) and as aging treatment (AT). The commercial Ti6Al4V ELI was also prepared as a standard of comparison test pieces. All corrosion samples were cut into disc shape with the thickness around 1-3 mm and diameter around ±15 mm so those suitable to be flatten using rotating of sand paper on polishing machines up to #2000 grids. The samples were mirror polished by using suspended of alumina powder in water at cloth polishes. The artificial saliva was prepared according to “Afnor” solution with composition shown in Table 1. The temperature of solution was set to hold at 10°C and at 50°C alternately.

Table 1. Chemical composition of “Afnor” artificial saliva. [7]

| Elemen     | NaCl | KCl  | KH2PO4 | NaHCO3 | NaH2PO4 | KSCN | UREA |
|------------|------|------|--------|--------|---------|------|------|
| g/l        | 0,7  | 1,2  | 0,2    | 1,5    | 0,26    | 0,33 | 0,13 |

All samples were immersed for 42 days (6 weeks) with three scheme hot-cold cycles as shown in Figure 1. In the scheme 1, the test pieces were held for 21 days at 50°C and 21 days at 10°C. In the scheme 2, the test pieces were held for 7 days at 50°C and for 7 days at 10°C and the cycle was repeated up to 42 days by 3 cycles. In the scheme 3, the test pieces were held for 3 days at 50°C and 3 days at 10°C and it was also repeated consecutively up to 42 days (7 cycles).
Figure 1. Scheme of testing variation; (a) 1 cycle, (b) 3 cycles, and (c) 7 cycles

Artificial saliva was put on the bottle with controlled environment. The low temperature of 10°C and the high temperature of 50°C were maintained by using the combination of a circulating heating simulator (Vivo Circulator iTherm RT2) and small ice blocks put on bottle surrounding. If the temperature drops below 10°C, the heating simulator will operate to increase temperature. Meanwhile, if temperature higher than 10°C, the heating simulator will operate by circulating ice blocks mixed in water to reduce temperature. Similarly, the high temperature of 50°C has resulted from the heater of the heating simulator.

The corrosion rate of samples was calculated by weight loss methods according to ASTM G1, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.

Characterizations of samples were performed by using Scanning Electron Microscope (SEM, S-3400N Type II). The initial condition of samples surfaces before corrosion was also evaluated using SEM for preliminary data. The hardness of samples before and after corrosion were evaluated with Vickers hardness tester (Shimadzu HMV-2).

III. RESULT AND DISCUSSION
3.1. Effect of immersion cycles hot-cold on corrosion rate

Figure 2 and Figure 3 show the quantitative corrosion rate of titanium alloy in “afnor” artificial saliva. Figure 3 was constructed from data in Figure 2 using formulation for corrosion rate based on ASTM G1 i.e:

\[
Cr = \frac{(K \times W)}{(D \times A \times T)}
\]

Where:
- \( Cr \) = Corrosion rate (miles per year)
- Constant for unit conversion = \( 3.45 \times 10^6 \)
- \( W \) = weight losses due to corrosion (g)
- \( D \) = Density of metal (g/cm\(^3\))
- \( A \) = Surface area (cm\(^2\))
- \( T \) = Time (hours)

There is no significant corrosion rate difference between those types of titanium alloys. Both as solution treatment and an aging condition of TNTZ elucidated similar corrosion rate after 42 days. The decline in the weight of the samples occurred due to formation metallic ion that suspended in the solution. As seen in Figure 2, weighing degradation is comparable with hot-cold immersion cycles i.e. more cycles resulted more weight reduction. It occurred for all types of titanium alloys. As seen in the Figure 2, the low corrosion rate occurred on samples with low cycles. Meanwhile, the samples with a high number of cycles have more weight reduction after completing 6 weeks immersed in the solution. Based on this result, the corrosion rate of dental wire would be affected by how often someone consumes meal at hot or cold temperature.

From Figure 2 is also revealed that weight reduction of Ti6Al4V Eli relatively similar to that of TNTZ AT for all cycles. However, TNTZ ST has the lowest corrosion rate than the Ti6Al4V has. The results are agreed with previous study[8], [9]. It was found that the corrosion rate of TNTZ ST is lower than corrosion rate of the Ti6Al4V after being tested by potentiodynamic methods at the constant temperature. This is due to present of Niobium and Zirconium elements in TNTZ which are the highly passivating metals. [10] The elements improve the corrosion resistance by the formation of more oxides at the surface of titanium such as ZrO\(_2\), TiO, Nb\(_2\)O\(_5\), and Ta\(_2\)O\(_5\). It strengthens the TiO\(_2\) passive film layer from oxygen attack. Moreover, non-toxic and non-allergic elements of Ti, Ta, Nb, and Zr support good biocompatibility with the tissues.[11], [12]
3.2 Observation of the surface morphology

Observation of surface corrosion were performed using SEM with 1000x magnification. As shown in Figure 4, the corrosion indication is marked as color differentiation, scrapping, or pitting in the surface of samples. The first row of the Figure 4 is condition of as polished samples for TNTZ ST, TNTZ AT and Ti6Al4V ELI respectively. As polished of TNTZ ST is homogenous distribution of single β phase. On the other hand, TNTZ AT and Ti6Al4V produce different surface morphology. Both of metal appears with other particle distributed on matrices β. As shown in Figure 4, the size of the second phase of Ti6Al4V seems to be larger than the second phase of TNTZ AT.

Along with increasing the cycle, crevice and pitting corrosion advanced in surface area. Samples of TNTZ ST with 1 hot-cold immersion cycle have induced pitting corrosion partially. An increasing in the number of cycles has promoted higher surface degradation where has shown as the pitting modes (Figure 4.b) changes into crevice of corrosion (Figure 4.c). Finally, the samples with 7 cycles yield more area of surface corrosion (Figure 4.d). Most of the surfaces have corroded. Similarly, the step of surface degradation also occurred on TNTZ AT samples but the corrosion appears worse than TNTZ ST samples as shown in Figure 4.g with larger crevice trace. Ti6Al4V samples revealed higher corrosion rate than TNTZ (Figure 4j- Figure 4l). There are some deep pitting and crevice at the surface of 3 and 7 cycles samples.

3.3 Hardness of samples

The hardness testing was performed in order to evaluate the effect of the corrosion process on the samples surface. The hardness of all samples showed in Figure 5. The initial hardness of samples before immersion in artificial saliva for TNTZ ST, TNTZ AT, and Ti6Al4V are 176.2 VHN, 332 VHN, and 346.8 VHN respectively. This result appropriates with the natural properties of the metal which content single or multiphase. TNTZ AT and Ti6Al4V consist of two-phase in the microstructure and thereby they have higher in hardness. The microstructure of multiphase has obtained increasing the strength through second phase strengthening mechanism.
The Figure 5 shows that the sharp drop of hardness belonging to Ti6Al4V in which the total hardness reduction was is 77.2 HVN. Meanwhile, the lowest hardness reduction of TNTZ ST was 26 HVN. It proved that the solution treatment condition has better corrosion resistance than the aging condition or multiphase microstructure.

Figure 4 SEM results of observation samples, the note (a, b, c, d) are TNTZ ST samples, (e, f, g, h) are TNTZ AT samples and (i, j, k, l) are Ti6Al4V. The first row showed the surface feature before immersion. The second, third and fourth row is the surface feature of 1 cycle, 3 cycles, and 7 cycles immersion, respectively.

Figure 4 SEM results of observation samples, the note (a, b, c, d) are TNTZ ST samples, (e, f, g, h) are TNTZ AT samples and (i, j, k, l) are Ti6Al4V. The first row showed the surface feature before immersion. The second, third and fourth row is the surface feature of 1 cycle, 3 cycles, and 7 cycles immersion, respectively.
IV. CONCLUSIONS

Based on the result, we may conclude that:

1. The corrosion rate of implantable titanium alloys was influenced by hot-cold immersion cycles in artificial saliva. The corrosion rate was proportional with number of hot-cold immersion cycles although they were immersed in similar periods (42 days).
2. The titanium alloys with solution treatment has better corrosion resistance than titanium multiphase for all hot-cold immersion cycles.
3. The lowest hardness reduction after corrosion has also occurred at solution treatment of titanium alloys.

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