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Corrosion resistance of new beta type titanium alloy, Ti-29Nb-13Ta-4.6Zr in artificial saliva solution

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Abstract. The corrosion resistance of Ti-29Nb-13Ta-4.6Zr (TNTZ) and Ti-6Al-4V alloys in oral cavity environment were studied by investigating its corrosion rate in artificial saliva solution. Corrosion measurement was conducted in 600 ml solution of Fusayama-Meyer artificial saliva containing 0.4g NaCl, 0.4g KCl, 0.795g CaCl₂·2H₂O, 0.69g NaH₂PO₄, and 1 g urea using a potentiostat controlled by a personal computer. The solution was maintained at pH 5.2 and controlled the temperature of 37°C to imitate oral cavity condition. After corrosion test, specimen surfaces were examined by SEM and EDX. The results show that the average corrosion rate of TNTZ and Ti-6Al-4V is 4.5×10⁻⁹ mmy⁻¹ and 6.4×10⁻⁸ mmy⁻¹, respectively, indicating that the corrosion resistance of TNTZ is slightly better than Ti-6Al-4V. This is suggested mainly due to the formation of multiple layers of Ti, Nb and Zr oxides in the surface of TNTZ. However, the formation of micro-pitting corrosion is more severe in TNTZ as compared to that of Ti-6Al-4V. The intense pitting corrosion in TNTZ is found strongly corresponded to its high impurities content and wide elemental segregation. It is recommended, therefore, a longer homogenizing process is required in TNTZ for reducing pitting corrosion attack. However, the details of corrosion mechanism are needed to be explored further.

1. Introduction
Titanium alloys, in particular Ti-6Al-4V, has been used as the most attractive dental materials due to their excellent combination of mechanical properties, corrosion resistance and biocompatibility [1-4]. However, the release of V and Al ions into the surrounded cell tissue by passive film dissolution [5] and wear corrosion [6], induce possible toxic effects in the human body [7]. Moreover, Young’s modulus of Ti-6Al-4V is still much greater compared to that of the cortical bone’s. This can be understood as these alloys are originally used for structural applications which need high modulus. Beta (β) type titanium alloys such as Ti-15Mo-5Zr-3Al and Ti-13Nb-13Zr with low Young’s modulus and greater strength have been, therefore, developed for biomedical applications [4,5]. A new beta type titanium alloy composed of non-toxic and non-allergic elements like Nb, Ta, and Zr, Ti-29Nb-13Ta-4.6Zr (TNTZ) [6], has been developed by Niinomi and co-workers in order to achieve much lower Young’s modulus and excellent mechanical performances. This alloy can have a wide range of mechanical properties by performing heat treatment or thermo-mechanical treatments on this alloy [6-8]. This alloy was found to have an excellent corrosion resistance in air and body fluids [9-13]. This may indicate that TNTZ also has potential to be used for orthodontic appliances. Some fundamental
works are still necessary to carry out in order to know the behavior of this alloy in oral cavity environment for such application.

Previous work on the corrosion test of TNTZ in 0.5% HCl and Ringer’s solution indicated that the corrosion rate of TNTZ varies according to the heat treatment and thermo-mechanical treatment where the cold-rolled of TNTZ has the highest corrosion rate among others [9]. The corrosion resistance of TNTZ, however, is slightly greater than those of forged Ti-15Mo-5Zr-3Al and Ti-6Al-4V ELI. While, measurement of corrosion rate in a modified artificial saliva using weight loss method indicates that the weight loss of TNTZ is zero up to exposure time of 480h [12]. At the same time, weight loss of two conventional alloys for dental application; stainless steel (SS) and cp-Ti can be easily obtained, that is 0.01g and 0.03 g, respectively. In order to understand the corrosion resistance of TNTZ in a artificial saliva, the corrosion rate is then measured by using a potentiostat in a Fusayama-Meyer artificial saliva medium at pH and temperature near oral cavity condition.

The corrosion rate of the most popular titanium, Ti-6Al-4V was also determined for comparison. The corrosion rates of these alloys are then compared to the corrosion rate of some conventional dental materials that are available in the literature.

2. Experimental Detail
As received samples in this study were rolled plates of TNTZ and bars of Ti-6Al-4V. Both materials were provided by Prof. Niinomi (Institute for Material Research, IMR, Japan). Some square plate specimens of TNTZ with a size of 10×10 mm and 3 mm thickness, and round Ti-6Al-4V with a diameter of 10 mm and 3 mm thickness were machined from the as-received materials (figure 1a). All sample surfaces were grinded gradually with emery papers from mesh size of #100 to #2000, and then polished and also cleaned prior to corrosion test to obtain smooth surface specimens. The surface of specimens was then fully covered with epoxy resin except for top surface for exposing to the artificial saliva solution (figure 1b).

![Figure 1](image_url)

**Figure 1.** Corrosion test samples (a) blank and (b) mounted specimens

Corrosion test was conducted in 600 ml solution of Fusayama Meyer artificial saliva solution containing 0.4g NaCl, 0.4g KCl, 0.795g CaCl₂·2H₂O, 0.69g NaH₂PO₄, and 1 g urea [14] which was provided by Faculty of Biomedical Engineering and Health Science, University Technology of Malaysia. This solution was maintained at pH 5.2 and 37°C during corrosion test using a potentiostat model (VERSA studio-200) controlled by a personal computer. Potentiodynamic polarization studies were carried out for 3h at a scan rate of 1 mV/s to obtain Tafel slot for each sample. Corrosion potential (Ecorr) and corrosion current density (Icorr) of each sample were then calculated from the Tafel slot. Corrosion rate (CR) of each sample was then determined using following formula (ASTM standards G01):

\[
CR = K_1 \frac{I_{corr} EW}{\rho}
\]  

where, CR is corrosion rate in mmpy, \( K_1 = 3.27 \times 10^{-3} \) mm g/µA Cm yr, \( I_{corr} \) = corrosion current.
density at $E_{\text{corr}}$, $EW =$ equivalent weight of material, and $\rho =$ density of material (g/cm$^3$).

Specimen surfaces were then observed by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS/EDX) and X-ray Photoelectron Spectroscopy (XPS). SEM examination was conducted at an acceleration voltage of 15 kV using Hitachi SEM S-340N. EDX was conducted at the same acceleration using EDX Horiba attached to the SEM machine. Both examinations were conducted at Andalas University, Padang, Indonesia.

3. Result and Discussion

Typical SEM micrograph of TNTZ and Ti-6Al-4V prior to corrosion process is shown in figure 2. The chemical composition of the alloy using EDX is tabulated in table 1. It can be seen that the presence of porosities and inclusions in both materials as indicated by black spots in the micrographs. The number of such impurities is more severe in TNTZ as compared to that of Ti-6Al-4V. This is due to the different preparation of both materials. TNTZ is still a new type material that has been manufactured for laboratory testing only. While, Ti-6Al-4V is a commercial one. The EDX result in Table 1 indicates that TNTZ, as expected, contains alloying elements of Nb (26.5%), Ta (13.5%) and Zr (3.9%) with a chemical composition close to the standard composition (29%Nb-13%Ta-4.6%Zr). While, Ti-6Al-4V contains alloying elements of Al (6.3%) and V (3.9%) which is also close to the standard one (6%Al and 4%V). However, the contents of other elements in TNTZ is much higher than that of Ti-6Al-4V. This verifies that TNTZ has much higher impurities than Ti-6Al-4V (Fig. 2).

![Figure 2. Surface condition of (a) TNTZ and (b) Ti-6Al-4V prior to corrosion process](image)

| Table 1. Chemical composition of the alloy by EDX |
|-----------------------------------------------|
| **TNTZ**                                      | **Ti-6Al-4V**                               |
| Element | %mass | %atom | Element | %mass | %atom |
|---- |---- |---- |---- |---- |---- |
| Ti    | 40.4 | 37.8 | Ti    | 86.9 | 77.1 |
| Zr    | 3.9  | 1.9  | Al    | 6.3  | 9.9  |
| Nb    | 26.5 | 12.8 | V     | 3.9  | 3.2  |
| Ta    | 13.5 | 3.3  | Others | 2.9  | 9.8  |
| Others | 15.7 | 44.2 |        |     |     |

Tafel curve of all samples obtained from the potensiosstat test is shown in figure 3. While, the calculation result of the Tafel curve is tabulated in table 2. It can be seen that $I_{\text{corr}}$ of TNTZ is much smaller than that of Ti-6Al-4V. As for the average $E_{\text{corr}}$ of TNTZ is also smaller than that of Ti-6Al-4V. However, the $E_{\text{corr}}$ of Ti-6Al-4V is more stable than that of TNTZ. Since corrosion rate (CR) is proportional to $I_{\text{corr}}$ value, the corrosion rate of TNTZ is much lower than that of Ti-6Al-4V. Averaged...
The corrosion rate of TNTZ is $4.48 \times 10^{-9}$ mmy$^{-1}$, while Ti6Al4V is $6.37 \times 10^{-8}$ mmy$^{-1}$. This value indicates that the corrosion rate of TNTZ is much smaller than the conventional dental wires of NiTi and stainless steel at pH 5 [7]. In orthopedic application, the low corrosion rate is essential as it minimizes the release of ion and particle to human digestion system, which in turns suppress the toxicity and allergic problems of elemental deposit inside human body [4].

![Figure 3. Tafel curve TNTZ and Ti-6Al-4V specimens](image)

| Specimen | $I_{\text{corr}}$ (A) | $E_{\text{corr}}$ (mV) | CR (mmy$^{-1}$) |
|----------|----------------------|------------------------|-----------------|
| TNTZ     | 1                    | $1.57 \times 10^{-7}$  | -350            | $1.36 \times 10^{-9}$ |
|          | 2                    | $6.99 \times 10^{-7}$  | -570            | $6.00 \times 10^{-9}$ |
|          | 3                    | $6.91 \times 10^{-7}$  | -380            | $6.07 \times 10^{-9}$ |
|          | **Avrg**             | $5.16 \times 10^{-7}$  | -433            | $4.48 \times 10^{-9}$ |
| Ti-6Al-4V| 1                    | $7.29 \times 10^{-6}$  | -406            | $6.33 \times 10^{-8}$ |
|          | 2                    | $7.51 \times 10^{-6}$  | -440            | $6.52 \times 10^{-8}$ |
|          | 3                    | $7.20 \times 10^{-6}$  | -490            | $6.25 \times 10^{-8}$ |
|          | **Avrg**             | $7.33 \times 10^{-6}$  | -463            | $6.37 \times 10^{-8}$ |

SEM observation result on the sample surfaces shows black spot in TNTZ and Ti-6Al-4V samples (figure 4). Elemental distribution in the black spots is tabulated in table 3. The high content of oxygen in the black spots indicates corrosion product. It can be seen clearly in Fig. 4 that corrosion area in TNTZ is wider than that in Ti-6Al-4V. The average content of oxygen in TNTZ is 46.7% that is much higher than that of Ti-6Al-4V (32.7%). This indicates that the formation higher amount oxides in TNTZ rather than Ti-6Al-4V. Moreover, the high content of Nb and Ta in the surface of the alloy may indicate that the oxide in TNTZ surface is not only titanium oxide, but also Niobium oxide and Tantalum oxide. In the case of Ti-6Al-4V, the oxide is predominantly titanium oxide as indicated by the very high content of Titanium in the corrosion area of Ti-6Al-4V. Elemental distribution in table 3 also confirms the corrosion attack in TNTZ is contributed directly by the artificial saliva solution. Almost all artificial saliva solution elements can be detected with a high content of chloride that is accumulation from NaCl, KCl, and CaCl$_2$.H$_2$O. However, the reason of the saliva elements undetected in all spots of Ti-Al-4V is not clear. A further investigation is needed to clarify this phenomenon, which will be reported separately.
Figure 4. Typical SEM micrograph of sample surfaces (a) TNTZ and (b) Ti-6Al-4V

Table 3. Elemental distribution near corrosion area of TNTZ and Ti-6Al-4V sample surfaces

| Sample   | Elements  | Spectrum 1 | Spectrum 2 | Spectrum 3 | Spectrum 4 | Avg  | Range |
|----------|-----------|------------|------------|------------|------------|------|-------|
| TNTZ     | Oxygen (O)| 70.9       | 27.7       | 36.4       | 50.0       | 46.7 | 43.3  |
|          | Titanium (Ti)| 7.2       | 36.0       | 24.6       | 23.2       | 23.3 | 28.8  |
|          | Niobium (Nb)| 6.3       | 22.7       | 18.8       | 16.8       | 15.7 | 16.4  |
|          | Tantalum (Ta)| 11.5      | 15.7       | 11.7       | 11.7       | 11.7 | 14.2  |
|          | Chloride (Cl)| 9.6       | 1.4        | 3.0        | 5.9        | 5.6  | 8.3   |
|          | Potassium (K)| 9.6       | 0.5        | 0.9        | 1.9        | 1.9  | 9.2   |
|          | Calcium (Ca)| 2.6        | 0.3        | 0.7        | 2.2        | 1.6  | 2.3   |
| Ti-6Al-4V| Oxygen (O)| 55.8       | 3.9        | 24.8       | 23.9       | 32.7 | 55.0  |
|          | Titanium (Ti)| 82.5      | 85.6       | 67.0       | 66.4       | 67.5 | 19.2  |
|          | Aluminium (Al)| 0.8      | 10.6       | 7.3        | 7.6        | 6.8  | 9.8   |
|          | Vanadium (V)| 0.6        | 0.8        | 2.1        | 1.3        | 1.3  | 1.5   |
|          | Sodium (Na)| 18.3       | -          | -          | -          | -    | -     |
|          | Chloride (Cl)| 17.1       | -          | -          | -          | -    | -     |
|          | Potassium (K)| 4.5        | -          | -          | -          | -    | -     |

SEM micrographs on the cross-section area at the surrounding of the corroded area and its elemental distribution are shown in figure 5 and table 4, respectively. Figure 5 shows pitting corrosion (or can be called as micro-pitting regard to the size of the pitting area) in both alloys, where, the micro-pitting in TNTZ is much deeper and swaller than that in Ti-6Al-4V. The oxygen content in the pitting area of TNTZ is also much higher than that of Ti-6Al-4V (table 4). This confirms that the formation of pitting corrosion in TNTZ is much more intense rather than in Ti-6Al-4V. Easier pitting corrosion attack in TNTZ is strongly suggested due to high element segregation in TNTZ. The range of alloying elements distribution in TNTZ is much wider than that of Ti-6Al-4V (table 3 and 4). The content of alloying elements (Nb, Ta, and Zr) is not detected in all spot of measurements. Moreover, high impurities content mentioned above is also contributed to induce more severe pitting corrosion attack in TNTZ (figure 2). In the case of Ti-6Al-4V, each alloying element is detected in all spectrum as can be seen in Table 4. Moreover, the range of composition of each alloying element in Ti-6Al-4V is tighter than that of TNTZ. This seems to provide a uniform protection on the surface of Ti-6Al-4V. In order to improve pitting corrosion resistance of TNTZ, an intense homogenizing process is necessary to apply in TNTZ prior to dental product application. It is well-known that homogenizing process is commonly applied to reduce element segregation in all alloys. Applying multi thermomechanical treatment is also improve element distribution in TNTZ [9].
Additional examinations on the surface of the sample are required to understand the corrosion resistance of TNTZ, e.g. by examining typical binding energy spectra of TNTZ using X-ray Photoelectron Spectroscopy (XPS) in order to determine the oxide compounds in the surface. The previous study showed the formation of multilayer (bi-layer) oxides in the surface of TNTZ [11]. The high intensity of oxygen and Titanium in TNTZ as compared to those of Ti-6Al-4V may indicate a high activation energy for uniform corrosion in TNTZ, and thus (uniform) corrosion resistance of TNTZ becomes better than that of Ti-6Al-4V.

### Table 4. Elemental distribution near micro-pitting area of TNTZ and Ti-6Al-4V

| Sample   | Elements | Spectrum 1 | Spectrum 2 | Spectrum 3 | Spectrum 4 | Avrg | Range |
|----------|----------|------------|------------|------------|------------|------|-------|
| TNTZ     | Oxygen (O)| 88.7       | 96.6       | 72.6       | 48.4       | 71.3 | 48.2  |
|          | Titanium (Ti)| 7.4     | 3.5        | 12.1       | 35.2       | 18.4 | 31.8  |
|          | Zirconium (Zr)| 3.2     | 4.8        | 3.7        | 3.6        | 3.6  | 1.6   |
|          | Niobium (Nb)| 0.8     | 10.5       | 12.7       | 8.2        | 8.2  | 12.0  |
| Ti-6Al-4V| Oxygen (O)| 2.1        | 41.8       | 35.1       | 27.1       | 27.1 | 39.7  |
|          | Titanium (Ti)| 82.5    | 45.5       | 54.8       | 58.0       | 58.0 | 37.0  |
|          | Aluminium (Al)| 2.2     | 2.1        | 3.7        | 2.6        | 2.6  | 1.6   |
|          | Vanadium (V) | 5.8     | 1.6        | 1.9        | 3.5        | 3.5  | 4.2   |
|          | Chloride (Cl)| 7.4     | 9.3        | 4.5        | 6.6        | 6.6  | 4.8   |

### 4. Conclusion
In order to understand the corrosion resistance of a new developed β type titanium alloy Ti-29Nb-13Ta-4.6Zr (TNTZ) in oral cavity environment, the corrosion rate of this alloy in a modified artificial saliva was investigated by using potentiostat. The corrosion rate of the most popular titanium, Ti-6Al-4V was also determined for comparison. The following results are obtained:

1. Corrosion resistance of TNTZ in the modified artificial saliva solution is greater than that of Ti-6Al-4V. It is suggested mainly due to the formation of multi-layer of Ti, Nb and Zr oxides, as compared to single-layer of Ti oxide in the surface of Ti-6Al-4V.
2. Micro-pitting is observed on the surface of both alloys, but micro-pitting in TNTZ is wider,
deeper and swallower than that in Ti-6Al-4V due mainly to a higher alloying element segregation in TNTZ as compared to that of Ti-6Al-4V. Moreover, high impurities of TNTZ is also contributed to the pitting corrosion attack.

3. In order to improve corrosion resistance, in particular pitting corrosion attack, an intense homogenizing process is recommended to apply in TNTZ for reducing the pitting corrosion.

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