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CORROSION BEHAVIOR OF NEW BETA TYPE TITANIUM ALLOY, TI-29NB-13TA-4.6ZR (TNTZ) IN FUSAYAMA-MEYER ARTIFICIAL SALIVA SOLUTION

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Abstract

In order to know precisely the corrosion behavior of a new developed β type titanium alloy Ti-29Nb-13Ta-4.6Zr (TNTZ) and ordinary titanium alloy Ti-6Al-4V (for comparison) in oral cavity environment, corrosion rate of these alloys in an artificial saliva solution was then investigated. Corrosion measurement was conducted in 600 ml solution of Fusayama-Meyer artificial saliva containing of 0,4 g NaCl, 0.4 g KCl, 0.795 g $CaCl_2.2H_2O$, 0.69 g NaH_2PO_4, and 1 g urea using a potentiostat model (VERSA studio-200) controlled by a personal computer. The solution was maintained at pH 5.2 and 37ºC to imitate oral cavity condition. After corrosion test, specimen surfaces were observed by SEM, EDX and XPS. The result show that the averaged corrosion rate of TNTZ and Ti-6Al-4V is 4.5×10^{-9} mmy^{-1} and 6.4×10^{-8} mmy^{-1}, respectively. This indicates that the corrosion resistance of TNTZ is relatively high, and it is better than that of Ti-6Al-4V. This is due to the formation of a multiple layer of Ti, Nb and Zr oxides in the surface of TNTZ. However, formation of micro-pitting corrosion is more intense in TNTZ due mainly to the alloying elements segregation and the presence of high impurities. It is recommended that, therefore, an intense homogenizing process is neccessary to apply in TNTZ for homogenizing the elemental distribution and, subsequently, for minimizing pitting corrosion attack. Having low pitting corrosion attack is an important thing for dental application in order to reduce stress concentration and crack initiation, and then to avoid mechanical failure during application.

Keywords: Artificial saliva, Corrosion rate, Dental material, Fusayama-Meyer, Titanium.

Nomenclatures

I_{corr}	Corrosion Current Density, A
E_{corr}	Corrosion Potential, mV
TNTZ	Ti-29Nb-13Ta-4.6Zr

Greek Symbols

β	Phase in titanium

Abbreviations

ASTM	American Standard for Testing Materials
CR	Corrosion Rate, mmy^{-1}
EDX	Energy Dispersive X-ray
ELI	Extra Low Interstitial
SEM	Scanning Electron Microscope
XPS	X-ray Photoelectron Spectroscopy

1. Introduction

Titanium alloys, in particular Ti-6Al-4V, up to now, 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], inducing possible toxic effects in the human body [7]. Beside, Young's modulus of Ti-6Al-4V, however, is still much greater comparing with that of the cortical bone [8]. This can be understood because these alloys are originally used for structural applications which needs 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 has also potential to be used for orthodontic appliances. Some fundamental works, therefore, 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 is varies according to the heat treatment and thermo-mechanical treatment where the cold-rollled of TNTZ has the highest corrosion rate among others [9]. The corrosion resistance of TNTZ, however, is slightly greater than 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 exposuring time of 480 h [12]. At the same time, weight loss of two conventional alloys for dental application; stainless steel (SS) and cp-Tican be easily measured, that is 0.01 g and 0.03 g, respectively. In order to know exactly the corrosion behavior of TNTZ in a modified artificial saliva, the corrosion rateisthen measured by using a potensiostat in a Fusayama-Meyer artificial saliva medium at pH and temperature near oral cavitity condition.

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

2. Experimental Procedure

As received samples in this study were a rolled plates of TNTZ and bars of Ti-6Al-4V that were provided by Institute for Material Research, Tohoku University, Japan. Three pieces of circular plate specimens of TNTZ and 3 pcs of those Ti-6Al-4V with a diameter of 10 mm and 3 mm thickness were machined from as-received bars. All sample surfaces were grinded, polished and 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.

Corrosion test were conducted in 600ml solution of Fusayama Meyer artificial saliva containing of 0.4 g NaCl, 0.4 g KCl, 0.795 g $CaCl_2.2H_2O$, 0.69 g NaH_2PO_4, and 1 g urea [14] which was provided by Faculty of Biomedical Engineering and Health Science, University Technology of Malaysia. This solution is maintained at pH 5.2 and 37^{o}C during corrosion test using a potentiostat model (VERSA studio-200) controlled by a personal computer. Potentiodynamic polarization studies were carried out at a scan rate of 1 mV/s to obtain Tafel slot of all 6 specimens. Corrosion potential (E_{corr}) and corrosion current density (I_{corr}) of each samples were then calculated from the Tafel slot. Corrosion rate (CR) of each sample was then determined using ASTM standars for corrosion test.

After corrosion test, specimen surfaces were observed by Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS/EDX) and X-ray Photoelectron Spectroscopy (XPS). SEM examination was conducted at acceleration voltage of 15 kV using Hitachi SEM S-340N. EDX was conducted at the same acceleration using EDX Horiba attached in the SEM machine. Both examinations were conducted in Andalas University, Padang, Indonesia. While, XPS analysis for measuring binding energy of chemical compounds was conducted in Tohoku University, Japan.

3. Result and Discussion

Typical SEM micrograhs of TNTZ and Ti-6Al-4V prior to corrosion process are shown in Fig. 1. Chemical composition of the alloy using EDX is tabulated in Table 1. It can be seen that the presence of porosities and inclusions in the both material 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 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 as shown in Fig. 1.

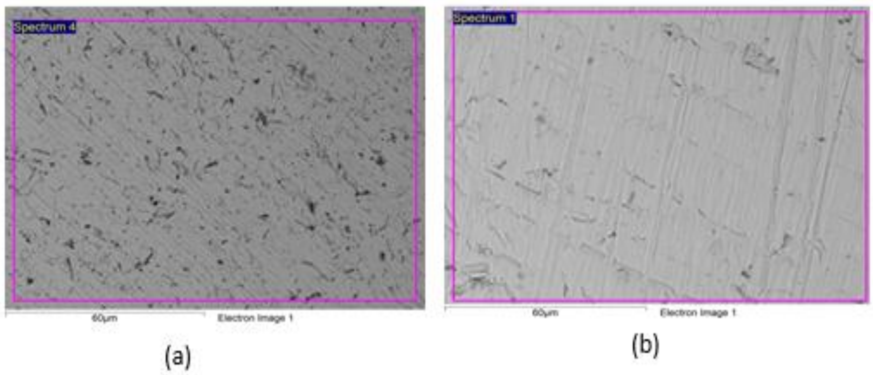


Fig. 1. Surface condition of(a) TNTZ, and (b) Ti-6Al-4V prior to corrosion process.

Table 1. Chemical composition of the alloy by EDX.

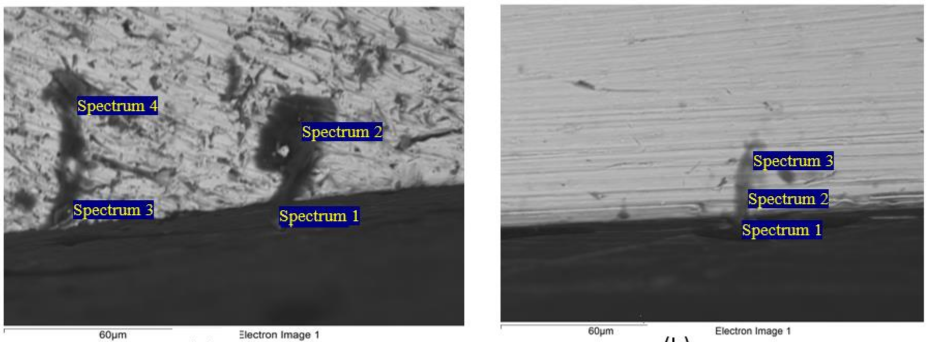
TNTZ			Ti-6Al-4V		
Element	% mass	% atom	Element	% mass	% atom
Ti	40.4	37.8	Ti	86.9	77.1
Zr	3.9	1.9	Al	6.3	9.9
Nb	26.5	12.8	V	3.9	3.2
Ta	13.5	3.3	Other	2.9	9.8
Other	15.7	44.2			

Tafel curve of all specimens that is obtained from potensiostat test is shown in Fig. 2. While calculation result of the Tafel curve is tabulated in Table 2. It can be seen that I_{corr} of TNTZ is much smaller than that of Ti-6Al-4V. As for the average E_{corr} of TNTZ is also smaller that of Ti-6Al-4V. However, the E_{corr} of Ti-6Al-4V is more stable than that of TNTZ. Since corrosion rate (CR) is proportional to I_{corr} value, the corrosion rate of TNTZ is much lower than that of Ti-6Al-4V. Averaged corrosion rate of TNTZ is 4.5×10^{-9} mmy^{-1}, while Ti-6Al-4V is 6.4×10^{-8} mmy^{-1}. This value is quite low as compared to corrosion rate of the conventional dental wires of NiTi and stainless steels. The corrosion rate of Ni-Ti alloy, for example, is around 4×10^{-8} at pH 5 [7].

Table 2. Result of potensiostat test on TNTZ and Ti-6Al-4V.

Specimen		I_{corr}**(A)**	E_{corr} **(mV)**	**CR (mmy^{-1})**
TNTZ	1	1.57×10^{-7}	-350	1.36×10^{-9}
	2	6.99×10^{-7}	-570	6.00×10^{-9}
	3	6.91×10^{-7}	-380	6.07×10^{-9}
	Avrg	5.16×10^{-7}	-433	4.48×10^{-9}
Ti-6A1-4V	1	7.29×10^{-6}	-406	6.33×10^{-8}
	2	7.51×10^{-6}	-440	6.52×10^{-8}
	3	7.20×10^{-6}	-490	6.25×10^{-8}
	Avrg	7.33×10^{-6}	-463	6.37×10^{-8}

SEM observation result on the cross section area of corroded samples shows that there is micro-pittings in TNTZ and Ti-6Al-4V samples (Fig. 3). It can be seen clearly in Figs. 3(a) and (b) that micro-pitting in TNTZ is deeper and shallower than that in Ti-6Al-4V. Elemental distribution near pitting area show that the content of oxygen in the pitting area of TNTZ is much higher than that of Ti-6Al-4V (Fig. 3(c)). This confirms that the formation of much more intense pitting corrosion in TNTZ rather than Ti-6Al-4V. Easier pitting corrosion attack in TNTZ is strongly suggested due to the element segregation in TNTZ where the content of alloying elements (Zr and Nb) is not detected in all spot of measurements especially in spectrum 2 (Fig. 3(c)). Moreover, high impurities content mentioned above is also contributed to induce more severe pitting corrosion attack in TNTZ. In the case of Ti-6Al-4V, each alloying element is detected in all spectra (Fig. 3(c)) in addition to its low impurities (Fig. 1(b)). Morever, the range of composition of each alloying element in Ti-6Al-4V is more tighter than that of TNTZ. This seems providing a uniform protection in 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 common applied to reduce element segregation in all alloys. Applying multi thermomechanical treatment is also improve element distribution in TNTZ [9].



(a) (b)

Sample	Element	Spectrum	Spectrum 2	Spectrum 3	Spectrum 4
	Oxygen (O)	88.69	96.55	72.59	48.36
	Titanium (Ti)	7.35	3.45	12.13	35.20
TNTZ	Zirconium (Zr)	3.20		4.82	3.71
	Niobium (Nb)	0.76		10.45	12.74
	Oxygen (O)	2.06	41.78	35.10	
	Titanium (O)	82.49	45.52	54.80	
Ti-6A1-4V	Aluminium (Al)	2.19	2.08	3.68	
	Vanadium (V)	5.83	1.62	1.91	
	Chlor (Cl)	7.43	9.30	4.51	

(c)

Fig. 3. SEM Micrograph of cross section sample (a) TNTZ and (b) Ti-6Al-4V, and (c) element distribution near micropitting of each indicated spectrum.

A typical binding energy spectrum of TNTZ is shown in Fig. 4, and the range of binding energy and intensity spectra of each alloy is tabulated in Table 3. This XPS result show that binding energy and intensity of Oxygen and Titanium is higher than those of Nb, Zr and Ta. This indicates that formation of predominantly titanium oxidelayer in the surface of TNTZ in addition to Nb, Zr and Ta oxides. The formation of multilayer (bilayer) oxides in the surface of TNTZ ia also observed previously [11]. While, the binding energy of Ti in Ti-6Al-4V is almost the same but with low intensity. The high intensity of oxygen and Titanium in TNTZ as compared to those of Ti-6Al-4V indicates a high activation energy or uniform corrosion in TNTZ, and thus (uniform) corrosion resistance of TNTZ becomes better than than that of Ti-6Al-4V.

Table 3. Range of Binding Energyand intensity of TNTZ and Ti-6Al-4V.

Sample	Element	Binding Energy (EV)	Intensity
TNTZ	Oxygen (O)	520 - 540	88.000
	Titanium (Ti)	450 - 470	44.000
	Niobium (Nb)	194 - 214	18.000
	Zirconium (Zr)	173 - 187	7.400
	Tantalum (Ta)	14 - 32	5.000
Ti-6A1-4V [14]	Oxygen (O)	528 - 540	12.000
	Titanium (Ti)	450 - 476	6.000
	Aluminium (A1)		
	Vanadium (V)		

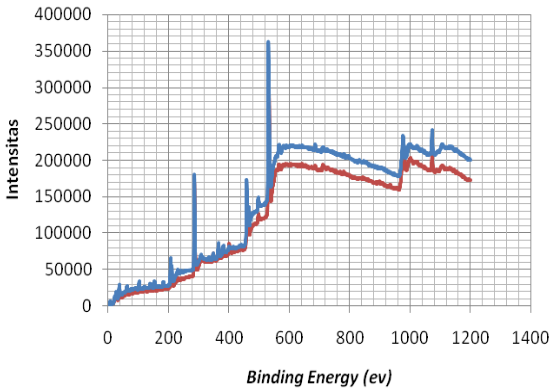


Fig. 4. Typical binding energy spectra of TNTZ.

As mentioned above, the new beta type titanium alloy, TNTZ, consists of non-toxic and non-allergic elements of Nb, Ta, and Zr. This provides the alloy as one the highest biocompatibility alloys for medical applications [4]. These alloying elements also contributes significantly to form low young's modulus alloy and controllable mechanical properties through heat treatment and thermomechanical treatments [4, 5]. In the point of view corrosion properties, this study reveals that this alloy also shows very low corrosion rate in the Fusayama-Meyer artificial saliva. Having low corrosion rate is an important thing for orthopedic application in order to minimize ion and particle release to human biological system, and then for reducing toxicity and allergic problems of elemental deposit inside human body [4]. With good combination of mechanical properties and corrosion resistance, this alloy becomes pottential for using in dental applications that really needs high strength materials and excellent in biocompatibility. The ordinary dental alloys, stainless steel (Fe-Cr-Ni alloys) and Ti-Ni alloys has excellent mechanical properties, but relatively low in biocompatibility. It is reported the use alloying element of Ni for medical applications leads to cause allergic problem to hypersensensitive patients [9].

One of the limitation of this alloy is the price due to using of such expensive alloying elements. Beside, from this study, the use of much type and high content elements has a problem on the elemental distribution (Fig. 3). TNTZ show segregation and the presence of high impurities that leads to induce pitting corrosion attack. However, this problem can be minimized by a longer homogenizing process as commonly applied to structural alloys. Having low pitting corrosion attack is also an important thing for dental application in order for reducing stress concentration, crack initiation, and subsequently to avoid mechanical failure during application.

4. Conclusion

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

- Corrosion resistance of TNTZ in the modified artificial saliva solution is greater than that of Ti-6Al-4V due mainly to formation of multi-layer of Ti, Nb and Zr oxides, as compared to single-layer of Ti oxide in the surface of Ti-6Al-V.
- Micro-pitting is observed in the surface of both alloys, but micro-pitting in TNTZ is deeper and shallower than that in Ti-6Al-4V due mainly to a higher alloying element segregation in TNTZ as compared to that of Ti-6Al-4V.
- It is recommended that an intense homogenizing process is necessary to apply in TNTZ for reducing pitting corrosion attack. Having low pitting corrosion attack is an important thing for dental application in order to reduce stress concentration and crack initiation, and then to avoid mechanical failure during application.

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