Corrosion Behaviour of New Beta Type Titanium Alloy TNTZ in Modified Artificial Saliva

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Abstract: A β type titanium alloy, Ti-29Nb-13Ta-4.6Zr (TNTZ) with high biocompatibility and low moduli has been recently developed for biomedical applications. This alloy also has potential to be used for orthodontic appliances. For such purpose, it is necessary to investigate the behaviour of this alloy in oral cavity environment. This work presents the corrosion rate of this alloy in a modified artificial saliva medium. The corrosion behaviour of the TNTZ was determined by static accelerated corrosion test in modified artificial saliva solution for 100 to 480h. Two common commercial dental materials, pure Ti and stainless steel (SS) are also tested for comparison. The corrosion tests were conducted at ambient atmosphere by immersing samples into the solution. Weight losses were measured every 12h using digital balance. Corrosion penetration rate was then calculated using the measurement data of weight loss, density of the material, corrosion area and exposure time. The result that the corrosion penetration rate of TNTZ in modified artificial saliva solution is slightly lower than that of cp-Ti, but much lower than that of SS. This is confirmed by the corrosion area, where the corrosion area of SS is relatively wider and more uniform than those of cp-Ti and TNTZ. This indicates that the corrosion resistance of TNTZ in the modified artificial saliva is greater than that of the commercial dental materials. Since all materials used in human mouth needs a high corrosion resistance, TNTZ has, therefore, high potential to be used for orthodontic appliances.
Keywords: Corrosion, titanium alloys, Ti-29Nb-13Ta-4.6Zr (TNTZ), biomaterial, dental, artificial saliva

1. Introduction

Stainless steels and cobalt alloys have been widely used for biomedical applications because of their excellent combination of strength and corrosion resistance. [1]. However, toxicity and allergic problems of alloying elements and high Young's modulus of these materials have been pointed out recently. [2,3]. Titanium alloys, in particular α+β type titanium alloys such as Ti-6Al-4V ELI and Ti-6Al-7Nb, have been then used as the most attractive biocompatible metallic materials due to their excellent combination of mechanical properties, corrosion resistance and biocompatibility [3]. Their Young's moduli are, however, still much greater comparing with that of the cortical bone. This can be understood because these alloys are originally used for structural applications which need high modulus. Beta type titanium alloys such as Ti-13Nb-13Zr and Ti-15Mo-5Zr-3Al 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. Previous research works on this alloy showed that TNTZ can have 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 indicates 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 behaviour of this alloy in oral cavity environment. This work presents the corrosion rate of this alloy in a prepared modified artificial saliva medium. Two conventional alloys; stainless steel (SS) and commercial pure (cp) Ti for dental applications has been also tested in this work for comparison.

2. Experimental Methods

Corrosion behaviours of the alloys were determined by static accelerated corrosion test in modified artificial saliva solution for long time (up to 480h). The solution used in this study consists of several elements as shown in Table 1. The corrosion tests were conducted at ambient atmosphere (300K) by immersing samples into 200 ml of the solution. The samples are TNTZ containing (in mass%) 31.5Nb, 11.6Ta, 4.7Zr, 0.03Fe,

Table 1. The content of modified artificial saliva [14]

Elements	Amount
Na_2HPO_4	0,426 g
$NaHCO_3$	168 g
$CaCl_2$	0,147 g
H_2O	800 ml
HCl-1M	2,5 ml

<0.02Al and bal.Ti and cp Ti (both provided by IMR, Tohoku Univ., Japan), and stainless steel that is commonly used as teeth brackets. All sample surfaces were prepared carefully by grinding, polishing and cleaning prior to immersing into the solution. Weight losses were measured every 12h using digital balance. Corrosion penetration rate, CPR, in mm/year was then calculated using equation 1 [15],

$$CPR = \frac{87.6 W_{loss}}{DAT} \quad \text{.........................} (1)$$

where W_{loss} = weight loss (g), D = density (g/cm^3), A= area (cm^3) and T=time (h). Sample surfaces and corrosion area were examined using a light microscope with an image measurement.

3. Results and Discussion

The averaged weight loss of each sample for the indicated range of exposure time in the modified artificial saliva solution is shown in Figure 1. It can be seen that the weight loss of TNTZ is not detected up to exposure time of 480h. While, in the same period, the weight loss of cp-Ti and SS is 0.1g and 0.3g, respectively. Figure 1 shows that the rate of weight loss of TNTZ is lower than cp-Ti and SS, and the weight loss is clearly detected after exposure time more than 100h. The rate of weight loss of SS is very high up to 400h, and then relatively small after 400h. While, the rate of weight loss of cp-Ti is relatively moderate among the three biomaterials. The rate of weight loss TNTZ is almost zero for the exposure time up to 480h.

Typical micrograph of the specimen surface of TNTZ using light microscope is shown in Fig. 2. It can be seen that corrosion area in TNTZ is narrow. Measuring result of corrosion area on some micrographs using Jenco Scientific Image Measurement show that the corrosion area of SS are relatively wider and more uniform than those of cp-Ti and TNTZ. The percentage of corrosion area of TNTZ is 3.07%. While, the percentage of corrosion area of cp-Ti, and SS after exposure time of 480h are 5.19 and 16.53%, respectively as shown in Figure 3.

The calculated CPR calculated of TNTZ is also much lower than that cp-Ti and SS. The value of CPR of each alloy is 0.001, 0.0015 and 0.0024 mm/y, for TNTZ, cp Ti and SS, respectively.

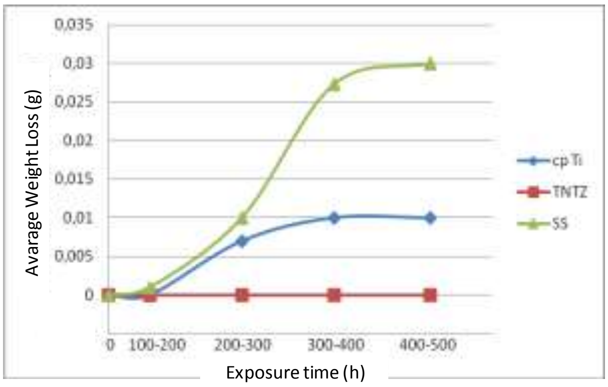

Figure 1. Weight loss of the indicated samples

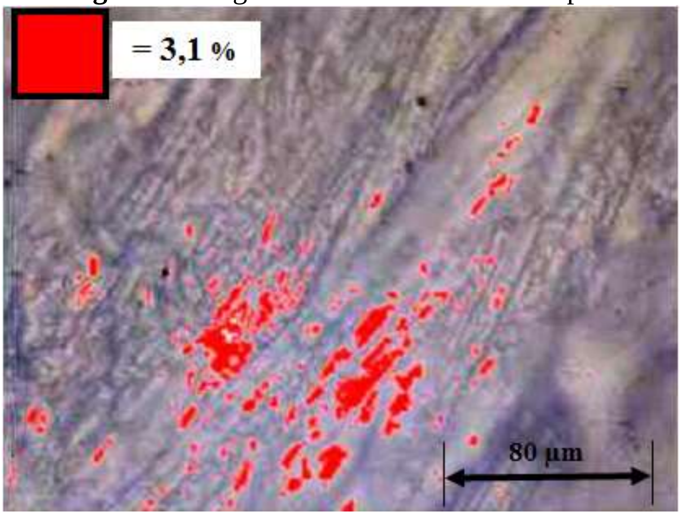

Figure 2. Typical micrograph of surface area of TNTZ after exposing 480h in the solution

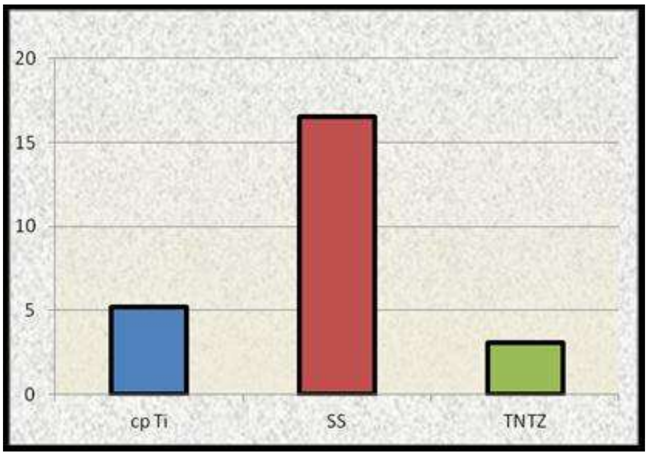

Figure 3. Percentage of corrosion area

The results shows that the corrosion resistance of TNTZ in modified artificial saliva solution is slightly greater than that of cp-Ti, but much higher than that of SS. Previous works [9-13] also showed that, in general, the corrosion of TNTZ is relatively higher than other titanium alloys in artificial body fluids. Corrosion behaviour of TNTZ also depends on the heat treatment process prior to corrosion test. The passive current density of the thermo-mechanical treated TNTZ, for instances, is much smaller than that of heat-treated TNTZ in either 5%HCl or Ringer's solutions.[9]. However, the values are a little smaller than those of annealed Ti-15Mo-5Zr-3Al and aged Ti-6Al-4V ELI.

The study of fretting-corrosion behavior of TNTZ and other titanium alloy in Hank's balanced salt solution showed that TNTZ and Ti–13Nb–13Zr are able to recover their passive state during fretting at open circuit potential [10]. TNTZ can also regain its passive state during fretting at an applied potential in the passive region. While, the response of Ti–13Nb–13Zr depends on the wear volume at the same electrochemical conditions. The ability of these alloys to recover their passivity despite fretting is a property which is beneficial to implant applications, since the release of metal ions and particles is expected to be limited. On the contrary, Ti–6Al–4Fe exhibited a widespread depassivation when fretting at a passive potential which led to the formation of large dissolution pits in the vicinity of the wear track.[10]. TNTZ seems to have an unique behaviour where a single layer of oxide film is available on the surface of the alloy [13]. These results confirm that the high corrosion resistance of TNTZ among some other mentioned biomaterials.

Since all materials used in human mouth needs a high corrosion resistance [16], TNTZ has, therefore, very high potential to be used for orthodontic appliences. This advantage may also useful to avoid allergic incidences, hypersensitivity reaction and other side effects, which suffer some patients using conventional othodentic appliences containing Ni such as SS and Ni-Ti [16,17].

4. Conclussion

1. The rate of weight loss of TNTZ is lower than cp-Ti and SS especially for exposure time more than 100h.
2. The corrosion area of SS is relatively wider and more uniform than those of cp-Ti and TNTZ. The percentages of corrosion area of TNTZ, cp-Ti, and SS after exposure time of 480h are 3.07, 5.19 and 16.53%.
3. The CPRs of TNTZ, cp-Ti and SS are obtained as much as 0.001, 0.0015 and 0.0024 mm/y.
4. The corrosion rate of TNTZ in modified artificial saliva solution is greater than that of conventional materials (SS and cp-Ti). This property gives more advantage for TNTZ to be use for orthodontic appliences.

5. References

1. R. Schenk: Titanium in Medicine, Springer, ed. by D. M. Brunette, P. Tengvall, M. Textor and P. Thomesen, (2001) 144–170.
2. M. Niinomi et al, Mater. Trans. 43 (2002) 2970–2977.
3. M. Semlitsch, F. Staub, H. Weber, Biomed. Technik. 30 (1985) 334–339.
4. I. Milosev, T. Kosec, H.-H. Strehblow, Electrochim. Acta 53 (2008) 3547–3558.
5. T.M. Lee, Mater. Sci. Mater. Med. 17 (2006) 15.
6. M . Niinomi, Mat. Mater. Trans. A 33A (2002) 477–486.
7. S. Li, Y. Hao, R. Yang, Y.Y. Cui, M. Ninomi, Mater. Trans. 3 (12) (2002) 2964.
8. N. Sakaguchi, M. Ninomi, T. Akahori, J. Takeda, H. Toda, Mater. Sci. Eng. C 25 (2005) 370.
9. T. Akahori et al, Materials Transactions, Vol. 45, No. 5 (2004) pp. 1540 to 1548
10. N. Diomidis, S. Mischler, N.S. More, M. Roy, and S.N. Paul, Wear 271(2011) 1093–1102
11. M. Karthega, V. Raman,and N. Rajendran, Acta Biomaterialia 3 (2007) 1019–1023.
12. Y. Tanaka *et al*, Corrosion Science 50 (2008) 2111–2116.
13. V. Raman, S. Nagarajan, and N. Rajendran, Electrochemistry Communications 8 (2006)

1309–1314
14. N.A. Mariano, et al (2009), Revista Materia 14:878-80.
15. ASTM G1-03 (1997), Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, ASTM Standards Vol. 3.02,
16. L. Canine et al (2003), MIKGI 10.5
17. M. Nurfadillah (2012), http:// maryamnurfadilah. wordpress. Com

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