Surface modification of β-Type titanium alloy by electrochemical potential pulse polarization

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Abstract. In the present work, we report the formation of a porous oxide / hydroxide surface layer on the Ti-29Nb-13Ta-4.6Zr (TNTZ) alloy achieved by the combination of an alkali immersion and a potential pulse polarisation process. The alkali treatment has been employed for pure titanium to produce amorphous and porous layer prior to hydroxyapatite (HAp) growth. But, in the case of TNTZ, immersion in 5M NaOH at the open circuit potential (OCP) at 60°C for 24 hours, did not yield any uniform layer, instead a thick deposited layer with highly cracked one. The cracks were attributed to the growth of a tantalum enriched particulate. In order to avoid the crack formation, the electrochemical behaviour of the alloy and the pure alloying elements (Ti, Nb, Ta and Zr) was investigated to produce a uniform surface with the application of a square wave modulated potential pulse polarization, leading to the formation of a relatively uniform porous layer on the alloy.

1. Introduction
Titanium and its alloys are widely used for orthopaedic implant applications due to their favourable mechanical properties and biocompatibility. The alloys such as Ti-6Al-4V and Ti-6Al-7Nb are suitable for implant materials, but, their elastic modulus is higher compared with that of bone. β type titanium alloy, such as Ti-29Nb-13Ta-4.6Zr (TNTZ) alloy, has been developed to achieve elastic modulus close to bone [1-4]. Similar to other biomedical titanium alloys, TNTZ alloy also might be difficult to attain favourable bonding with bone and tissues directly. Therefore, some surface modification is required to improve its biocompatibility.

Various surface modification methods have been proposed to establish biocompatibility [5]. One such treatment includes the alkali treatment where titanium and titanium alloys are immersed in a high concentration of NaOH solution, which leads to the formation of a thin-amorphous sodium titanate layer on the surface [6-8]. The sodium titanate layer has a sponge-like homogeneous porous structure with the pore size of approximately 1 µm as shown in Fig 1. A subsequent heat treatment of the alkali treated specimens modifies the layer. The heat-treated layer when immersed in a simulated body fluid (SBF), results in the
formation of Ca-P layer [9]. This alkali treatment is much simpler, more economical and capable of producing uniform coating on complex shape implant. On the other hand, such homogeneous porous structure is hard to form on Ti alloys. In the present work, we report the electrochemical behaviour of each alloying elements contained, then propose the process to produce a porous layer on TNTZ alloy with the combination of the alkali treatment and an electrochemical pulse polarization.

2. Experimental
Specimens examined were pure Ti, pure Nb, pure Ta, pure Zr (the purity level of all the metals are in the range of 99.95% up) and the TNTZ alloy with the dimensions of 10mm x 10mm x 2mm. The specimens were mechanically ground with emery paper up to 2000 grit, and further polished to mirror finish with 3 µm alumina. The specimens were ultrasonically degreased in acetone and distilled water, successively, followed by rinsing with distilled water and finally drying in air.

For electrochemical measurements the conventional three-electrode electrochemical cell was used with Pt wire and Ag/AgCl as the counter and reference electrode, respectively. The specimens were pressed against an O-ring with Cu plate in the electrochemical cell, leaving approx. 60mm² exposed to an electrolyte. All experiments were carried out in 5M NaOH at 60°C. The electrolyte was prepared from analytical grade chemicals and demonised water.

For immersion tests, the specimens were immersed with a 1mm platinum wire in a 5M NaOH solution for a period of 1 day at 60°C. The specimens were prepared by holding potential at an open-circuit potential (OCP) and desired applied potentials. The morphology of the specimens were observed using a JEOL 6500 series Field Emission Scanning Electron Microscope (FE-SEM) with the Energy Dispersed X-ray (EDX) unit.

3. Results and discussion

2.1.1 Alkali treatment.
The conventional surface treatment for a bioactive surface was prepared for the TNTZ alloy by immersing in 5M NaOH at 60°C for 24 hours. Morphology of the surface was examined with SEM. The TNTZ alloy produced a thick, highly cracked surface. In order to understand the crack growth, the morphology was studied at different exposure time.

After 1 hour of exposure, the surface exhibited particulates incorporated in a continuous film as seen in Fig. 2(a). Fig.2(b) shows the morphology after 3 hours of exposure time, the surface exhibited some cracks, which initiate around the particle. After 24 hours, the surface was highly cracked as shown in Fig.2 (c). The layer and white particulates grew in thickness and in size and amount, respectively, with time. Therefore, the excessively broken film with the growing thickness can be attributed to the continuous growth of the white particulate. EDX analysis was carried out to characterize the chemical composition of the white particulates. The position analysed is marked as A in Fig.3. For comparison, the surrounding area indicated as B in Fig.3 is also examined. The EDX analysis revealed that tantalum is enriched in the particulate (Table 1), compared with the surrounding layer with trace amounts of oxygen, sodium and the other elements. Fig.4(a) shows an as-polished specimen of the TNTZ alloy exhibiting few tantalum enriched spots. After 30 minutes of immersion in

![Fig.2 TNTZ alloy treated at open circuit potential for (a) 1 hr, (b)3 hrs and (c) 24 hrs](image-url)
5M NaOH at 60°C, on the other hand, many localised tantalum enriched spots were identified as shown in Fig.4 (b). In other words, the localized enrichment of tantalum occurred during immersion in the alkali medium. Kokubo et al., reported the formation of a crystalline Na$_2$Ta$_4$O$_{11}$, sodium tantalate, over the tantalum substrate after immersion in a 0.5M NaOH at 60°C for 24 hours[10]. The tantalum enriched particulates observed in the present work might be the localised formation of a crystalline sodium tantalite. Considering that these spots were not observed when specimen is immersed within 30 minutes, the tantalum enriched particulates grow into the surface layer from the bottom of the layer, resulting in destructing the uniform nature of the film. These small cracks propagate and the film fragments into many pieces with the growing thickness of the layer as shown in Fig. 2. In order to overcome this problem, electrochemical methods can be adopted. Hence, the electrochemical behaviour of the alloy and its constituent elements was measured.

2.1.2 Open Circuit Potential
The changes in the open circuit potentials for the TNTZ alloy and its elements with time measured in 5M NaOH at 60°C for 24 hours are shown in Fig.5. After 24 hours, all the metals attained a noble potential compared to the initial potential. The OCP of TNTZ alloy was comparable with that of Ta and Nb rather than that of Ti or Zr. During the first one-hour immersion, OCP of all the metals dropped in the less noble direction and then stabilized with exposure time. The decrease of OCP with time indicates the dissolution of the air formed films. It was also noted that there was no distinct change in the order of the nobility compared to 24 hours immersion. The TNTZ alloy exhibited OCP as low as –1.41V, a potential lower than that of pure Nb and Ta. The potentials of pure Ta and the TNTZ alloy shifted less noble with exposure time until 24 hours. The behaviour of TNTZ alloy was more closely comparable to pure Ta or Nb rather than Ti although the mass % of Ti in the alloy

### Table 1  EDX data of TNTZ alloy treated at OCP for 12 hours. (mass%)

| Elements | A      | B      |
|----------|--------|--------|
| O (K)    | 3.78   | 21.36  |
| Na (K)   | 0.54   | 8.78   |
| Ti (K)   | 10.73  | 43.69  |
| Zr (L)   | 1.52   | 6.49   |
| Nb (L)   | 4.46   | 7.21   |
| Ta (M)   | 78.97  | 12.47  |
| Total    | 100.00 | 100.00 |
composition was higher. This behaviour of the alloy can be attributed to the high alloying content in the alloy. Furthermore, Nb and Ta are more reactive to aggressive alkali medium than Ti.

2.1.3 Polarization studies
Anodic polarization curves were also measured for the TNTZ alloy and its constituent elements after 1 hour and 24 hours of immersion in 5M NaOH at 60°C with a scan rate of 60mVs⁻¹.

Fig. 6(a) shows the anodic polarization curves obtained after 1 hour of immersion. Nb and Ta exhibited relatively high current densities in both active and passive regions, while Zr showed the lowest current density with a highly stable passive region. Ti exhibited essentially no active dissolution peak, while showing a small current increase at around 0.4 V, which might be due to a change in the stability of the oxide film. The TNTZ alloy had a current density pattern similar to that of Ti with a pronounced increasing current at more noble than 0.4 V.

Fig. 6(b) shows the anodic polarization curves measured after 24 hours of immersion. Nb, Ta and TNTZ alloy had a very low initial OCP, while Ti had a nobler one compared to the TNTZ alloy and Zr had the initial OCP as high as –0.4V. The polarization behaviour of these metals was similar to that after 1 hour immersion. A significant observation after 24 hours was that the active dissolution peak of Nb which had two peaks during 1 hour immersion merged into a single broad peak and the current density of Ta was increased by a decade. The passive current density of Ta was higher than that of Nb in the passive region. On the other hand, there was no remarkable change in the current density behaviour of the TNTZ alloy and Ti.

The OCP studies together with the polarisation studies reveal the complex oxide growth on the TNTZ alloy. The alloy has exhibited a potential change resembling Nb and Ta, and also the
polarization curve resembling Ti. As the content of Zr was small, there was no significant participation of Zr in the electrochemical behaviour of the TNTZ alloy.

2.1.4 Electrochemical – alkali treatment

In order to produce a uniform layer over the TNTZ alloy, a potential pulse polarization is introduced. The alloy is immersed in 5 M NaOH at 60 °C, then polarized with the applied potential modulated as square wave. The higher and lower potential of square wave pulses, \( E_H \) and \( E_L \), respectively, and the duration of each pulse, \( t_H \) and \( t_L \), are varied. The film was formed in the following condition, \( E_L = -1.2 \) V, \( E_H = -0.94 \) V; \( t_L = 2 \) s, \( t_H = 5 \) s. The applied potentials for \( E_L \) and \( E_H \) were chosen from the electrochemical behaviour of the TNTZ alloy and the alloying elements. The anodic polarisation behaviour of tantalum, after 1 hour and 24 hours of immersion, reveal an active dissolution peak at -1.2 V (\( E_L \)). While, the \( E_H \) (-0.94 V) was determined from the OCP of pure titanium after 24 hours of immersion. After the treatment, the morphology of the surfaces produced by pulse polarization technique appeared as shown in Fig.7. There was no particulate (a) after 1 hour of treatment. A few spots with the tantalum rich particles were seen after (b) 3 hours of treatment. At the end of 24 hours, a uniform film with a few cracks was observed.

The variation in current with the applied square wave modulated potential was cathodic during the application of \( E_L \) and anodic during \( E_H \). The cathodic behaviour of the alloy shifts the equilibrium of reaction of tantalum with the medium. Hence, during the 1 hour treatment, no particulate was observed. But with time the equilibrium could have been attained and the particles emerge, cracking the uniform layer. The application of \( E_H \) might enhance the growth of the film. The thickness of the film after 24 hours was observed.

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Fig.7 SEM images of a uniform layer formed on TNTZ alloy by pulse polarisation after (a) 1 hr, (b) 3 hrs and (c) 24 hrs.

Fig.8 (a) Cross sectional view of the layer formed over TNTZ alloy by alkali treatment at OCP, (b) Cross sectional view of the layer formed over TNTZ alloy by pulse polarisation.
hours of treatment was approx. 2 µm. This was comparable with the thickness of the film observed after the conventional alkali treatment as apparent from Figs.8 (a) and (b).

4. Conclusion
In the present work, the electrochemical behaviour of the β-type TNTZ alloy in 5 M NaOH at 60 °C is examined in order to establish a surface modification process using alkali treatment. The fragmented nature of the layer, which is obtained by the simple natural immersion, is associated to the localised precipitation of a tantalum enriched particulate oxide during the initial stage of the immersion. Application of a square wave modulated potential over the TNTZ alloy apparently hindered the growth of those tantalum enriched particulates resulting in the formation of the uniform layer of sodium titanate / titanium hydroxide layer with a porous network structure.

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