Wear and Mechanical Properties, and Cell Viability of Gas-Nitried Beta-Type Ti-Nb-Ta-Zr System Alloy for Biomedical Applications

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Frictional wear resistance is one of the important properties of metallic biomaterials. Surface hardening treatments such as oxidizing, nitriding and ion implantation tend to be applied for improving the wear resistance of titanium and its alloys. The simple gas nitriding process is expected to further improve the wear resistance of newly developed beta-type Ti-29Nb-13Ta-4.6Zr alloy (TNTZ) for biomedical applications. However, there is a possibility for the mechanical properties such as tensile and fatigue strength of TNTZ to be degraded through gas nitriding process. Therefore, the gas nitriding process was carried out in this study to improve the wear resistance of TNTZ and alpha-beta-type Ti-6Al-4V ELI alloy (Ti64), which is one of the representative titanium alloys practically applied for biomedical applications, in simulated body fluid (Ringer’s solution). The tensile and fatigue properties and cell viability was also investigated in order to confirm the reliability as biomedical materials.

The Vickers hardness near the specimen surface of nitried TNTZ and Ti64, where TiN and Ti2N forms, increases significantly as compared to that of their matrices. The wear resistances of TNTZ and Ti64 are improved significantly in Ringer’s solution by nitriding process as compared to those of as-solutionized TNTZ (TNTZST) and Ti64 (Ti64ST). The tensile strength of nitried TNTZ increases by around 90 MPa as compared to that of TNTZST. The tensile strength of nitried Ti64 does not change significantly at all nitriding temperatures. On the other hand, the elongation decreases with increasing the nitriding temperature. The run out (plain fatigue limit) of TNTZ subjected to a nitriding process at 1123 K, which has relatively good balance between wear resistance and tensile properties, is around 300 MPa, and is nearly equal to that of Ti64 subjected to a nitriding process at 1123 K, although the tensile strength of the nitried TNTZ is around 200 MPa smaller than that of the nitried Ti64. The cell viabilities of nitried TNTZ and Ti64 range from 1.4 to 1.6 against that of control (cell disc), and are a little higher than that of TNTZST and Ti64ST. The cell viabilities of nitried TNTZ and Ti64 after removing the oxide layer on their surfaces are similar to that of control and are not significantly degraded.

Therefore, in this study, the wear characteristics of TNTZ and Ti-6Al-4V ELI alloy (Ti64), which is one of representative titanium alloys for biomedical applications, subjected to gas nitriding were investigated in a simulated body fluid (Ringer’s solution). In addition, the tensile and fatigue properties of TNTZ and Ti64 subjected to gas nitriding process were also investigated, where the change of mechanical properties in air are only done due to compare to TNTZST and Ti64ST. The cell viabilities of nitried TNTZ and Ti64 after removing the oxide layer on their surfaces are similar to that of control and are not significantly degraded. [doi:10.2320/matertrans.MRA2007210]

1. Introduction

Biocompatible Ti-29Nb-13Ta-4.6Zr alloy (TNTZ) developed by the authors can be used in biomedical applications due to its good mechanical properties such as high specific strength and elongation.1-4) TNTZ subjected to a solution treatment (TNTZST) has a low Young’s modulus of around 55 GPa, very low cyto-toxicity, similar to that of commercial pure Ti (grade II), and good biocompatibility with living tissues.5) Therefore, TNTZ is expected that it would be put into practical use as a next generation biomedical material. However, titanium alloys are generally inferior in wear resistance when compared to Co based alloys or ceramics.

Surface hardening is effective to improve the wear resistance, and various types of surface hardening processes have been applied to titanium alloys.6) The authors conducted the oxidizing process with TNTZ in air, and reported that the wear resistance of TNTZ in Ringer’s solution was improved remarkably.6) Nitrides such as TiN and Ti2N are around twice harder as compared to TiO2. The wear resistance of TNTZ is expected to improve further by nitriding process. Thus, it is relatively high possibility that TNTZ subjected to nitriding process is applied to the bone head and the cup, which are parts of the artificial hip joint. The gas nitriding process is relatively convenient one to form nitrides on the surface of metallic materials, and has been applied to harden the surface of titanium alloys.7)

2. Experimental Procedures

2.1 Materials

The materials used in this study were hot forged bars of TNTZ (Nb: 29.1, Ta: 12.5, Zr: 4.60, N: 0.01, O: 0.07, Ti: bal., mass%) with a diameter of around 20 mm and hot rolled plates of Ti64 (Al: 6.34, V: 4.10, N: 0.01, O: 0.12, Ti: bal., mass%) with a thickness of about 4.0 mm, which were used for comparison. The bars of TNTZ were cold-rolled to form plates with a thickness of 2.5 mm with a reduction of around 88% in ambient temperature. The plates of TNTZ were subjected to a solution treatment at 1063 K, which is 50 K above the β transus temperature, for 3.6 ks in vacuum.
followed by water quenching. The plates of Ti64 were subjected to a solution treatment at 1223 K, which is 50 K below the β transus temperature, for 3.6 ks in vacuum followed by air cooling. The solution treated TNTZ and Ti64 are referred to as TNTZ_{ST} and Ti64_{ST}, respectively. In addition, a hot-forged bar of commercially pure Ti (grade II: CP Ti) in as-received condition was also used for comparison.

2.2 Specimens
Square-type specimens with dimensions of 20 × 20 × 2.0 and 10 × 10 × 2.0 mm³ for frictional wear test and evaluation of cell viability, respectively, and plate-type specimens with a cross section of 3.0 × 1.5 mm² and a gage length of 13 mm for tensile and plain fatigue tests were machined from heat-treated materials as stated below. These specimens were wet-polished using emery papers up to #1500.

2.3 Surface hardening treatment
After inserting the specimens into a furnace, the process of vacuum drawing and introduction of nitrogen gas were repeated three times in order to eliminate the effect of oxygen in the furnace. The TNTZ_{ST} and Ti64_{ST} specimens were heated to 1023, 1073, 1123, and 1223 K, respectively, in the vacuum, and then the nitrogen gas pressure was reduced to 0.01 MPa. The TNTZ_{ST} and Ti64_{ST} specimens were kept in the nitrogen gas at 1023, 1073, 1123, and 1223 K, respectively, for 21.6 ks followed by furnace cooling. The nitried TNTZ and Ti64 at various temperatures are referred to as TNTZ1023NP, TNTZ1073NP, TNTZ1123NP, TNTZ1223NP, Ti641023NP, Ti641073NP, Ti641123NP, and Ti641223NP, respectively. Some of the TNTZ_{ST} were heated to 1023, 1073, and 1223 K, respectively, for 21.6 ks in the vacuum to clarify the strengthening mechanism of mechanical strength, which is related to diffused nitrogen or precipitated phase through the nitriding process. The heat-treated TNTZ_{ST} at 1023, 1073, and 1223 K are referred to as TNTZ1023HT, TNTZ1073HT, and TNTZ1223HT, respectively.

Some of the TNTZ_{ST} and Ti64_{ST} specimens were subjected to oxidizing process in air at 1073 K for 21.6 ks for comparing the friction wear characteristics of the nitried TNTZ and Ti64. The oxidized TNTZ and Ti64 specimens are referred to as TNTZ_{OP} and Ti64_{OP}, respectively. The oxidized specimens were subjected to only weight loss measurements in friction wear tests.

2.4 Microstructural observations
For microstructural observations, each specimen was wet-polished using emery papers up to #1500 and subsequently buff-polished with alumina powder and SiO₂ suspension liquid, and finally etched in a 5%HF solution. Microstructures and 3D accurate surface topographies of cross section near specimen surface and specimen surface were observed using an optical microscope and optical profiler, respectively.

The phase constitution of the specimens was determined by an X-ray diffractometer using Cu-Kα radiation with an accelerating voltage of 40 kV and a current of 30 mA, and an X-ray spectroscopy with a spot size of 600 µm and a measuring time of 10.8 ks in vacuum. The qualitative depth profile of each element of the specimen, which is assumed by the sputter rate of SiO₂ (0.5 nm/s), was evaluated using an Auger electron spectroscopy (AES) at a pressure below 1.3 × 10⁻⁷ Pa with a spot size of 3.0 µm and a voltage of 10 kV. In this analysis, the specimen was etched in the depth direction using an argon ion beam with a voltage of 3.0 kV.

The morphologies of the wear traces obtained from the friction wear tests and fracture surfaces obtained from the tensile and fatigue tests as states below were observed using a scanning electron microscopy (SEM).

2.5 Wear and mechanical tests
The cross section of square-type specimen was wet-polished using water proof emery papers up to #1500 and subsequently buff-polished with alumina powder and SiO₂ suspension liquid. The Vickers hardness was measured at every 20 or 50 µm into a depth of 100–300 µm from the surface of the specimen using a Vickers hardness tester with a weight of 0.49 N and a holding time of 15 s.

The friction wear characteristics of each specimen versus zirconia ball with a diameter of 5.0 mm were evaluated in Ringer’s solution at 310 K at a sliding speed of 31.4 mm/s, sliding distance of 3.14 × 10³ mm and load of 9.8 N. The wear characteristics were evaluated by measuring the weight loss (W_loss) in the specimen. The weight of each specimen before and after friction wear test was measured using an electric balance, and then the W_loss was calculated using a weight difference of the specimen before and after the friction wear test using the following equation:

\[ W_{\text{loss}} = W_1 - W_2 \]  

where W₁ and W₂ are the weight of specimen before and after friction wear test.

Tensile tests were carried out on the plate-type specimens finished as stated above using an Instron type machine with a cross-head speed of 8.33 × 10⁻⁶ m/s in air at 295 K. The strain was measured using a foil strain gage attached directly to the parallel portion of the specimen. The elongation was measured using reading microscopy.

Plain fatigue tests were carried out on the plate-type specimens finished as stated above using an electro-servo-hydraulic machine. The plain fatigue tests were performed at a frequency of 10 Hz with a stress ratio, R = 0.1, under the tension-tension mode in air at 295 K. The maximum cyclic stress, at which the specimen was not failure at 10⁷ cycles, was defined as the run out (plain fatigue limit) in this study.

2.6 Evaluation of cell viability
The cell viability was evaluated by the survival ratio of L-929 cell, which is a mouse fibroblast cell. The L-929 cells were subcultured in MEM (minimum essential medium) supplemented with 10% FBS, 100 U/ml penicillin, and 100 µg/ml streptomycin at 310 K for 172.8 ks in incubator, which is filled in 5%CO₂ at a humidity of 95%. The subcultured L-929 cells were isolated with 0.25% trypsin. The number of cells was counted in a cytometer plate. The square-type specimens of TNTZ_{ST}, Ti64_{ST}, nitried TNTZ and Ti64, where some specimen surfaces of nitried TNTZ and Ti64 were wet-polished using emery papers of #1500 to remove the oxide layer, CP Ti, and a control (cell disc) made of a fluoro-plastic for cell adhesion (Sumitomo Bakelite,
Japan) were placed in micro-plate with 24 wells, and then 600 μl (2 × 10⁴ cells/ml) of L-929 cells were disseminated on the specimen. The numbers of cells were counted at every 86.4 ks, up to 432 ks, using a CellTiter 96 Aqueous One Solution Reagent (Promega, USA). The absorbance was determined with a microplate reader with a wavelength of 492 nm.

3. Results and Discussion

3.1 Microstructures

The X-ray diffraction (XRD) profiles of the surface and those for a distance of 1000 μm from the surface (center of the specimen) for the nitrided TNTZ (TNTZ1023NP, TNTZ1073NP, TNTZ1123NP, and TNTZ1223NP) and Ti64 (Ti641023NP, Ti641073NP, Ti641123NP, and Ti641223NP) are shown in Figs. 1 and 2. Peaks attributed to β phase, α phase, TiN, and Ti₂N are observed on the surfaces of TNTZ1023NP, TNTZ1073NP, TNTZ1123NP, TNTZ1223NP, Ti641023NP, Ti641073NP, Ti641123NP, and Ti641223NP, respectively, as shown in Figs. 1(a) and 2(a). Therefore, nitride layers, comprising TiN and Ti₂N, are formed on the surfaces of the nitrided TNTZ and Ti64. The intensity of the TiN peak increases with the nitriding temperature. A strong peak of the β phase and a weak or very weak peak of the α phase are observed at a distance of 1000 μm from the surface of the specimen.
TNTZ_{1023NP}, TNTZ_{1073NP}, TNTZ_{1123NP}, and TNTZ_{1223NP} as shown in Fig. 1(b). The peak of the $\alpha$ phase on the surface of the nitrided TNTZ becomes relatively sharper. The precipitation of the $\alpha$ phase inside the nitrided TNTZ is mainly due to the slow cooling rate after nitriding, while the precipitation of the $\alpha$ phase near the surface of the nitrided TNTZ is due to the slow cooling rate after nitriding and the increase in the dissolved nitrogen content, which is a $\alpha$ phase stabilizing element. For nitrided Ti64, nearly the same trend of XRD profiles is observed in the nitrided TNTZ.

The 3D accurate surface topographies of specimen surfaces and optical micrographs of cross section near specimen surface of TNTZ_{1223NP} and Ti64_{1223NP} are shown representatively in Fig. 3. The nitrides on surface of TNTZ_{1223NP} show mainly transgranular growth, although it is difficult to find the same trend on Ti64_{1223NP}. The microstructures of cross section near specimen surface of TNTZ_{1223NP} and Ti64_{1223NP} are comprised of nitride layer including TiN and Ti$_2$N with a thickness of around 10 $\mu$m from their specimen surface and subsequently exist a region of a large amount of $\alpha$ phases in their matrices. It is easy to form $\alpha$ phase beneath the nitride layer because there are a large amount of solved nitrogen, which is an $\alpha$ stabilizer as mentioned above. Their thickness of both the nitriding layer and region of $\alpha$ phase decreased proportionally according to a decrement of the nitriding temperature.

### 3.2 Depth profile of elements

The AES depth profile of each element in TNTZ$_{ST}$, TNTZ$_{1223NP}$, Ti64$_{ST}$, and Ti64$_{1223NP}$ are representatively shown in Fig. 4. It is difficult to determine the N peak
individually because it overlaps with the Ti peak (see the depth profile indicated by titanium nitride (TN) in the figure). However, since there is another Ti peak (see the depth profile indicated by Ti in the figure), the concentration of N can be estimated by evaluating the ratio between the intensities of two N peaks—one that overlaps with that of Ti and another that does not overlap with that of Ti. A very narrow area, where the concentration of oxygen (O) is the highest, exists from the surface to the inside of each specimen. This area is considered to be a very thin oxide layer, which cannot be detected using an X-ray diffractometer. It was found by AES to be mainly composed of TiO$_2$.

By considering the results of the microstructural observations, the area where the nitrides exist can be considered to exist at the depth where the depth profile line of TN crosses that of Ti. The thickness of the nitride layers in TNTZ$_{1223}$NP and Ti64$_{1223}$NP are estimated to be around 14 and 12μm, respectively.

3.3 Depth profile of hardness

The Vickers hardness profiles of TNTZ$_{ST}$, TNTZ$_{1023}$NP, TNTZ$_{1073}$NP, TNTZ$_{1123}$NP, TNTZ$_{1223}$NP, Ti64$_{ST}$, Ti64$_{1023}$NP, Ti64$_{1073}$NP, Ti64$_{1123}$NP, and Ti64$_{1223}$NP are shown in Fig. 5. The Vickers hardness of nitrided TNTZ or Ti64 is higher than that of the TNTZ$_{ST}$ or Ti64$_{ST}$ matrices and increases with the nitriding temperature as the distance from the surface of the specimen increases. For nitrided TNTZ, the Vickers hardness decreases rapidly from its value at the surface to that at a distance of around 100μm from the surface, and then gradually decreased with an increase in the distance from the surface of the specimen. For nitrided Ti64, the Vickers hardness decreases rapidly from its value at the surface to that at a distance of around 150μm from the surface. Subjecting to nitriding at the highest nitriding temperature shows the highest value of Vickers hardness in both TNTZ and Ti64, which are around 630 and 920 HV, respectively. The Vickers hardness close to the surface of the nitrided Ti64 was much higher than that for the nitrided TNTZ. This higher amount of TiN in the nitrided Ti64 as compared to that in the nitrided TNTZ is considered to be the cause of this observation.

The increasing ratio of Vickers hardness at around 100μm and later from the specimen surface of nitrided TNTZ to TNTZ$_{ST}$ is much higher than that of nitrided Ti64 to Ti64$_{ST}$. Figure 6 shows the Vickers hardness profiles of TNTZ$_{ST}$ subjected to heat-treatments, TNTZ$_{1023}$HT, TNTZ$_{1073}$HT, and TNTZ$_{1223}$HT, in vacuum. Comparing this figure to Fig. 5(a), the values of Vickers hardness at around 100μm and later from the specimen surface of both nitrided TNTZ and heat-treated TNTZ at various temperatures are almost similarly...
except for TNTZ\textsubscript{1223NP}, which is around 30 Hv higher than that of TNTZ\textsubscript{1223HT}. This increasing of Vickers hardness in nitrided TNTZ is mainly contributed to the age-hardening by precipitation of $\alpha$ phase in $\beta$ phase during furnace cooling, although there is a possibility of existence of diffused nitrogen at around 100 $\mu$m and later from the specimen surface of TNTZ\textsubscript{1223NP}. But, it needs further investigation because the trend also seems to take place in Ti64\textsubscript{1223NP}.

### 3.4 Frictional wear characteristics

The $W_{\text{loss}}$ in TNTZ\textsubscript{ST}, TNTZ\textsubscript{1023NP}, TNTZ\textsubscript{1073NP}, TNTZ\textsubscript{1123NP}, TNTZ\textsubscript{1223NP}, Ti64\textsubscript{ST}, Ti64\textsubscript{1023NP}, Ti64\textsubscript{1073NP}, Ti64\textsubscript{1123NP}, and Ti64\textsubscript{1223NP} in Ringer’s solution are shown representatively in Fig. 7. The $W_{\text{loss}}$ in TNTZ\textsubscript{OP} and Ti64\textsubscript{OP} in Ringer’s solution are also shown in this figure.

The friction wear resistance of TNTZ in Ringer’s solution, the friction wear resistance of all nitrided or oxidized TNTZ increases as compared to that of TNTZ\textsubscript{ST}, and increases with the nitriding temperature. The friction wear resistance is improved when the nitriding temperature is 1223 K as compared to the oxidizing process in the Ringer’s solution where the thickest nitride layer is formed on the surface of TNTZ\textsubscript{matrix}.

In the case of Ti64, the friction wear resistance is also improved by nitriding or oxidizing process in Ringer’s solution. The friction wear resistance of Ti64 increases with the nitriding temperature in Ringer’s solution. In Ringer’s solution, the wear resistance of the nitrided Ti64 at temperatures of 1073, 1123, and 1223 K is better as compared to that of the oxidized one. The surface modification by nitriding is effective in improving the wear resistance of TNTZ and Ti64 in Ringer’s solution.

The SEM micrographs of wear traces in TNTZ\textsubscript{ST}, TNTZ\textsubscript{1223NP}, Ti64\textsubscript{ST}, and Ti64\textsubscript{1223NP} in Ringer’s solution are shown representatively in Fig. 8. The wear morphology in Ringer’s solution changes from severe wear morphology to mild wear morphology\textsuperscript{9} by subjecting to nitriding, where the separation of adhesive debris (wear trace area in white) is extremely restricted. Thus, the width of wear trace of TNTZ\textsubscript{1223NP} and Ti64\textsubscript{1223NP} is around one third of that of TNTZ\textsubscript{ST} and Ti64\textsubscript{ST} where the bottom of wear trace is located in a region of nitride and nitrogen rich layer as shown in Fig. 9. The results of the SEM observation of wear traces in TNTZ and Ti64 coincide with the trend observed in the $W_{\text{loss}}$ in Ringer’s solution.

### 3.5 Tensile properties

The tensile strength, 0.2\% proof stress, and elongation of TNTZ\textsubscript{ST}, TNTZ\textsubscript{1023NP}, TNTZ\textsubscript{1073NP}, TNTZ\textsubscript{1123NP}, TNTZ\textsubscript{1223NP}, Ti64\textsubscript{ST}, Ti64\textsubscript{1023NP}, Ti64\textsubscript{1073NP}, Ti64\textsubscript{1123NP}, and Ti64\textsubscript{1223NP} are shown in Fig. 10. The tensile strengths of nitrided TNTZ and Ti64 are around 710 and 930 MPa, respectively, regardless of change in the nitriding temperature. The tensile strength of nitrided TNTZ is 90 MPa higher than that of TNTZ\textsubscript{ST}. While the tensile strength of nitrided Ti64 is nearly equal to that of Ti64\textsubscript{ST}. The effect of nitrogen
in titanium is presumably similar to the solid solution strengthening effect of oxygen. However, it is a little low one in improvement of strength because the diffused nitrogen is not homogeneously dissolved into the whole specimen and forms a brittle nitride layer. The tensile strength of forged and cold-rolled TNTZ increases twice or more of that of as-solutionized one with increasing amount of precipitates such as \( \omega \) or \( \alpha \) phase after a solution treatment followed by an aging treatment.\(^{10}\) The increase of strength of nitrided TNTZ can be mainly contributed to the age-hardening by the precipitation of \( \alpha \) phase during slow cooling in a furnace as stated above. However, the tensile strength of nitrided TNTZ is 200 MPa smaller than that of nitrided Ti64. On the other hand, their elongation decrease with increasing the nitriding temperature. In particular, the elongation of TNTZ\(_{1223NP}\) shows a few %. The degraded elongation of TNTZ\(_{1223NP}\) may contribute to the diffusion of nitrogen into the center of specimen as mentioned above, which strongly enhances the brittleness of the matrix. According to increasing the nitriding temperature, the reduction ratio and the diameter of dimple decreased slightly in both TNTZ and Ti64.

TNTZ\(_{1123NP}\) is a candidate for biomedical applications, which has relatively good balance between tensile strength (710 MPa) and elongation (around 15\%) in addition to relatively high wear resistance as mentioned above, although the Young’s modulus seems to increase to some degree because of the precipitation of \( \alpha \) phases, which are enhanced near the tensile specimen surface by diffused nitrogen of \( \alpha \) stabilizer and precipitated in the tensile specimen during furnace cooling, and formation of nitride layers.

### 3.6 Fatigue properties

The S-N curves of TNTZ\(_{ST}\), TNTZ\(_{1123NP}\), TNTZ\(_{1223NP}\), Ti64\(_{ST}\), Ti64\(_{1123NP}\), and Ti64\(_{1223NP}\) are shown in Fig. 11. The run out, which is a maximum cyclic stress not to break at \( 10^7 \) cycles, of TNTZ\(_{1123NP}\) was around 300 MPa, and is nearly equal to that of Ti64\(_{1123NP}\), although the tensile strength of TNTZ\(_{1123NP}\) was around 200 MPa smaller than that of Ti64\(_{1123NP}\). The value was a little smaller than that of TNTZ\(_{ST}\). The fatigue crack seems to be easily initiated at a little thicker brittle nitride layer, TiN or Ti\(_2\)N, of nitrided Ti64 as compared with that nitrided TNTZ. Particularly, the elastic modulus of the TiN is two or more times higher of the matrix\(^{11}\) and thus the TiN layer of nitrided TNTZ and Ti64 is severely deformed under cyclic loading, where localized fatigue deformation could be took place. This seems to occur the brittle cracking and shorten the crack initiation life, in particular, on nitrided Ti64 with relatively high Vicker hardness, and thickness of nitride and nitrogen rich layers. In addition, the notch factor (run out of smooth specimen/ run out of notch specimen), which means a notch sensitivity, of aged TNTZ decreases with increasing the volume fraction of \( \alpha \) phase, and is lower than that of annealed Ti64 with the equiaxed \( \alpha \) structure.\(^{12}\) From these points of view, the plain fatigue strength of TNTZ is not so degraded as compared to that of Ti64 by nitriding process.

SEM images of the fracture surface in TNTZ\(_{ST}\) and TNTZ\(_{1223NP}\) are representatively shown in Fig. 12. There is a clear difference in morphologies between TNTZ\(_{ST}\) and TNTZ\(_{1223NP}\). In TNTZ\(_{ST}\), the crack is considered to initiate at an intrusion and extrusion in \( \beta \) phase and then grow concentrically. On the other hand, the crack of TNTZ\(_{1223NP}\) tends to initiate in a nitride layer and then grow perpendic-

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**Fig. 10** Tensile properties of TNTZ and Ti 64 subjected to solution treatment and nitriding process.

**Fig. 11** S-N curves of TNTZ and Ti 64 subjected to solution treatment and nitriding process.
ularly to the specimen surface. These features in SEM morphologies of the fracture surfaces were also obtained in Ti64.

It is difficult to improve the fatigue properties of TNTZ and Ti64 with a brittle nitride layer of TiN and Ti$_2$N, which becomes the crack initiation site, through the gas nitriding process, even if they have relatively high tensile strength and elongation more than 700 MPa and 15%, respectively.

3.7 Cyto-toxicity

The cell viabilities on specimen surfaces of TNTZ$_{ST}$, TNTZ$_{1073NP}$, TNTZ$_{1223NP}$, Ti64$_{ST}$, Ti64$_{1023NP}$, Ti64$_{1073NP}$, Ti64$_{1123NP}$, and Ti64$_{1223NP}$ are shown in Fig. 13 with those of CP Ti and control for comparison. The cell viabilities of nitrided TNTZ and Ti64 range from 1.4 to 1.6 against that of control (cell disc), which is 1.0, and is a little higher than that of TNTZ$_{ST}$ and Ti64$_{ST}$. The graded cell viabilities of nitrided TNTZ and Ti64 may contribute to the existence of thin TiO$_2$ layer on the very edge of specimen surface, which has a bactericidal action, although their specimen surfaces are relatively rough due to the formation of nitrides. Therefore, the cell viability of CP Ti, which is covered with smoothly homogeneous TiO$_2$ layer, is around 1.7, and was the highest in the others. But, a result of XPS spectra on the surface of nitrided TNTZ and Ti64 showed the existence of oxidized state of Nb$^{5+},$ Ta$^{5+},$ Zr$^{4+},$ Al$^{3+},$ and V$^{4+},$ respectively, although their formed oxides seem to be in amorphous or low-crystalline thin film states. From this report, the cell viabilities of nitrided TNTZ and Ti64 seems to be changed and show a little lower value as compared to that of CP Ti covered fully with TiO$_2$. The cell viabilities of TNTZ$_{1073NP}$, TNTZ$_{1223NP}$, Ti64$_{1073NP}$, and Ti64$_{1223NP}$ removed their oxide layers by wet-polishing were 1.1 and 0.9, respectively, which were almost similar to that of control, and were not significantly degraded.

4. Conclusions

In this study, Ti-29Nb-13Ta-4.6Zr alloy (TNTZ) and Ti-6Al-4V ELI alloy (Ti64) for biomedical applications were subjected to the surface hardening treatment by gas nitriding process in order to improve their wear resistance in a simulated body fluid (Ringer’s solution). Furthermore, the tensile and fatigue properties, and cell viabilities of nitrided TNTZ and Ti64 were also investigated in this study. The following results were obtained.

(1) The Vickers harnesses near the specimen surface of nitrided TNTZ and Ti64, where TiN and Ti$_2$N forms, increases significantly as compared to that of their matrices.

(2) The wear resistances of TNTZ and Ti64 are improved significantly in Ringer’s solution by nitriding process as compared to those of as-solutionized TNTZ (TNTZ$_{ST}$) and Ti64 (Ti64$_{ST}$).

(3) The tensile strength of nitrided TNTZ increases by around 90 MPa as compared to that of TNTZ$_{ST}$. The tensile strength of nitrided Ti64 does not change significantly at all nitriding temperatures. On the other
hand, their elongation decrease with increasing the nitriding temperature.

(4) The run out of TNTZ subjected to nitriding at 1123 K is around 300 MPa, and is nearly equal to that of Ti64 subjected to nitriding at 1123 K, although the tensile strength of TNTZ subjected to nitriding at 1123 K was smaller than that of Ti64 subjected to nitriding at 1123 K.

(5) The cell viabilities of nitrided TNTZ and Ti64 range from 1.4 to 1.6 against that of control, and is a little higher than that of TNTZST and Ti64ST. The cell viabilities of nitrided TNTZ and Ti64 after removing their oxide layers are similar to that of control, and are not significantly degraded.

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