Change in Mechanical Strength and Bone Contactability of Biomedical Titanium Alloy with Low Young’s Modulus Subjected to Fine Particle Bombarding Process

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Beta-type Ti-29Nb-13Ta-4.6Zr (TNTZ), which is a recently developed biomedical titanium alloys, shows a relatively low Young’s modulus of around 60 GPa when subjected to a solution treatment. However, our focus in this study was on the practical applications of TNTZ in vivo because its mechanical strength decreases with solution treatment progress. Therefore, we investigated the effect of fine particle bombardment (FPB) on the mechanical properties of TNTZ subjected to a cold-swaging treatment in order to maintain its relatively low Young’s modulus and to improve its mechanical properties. The relative bone contact ratios between the cancellous bones of Japanese white rabbits and column-shaped TNTZ samples subjected to FPB were also evaluated.

The microstructure of cold-swaged TNTZ showed a single beta-phase with a marble-like structure. Moreover, its Vickers hardness did not increase remarkably with changes in its diameter, although the average diameter of the beta-grains of solutionized TNTZ ranged from 5.0 to 20 μm, depending on the increase in the holding time of the solution treatment. The Vickers hardness and Young’s modulus of TNTZ subjected to FPB increased at the edge of the specimen surface to be around 70% and 15%, respectively, more than those of cold-swaged TNTZ. Further, the fatigue strength of TNTZ subjected to FPB became significantly higher than that of cold-swaged TNTZ in the high-cycle fatigue life region. Lastly, TNTZ with a rough surface texture (Ra: 0.65 μm) showed a relative bone contact ratio of more than 80% after undergoing FPB; this value was significantly higher than that of cold-swaged TNTZ with a very smooth surface texture (Ra: 0.07 μm).

1This Paper was Originally Published in Japanese in J. Japan Inst. Met. Mater. 78 (2014) 163–169.
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Keywords: metallic biomaterial, microstructure, tensile and fatigue properties, Young’s modulus, biocompatibility

1. Introduction

Ti-6Al-4V ELI alloy (Ti64), which has a high specific strength and good corrosion resistance, has been widely applied in biomedical devices such as the stem of artificial hip and knee joints. However, since Ti64 is an alloy developed for use as a structural material in aircraft, the biocompatibility of the alloying elements and the deformation response of Ti64 as compared to bone during physiological loading (such as walking and running) are not taken into consideration when discussing biomedical applications. For instance, there are concerns about the toxicity of V ions released in vivo and the stress shielding related to the high Young’s modulus of the implanted material.1) For these reasons, the Ti-29Nb-13Ta-4.6Zr alloy (TNTZ), which consists of only alloying elements with relatively good biocompatibility, has been developed.2,3) Although as-solutionized TNTZ has an equiaxed single beta phase with a relatively low Young’s modulus, nearly equal to 60 GPa, it has poor mechanical strength as compared with Ti64.

Generally, the techniques for improving the mechanical strength of β-type titanium alloys are thermo-mechanical treatment and mechanical or chemical surface hardening. It has been reported that Young’s modulus for TNTZ increases with thermo-mechanical treatment such as solution treatment and aging (STA) after rolling, although the mechanical strength can approach that of Ti64 by controlling the microstructure. In this study, we applied shot peening (SP), which is one of the simplest surface hardening processes, for improving the mechanical strength.4,5) Although conventional SP is used for raising fatigue strength by introducing some compressive residual stresses into the outermost layers of the specimen, it has been pointed out that the fatigue strength is sometimes degraded by the drastically increased surface roughness.6-9) On the other hand, it has been reported that the fine-particle bombardment (FPB), which uses shot particles with diameters between 50 and 200 μm at high velocities (more than 100 m·s-1), is an attractive processing technique because it produces only small changes in surface roughness, refinement of the micro-structure, and the aforementioned compressive residual stresses.9-12) Therefore, it is possible to increase the mechanical properties of TNTZ by using FPB. This study investigated the effects of surface modification by FPB on the mechanical properties of TNTZ in order to maintain a relatively low elastic modulus. The bone contact characteristics of TNTZ samples subjected to surface modification and cancellous bone were also compared.

2. Experimental Methods

The materials used in this study were cold-swaged bars at a working rate: around 94% of TNTZ with a diameter of 7.0 mm (SW). The chemical composition is shown in Table 1. Some samples of SW were solutionized at 1063 K for 0.3, 0.6, 1.2, 1.8 and 3.6 ks in a vacuum followed by water quenching (WQ), and they were designated as ST0.3-3.6, which is classified as holding time.

Surface modification by FPB was applied to some specimens of SW and ST3.6, which were designated as...
SW/FPB and ST/FPB, respectively. FPB was done by fine steel particles with a diameter of around 200 µm at a rotation rate of 70 rpm and pressure for controlling the amount of particle and its particle rate of 0.5 MPa and 0.6 MPa, respectively. The distance between the injection tip and the specimen surface and time for FPB were 30 mm and 0.6 ks, respectively. Some samples of SW, ST0.3-3.6, SW/FPB, and ST/FPB machined into the half, and then their cross sections were etched in 0.5HF solution after wet-polishing with a wet emery paper with a grid of #4000 and then buff-polishing with the colloidal silica suspension.

Microstructures and constitutional phases of all samples were examined through optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis.

Measurement of hardness for all samples was done at their around centers of cross sections, which were polished with a wet emery paper with a grid of #4000, by micro Vickers hardness (HV) testing machine at a load of 200 g for a holding time of 10 s. Moreover, HV profiles of SW/FPB and ST/FPB were also measured from very edge of specimen surface to around 1.0 mm from that on the cross sections.

Young’s modulus was calculated by a gradient obtained from a load-unload curve by using a nano-indentation tester at a load of 392 mN for a holding time of 10 s.

For the tensile test, the dog-bone-type tensile specimens with a diameter of 3.0 mm and a gage length of 10 mm were machined from SW and ST3.6. These specimens were then wet-polished with a wet emery paper with a grid of #4000. The gage parts of tensile specimens for SW/FPB and ST/FPB were conducted with FPB as mentioned above. The tensile test was done using an Instron type machine at a cross-head speed of 8.33 × 10⁻⁶ m·s⁻¹ in air at 295 K. The load was detected by the load cell of the machine. The strain was detected by a strain gage attached to the gage part of the tensile specimen and calculated by the change of gage length before and after the tests by a measurement microscopy.

For the fatigue test, the geometry of specimen was the same as that for tensile test. The fatigue tests were conducted by using an electro servo-hydraulic-machine at a frequency of 10 Hz and a stress ratio (R) of 0.1 in air at 295 K.

For evaluating the bone contactability, the column shape samples of SW/FPB and SW with mirror surface (SW/mirror) were implanted into the lateral condyles of the femurs of Japanese white rabbits, which were male at around one year old, and then were taken out along with the some parts of femur after 12 weeks. Their samples were dehydrated in alcoholic solution and then were conducted with the fuchsin staining process and embedding in the resin of methyl methacrylate polymer. Their samples in the resin were machined into the thin layers with a thickness of around 150 µm for observing the contact micro radiogram (CMR) image. Evaluating the bone contactability was carried out by analyzing the CMR images of the contacted area between the implants and bony tissue as shown in Fig. 1.13,14 The image was converted into the rectangle shape for easily analyzing the level of gray value obtained from implant surface to distance of around 50 µm thick. The lower limit of gray value between those was defined as the bone contact threshold (BCT) although BCT was different value in each sample. The values more and less than BCT were defined as the bone contact and non-bone contact regions. Moreover, the non-bone contact region was classified into two phenomena surrounded by the bony tissue without the contact of implant surface and no formation of bony tissue near the surface, respectively. The bone contact region over the circumference length of the implant (bone contact ratio) and the bone contact region over total length surrounded by bony tissue (relative bone contact ratio) were calculated due to the individual difference of animal and the slight difference of implant location. The roughness profiles and the average surface roughness (Ra) of all implants before implantation were measured by a roughness tester manufactured by Mitsutoyo Japan.

3. Result and Discussion

3.1 Microstructures

The microstructures of SW and ST0.3-3.6 are shown in Fig. 2. The microstructure of SW shows the unshaped marble-like structure (Fig. 2(a)) because of severe cold swelling at a working ratio of around 94%.15 However, all ST samples indicate recrystallization, and the average grain diameter increases proportionally with the logarithm of the holding time from 0.3 to 3.6 ks. The average grain diameter of ST0.3-3.6 changes from around 5.0 to 20 µm.

The results of the XRD profiles near the β(110) peak of SW and ST0.3-3.6 are detailed in Fig. 3. The (110) diffraction peak shifts slightly toward the high-angle side with increases in the holding time of ST, and the peaks show narrower full width at half-maximum values as compared with that of SW. The spreading of the (110) diffraction peak of SW is attributed to a large amount of strain introduced by work hardening during swaging. On the other hand, the shift towards high angles and the sharp shapes of the (110) diffraction peaks are attributed to the relaxation of strain with increased holding time of ST. There are other diffraction

### Table 1 Chemical compositions of Ti-29Nb-13Ta-4.6Zr.

<table>
<thead>
<tr>
<th>Nb</th>
<th>Ta</th>
<th>Zr</th>
<th>Fe</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>13</td>
<td>4.6</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.07</td>
<td>Bal.</td>
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© ¹ 6 m·s⁻¹ 10 ¹ 13,14 The image

![Fig. 1 Line density profile obtained from contact-microradiogram (CMR) image.](image)
peaks confirmed in Fig. 4 aside from those of the β phase ((110), (200) and (211)). These diffraction peaks correspond to those of stress-induced martensite (α’ phase), which seem to be formed by FPB.

3.2 Change in HV and Young’s modulus

Figure 5 shows the HV of ST_{0.3-3.6}, which were measured near the center of the samples, and SW/FPB and ST/FPB, which were measured at the very edge of the samples. The HV of ST_{0.3-3.6} does not change drastically with the change in the average diameter of the grains; the hardnesses are all nearly equal to each other. On the other hand, although the hardness of work-hardened SW is 60 HV, higher than that of the ST_{0.3-3.6}, those collected at the very edge of the specimen surface of SW/FPB and ST/FPB are 410 HV and 380 HV, respectively, which are greater than those of ST and SW by around 70% and 110%, respectively. The HV and Young’s modulus profiles from very edge of the specimen surface to around the center of the specimen are shown in Fig. 6. The HV and Young’s modulus of SW/FPB and ST/FPB at around the center of specimen are nearly equal to those of SW and ST, while very edge of the specimen surfaces of SW/FPB and ST/FPB have the high values mentioned above. Moreover, in SW/FPB, there is a soft region of lesser hardness around the center of the specimen, and the hardness decreases simply up to around 130 µm in depth from specimen surface. This trend is reproduced in the Young’s modulus profile of SW/FPB.

The microstructure near the soft region is shown in Fig. 7. It is clear that the plastic deformation layer extends up to around 40 µm in depth from the specimen surface. In addition, the microstructure is comprised of equiaxed grains produced by recrystallization and exists at around 100–160 µm in depth from the specimen surface. The existence of the microstructural change produced by FPB correlates with the specific region where softening occurred. However, further investigation about this point is required. On the other hand, in ST/FPB, the hardness decreases simply from the specimen surface to inside of specimen, up to 350 µm in depth. Furthermore, the hardness is similar to that around the center of specimen. The trend is the same in Young’s modulus of ST/FPB.
Generally, the main reasons for the improvement in hardness near the specimen surface are because of the increase strain produced by work hardening, the refinement of the microstructure, and the precipitation of the secondary phase. Furthermore, it is reported that the strain rate during the collision between the shot particles and metallic material during FPB increases proportionally with decreases in the diameter of the shot particle and the increase in the velocity of the particle. From these reports, it is considered that the region with drastically higher hardness near specimen surface is formed by the development of stress-induced martensite and subsequent development of the mixed phase, which are effectively hardened by work hardening. Moreover, the increased temperature of the specimen surface induced by the collision of shot particles is reported to reach around 1000 K, ideally. Therefore, it is hard to believe that the remarkable rise in specimen surface temperature only contributes to the existence of the stress-induced martensite. Therefore, it seems to indicate other influences, like the secondary phase precipitation during cooling after FPB or the diffusion of shot partial element like Fe, which is partially adhered by collision during FPB, by severe deformation and exposure at relating high temperature as mentioned above.

3.3 Tensile properties

Figure 8 shows the tensile properties of SW, ST, SW/FPB, and ST/FPB. The tensile strength of SW is around 985 MPa, which is larger than the others because of the large amount of strain produced by severe cold working during swaging as mentioned in Section 3-1. Additionally, the elongation is also relatively high, around 14%. On the other hand, the elongation of ST is the largest (around 60%), although the tensile strength decreases by around 35%, as a result of recrystallization. The tensile strength of SW/FPB shows around 8.0% reduction compared with that of SW. Moreover, comparing the reduction areas of the tensile fracture surfaces of SW and SW/FPB, their values were around 42% and 57%, respectively, and the ductility was degraded by FPB. The specimen surface is work-hardened by FPB, and a residual compressive stress is also introduced. Therefore, it is considered that the poor ductility shown in SW/FPB is because of the early formation of voids in areas that be not influenced by residual compressive stresses. The 0.2% proof stress of ST/FPB increases by around 20% as compared with that of ST, although the tensile strength and elongation of ST/FPB is almost identical to those of ST. This enhancement is because of the early formation of voids in areas that be not influenced by residual compressive stresses. The 0.2% proof stress of ST/FPB increases by around 20% as compared with that of ST, although the tensile strength and elongation of ST/FPB is almost identical to those of ST. This enhancement is because of the early formation of voids in areas that be not influenced by residual compressive stresses. The 0.2% proof stress of ST/FPB increases by around 20% as compared with that of ST, although the tensile strength and elongation of ST/FPB is almost identical to those of ST. This enhancement is because of the early formation of voids in areas that be not influenced by residual compressive stresses. The 0.2% proof stress of ST/FPB increases by around 20% as compared with that of ST, although the tensile strength and elongation of ST/FPB is almost identical to those of ST. This enhancement is because of the early formation of voids in areas that be not influenced by residual compressive stresses.
around 310 MPa. This tendency is similar in SW/FPB, and the fatigue limit is around 400 MPa. However, the fatigue limit is slightly lower than the minimum value of the fatigue limit for Ti64. As compared with the fatigue strength of SW, the fatigue limit is slightly lower than the minimum value of the fatigue limit. Therefore, the fatigue limit is around 400 MPa. However, the fatigue limit is around 310 MPa. This tendency is similar in SW/FPB, and the fatigue limit is around 400 MPa. However, the fatigue limit is slightly lower than the minimum value of the fatigue limit for Ti64. As compared with the fatigue strength of SW, the fatigue limit is slightly lower than the minimum value of the fatigue limit.

Therefore, it is considered that fatigue crack initiation is restricted by the fully effective residual compressive stresses (without damping) in the high-cycle fatigue-life region.

### 3.5 Bone contactability

Figure 10 shows the CMR images at 12 weeks after implantation, the surface roughness profiles, the average roughness (Ra) and CMR image of SW with a mirror surface and SW/FPB. The Ra of SW/mirror as a comparison material is 0.07 µm, and the maximum height of the surface roughness profile is around 0.25 µm. On the other hand, the Ra of SW/FPB is 0.65 µm, and the maximum height of the surface roughness profile is around 100 µm. In the high cycle fatigue life region, while it drastically increases by around 310 MPa. This tendency is similar in SW/FPB, and

![Fig. 9 S-N curves of SW and SW/FPB along with fatigue limit range of annealed Ti-64.](image)

Table 2 Average of bone formation ratio, bone contact ratio and relative bone contact ratio of SW/mirror and SW/FPB.

<table>
<thead>
<tr>
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<th>Bone formation ratio [%]</th>
<th>Bone contact ratio [%]</th>
<th>Relative bone contact ratio [%]</th>
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<tbody>
<tr>
<td>SW/mirror</td>
<td>88.6 ± 7.4</td>
<td>12.3 ± 4.0</td>
<td>8.8 ± 4.3</td>
</tr>
<tr>
<td>SW/FPB</td>
<td>99.1 ± 1.5</td>
<td>20.1 ± 8.1</td>
<td>20.1 ± 8.1</td>
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![Fig. 10 Roughness profiles, average surface roughness (Ra) and CMR image of SW/mirror and SW/FPB.](image)
SW/mirror and SW/FPB. The surface roughness of SW/FPB is nearly equal to that of a polished surface and is located within the region required for successful implantation, while that of SW/mirror, with a surface roughness less than 0.1 µm is outside of this region. From the results in this study, it is possible to easily change the surface morphology of these alloys by FPB under various conditions, such as the type of shot material and the shot velocity. Therefore, there is a possibility of further improvement of bone formation on implants treated by FPB under optimum shot conditions.

4. Conclusions

This study investigated the effects of surface modification by fine particle bombarding (FPB) on the mechanical properties of Ti-29-13Ta-4.6Zr alloy (TNTZ), which were severe cold swaging, in order to maintain a relatively low elastic modulus. The bone contact characteristics of TNTZ samples subjected to surface modification and cancellous bone were also compared. The following results were obtained.

1) The microstructure of severe cold swaged TNTZ (SW) showed single β phase with unshaped marble-like structure. However, all as-solutionized TNTZ (ST) indicated recrystallization, and the average grain diameter of ST for holding times of 0.3 to 3.6 ks changed from around 5.0 to 20 µm. Their HV did not change drastically with the change in the average diameter of the grains.

2) Although the hardness of work-hardened SW was 60 HV, higher that of the ST for holding times of 0.3–3.6 ks, those collected at the very edge of the specimen surface of SW and ST subjected to FPB (SW/FPB and ST/FPB) were 410 HV and 380 HV, respectively, which were greater than those of ST and SW by around 70% and 110%, respectively.

3) The fatigue strength of SW/FPB improved in the high-cycle fatigue-life region because of the residual compressive stresses at very edge of the specimen surface.

4) The specimens of SW/FPB with a rough surface texture (average roughness, \( Ra \), of 0.65 µm) and TNTZ with a very smooth surface texture (\( Ra \) of 0.07 µm) were surrounded by neonatal bone to the circumference of the specimen. The relative bone contact ratio of SW/FPB was around 80%, much higher than that of SW/mirror (around 13%).

Acknowledgements

This work was supported in part by The Light Metal Educational Foundation, The Amada Foundation, The Tatamatsu Foundation and The Japan Titanium Society.

REFERENCES