Change in Mechanical Properties of Biomechanical Ti–12Cr Subjected to Heat Treatment and Surface Modification Processing

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In recent years, metallic biomaterial applications have demanded a relatively low Young’s modulus that is nearly equal to that of bone (around 30 GPa). However, in the case of spinal fixture applications, metallic materials with a relatively high Young’s modulus are required to suppress spring-back by elastic and plastic deformation during implantation. We recently proposed Young’s modulus control by stress-induced transformation to produce the biomedical β-type Ti–12Cr alloy. However, the relationship between the microstructure and the mechanical properties of Ti–12Cr has not been fully investigated. In this study, the changes in the mechanical properties of Ti–12Cr were investigated through the heat treatment and the fine particle bombarding process (FPB), which is a surface modification process. Peak aging (PA) of Ti–12Cr heated at 673 K occurred for around 2.4 ks. The Vickers hardness of Ti–12Cr at the PA condition at 673 K (HV 524) was around 90% higher than that after solutionized treatment (ST) (HV 294). Both the 0.2% proof stress and tensile strength of Ti–12Cr at the PA condition at 673 K were also around 50% higher those after ST. However, the ductility of Ti–12Cr at the PA condition at each temperature significantly decreased. Therefore, only ST was judged to be optimal for Ti–12Cr with an excellent combination of strength and ductility. The Vickers hardness and Young’s modulus of solutionized Ti–12Cr subjected to FPB increased by around 40% and 70%, respectively, at the edge of the specimen surface compared with the corresponding values of the unprocessed sample. Furthermore, the run-out (770 MPa) of Ti–12Cr subjected to FPB increased by around 70 MPa. The bone contact ratio of Ti–12Cr slightly increased with an increase in the implantation period from 24 to 52 weeks.

Keywords: metallic biomaterial, stress-induced phase, mechanical strength, surface modification, biocompatibility

1. Introduction

In recent years, stainless steel (SS) and the Ti–6Al–4V ELI alloy (Ti64) have been used for manufacturing spinal fixations as metal-based biomaterials. However, application of both of these alloys in spinal fixations is limited because of the significant weight of SS along with its high density and the spring-back after working of Ti64 with a relatively low Young’s modulus. Spring-back is a phenomenon in which the material recovers from deformation to its no-load state. In general, spring-back easily occurs using metallic materials with a relatively low Young’s modulus in the manufacture of spinal fixations. In addition, there are some problems regarding the operability of spinal fixtures with respect to plastic deformation during operation and shape recovery after operation.

Material development is therefore required for spinal fixations so that they are non-toxic to the body and do not undergo significant spring-back. We previously proposed that for metastable β-type Ti–Cr system alloys for biomedical applications, it is possible to control the Young’s modulus by the stress-induced phase, thereby providing new metallic biomaterials.

Moreover, spinal fixations need to endure high fatigue strength to be implanted in the body for a long period of time. Mechanical surface modification processing and heat treatment, such as aging treatment, can drastically improve the fatigue strength of the alloy. In this study, we focused on shot peening (SP), which is widely used in industry. Conventional SP increases the fatigue strength and creates residual compressive stress. However, it has been suggested that it decreases the fatigue strength when the surface becomes rough. Therefore, the fine particle bombarding process (FPB) is performed using smaller particles than those used in SP. In addition to the SP effect, various effects have been reported, such as control of the surface roughness, grain refinement of the surface layer, and induced phase transformation.

In this study, we investigated the changes in the mechanical properties of Ti–12Cr subjected to various heat treatments and mechanical surface modification processing.

2. Experimental Methods

In this study, we used a forging round bar specimen made of the Ti–12Cr alloy. The chemical composition is listed in Table 1. This material was solutionized for 3.6 ks at a temperature above the β-transus temperature of 953 K. The Ti–12Cr alloy was solutionized at 1003 K, was and this sample is referred to as ST. This material was then water quenched (WQ) and aged at 573 K, 673 K, or 723 K for various times, and these samples are referred to as STA573 K, STA673 K, and STA723 K, respectively. The solutionized images are shown in Fig. 1. The heat treatments were performed in vacuum. These solutionizing heat treatments gave the single β phase.

Surface modification through FPB was applied to some ST specimens. During the process of FPB, the medium was high-

**Table 1 Chemical composition of Ti–12Cr (mass%).**

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-12Cr</td>
<td>11.9</td>
<td>0.04</td>
<td>0.01</td>
<td>0.11</td>
<td>0.004</td>
<td>Bal.</td>
</tr>
</tbody>
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speed steel beads with a diameter range of 50–150 µm. The parameters were as follows: particle control pressure of 0.6 MPa, distance of 30 mm, and shot time of 0.09 ks, 0.18 ks, and 0.36 ks, and these samples are referred to as ST/FPB0.09 ks, ST/FPB0.18 ks, and ST/FPB0.36 ks, respectively. The heat-treated materials were mirror-surface finished by polishing them with wet emery paper with a grid of #4000 and buff polishing by colloidal silica suspension (average diameter of particle of 0.04 µm). The mirror-surface-finished materials were etched using 0.5% HF solution, and they were then subjected to microstructural observation by optical microscopy (OM) (OLYMPUS: BX60M) and scanning electron microscopy (SEM) (KEYENCE: VE-8800). The X-ray diffraction (XRD) (RIGAKU: MiniFlex 300) patterns of the samples were recorded using an X-ray diffractometer with Cu-Kα radiation under 30 kV/10 mA at room temperature. The other parameters were as follows: 30°–90° diffraction angle range and a scan speed of 20°/10min.

The residual stresses were measured with a portable X-ray stress analyzer (PULSTEC: μ-X360) with Cr-Kα radiation under 30 kV/1.0 mA, an X-ray incidence angle of 25°, and a measured distance of 29 mm at room temperature. Using the diffraction ring obtained in the measurement, the compressive residual stresses were calculated from the X-ray intensity around the diffraction ring.

The hardness measurements of all of the samples were performed around the centers of their cross-sections, which were polished with wet emery paper with a grid of #4000, using a micro-Vickers hardness testing machine (MITSUTOYO: HM-102) at a load of 2.0 N for a holding time of 10 s. HV profiles of the ST/FPB0.09–0.36 ks samples were also measured from every edge of the specimen surface to around 3.0 mm from that on the cross-section.

The Young’s modulus was calculated using the gradient obtained from the load–unload curves using a nano-indentation tester (SHIMADZU: DUH-211) at a load of 392 mN for a holding time of 10 s.

For the tensile tests, dog-bone-type tensile specimens with a diameter of 3.0 mm and a gauge length of 18 mm were machined from the ST and STA573–723 K samples (Fig. 2(a)). These specimens were then wet-polished using wet emery paper with a grid of #4000. The tensile tests were performed using an Instron-type machine (SHIMADZU: AGS-20kNG) at a crosshead speed of 8.33 × 10⁻⁶ m s⁻¹ in air at room temperature. The load was detected through the load cell of the machine. The strain was detected by a strain gauge attached to the gauge part of the tensile specimen and calculated from the change in the gauge length before and after the tests through a microscopy measurement.

For the fatigue tests, dog-bone-type tensile specimens with a diameter of 4.0 mm and a gauge length of 5.0 mm were machined from ST (Fig. 2(b)) after having been subjected to FPB. The fatigue tests were performed using an electro-servo-hydraulic machine (mts: FlexTest SE) at a capacity of 98 kN, a frequency of 10 Hz, and a stress ratio (R) of 0.1 in air at room temperature. In this study, the maximum cyclic stress, where the fatigue specimen is not broken at 10⁶ cycles, is designated as the run out.

For evaluation of the bone contactability, column-shaped samples of ST and commercial pure titanium (CP-Ti) with mirror-surfaces were implanted into the lateral condyles of the femurs of Japanese white rabbits, which were approximately one-year-old males. They were then extracted along with some parts of the femur 24 and 52 weeks after implantation. The samples were processed using the fuchsin staining process and embedded in a resin of methyl methacrylate polymer. The samples in the resin were machined into thin layers with a thickness of around 150 µm to observe the contact micro-radiogram (CMR) image. Evaluation of the bone contactability was performed by analyzing the CMR images of the contact area between the implants and the bony tissue. The image was converted to a rectangular shape to easily analyze the level of the gray value obtained from the implant surface up to a thickness of approximately 50 µm. The lower limit of the gray value was defined as the bone contact threshold (BCT), although the BCT value was different in each sample. Values above and below the BCT were defined as the bone contact and non-bone contact regions. Moreover, the non-bone contact region was classified into two categories depending on whether it was surrounded by bony tissue, in contact with the implant surface, and whether there was formation of bony tissue near the surface. The bone contact region around the circumference of the implant (bone contact ratio) and the bone contact region around the circumference of the implant surrounded by bony tissue (relative bone contact ratio) were calculated considering the individual differences in the animals and the slight differences in the implant locations.

3. Results and Discussion

3.1 Change in the Vickers hardness and Young’s modulus after aging treatment

Figure 3 shows the change of the Vickers hardness with aging for Ti–12Cr heated at 573 K, 673 K, and 723 K after ST. The Vickers hardness values of STA573–723 k significantly
increase at the early stage of aging. In this case, the PA condition of STA673 K has the highest value (524 HV). However, the rate of increase of the hardness is 174.2 HV/ks for STA723 K, which is 45 to 88% higher than the samples subjected to the other aging treatments. As a result, Ti–12Cr reaches the PA condition significantly earlier than the biomedical Ti–29Nb–13Ta–4.6Zr (TNTZ)\textsuperscript{12}. For example, TNTZ reaches the PA condition in around 614.4 ks when subjected to aging treatment at 723 K. The rate of increase of the hardness is 0.198 HV/ks for TNTZ at the PA. The shorter PA times for Ti–12Cr are because of the faster diffusion rate of Cr in Ti than those of Nb and Ti\textsuperscript{13}.

Figure 4 shows the change in the Young's modulus of Ti–12Cr aged at 573 K, 673 K and 723 K after ST. The Young's modulus of ST is about 68 GPa, which is about 40 GPa lower than that of CP-Ti and slightly higher than that of TNTZ. The Young’s modulus of STA673 K is 111 GPa at the PA condition, which is equivalent to the respective value of CP-Ti. It is considered that aging treatment causes the volume fraction of the \(\alpha\) phase to increase and coarsening\textsuperscript{14}. The increasing trends of the Vickers hardness and Young's modulus are similar with aging time.

3.2 Microstructures after the heat treatments

Figure 5 shows optical microscope images of the microstructures of ST and STA573–723 K at the PA condition. The microstructure of ST is the single \(\beta\) phase with an average grain size of 70 \(\mu\)m, and its precipitates cannot be observed in the grain and grain boundary. It is considered that the microstructures of STA573–723 K are the precipitation phase, such as the \(\alpha\) phase and \(\omega\) phase\textsuperscript{15,16}, but detailed observation is difficult by optical microscope. The average grain sizes after aging treatment are not significantly different from that of ST. However, STA673 K contains light and dark regions. It is considered that these precipitate areas correspond to fluctuation regions of the Cr element. STA673 K and STA723 K do not show such fluctuation because diffusion of Cr is promoted by higher aging temperature.

Figure 6 shows XRD profiles of ST and STA573–723 K in the PA condition. The XRD profile of ST only shows a diffraction peak of the \(\beta\) phase, but the XRD profiles of STA573–723 K show diffraction peaks of the \(\alpha\) phase as well as the \(\beta\) phase. In addition, the diffraction peak intensities of the \(\alpha\) phase peaks in STA673 K are the highest. As a result, it is considered that STA673 K has higher Vickers hardness and Young's modulus than the samples produced with the other aging temperatures.
3.3 Tensile properties after the heat treatments

Figure 7 shows the tensile strength, 0.2% proof stress, elongation, and reduction area of ST and STA573–723 K at the PA condition. The tensile strength, 0.2% proof, and elongation of ST are 936 MPa, 890 MPa, and 23%, respectively. The tensile strength and 0.2% proof of STA573–723 K are 1390–1440 MPa and 1310–1400 MPa, respectively, which are significantly higher than the corresponding values of ST. However, the elongation of ST is approximately 23% while the elongation values of the STA samples at the PA condition are only a few percent. The reduction area of ST is approximately 38%, but the reduction areas of STA573–723 K are approximately 1%, which indicates significant embrittlement.

Figure 8 shows the tensile fracture surfaces of ST and STA573–723 K at the center of the tensile test specimen. The tensile fracture surface of ST has dimples with an average diameter of 1.72 μm, which indicates typical ductile fracture. In contrast, the tensile fracture surfaces of STA573–723 K have many facets and a few fine dimples, which indicate relatively brittle fracture morphologies. Therefore, it is considered that Ti–12Cr does not require aging treatment because of the excellent balance between the strength and ductility of ST.

In the following experiments, only ST was used for the surface modification processing.

3.4 Change in the Vickers hardness and Young’s modulus after FPB

Figure 9 shows the Vickers hardness profiles of ST/FPB₀.₀₉–₀.₃₆ ks as a function of the distance from the specimen surface. The average Vickers hardness of ST is 294 HV. The specimen surfaces of ST/FPB₀.₀₉–₀.₃₆ ks have higher Vickers hardness values than ST. The Vickers hardness values of the specimen surfaces of ST/FPB₀.₀₉ ks and ST/FPB₀.₃₆ ks are 330 HV and 360 HV, respectively. The rates of increase of the hardness are 4.0 HV/s and 3.8 HV/s for ST/FPB₀.₀₉ ks and ST/FPB₀.₃₆ ks, respectively, which is no significant difference. However, ST/FPB₀.₃₆ ks has a Vickers hardness of 379 HV on the specimen surface, which is the rate of increase of the hardness of 2.4 HV/s, which is slightly lower than the other specimens subjected to FPB. ST/FPB₀.₁₈ ks and ST/FPB₀.₃₆ ks have large regions of increasing Vickers hardness from the surface of 80 μm, while that of ST/FPB₀.₀₉ ks is 50 μm.

Figure 10 shows the microstructures of the specimen surfaces of ST/FPB₀.₀₉ ks and ST/FPB₀.₁₈ ks. The ST/FPB₀.₀₉ ks and ST/FPB₀.₁₈ ks specimens have remarkable plastic deformation areas to depths of 5.0 μm and 10 μm from the specimen surfaces, respectively. It is considered that the difference of the hardness affected areas of ST/FPB₀.₀₉ ks and ST/
FPB_{0.18 \text{ ks}} are because of the difference of the plastic deformation areas. From these plastic deformation areas, the increase in the hardness of ST/FPB compared with ST can be attributed to work hardening, the stress induced ω phase, or refinement of grains\(^{17,18}\). As a result, hereafter, we will focus on ST/FPB_{0.18 \text{ ks}} considering the ratio of the Vickers hardness and the operability of FPB.

Figure 11 shows the Young’s modulus profile of ST/FPB_{0.18 \text{ ks}} as a function of the distance from the specimen surface. Generally, an increase in the Young’s modulus is not because of the metastable β-type titanium alloy being subjected to cold working, but the Young’s modulus of the specimen surface of ST/FPB_{0.18 \text{ ks}} increases to 93.8 GPa. It is considered that an increase in the Young’s modulus is because of precipitation of the stress induced phase, which has a higher Young’s modulus than the β phase of the parent phase\(^{19}\).

Figure 12 shows XRD profiles of the specimen surfaces of ST and ST/FPB_{0.09–0.36 \text{ ks}}. The XRD profile of ST only shows a diffraction peak of the β phase, but the XRD profiles of ST/FPB_{0.09–0.36 \text{ ks}} show diffraction peaks of fine particles in addition to the β phase. However, the peak of the ω phase of the stress-induced phase cannot be observed. In the case of cold-worked Ti–12Cr, there are some stress-induced ω phases observed by transmission electron microscopy\(^{20,21}\), although the microstructure of solutionized Ti–12Cr only shows the β phase. As a result, it is expected that after being subjected to FPB, work hardening becomes greater with mixed β and ω phases.

### 3.5 Fatigue property

Figure 13 shows S–N curves of ST and ST/FPB_{0.18 \text{ ks}} along with the run-out range of Ti64 with various microstructures\(^{22–24}\). The run-out of ST is 710 MPa. It has high fatigue strength with a fatigue ratio (fatigue strength/tensile strength) of 0.86 when considering the tensile strength of this alloy (830 MPa). However, the run-out is located slightly at the lower side of the run-out range of Ti64. Conversely, in the S–N curve of ST/FPB_{0.18 \text{ ks}}, there is an increase in the fatigue strength in the low- and high-cycle fatigue life regions compared with the corresponding curve of ST. The run-out of ST is 770 MPa and it is located at the higher side of the run-out range of Ti64.

Figure 14 shows the fatigue fracture surface of ST in the low- and high-cycle fatigue life regions. Fatigue crack initiation is generated in the β phase of the specimen surface, and fatigue crack propagation occurs radially inwards towards the inside of the specimen. In addition, obvious striation is observed at the fracture surface of the fatigue crack propagation area, and the fast fracture area forms an equiaxial dimple.
fracture surface. The fatigue fracture morphology is characteristic of common ductile materials.

Figure 15 shows the fatigue fracture surface of ST/FPB0.18 ks in the low- and high-cycle fatigue life regions. Fatigue crack initiation of ST occurs on the specimen surface, but in ST/FPB0.18 ks it occurs inside the specimen because of formation of the plastic deformation area. The fatigue crack then radially propagates towards the inside of the specimen, which is similar to the case of ST. Obvious striation is observed at the fracture surface of the fatigue crack propagation area. The fast fracture area forms an equiaxial dimple fracture surface, which is also observed for ST. As a result, it is considered that FPB increases the fatigue life where the plastic deformation areas occur.

When this alloy is subjected to FPB, it is considered that microcrack initiation resistance greatly increases. Metallic materials subjected to ST generally show little residual tensile stress\(^{25,26}\), but the residual stress of ST/FPB0.18 ks is around \(-1100\) MPa. In this case, it is considered that the fatigue strength of ST/FPB0.18 ks improves to increase the microcrack initiation life, where the residual compressive stress occurs after ST/FPB0.18 ks has been subjected to FPB.

### 3.6 Bone contactability

In Section 3.5, we mainly focused on ST/FPB0.18 ks. In this section, we mainly focus on the bone contactability of ST compared with that of CP-Ti, where an existing biomaterial was used to investigate the influence of the constituent elements.

Figure 16 shows CMR images and profiles of ST on 24 and 52 weeks after implantation. ST is generally surrounded by bone tissue around almost its entire periphery on both 24 and 52 weeks after implantation, and the surrounding bone tissue matures and thickens with increasing postoperative time. However, in the concentration profile, the bone-forming section shows that there is no new bone part of the specimen on 24 weeks after implantation. The vacancy derived from the shape of cancellous bone was confirmed by optical microscope observation.

Figure 17 shows the bone formation and relative bone contact ratios of ST and CP-Ti on 24 and 52 weeks after implantation. The bone formation and relative bone contact ratios increase with postoperative time. However, the bone formation and relative bone contact ratios of ST are not very different from those of CP-Ti on 24 weeks. ST does not show a significant increase of the two ratios compared with CP-Ti at a postoperative time of 52 weeks. It is considered that close contact between titanium and bone formation results in osteogenesis\(^{27}\), and the bone contact ratio of ST is not good for bone formation. Therefore, it is considered that ST has mediated osteogenesis similar to SS and the Co–Cr alloy. In this case, SS and the Co–Cr alloy precipitate chromium oxide in the specimen surface.\(^{28,29}\) It is expected that the Ti–Cr sys-
tem alloy forms some chromium oxide in addition to titanium oxide in the specimen surface. However, this requires further investigation.

4. Conclusions

We have investigated the effects of various heat treatments and surface modification processing by FPB on the mechanical properties of the Ti–12Cr alloy. The bone contactability of Ti–12Cr was also compared with that of CP-Ti. The following results were obtained.

(1) Ti–12Cr subjected to some aging treatments has high mechanical strength and low ductility owing to the rapid diffusion rate of Cr. In this case, Ti–12Cr subjected to ST has an excellent balance between strength and ductility.

(2) It is considered that the specimen surface of Ti–12Cr subjected to FPB has mixed β and ω phases because of the precipitate of the stress-induced phase. Therefore, the maximum Vickers hardness is around 360 HV because of acceleration of work hardening.

(3) Ti–12Cr subjected to FPB has high microcrack initiation resistance owing to the combination of the compressive residual stress and the precipitate of the stress-induced phase. Therefore, run-out is around 770 MPa, which is around the upper limit of the fatigue of Ti–6Al–4V ELI.

(4) The bone formation and relative bone contact ratios of Ti–12Cr slightly increase with postoperative elapsed time.

Acknowledgements

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Fig. 17 Bone formation and relative bone contact ratios of Ti–12Cr and CP-Ti after implantation on 24 and 52 weeks.