Mechanical Properties of Biocompatible Beta-Type Titanium Alloy Coated with Calcium Phosphate Invert Glass-Ceramic Layer

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The presence of calcium phosphate invert glass-ceramic (designated as CPIG) layer on the surface of artificial implant products can improve the bonding between these products and bones. In this study, the morphology of the CPIG layer on the surface of a β -type titanium alloy, Ti-29Nb-13Ta-4.6Zr (TNTZ), was investigated for biomaterial applications by a dip-coating treatment. Furthermore, the mechanical properties of TNTZ coated with the CPIG layer were also investigated.

In the CPIG layer, a compositionally gradient zone with a thickness of approximately 2.0 μ m exists on the surface of the TNTZ. The titanium concentration in the zone increases with the decreasing distance from the CPIG surface toward the base materials. On the other hand, calcium and phosphorus concentrations in the zone increase with the distance from the TNTZ surface. The tensile bonding strength between TNTZ and the CPIG layer is 25 MPa and that between aged TNTZ and the CPIG layer is 18.6 MPa.

For easily understanding the change in mechanical properties by a dip-coating treatment, the values of those on TNTZ and TNTZ coated with CPIG layer were shown as follows. The tensile strength increases remarkably by a dip-coating treatment as compared with that of as-solutionized TNTZ while the elongation is a reverse trend. Young's modulus of TNTZ and aged TNTZ coated with the CPIG increases by 15 to 27 GPa after the dip-coating treatment as compared with that of as-solutionized TNTZ (approximately 60 GPa). The fatigue limit of TNTZ coated with the CPIG layer is nearly equal to that (approximately 300 MPa) of as-solutionized TNTZ. On the other hand, the fatigue limit of aged TNTZ coated with the CPIG layer is a 100 MPa higher than that of as-solutionized TNTZ.

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1. Introduction

Biocompatible Ti-29Nb-13Ta-4.6Zr (TNTZ) developed by the authors can be used in biomedical applications due to its good mechanical properties such as high specific strength and elongation.¹⁻⁵⁾ TNTZ has a low Young's modulus of approximately 60 GPa, very low cyto-toxicity, similar to that of pure Ti, and good biocompatibility with living tissues.⁶⁾ However, it lacks bioactivity, which is the ability to directly form a chemical bond with bones although its biocompatibility is inadequate. A stem—a part of artificial joints—and dental implants made of metallic materials are required to strongly bond with living bone. However, they themselves cannot form a chemical bond with living bone.

The bioactive ceramic surface modification is effective in improving the biocompatibility of TNTZ. Calcium phosphate ceramics such as hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$; HA) or β -tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$; TCP) possess bioactivity.^{7,8)} Bioactivity is required in some portions of artificial substitutes for hard tissues. Many types of HA- and TCP-coating methods on titanium or titanium alloys have been reported so far.⁹⁻¹⁶⁾ Among them, the calcium invert glass-ceramic coating method, which is the dip-coating treatment, is simple and highly applicable to TNTZ.^{17,18)} This method includes heating at 1073 K. Since firing is conducted above the beta transus temperature of TNTZ during-coating process, there is a possibility that the mechanical properties of TNTZ are degraded during firing. In such a case, heat treatments such as aging, etc., are needed to improve the mechanical properties of TNTZ after conducting the calcium invert glass-ceramic coating process. However, there is a

possibility that the characteristics of the aged TNTZ coated with a calcium invert glass-ceramic layer might be degraded as compared with those of TNTZ that has undergone general aging after the solution treatment. Furthermore, there is a possibility that the coating layer will be exfoliated due to the difference in thermal expansion coefficients between the TNTZ matrix and the coating layer when the aging is conducted.

Therefore, the morphology of calcium phosphate invert glass-ceramic layer, and the mechanical properties of TNTZ and heat-treated TNTZ coated with this layer were investigated, where the change of mechanical properties in air are only done due to compare to TNTZ subjected to solution treatment (ST) and aging after ST although that in vitro is very important.

2. Experimental Procedures

The material used in this study was hot forged bars of Ti-29Nb-13Ta-4.6Zr (TNTZ), 11 mm in diameter.

Prior to the dip-coating of calcium phosphate invert glass, the solution treatment was conducted in vacuum on TNTZ bars at 1063 K—the temperature above the beta transus temperature of TNTZ (approximately 1013 K). As-solutionized TNTZ is termed as ST.

In this study, specimens with a diameter of 10 mm and thickness of 2.0 mm for the Vickers hardness tests were machined from ST. The surfaces of specimens of these specimens were subjected to polishing using a wet emery paper with a grid of #600.

The bonding strength between the coated layer and the

base material is measured using specimens with a diameter of 10 mm and a height of 20 mm machined from ST. To enhance the adhesion between the TNTZ matrix and coating layer, the surfaces of these specimens were subjected to sand-blasting, where the surface roughness achieved was approximately $1.29\text{ }\mu\text{m}$ on the average, after polishing using a wet emery paper with a grid of #600.

For the tensile and plain fatigue tests, round bar tensile specimens with a diameter of 10 mm and a gauge length of 20 mm were machined from ST. These specimens were then subjected to sand blasting after polishing using a wet emery paper with a grid of #600. In particular, for the fatigue test, the specimens in the solutionized condition were buff-polished to get a mirror surface having a roughness of approximately $0.01\text{ }\mu\text{m}$ on the average after polishing using a wet emery paper with a grid of #1500.

For the measurement of Young's modulus, specimens with a diameter of 10 mm and a length of 70 mm were machined. These surfaces of specimens were subjected to sand blasting after polishing using a wet emery paper with a grid of #600.

Each specimen was dipped into the slurry of calcium phosphate invert glass powder ($60\text{CaO}-30\text{P}_2\text{O}_5-7\text{Na}_2\text{O}-3\text{TiO}$) and methanol and lifted at a speed of 1.4 mm/s . The dipped specimen was dried in air at room temperature for 1.8 ks. The thickness of calcium phosphate invert glass-ceramic (designated as CPIG) layer was controlled at approximately $5\text{ }\mu\text{m}$ by the concentration of slurry. After the dip-coating of CPIG, the coated specimen was heated at 1073 K for 0.9 ks followed by furnace cooling to room temperature. The coated specimen is termed as DC_5 . The dip-coating treatment process carried out for TNTZ is schematically shown in Fig. 1.

Part of DC_5 specimens were aged at 723 K for 259.2 ks in vacuum followed by air-cooling in order to improve their mechanical properties. These specimens are termed as the aged DC_5 and their aging process is also schematically shown in Fig. 1.

Microstructural observations of ST, DC_5 , and aged DC_5 were carried out using a scanning electron microscopy (SEM) after buff polishing and etching.

The X-ray diffraction analysis was carried out using a Cu target with an accelerating voltage of 40 kV and a current of 30 mA .

The Vickers hardness was measured using a Vickers hardness tester with a load of 0.49 N and a holding time of 15 s after buff polishing the specimen.

The coating layer boundary and near the surface of the TNTZ matrix were observed using an SEM with an energy dispersive X-ray (EDX) after polishing the specimen and coated it with Pt.

The aforementioned columnar specimens of DC_5 and aged DC_5 were used to evaluate the tensile bonding strength of the coating layers. A bonding agent for dental applications, (super bond orthomite), was applied to the surface of the coating layer of each specimen, and the surface was then bonded with a columnar stainless steel fixture whose size was identical to that of the columnar specimens of DC_5 and aged DC_5 . Subsequently, the bonded specimens were dried in air at room temperature for 86.4 ks and subjected to the tensile bonding test. The tests were conducted at a crosshead speed of $1.67 \times 10^{-5}\text{ m/s}$ in air at room temperature by using an Instron type tensile testing machine. The specimens were carefully set up the chucking jig not to occur some shear stresses at the boundary between TNTZ and the fixture. The tensile bonding strength test system was schematically shown in Fig. 2.

The tensile test of each specimen was conducted using an Instron type machine at a crosshead speed of $8.33 \times 10^{-6}\text{ m/s}$ in air at room temperature. A load cell of the machine detected the load and the strain was detected by a strain gauge attached to the gauge part of the specimen.

The fatigue tests were conducted on the plain fatigue test specimens using an electro-servo-hydraulic machine. The test was conducted at a frequency of 10 Hz with a stress ratio, $R = 0.1$, in air at 295 K . The maximum cyclic stress, at which the specimen was not failure at 10^7 cycles, was defined as the plain fatigue limit in this study.

The fracture surface observation was carried out using an SEM.

The Young's modulus of each specimen was measured in air at room temperature using a resonance method. This method is based on the measurement of the fundamental resonant frequencies of the material during vibration.

3. Results and Discussion

3.1 Microstructure and age hardening characteristics

The microstructures of ST, DC_5 aged DC_5 were comprised

Fig. 2 Schematic drawing of tensile bonding strength testing system.

Fig. 1 Schematic drawings of (a) solution treatment, (b) dip-coating treatment and (c) aging treatment. RT, WQ, FC and AC indicate room temperature, water quenching, furnace cooling and air cooling, respectively.

Fig. 3 Aging curves of Ti-29Nb-13Ta-4.6Zr, TNTZ, conducted with solution treatment, ST, and TNTZ coated with calcium phosphate invert glass-ceramic, CPIG, layer, DC₅.

of β phase grains of a diameter of approximately 20 μm . Alpha and omega phase, which is expected to exist, are not observed by SEM observation probably due to the super fine precipitation.

Figure 3 shows the age hardening curves of ST and DC₅ specimens. The Vickers hardness of DC₅ before aging is higher than that of ST due to the ω phase precipitation during furnace cooling after the firing. The Vickers hardness of DC₅ gradually increases up to 259.2 ks. The Vickers hardness of DC₅ at an aging time of 86.4 ks is nearly equal to that of ST. The rate of increase in the hardness of DC₅ is nearly equal to that of ST up to an aging time of 43.2 ks. For the aging time from 43.2 to 259.2 ks, the rate of increase in Vickers hardness of ST is higher than that of DC₅. The average Vickers hardness of DC₅ and ST for an aging time of 259.2 ks is 241 and 270 HV, respectively. It has been reported that Vickers hardness at the peak of aging of cold-rolled TNTZ subjected to aging at 723 K is over 3.0 Ms.¹⁹⁾ Therefore, the aging time selected in this study is in under-aging conditions.

Figure 4 shows the change of Vickers hardness of DC₅ specimens at the different position in the specimen thickness measured of various aging time. The Vickers hardness for the aging time range of 18.0 to 86.4 ks increases in keeping with the hardness gradient near the surface of the specimen because the oxide layer and the α case exist near the surface of specimen when heating is carried out in air. The Vickers hardness of near the surface of the specimen for aging of 259.2 ks is the greatest with a value of 376 HV.

3.2 Morphology of coating layer

Figure 5 shows SEM micrographs of specimen surfaces and cross sections of DC₅ and aged DC₅. The CPIG layers of DC₅ and aged DC₅ show microstructures with a large number of pores, few micrometers in diameter and approximately 5.0 μm in thickness. There are no cracks at the boundary between the CPIG layer and each TNTZ and no exfoliations on the CPIG layer on DC₅ and aged DC₅ although the thermal expansion coefficients of titanium and TCP range from 8×10^{-6} to $10 \times 10^{-6} \text{ deg}^{-1}$ and 11×10^{-6} to $15 \times 10^{-6} \text{ deg}^{-1}$, respectively.¹⁸⁾ A number of cracks and exfoliations were observed on the surface of TNTZ coated with

Fig. 4 Change in Vickers hardness of DC₅ at various aging time as a function of distance from surface.

Fig. 5 SEM micrographs of morphologies of (a) DC₅, and (b) aged DC₅, and cross section of near CPIG layer of (c) DC₅ and (d) aged DC₅.

CPIG layer with a thickness of 15 μm after heating.²⁰⁾ It is considered that the CPIG layer with a thickness of 5 μm composed of the compositional gradient zone (3 μm) is optimum size.

Figure 6 shows an SEM micrograph of the cross section of DC₅ and results of the line analysis of elements measured by EDX along the indicated line. The composition of elements shows gradient within the thickness of the layer, thus forming the compositional gradient zone. The titanium concentration in the zone increases with the decreasing distance from the CPIG surface toward the base materials. On the other hand, calcium and phosphorus concentrations in the zone increase with the distance from the TNTZ surface. And the matrix, almost devoid of no calcium, comes in contact with the surface.

The X-ray diffraction profiles of the surfaces of DC₅ and aged DC₅ show the phases of β -TPC, β -CPP, β , α , and TiO₂, as shown in Fig. 7. As indicated by the results of the X-ray profile, it is considered that the coating layers comprise of a large amount of β -TCP and a small amount of β -CPP. The peak strength of TiO₂ is clearly observed as compared with TNTZ subjected to solution treatment in vacuum¹⁹⁾ because TNTZ is conducted with a heating in air.

Figure 8 shows the X-ray diffraction profiles, measured at

Fig. 6 SEM micrograph of cross section of DC₅, and Ti, P and Ca concentration profiles along detected line.

Fig. 7 X-ray diffraction profiles of surfaces of (a) DC₅ and (b) aged DC₅.

Fig. 8 X-ray diffraction profiles of DC₅ as a function of distance from surface of specimen.

the different depth from surface of DC₅ specimen, the CPIG layer. The surface is removed from the specimen surface. The oxide layer (TiO₂) is observed up to 20 μm from the boundary between the CPIG layer and the TNTZ matrix. Subsequently, the oxygen-rich region, which is considered to be an α case, and consists of the α phase, exists up to approximately 100 μm from the boundary. The same phenomenon is also observed in aged DC₅.

No ω phase was detected up to a depth of approximately 200 μm from the specimen surface of aged DC₅. A peak of ω phase was detected at approximately the same distance from

Fig. 9 SEM fractographs of (a) DC₅ and (b) aged DC₅ after tensile bonding strength tests.

the specimen surface of DC₅. As mentioned earlier, ω phase is considered to precipitate during the firing treatment.

3.3 Tensile bonding strength of coating layer

The tensile bonding strengths between the base material and the CPIG layer of DC₅ and aged DC₅ were approximately 25.0 and 18.6 MPa, respectively. The tensile bonding strengths of DC₅ and aged DC₅ are much greater than that of pure titanium and its alloys, whose tensile bonding strength is in the range of 4.15–13.9 MPa and on which the HA powders and AW glass layer were mechanically coated.^{21,22} Therefore, applied to pure titanium and its alloys, this coating method is expected to acquire relatively high tensile bonding strength.

All specimen surfaces of DC₅ and aged DC₅ from tensile bonding tests are observed fractured CPIG and a portion of an adhesive (super bond orthomite), where the zone of TNTZ is not observed, as shown in Fig. 9. In other words, the coating layer is strongly adhered to the TNTZ matrix due to the presence of the compositionally gradient zone within the CPIG layer and the wedge effect of the TNTZ surface by shot blasting. Therefore, it is difficult to investigate the true tensile bonding strength due to very high interface bonding between the TNTZ and the CPIG layer.

3.4 Tensile properties

The tensile strength, 0.2-% proof stress and elongation of ST, DC₅, and aged DC₅ are shown in Fig. 10. The values of tensile properties of ST, DC₅, and aged DC₅ are shown as follows for easily understanding the change in those by a dip-coating process or compare with those of the others metallic

Fig. 10 Tensile properties of (a) ST, (b) DC₅ and (c) aged DC₅.

Fig. 11 Young's moduli of (a) ST, (b) DC₅ and (c) aged DC₅.

materials for biomedical applications. The tensile strength of ST is 549 MPa, and is minimum. However, its elongation is 41.6% and is the highest. The tensile strengths of DC₅ and aged DC₅ are 713 MPa and 897 MPa, respectively. The tensile strength of aged DC₅ is greater than that of ST by 300 MPa. However, the elongations of DC₅ and aged DC₅ are 21.7% and 10.5%, respectively; these values are half and one-fourth of that of ST, respectively.

The increase of strength of DC₅ can be mainly contributed to the age hardening by the precipitation of ω phase during cooling in air.

The tensile strength of aged DC₅ is pretty high, but its elongation shows a reverse trend. This inverse relationship between the tensile strength and elongation may become evident with on increasing the volume fraction of the fine α phase that relatively enhances the brittleness of the matrix.

3.5 Young's modulus

The Young's moduli of ST, DC₅ and aged DC₅ are shown in Fig. 11. The Young's moduli of ST and DC₅ are approximately 60 and 75 GPa, respectively. Therefore, Young's modulus of TNTZ increases by approximately 15 GPa after the dip-coating treatment. This increase in Young's modulus is due to the precipitation of the ω phase during firing and subsequent cooling. The Young's modulus of aged DC₅ increases further and has a value of approximately 87 MPa. The Young's modulus of TNTZ subjected to aging treatment at 723 K for 259.2 ks after the solution treatment at 1063 K for 3.6 ks was approximately 88 GPa.²³⁾

3.6 Fatigue properties

Figure 12 shows the relationship between maximum cyclic stress and number of cycles to failure of ST, DC₅, and aged DC₅. The fatigue strength of DC₅ is similar to that of ST in low cycle fatigue life ($< 10^5$ cycles) and high cycle fatigue life ($> 10^5$ cycles) regions. The fatigue limits of ST, DC₅ are 330 MPa and 325 MPa, respectively. However, the fatigue ratio (f ; fatigue limit/tensile strength) of DC₅ is 0.46, and this value is smaller than that of ST (0.60). In general, the fatigue strength increases proportionally with increasing tensile strength and 0.2% proof stress. The tensile strength and 0.2% proof stress of DC₅ are much greater than those of ST. This is attributed to the difference in the surface roughness between DC₅ and ST. The surface of DC₅, subjected to sand-blasting before the dip-coating treatment, is considerably rough as compared with that of the buff-polished ST. In general, the fatigue strength of titanium and

Fig. 12 S-N curves of (a) ST, (b) DC₅ and (c) aged DC₅.

its alloys, which have high notch sensitivity, deteriorate remarkably with increasing surface roughness.^{24,25)} The fatigue crack initiation lives of typical titanium alloys such as Ti-6Al-7Nb and Ti-6Al-4V ELI, used in biomedical applications, have 50% or more of their total fatigue life.²⁶⁾ Hence, due to the decrease in the fatigue crack initiation life of DC₅, its total fatigue life also decreases significantly.

In particular, the fatigue strength of aged DC₅ in the high cycle fatigue life region is much greater than that of DC₅. Its fatigue limit and f are 400 MPa and 0.46, respectively. The fatigue limit of cold-rolled TNTZ subjected to aging at 723 K for 259.2 ks after the solution treatment is 680 MPa,²³⁾ whereas that of aged DC₅ is decreased by 280 MPa, where the values of fatigue limits are shown for easily understanding the change in those by a dip-coating process.

All fatigue cracks of DC₅ and aged DC₅ initiate at the very edge of the fatigue specimen surface composed of TiO₂ and α case as shown in Fig. 13. While, that of ST was initiated at β phases. Striations were formed at the stable crack propagation area of all types of material studied.

Figure 14 shows the SEM micrograph of the specimen surface of DC₅ obtained from the fatigue test. The exfoliation of the CPIG layer is not observed on the surface. However, there are a number of micro-cracks in the CPIG layer because of a large difference in the Young's modulus between TNTZ and CPIG layer. Similar surface were observed in aged DC₅ specimen.

It needs to investigate the fatigue properties in vitro in detail to acquire the credibility for practical applications.

4. Conclusions

The morphology of the calcium phosphate invert glass-ceramic (designated as CPIG) layer on the surface of β -type titanium alloy, Ti-29Nb-13Ta-4.6Zr (designated as TNTZ) was investigated for biomaterial applications by the dip-coating treatment. Furthermore, the mechanical properties of TNTZ coated with the coating layer were also investigated. The following results were obtained.

- (1) There exists a compositionally gradient zone within the CPIG layer with a thickness of approximately 2.0 μm on the surface of the TNTZ. The tensile bonding strength between TNTZ and the CPIG layer is 25 MPa and that

Fig. 13 SEM fractograph of DC₅ in low cycle fatigue life region.

Fig. 14 SEM micrographs of specimen surface of DC₅ after fatigue test.

between the aged TNTZ and the CPIG layer is 18.6 MPa, respectively.

- (2) The tensile strengths of TNTZ and aged TNTZ coated with CPIG layer are 713 and 897 MPa, respectively. On the other hand, their elongations are 21.7 and 10.5%, respectively, which are a half to quarter smaller than that of as-solutionized TNTZ.
- (3) Young's moduli of TNTZ and aged TNTZ coated with the CPIG layer are approximately 75 and 87 GPa, respectively. Therefore, Young's modulus of TNTZ increases by approximately 15 GPa by the dip-coating treatment process as compared with that of as-solutionized TNTZ.
- (4) The fatigue limit of TNTZ coated with the CPIG layer is nearly equal to that of as-solutionized TNTZ subjected to solution treatment, while the fatigue limit of aged TNTZ coated with the CPIG layer is approximately 80 MPa greater than that of as-solutionized TNTZ.
- (5) TNTZ and aged TNTZ subjected to dip-coating treatment process exhibit sufficiently good mechanical properties such as tensile properties and a small Young's modulus for biomaterials except for relatively low fatigue strength. The mechanical properties of TNTZ subjected to the dip-coating treatment process are expected to sufficiently improve with aging conditions.

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