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Comparison of Various Properties between Titanium-Tantalum Alloy and Pure Titanium for Biomedical Applications

Ying-Long Zhou[1,*], Mitsuo Niinomi[2], Toshikazu Akahori[2],
Masaaki Nakai[2] and Hisao Fukui[3]

[1]*Department of Mechatronics Engineering, School of Mechatronics and Information Engineering,*
Foshan University, Foshan 528000, P. R. China
[2]*Department of Biomaterials Science, Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[3]*School of Density, Aichi-Gakuin University, Nagoya 464-8650, Japan*

The mechanical properties, corrosion resistance and biocompatibility of the titanium-tantalum alloys together with pure titanium are comparatively studied for biomedical applications in this study. The experimental results confirm the previous theoretic investigation that tantalum has a potential to enhance the strength and reduce the elastic modulus of titanium alloys at the same time, and indicate that the titanium-tantalum alloys are more suitable than pure titanium for biomedical applications because of their lower elastic modulus, higher strength and enhanced corrosion resistance than pure titanium used as a standard metallic biomaterial, and the same excellent compatibility to pure titanium. [doi:10.2320/matertrans.48.380]

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1. Introduction

Requirements for metallic materials such as joint replacement, bone pin, plate and screw continue to grow as people in most of the countries live longer or damage themselves more through hard sports play or jogging, or are seriously injured in road traffic and other accidents.[1,2] To meet the demand of long service life and implantation in younger patients, the metallic implants should provide a low elastic modulus as close to that of a human bone as possible, high strength, excellent corrosion resistance and biocompatibility in the human body environment. The closer the elastic modulus of a metallic implant to that of a human bone, the more favorable for bone healing and remodeling.

Pure titanium (Ti) is one of few materials that naturally match the requirements for implantation in the human body, and has been successfully used as an implant material since 1950s.[3] The natural selection of pure Ti for implantation is determined by a combination of most favorable characteristics including immunity to corrosion, excellent biocompatibility, specific strength, relatively low modulus and density, and the capacity for joining with bone and other tissue among the metallic biomaterials. Pure tantalum (Ta) is another good candidate successfully used as an implant material such as sutures, bone screws and plates for many year due to its excellent corrosion resistance and biocompatibility.[4] The poor mechanical properties of pure Ti and pure Ta, including the mismatched elastic modulus to that of a human bone, however, have restricted their extensive applications. The metallurgical practices indicate that the mechanical properties of Ti can be improved by alloying Ta, and recent theoretic research based on the first principal calculation using the discrete variation cluster method has suggested that Ta has the potential to enhance the strength and reduce the modulus of Ti alloys at the same time.[5] Therefore, the Ti-Ta alloys are expected to be more suitable than pure Ti and pure Ta for biomedical applications due to their improved mechanical properties, including reduced elastic modulus than pure Ti. Although the previous studies[6,7] revealed that the superior corrosion resistance and biocompatibility of Ti-Ta alloys couldn't be modified by alloying treatment because the solid solutioning process neither destroys the corrosion-proof mechanism of pure Ti and pure Ta nor results in toxicity, various properties of Ti-Ta alloys have been not yet studied systematically for biomedical applications.

In this study, the mechanical properties, corrosion resistance and biocompatibility of Ti-Ta alloys are investigated together with pure Ti used as a standard biomaterial for biomedical applications.

2. Experimental Procedure

2.1 Material preparation

The Ti-Ta alloys with Ta contents from 10 to 70 mass% (hereafter, 'mass%' will be referred to as '%') were prepared from high purity sponge Ti (99.5%) and sheet Ta (99.95%). Melting was carried out in a high purity argon atmosphere by a tri-arc furnace with water-cooled copper hearth. All ingots were homogenized in vacuum at 1273 K for 21.6 ks to eliminate the as-cast microscopic segregation, and then rolled into plates 3 mm thick by a total thickness reduction of 80%. In order to remove the influences of residual stresses caused by plastic deformation on the elastic modulus, the rolled plates were solution-treated in vacuum above β transus temperature[8] at 1223 K for 3.6 ks, and then rapidly quenched in ice water (STQ).

It is difficult to get a homogeneous Ti-Ta alloy in both composition and microstructure due to a large difference in melting point and density between pure Ti and pure Ta. In order to check the true chemical compositions of the Ti-Ta alloys, some of them were chosen for the chemical analysis. The results are shown in Table 1, indicating that the actual

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[*] Corresponding author, Email: ylzhou_2@yahoo.com

Table 1 Chemical compositions of typical Ti-Ta alloys.

Alloy code	Ta (%)	O (%)	Ti (%)
Ti-10% Ta	10.0	0.075	Bal.
Ti-30% Ta	29.6	0.088	Bal.
Ti-50% Ta	49.7	0.071	Bal.
Ti-70% Ta	69.9	0.034	Bal.

chemical composition of each alloy is close to its nominal composition.

2.2 Measurement of elastic modulus and tensile properties

There are two methods to measure an elastic modulus of a material: one is dynamic method, and the other is static method. The dynamic method is based on the measurement of the fundamental resonant frequencies of the material during vibration to determine its elastic properties. During the measurement, the specimen is supported horizontally at its nodal points by two parallel, fine nickel wires. The sample is driven electrostatically in flexural vibration. The vibration amplitude is recorded as a function of frequency. For rectangular bar specimens, the dynamic Young's modulus, E, is calculated according to the following equation[9]

$$E = 0.9694 mL^3 {f_r}^2/(wd^3) \quad (1)$$

where m, L, w and d are the mass, the length, the width and the thickness of specimens, respectively, and f_r is the intrinsic resonance frequency. Obviously, this experimental accuracy is only determined by the precisions of the mass and length measurements. Since its errors can be minimized by using high-precision electron balance and measurement microscope, the dynamic method is more accurate than the static method which evaluates the elastic modulus from tensile stress-strain curves. Hence the dynamic method was used to determine the modulus of Ti-Ta alloy and pure Ti in this study.

Tensile specimens have a thickness of 2 mm, a width of 3 mm and a gage length of 12 mm with their longitudinal directions parallel to rolling direction. The strain gage was attached at the gage section of each specimen to measure the strain change during tensile test. The uniaxial tensile tests were conducted at a crosshead speed of 8.33×10^{-6} m/s at room temperature using an Instron type machine. For each Ti-Ta alloy and pure Ti, at least 3 pieces of specimens were used for the measurement in order to minimize the experimental errors.

2.3 Corrosion test and evaluation of cyto-toxicity

Since the previous studies[6,7] have already investigated the corrosion resistance and biocompatibility of the Ti-Ta alloys with Ta contents of 5, 40 and 50%, only Ti-10, 30 and 70% Ta alloys were chosen to test these properties in order to simplify this research work.

A metallic material in living tissue is usually prone to corrosion. In order to evaluate the corrosion resistance of the Ti-Ta alloys, the anodic polarization tests were carried out by an automatic potentiostat in 5% HCl solution at 310 K. The specimens with a square surface area of 1 cm^2, *i.e.* the working electrode, were embedded with epoxy resin and ultrasonically cleaned in distilled water after being polished with waterproof emery papers up to 1500 grit under running water. The cathodic treatment was then carried out at -0.9 V for 600 s to remove any oxide films present on the surface of each specimen. After the natural electrode potential was held for 1.2 ks, the anodic polarization test was performed in air at a sweep rate of 3.33×10^{-4} V/s. A saturated calomel electrode (SCE) was used a reference electrode and a platinum wire as a counter electrode. The anodic test was repeated for three times for each specimen which was polished using waterproof emery papers before each test.

Since cyto-toxicity testing is a rapid, standardized, sensitive and inexpensive means to determine whether a material contains significant quantities of biologically harmful extractables, it was employed in this study. Biocompatibility of the Ti-Ta alloys and pure Ti was judged by evaluating the cyto-toxicity through MTT assay. Two specimens with a size of ϕ10 mm × 2 mm and ϕ15 mm × 2 mm were prepared for each Ti-Ta alloy and pure Ti, respectively, and then polished using waterproof emery papers up to 1500 grit under running water. The vessel with 10 ml Eagle's culture solution at a temperature of 310 K was rotated with a speed of 240 rpm, and extraction periods were 7 and 14 days. As-extracted solution and filtrated extract solution using 0.22 µm membrane filter were prepared. In the as-extracted solution and filtrated extract solution, the survival rate of L-929 cells derived from mice was evaluated using MTT methods as detailed in the previous investigation,[10] which indicates the cyto-toxicity level of the extracts.

3. Results and Discussion

3.1 Elastic modulus of the Ti-Ta alloy

The measured elastic modulus of the Ti-Ta alloy is shown in Fig. 1 as a function of Ta content. It can be seen that the elastic modulus first decreases with increasing Ta content, and reaches a minimum value of 69 GPa at 30% Ta. Then it gradually increases to 88 GPa at 50% Ta, and drops again to another minimum value of 67 GPa at 70% Ta.

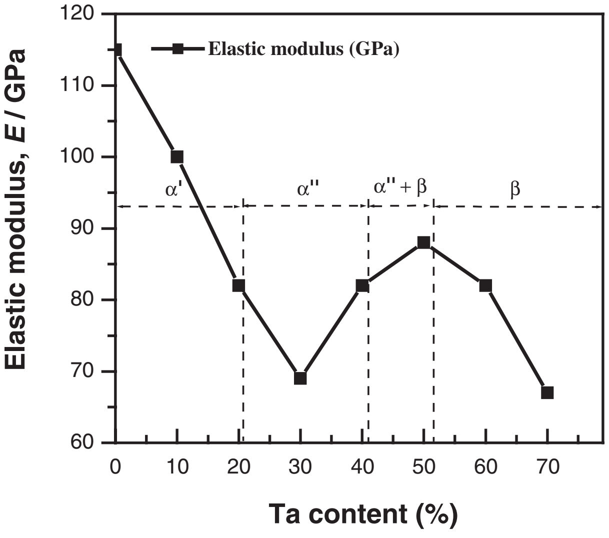


Fig. 1 Elastic modulus of pure Ti and Ti-Ta alloys.

Table 2 Constitutional phases and their morphologies of Ti-Ta alloys.

Ta content	Formed phase	Morphology
10∼20%	α'	Lamellar
30∼50%	α''	Needle-like
60%	$\beta+\alpha''$	Equiaxed β + needle-like α''
70%	β	Equiaxed β with unrecrystallized structure

The Young's modulus, which is an intrinsic materials property, depends on atomic bonding force. Any change in the distance between atoms of the material possibly leads to variation in the atomic bonding force and resulting elastic modulus. For example, a heat treatment or alloying addition or thermo-mechanical processing (deformation texture) often renews the elastic modulus value of a metallic material.[11,12] The most common phenomenon is that a phase change caused by a heat treatment or stress may alter the elastic modulus of a metallic material because it changes the distance between atoms, which is why the different phase (crystal structure) has different elastic modulus. In the Ti alloys, it was extensively reported that the ω phase has the highest elastic modulus, and the α'' or β phase can reach the lowest.[13–15] Combining Fig. 1 with the microstructures of the Ti-Ta alloys (Table 2) which were examined by an X-ray diffraction (XRD) and a scanning electron microscopy (SEM), it can been seen that there are two minima of elastic modulus in the Ti-Ta alloys: one is for the Ti-30% Ta alloy with α'' phase, and the other is for the Ti-70% Ta alloy with β phase, which are in agreement with the previous reports.[13–15]

While maintaining the same phase, since the atom size of solute is usually different to that of the solvent, increasing alloying content in an alloy leads to the increasing degrees of supersaturation and lattice distortion with addition of alloying content, which also changes the distance between atoms and results in change of the elastic modulus. Because the atom size of Ta is bigger than that of Ti, it is easy to understand the variations in elastic modulus of single α' and α'' phases with increasing Ta content as shown in Fig. 1. Therefore, the phase change and degrees of lattice distortion with increasing Ta content lead to the variations in elastic modulus of the Ti-Ta alloy, which indicate that the elastic modulus of quenched Ti-Ta alloy depends on both crystal structure and Ta content.

3.2 Tensile properties of Ti-Ta alloy

The measured tensile strength, yield strength and elongation at fracture of the Ti-Ta alloys are summarized in Fig. 2. Both the tensile strength and yield strength of all the studied Ti-Ta alloys are much higher than those of pure Ti, and varies between 510 and 690 MPa for the former, and 400 and 610 MPa for the latter. It can be seen that the tensile strength is 510 MPa at 10% Ta, slowly increases with increasing Ta content, and reaches the peak value of 690 MPa at 60% Ta, and then slightly decreases.

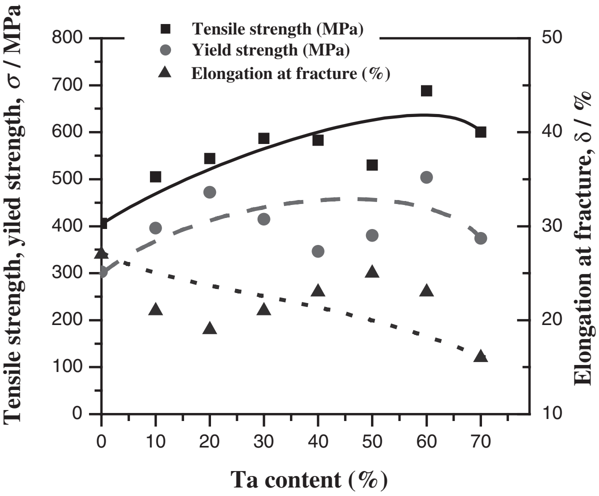


Fig. 2 Variation of tensile properties of pure Ti and Ti-Ta alloys.

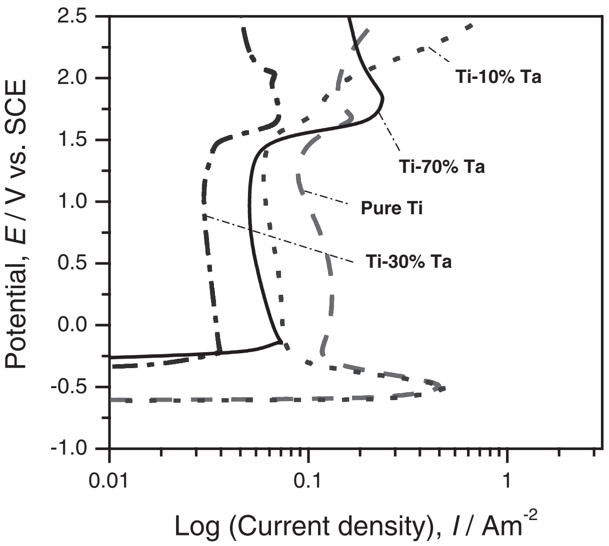


Fig. 3 Anodic curves for pure Ti and Ti-Ta alloys in 5% HCl solution at 310 K.

It is considered that the variations in strength of the Ti-Ta alloys with Ta content are due to the changes in microstructures caused by Ta content. The strength of the Ti-Ta alloy increases with Ta content because the solid solution strengthening increases with alloying content, and the Ti-60% Ta alloy has the highest strength among all the studied materials due to the combination of the solid solution strengthening and the precipitation strengthening, and the strength of Ti-70% Ta alloy slightly decreases due to the disappearance of precipitation strengthening from the α'' phase. The elongation at fracture of the Ti-Ta alloy decreases with increasing Ta content, which is consistent with the ordinarily observed relationship between strength and ductility: when the yield strength increases, the ductility accordingly decreases.

3.3 Corrosion resistance of Ti-Ta alloy

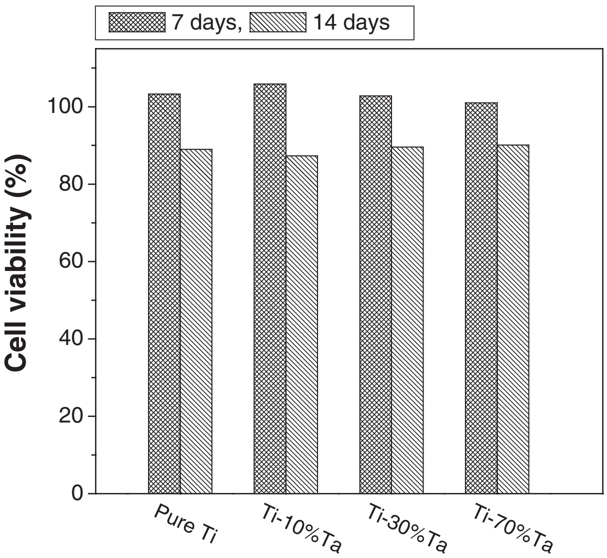
The anodic polarization curves for the Ti-Ta alloys together with pure Ti are shown in Fig. 3. It can be seen that the Ti-Ta alloys show the similar corrosive behavior. Like pure Ti, all the studied alloys reach respectively their stable passive current densities as the potential increases, indicating the existences of their passive behaviors in the 5% HCl solution. The Ti-10% Ta alloy shows the close critical current density (I_{cc}) and similar primary passivation potential (E_{pp}) to those of pure Ti, suggesting their similar corrosion resistance. In contrast, the current densities of the Ti-30% and 70% Ta alloys are much smaller that those of pure Ti and Ti-10% Ta alloy, which indicates that these two Ti-Ta alloys show better corrosion resistance than pure Ti and Ti-10% Ta alloy, and that the more passive oxides layers of Ta_2O_5 form on the surfaces of these two alloys because the passive oxide layer of Ta_2O_5 is stronger and more stable than that of TiO_2.[16,17] It also can be seen that the anodic polarization curve of the Ti-Ta alloy shifts to the noble (positive) direction with increasing Ta content, which is related to the free energy of Ta_2O_5 relatively higher than that of TiO_2 oxide.[18] This phenomenon is similar to the effect of addition of platinum[19] or molybdenum[20,21] on the corrosion behavior of Ti alloys.

3.4 Cyto-toxicity of Ti-Ta alloy

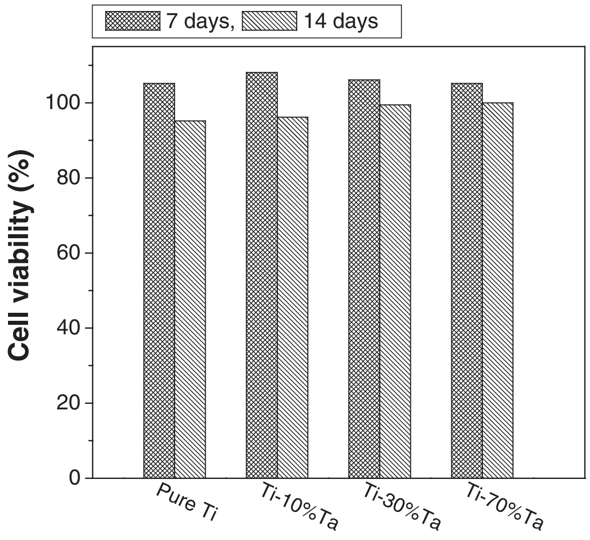
Figure 4 shows the cell viability of filtrated extracts and non-filtrated extracts of studied Ti-Ta alloys and pure Ti after extracting for 7 and 14 days evaluated through MTT assay. It can be seen that the cell viability of the Ti-Ta alloys is almost the same to that of pure Ti in both filtrated extracts and non-filtrated extracts, indicating the excellent biocompatibility of the Ti-Ta alloys like pure Ti since pure Ti has been extensively evaluated to be totally biocompatible. The biocompatibility of a metallic material is determined by its corrosion resistance and toxicity of its corrosion products.[22–24] It has been proven that the Ti-Ta alloy shows the excellent corrosion resistance like pure Ti as shown in this study, and that the corrosion products of the TiO_2 and Ta_2O_5 oxide films exhibit to be inert in the body fluids.[24] Those accounts for why the Ti-Ta alloy possesses the excellent biocompatibility.

As mentioned in the introduction, ideal implants are required to have a high strength, low elastic modulus comparable to that of a human bone, excellent corrosion resistance and biocompatibility to meet the demand of long service life and implantation in younger patients. This investigation shows that the Ti-Ta alloys have lower elastic modulus, higher strength, enhanced corrosion resistance than pure Ti, and the same excellent compatibility to pure Ti, therefore they are more suitable for biomedical applications than pure Ti. The strength of Ti-Ta alloy increases and its elastic modulus decreases with Ta content, which confirms the previous theoretical result that Ta has a potential to enhance the strength and reduce the modulus of Ti alloys at the same time.[5]

The Ti-Ta alloys have better mechanical compatibility than pure Ti, however, they are needed to further increase the strength and reduce the elastic modulus to approach that of a human bone. Since precipitation strengthening, which is one of the typical strengthening mechanisms in alloys, results in an increase in both elastic modulus and strength of a Ti alloy.[13,25–27] Therefore, the best way to achieve this goal is by reducing grain size, especially when the grain size is reduced into the nano-meter scale where the Hall-Petch relation does not work, the strength will significantly increase while maintaining the good ductility. At the same time, the elastic property in nano-structure is governed not only by classical bulk elastic strain energy, but also by the interfaces (or grain boundaries) in which there are plenty of lattice defects, such as grain-boundary and interface dislocations, lattice parameter mismatch, voids, etc. Thus, the grain boundary has lower elastic modulus than that of grains due to the high dense defects (such as voids, dislocation, etc.). As a result, the nano-structured metallic materials simultaneously have lower elastic modulus than that of their normal grain-sized counterparts because the volume fraction of grain boundary in the nano-structure significantly increases.[28] Therefore, the nano-structured Ti-Ta alloys are expected to have very high strength, low elastic modulus and the other attractive properties for biomedical applications, promising to be good candidates of implants in the future.



(a) Non-filtrated



(b) Filtrated

Fig. 4 Cell viability of L-929 in (a) non-filtrated and (b) filtrated solutions evaluated by MTT method for pure Ti and Ti-Ta alloys.

4. Summary

The mechanical properties, corrosion resistance and biocompatibility of the Ti-Ta alloys under the solution treatment together with pure Ti are comparatively studied for biomedical applications. The following conclusions can be obtained:

(1) Ta has a potential to enhance the strength and reduce the elastic modulus of Ti alloys at the same time.

(2) The Ti-Ta alloys are more suitable than pure Ti for biomedical applications due to their lower elastic modulus, higher strength and enhanced corrosion resistance than pure Ti used as a standard metallic biomaterial, and the same excellent compatibility to pure Ti.

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