Effect of Alloying Elements on Mechanical Properties of Titanium Alloys for Medical Implants[†]

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Titanium alloys for medical implants were cast using 5~20 mass%Zr, 10~20%Sn, 4~8%Nb, 2~4%Ta and 0~0.2%Pd as alloying elements instead of using harmful Al and V.

The alloys were forged in their α and $\alpha + \beta$ regions and then annealed at 973 K for 7.2 ks. The annealed microstructures of the alloys consisted mainly of the acicular structure containing 10 to 30 volume% elongated β grains.

While the room temperature tensile strength of the Ti-(5~15%)Zr-4%Nb-2%Ta-0.2%Pd alloys increased slightly with increasing Zr content, the strength of the Ti-(10~20%)Sn-4%Nb-2%Ta-0.2%Pd alloys increased markedly with increasing Sn content. The Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloy surpassed the Ti-6%Al-4%V extra low interstitial (ELI) alloy for medical implants (ASTM F136-84 Standard) in tensile strength as well as in elongation and reduction of area. The tensile strength was further improved by the additions of nitrogen and oxygen.

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I. Introduction

With the prolonged average duration of life, there is an increasing concern for repair of bone, joints and teeth which deteriorate and lose their function. Thus, research of artificial bone, joints, and teeth is rapidly becoming more important.

Among the standard surgical implant materials such as stainless steel (SUS316L), Co-Cr alloy, and pure titanium, Ti-6 mass%(hereafter, unless otherwise noted, % denotes mass%)Al-4%V extra low interstitial (ELI) alloy is watched with keen interest. Diverted to use in medical implants from its original aerospace applications, Ti-6%Al-4%V ELI alloy has undergone recent concerns due to the suspected effects of Al and the cytotoxicity of V. The presence of Al ions results in a phosphorus deficiency in blood and bone due to the combination of Al with inorganic phosphorus. A causal relationship between Al and the occurrence of senile dementia of Alzheimer type of Al is suspected as well. To address the cytotoxicity of V and examine alternative alloying elements, studies of the corrosion resistance and mechanical properties of Ti-6%Al-7%Nb and Ti-5%Al-2.5%Fe alloys have been conducted⁽¹⁾.

In this study, the effects of alloying elements other than Al and V on microstructure and mechanical properties were investigated to develop alternative titanium alloys with higher biological safety, strength and ductil-

ity for medical implants.

II. Experimental Method

1. Alloy design

Kawahara *et al.*⁽²⁾ and Steinemann⁽³⁾ reported the cytotoxicity of pure metals and the relationship between biocompatibility and polarization resistance of surgical implant materials. These results are summarized in Fig. 1(a) and (b).

Figure 1(a) plots the coefficient of fibroblastic outgrowth in embryo heart muscle versus the relative growth rate of L929 cells in mouse fibroblastic tissue. Toxicity increases with decreasing coefficient of fibroblastic outgrowth and decreasing relative growth rate of L929 cells.

Figure 1(a) illustrates the high toxicity of common surgical implant alloying elements such as V, Fe, Co, and Ni, while Fig. 1(b) reports a lower biocompatibility of Co-Cr alloy, SUS316L stainless steel, Al and Fe due to capsulation, the biological defense reaction against toxicity. Sn, Zr, Ti, Ta and Pd exhibit low toxicity, while Zr, Ti, Nb, Ta and Pt demonstrate excellent biocompatibility. Thus, the pure metallic elements Zr, Sn, Nb, Ta and Pd, which can be expected to improve mechanical properties, corrosion resistance and biocompatibility, were selected as alloying elements.

Sn and Zr were selected as the first additional alloying element to increase strength, while Ta and Pd were added to improve corrosion resistance and Nb, a high β stabilizer element, was added to obtain $\alpha + \beta$ two-phase fine structure and improve hot workability. From the

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Fig. 1 Biological safety of metals. (a) cytotoxicity of pure metals, (b) relation between polarization resistance and biocompatibility of pure metals, Co-Cr alloy and stainless steels⁽³⁾⁻⁽⁵⁾.

view point of castability, the concentrations of Nb and Ta, alloying elements of high melting point, were lowered. The composition of Pd, a β eutectoid element, was minimized to reduce the precipitation of brittle phase. Hence, the following alloying composition was determined; Zr and Sn: less than 20%, Nb: less than 8%, Ta: less than 4%, and Pd: less than 0.2%.

2. Melting, forging and heat treating process

Various titanium alloys having the composition of Ti-(0~20%)Zr-(0~20%)Sn-(4~8%)Nb-(2~4%)Ta-(0~0.2%)Pd-(0~0.15%)N-(0~0.3%)O were melted and cast by vacuum arc melting. After the 0.6 kg ingot was held at 1373 K for 7.2 ks, the ingot was forged to a rod of 35 mm diameter and 160 mm length by β forging. After reheating again at 1223 K, the rod was forged to a 15 mm diameter by α - β forging. Annealing at 973 K was carried out for 7.2 ks to remove internal strain induced by the α - β forging process. The chemical com-

positions of these alloys are shown in Table 1.

3. Microstructural observation and mechanical properties

Microstructural observation and phase identification of $10 \times 10 \times 5$ mm block specimens were performed using optical microscopy, scanning electron microscopy and X-ray diffraction. Etching with nitric and hydrofluoric acid solution ($\text{HF}:\text{HNO}_3:\text{H}_2\text{O}=3 \sim 2 \text{ cc}:20 \text{ cc}:77 \sim 78 \text{ cc}$) was performed prior to structural observation. The volume fraction of β phase was measured by image analysis of the SEM photograph using PIAS LA500. X-ray diffraction with the Cu target was performed under the conditions of 40 KV tube voltage, 0.2 A tube current and $1 \sim 2^\circ/\text{min}$ scanning speed (2 θ).

To investigate the effect of alloying elements on mechanical properties, a tensile test was carried out at room temperature. A test specimen of 6.25 mm diameter and 25 mm parallel length was pulled at a load speed of $8.33 \times 10^{-6} \text{ m/s}$ (0.5 mm/min) until the 0.2% proof strength was reached. The load speed was then changed so that the specimen broke within 60s according to ASTM E8. A hardness test at the load of 98N (10 kgf) and a Charpy impact test at room temperature were performed. The Charpy impact test was carried out according to JIS Z 2242 with a JIS No. 4 full size test piece to investigate the effect of oxygen and nitrogen on Charpy impact energy.

III. Experimental Results and Discussion

1. Effect of substitutional alloying elements

(1) Mechanical properties

To investigate the alloying effect of Sn, Zr, Nb, Ta and Pd on the mechanical properties, a tensile test at room temperature was carried out according to ASTM-E8. The effects of Zr, Sn, Nb, Ta and Pd contents on 0.2% proof strength, ultimate tensile strength, total elongation and reduction of area are summarized in Fig. 2. The strength increases linearly with the addition of Sn and Zr. Addition of Sn is more effective while addition of Zr in excess of 15% does not show a remarkable increase in strength. The effects of β stabilizer element Nb, Ta and β eutectoid element Pd contents are very small. While the effects of the alloying element Nb are small, a slight increase in strength is noted for the Ti-10%Sn-(4~8%)Nb-2%Ta-0.2%Pd alloys compared to the Ti-10%Zr-(4~8%)Nb-2%Ta-0.2%Pd. While total elongation and reduction of area remains fairly constant with alloying content, both quantities decrease for Sn and Zr alloying content greater than 15%. The higher strength Ti-(10~20%)Sn-4%Nb-2%Ta-0.2%Pd alloys experience a more rapid decrease as well as a lower total elongation and reduction of area.

For comparison, ASTM specification values (F136-84) of Ti-6%Al-4%V ELI alloy for surgical implant are plotted in Fig. 2. Compared to the Ti-6%Al-4%V ELI alloy ultimate strength value of 860 MPa, the strength of Ti-15%Zr-4%Nb-2%Ta-0.2%Pd is lower at 726 MPa

Table 1 Chemical composition (mass%) of materials used in the present study.

Titanium alloys	Zr	Sn	Nb	Ta	Pd	O	N	Ti
Ti-5Zr-8Nb-2Ta	5.05	—	7.61	2.05	—	0.075	0.0040	Bal.
Ti-10Zr-8Nb-2Ta	10.04	—	7.63	2.04	—	0.089	0.0044	Bal.
Ti-15Zr-8Nb-2Ta	14.84	—	7.62	2.05	—	0.088	0.0047	Bal.
Ti-10Zr-4Nb-2Ta	10.04	—	4.09	2.00	—	0.067	0.0074	Bal.
Ti-10Zr-8Nb-4Ta	10.02	—	7.69	4.05	—	0.084	0.0044	Bal.
Ti-10Zr-8Nb-2Ta-0.2Pd	9.90	—	7.68	2.04	0.20	0.083	0.0041	Bal.
Ti-10Sn-8Nb-2Ta-0.2Pd	—	9.93	7.77	1.98	0.19	0.089	0.0038	Bal.
Ti-15Zr-4Nb-2Ta-0.2Pd	15.27	—	3.94	1.97	0.19	0.127	0.0034	Bal.
Ti-20Zr-4Nb-2Ta-0.2Pd	20.53	—	3.98	1.97	0.19	0.095	0.0034	Bal.
Ti-10Sn-4Nb-2Ta-0.2Pd	—	9.83	3.92	1.96	0.20	0.090	0.0031	Bal.
Ti-15Zn-4Nb-2Ta-0.2Pd	—	14.74	3.93	1.97	0.20	0.093	0.0031	Bal.
Ti-20Sn-4Nb-2Ta-0.2Pd	—	19.57	3.93	1.97	0.19	0.086	0.0031	Bal.
Ti-15Zr-4Nb-4Ta-0.2Pd	15.07	—	3.98	4.01	0.19	0.064	0.0293	Bal.
Ti-15Sn-4Nb-4Ta-0.2Pd	—	14.69	3.99	3.99	0.17	0.055	0.0041	Bal.
Ti-10Zr-4Nb-2Ta-0.13%O -0.14%N	10.07	—	3.84	2.01	—	0.130	0.135	Bal.
Ti-15Zr-4Nb-2Ta -0.2Pd-0.2%O-0.05%N	15.13	—	3.98	1.98	0.19	0.198	0.0450	Bal.
Ti-15Zr-4Nb-2Ta -0.2Pd-0.2%O-0.10%N	15.33	—	4.00	1.99	0.19	0.201	0.0900	Bal.
Ti-15Zr-4Nb-2Ta -0.2Pd-0.2%O-0.15%N	15.28	—	3.98	1.99	0.18	0.198	0.142	Bal.
Ti-15Zr-4Nb-2Ta -0.2Pd-0.3%O-0.05%N	15.35	—	4.04	1.96	0.19	0.300	0.0456	Bal.
Ti-15Sn-4Nb-2Ta -0.2Pd-0.2%O-0.05%N	—	14.63	3.95	1.97	0.19	0.195	0.0446	Bal.
Ti-15Sn-4Nb-2Ta -0.2Pd-0.2%O-0.10%N	—	14.57	3.93	1.96	0.19	0.184	0.0911	Bal.
Ti-15Sn-4Nb-2Ta -0.2Pd-0.2%O-0.15%N	—	14.64	3.94	1.97	0.19	0.177	0.148	Bal.

$C \leq 0.0088$ $H \leq 0.011$

while the strength of Ti-15%Sn-4%Nb-2%Ta-0.2%Pd is higher at 990 MPa. The total elongation and reduction of area of both Ti-Zr and Ti-Sn are higher than that of Ti-6Al-4V.

(2) Relation between structures and mechanical properties

To investigate the effects of Sn, Zr, Nb, Ta and Pd on the annealed structures, microscopic observation by optical microscope and SEM was carried out.

The alloying effect of Nb, Ta and Pd on the optical microstructure after annealing at 973 K for 7.2 ks is very small. However, the Ti-Sn alloy does exhibit a slightly finer acicular structure than that of Ti-Zr.

The Fig. 3 plots the volume fraction of the β phase measured by image analysis of SEM photograph as a function of the alloying content. The β phase volume fraction varies between 10~30 vol% for the alloy composition used in this study. As expected, the increasing addition of Nb, Ta, Zr, and Pd increases the volume fraction of the β phase, while increased Sn results in a slight decrease in volume fraction of β phase. Nb and, to a lesser extent, Ta, both act as β stabilizers to form homogeneous solid solutions, while Zr acts as a neutral element for forming a homogeneous solid solution in the α and β phases. Pd, a β eutectoid element, increases the volume fraction of the β phase as well. Less than 10%Sn,

however, stabilizes the β phase while over 15%Sn stabilizes the α phase, as observed on the Ti-Sn binary phase diagram⁽⁴⁾. Thus, Sn has weak β stabilizing ability and is designated as an α stabilizer element.

Figure 4(a) and (b) show the SEM structures of Ti-15%Zr-4%Nb-2%Ta-0.2% Pd and Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloys, respectively. While the Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloy exhibits a finer β phase, Ti-20%Sn-4%Nb-2%Ta-0.2%Pd alloy exhibits both the rough and fine structures in the β phase. This inhomogeneity of structure might be related to the rapid lowering of ductility for Sn alloying content of greater than 15%. A more detailed study is necessary.

2. Effect of interstitial alloying elements on mechanical properties

Mechanical properties and corrosion resistance of Ti alloys remarkably change according to the contents of impurities. Consequently, in the ASTM specification for surgical implant, the acceptable limits of such impurities as nitrogen (less than 0.05%), oxygen (less than 0.13%), carbon (less than 0.08%), hydrogen (less than 0.0125%) and iron (0.25%) are specified. However, as the total elongation and reduction of area of titanium alloys in this study are higher than the ASTM specification values, ductility and toughness requirements are not deficient. Thus, we investigated the effects of N and O to improve

Fig. 2 Effect of alloying contents on 0.2% proof strength, ultimate tensile strength, total elongation and reduction of area in Ti-(0~20%)Zr-(0~20%)Sn-((4~8%)Nb-(2~4%)Ta-(0~0.2%)Pd alloys at room temperature.

Fig. 3 Relation between volume fraction of β phase in the titanium alloys and alloying contents.

strength at room temperature.

Figure 5 illustrates the effects of N and O content on 0.2% proof strength, ultimate tensile strength, elongation and reduction of area. 0.2% proof strength and ultimate tensile strength increase linearly with increased nitrogen and oxygen in both Ti-15%Zr-4%Nb-2%Ta-0.2%Pd and Ti-15%Sn-4%Nb-2%Ta-0.2%Pd. Elongation and reduction of area decrease with the addition

Fig. 4 Optical and Scanning electron micrographs of Ti-15%Zr-4%Nb-2%Ta-0.2%Pd and Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloys annealed at 973 K for 7.2 ks.

of nitrogen and oxygen in Ti-15%Zr-4%Nb-2%Ta-0.2%Pd, but remain fairly constant in Ti-15%Sn-4%Nb-2%Ta-0.2%Pd.

The effect of alloying elements on ultimate tensile strength was analyzed by multiple regression analysis to yield the following equation:

$$\begin{aligned} \sigma_{UTB}/\text{GPa} = & 10^{-3}(487 + 28.2[\% \text{Sn}] + 10.9[\% \text{Zr}] \\ & + 4.9[\% \text{Nb}] + 2.9[\% \text{Ta}] \\ & + 514[\% \text{O}] + 1491[\% \text{N}]). \end{aligned} \quad (1)$$

A clear correlation between estimated and measured values can be observed with a multiple correlation coefficient of $R^2=0.96$. The ultimate tensile strength of the annealed material can be calculated from the chemical composition of the alloy by using eq. (1). Among substitutional alloying elements, the coefficient decreases in the order of Sn, Zr, Nb and Ta. Among interstitial elements, that the coefficient for nitrogen is considerably higher than that for oxygen.

3. Relation between strength and hardness in Ti alloy for medical implants

Figure 6 illustrates the relationship between hardness

Fig. 5 Effect of nitrogen and oxygen contents on 0.2% proof strength, ultimate tensile strength, total elongation and reduction of area in Ti-15%Zr-4%Nb-2%Ta-0.2%Pd and Ti-15%Sn-4%Nb-2%Ta-2%Pd alloys at room temperature.

Fig. 6 Relation between Vickers hardness and tensile properties at room temperature.

and strength for the alloys used in this study, Ti-(5~20%)_x-(4~8%) Nb-(2~4%) Ta-(0~0.2%) Pd-(0~0.15%)N-(0~0.3%)O, where x represents the alloying element Zr or Sn. A linear relation is established between hardness and 0.2% proof strength as well as ultimate tensile strength in the annealed material (973 K-7.2 ks), using regression analysis. The multiple correlation coefficient is $R^2=0.95$:

$$\sigma_{0.2\%PS}/\text{GPa} = 10^{-3}(-85.7 + 3.21[H_v]) \quad (2)$$

$$\sigma_{UTS}/\text{GPa} = 10^{-3}(-55.6 + 3.41[H_v]). \quad (3)$$

4. Comparison of strength properties between Ti alloys for medical implants and commercial Ti alloys

Figure 7 plots total elongation and reduction of area of several titanium alloys as a function of ultimate tensile strength. Reference data for titanium alloys of α , $\alpha+\beta$, and β structures investigated by Shouichi Tokuda, *et al.*⁽⁵⁾ and for commercial titanium alloys⁽⁶⁾ are plotted against the data for titanium alloys under investigation in this study. The total elongation versus tensile strength obtained in this study is similar to that obtained for the heat-resistant α and $\alpha+\beta$ type alloys while reduction of area is relatively higher than that of commercial titanium alloys. To determine whether these findings are a feature of the composition system or are due to the fusing procedure, further investigation is necessary.

5. Toughness of Ti alloy for medical implants

As shown in Fig. 5, the combined addition of nitrogen and oxygen was effective for improving strength without lowering ductility.

Figure 8 illustrates the effects of nitrogen and oxygen on toughness as measured by a Charpy impact test at room temperature. The addition effect of nitrogen and oxygen resulted in a decrease of Charpy impact energy with increasing N and O contents for both Ti-15%Sn-

Fig. 7 Total elongation and reduction of area as a function of ultimate tensile strength at room temperature.

Fig. 8 Effect of nitrogen and oxygen contents on Charpy impact energy of Ti-15%Zr-4%Nb-2%Ta-0.2%Pd and Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloys at room temperature.

4%Nb-2%Ta-0.2%Pd-0.2%O-(0.5~0.15%)N and Ti-15%Zr-4%Nb-2%Ta-0.2%Pd-0.05%N-(0.2~0.3%)O alloys.

Further characterization of corrosion resistance, cell compatibility, toughness and fatigue resistance is necessary to determine the practical applications for medical implants.

IV. Summary

To develop a safer biological Ti alloy with high strength and high ductility, biocompatible alloying elements were examined as alternatives to V and Al. The effect of alloying elements on the structure and mechanical properties was investigated and the following conclusions were obtained:

(1) The strength at room temperature increases with increasing Zr and Sn contents. Sn is more effective than Zr, while Nb, Ta and Pd are less effective. The tensile strength of Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloy [990 MPa] is higher than ASTM specification value of Ti-6%Al-4%V ELI alloy for medical implants [860 MPa] while that of Ti-15%Zr-4%Nb-2%Ta-0.2%Pd

alloy [726] is lower. Total elongation and reduction of area were higher than the ASTM specification in both alloys.

(2) In Ti-(5~20%)Zr-(4~8%)Nb-(2~4%)Ta-(0~0.2%)Pd and Ti-(10~20%)Sn-4%Nb-(2~4%)Ta-0.2%Pd alloys, optical microscopy revealed an acicular structure. SEM image analysis revealed a 10~30% volume fraction of β phase. The volume fraction of β phase increases with increasing Nb, Ta, Pd and Zr, but decreases slightly with Sn content in excess of 10%. The change of volume fraction of β phase suggested that the refinement of β phase contributes to the increase of strength at room temperature.

(3) Strength increased linearly with increasing nitrogen and oxygen contents in the Ti-15%Zr-4%Nb-2%Ta-0.2%Pd and Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloys without loss of ductility. The following correlation equation between tensile strength and alloy composition was obtained:

$$\begin{aligned} \sigma_{\text{UTS}}/\text{GPa} = & 10^{-3}(487 + 28.2[\% \text{Sn}] + 10.9[\% \text{Zr}] \\ & + 4.9[\% \text{Nb}] + 2.9[\% \text{Ta}] + 514[\% \text{O}] \\ & + 1491[\% \text{N}]). \end{aligned}$$

The linear relationships between the hardness and 0.2% proof strength as well as tensile strength, respectively, were obtained:

$$\begin{aligned} \sigma_{0.2\% \text{PS}}/\text{GPa} = & 10^{-3}(-85.7 + 3.21[Hv]) \\ \sigma_{\text{UTS}}/\text{GPa} = & 10^{-3}(-55.6 + 3.41[Hv]). \end{aligned}$$

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