Effects of Mo and Pd on Corrosion Resistance of V-Free Titanium Alloys for Medical Implants[†]

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The corrosion resistances of Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N and Ti-15%Sn-4%Nb-2%Ta-0.2%Pd-0.2%O alloys were compared with pure Ti grade 2, Ti-6%Al-4%V ELI (Extra low interstitial), Ti-6%Al-2%Nb-1%Ta and β type Ti-15% Mo-5%Zr-3%Al alloys for medical implants by anodic polarization and immersion tests at 310 K in various pseudo saline solutions.

The change in current density was small up to passivity zones in 1 mass% lactic acid, PBS (Phosphate-buffered saline solution) (-), calf serum and Eagle's MEM (Minimum essential medium) + bovine serum solutions except 5% HCl. The current density change of Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N alloy was lowest among the whole Ti alloys. The current densities in a region higher than 2 V tend to increase in the following relation; Ti-6%Al-4%V ELI > Pure Ti grade 2 > Ti-6%Al-2%Nb-1%Ta > Ti-15%Sn-4%Nb-2%Ta-0.2%Pd-0.2%O > Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N alloy in $\alpha + \beta$ type alloys. Otherwise the passive current density of the β type Ti-15%Mo-5%Zr-3%Al alloy was higher than that of $\alpha + \beta$ type alloys. Passive films formed on the Ti-15%Mo-5%Zr-3%Al alloy in the calf serum consisted mainly of Ti^{4+} , Zr^{4+} , Al^{6+} and Mo as demonstrated by X-ray photoelectron spectroscopy (XPS).

The rate of Ti ions released from Ti alloys in a deaerated 5% HCl solution decreased with increasing Zr, Nb, Ta, and Pd contents. Especially, the rate of Ti ions released from Ti-15%Zr-4%Nb-(2~4%)Ta-Pd alloys containing Pd in the range from 0 to 0.2% decreased remarkably compared to 0.2 to 0.5%Pd. The passive films formed on the Ti-Zr-Nb-Ta-Pd and Ti-Sn-Nb-Ta-Pd alloys containing 0.2% Pd in the immersion test consisted mainly of Ti^{4+} , Zr^{4+} , Sn^{4+} , Sn, Nb^{5+} , Ta^{5+} and Pd. The rate of released Ti increased by the following relation; Ti-15%Sn-4%Nb-2%Ta-0.2%Pd-0.2%O $\geq$ Ti-6%Al-2%Nb-1%Ta $\geq$ Ti-6%Al-4%V ELI $\geq$ Pure Ti grade 2 > Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N $\geq \beta$ type Ti-15%Mo-5%Zr-3%Al alloy.

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I. Introduction

The use of pure Ti grade 2 and Ti-6%Al-4%V ELI (Extra Low Interstitial) alloys (all the contents in mass%) is increasing every year as orthopedic and dental implants. Ti-6%Al-4%V ELI alloys were originally developed for aircraft material, but is now presently being used as an implant material, even though the vanadium content is strongly cytotoxic in⁽¹⁾⁻⁽¹¹⁾. As $\alpha + \beta$ -type alloys for medical implants not containing V, the alloys such as Ti-6%Al-7%Nb⁽¹²⁾, Ti-5%Al-2.5%Fe⁽¹²⁾, Ti-6%Al-6%Nb-1%Ta⁽¹²⁾, Ti-5%Al-3%Mo-4%Zr⁽¹³⁾, Ti-6%Al-2%Nb-1%Ta and β -type alloys such as Ti-12%Mo-6%Zr-2%Fe⁽¹⁴⁾, Ti-15%Mo-3%Nb-0.2%Si-0.3%O⁽¹⁵⁾, Ti-15%Mo-3%Nb-3%Al-0.2%Si⁽¹⁵⁾, Ti-13%Zr-13Nb⁽¹⁶⁾ and Ti-15%Mo-5%Zr-3%Al⁽¹⁷⁾ alloys are being devel-

oped into medical implants. In the present research, the electrochemical evaluation of corrosion resistance of Ti-6%Al-2%Nb-1%Ta and Ti-15%Mo-5%Zr-3%Al alloys under a simulated biological environment which are in practical application after various clinical experiments as prescribed by The Ministry of Health and Welfare, and the new Ti alloys without V and Al, currently under development by the authors for medical implants⁽¹⁸⁾⁻⁽²²⁾, are being investigated. The effect of Mo in the passive film formed on the β type alloy was also examined. Moreover, the effect of Pd on the corrosion resistance of titanium alloys was investigated by immersion tests in an aerated and a deaerated 5 mass% HCl solutions, since the effect of Pd by anodic polarization investigations alone is not amply sufficient.

II. Experimental Procedures

The following alloys were designed with better biocompatible alloying elements than V and Al, Ti-(5-20%)Zr-(4-8%)Nb-(2-4%)Ta-(0-0.5%)Pd-(0.1-0.3%)O-

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Table 1 Chemical composition (mass%) of materials used.

Titanium alloy	Zr	Sn	Nb	Ta	Pd	Al	V	Mo	Fe	O	N	H	C	Ti
Pure Ti Grade 2	—	—	—	—	—	—	—	—	0.062	0.078	0.0037	0.0012	0.007	Bal.
Ti-6%Al-4%V ELI	—	—	—	—	—	6.42	4.19	—	0.198	0.101	—	0.0052	0.011	Bal.
Ti-6%Al-2%Nb-1%Ta	—	—	1.91	0.95	—	5.90	—	0.77	0.214	0.055	0.0047	0.0010	<0.005	Bal.
Ti-15%Mo-5%Zr-3%Al	5.12	—	—	—	—	2.92	—	15.19	0.028	0.099	0.009	0.0073	0.007	Bal.
Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N	15.24	<0.01	3.90	3.92	0.22	—	—	—	0.022	0.162	0.0480	0.0110	0.002	Bal.
Ti-15%Sn-4%Nb-2%Ta-0.2%Pd-0.2%O	0.003	14.77	3.87	1.92	0.20	—	—	—	0.026	0.236	0.0046	0.0080	0.003	Bal.
Ti-15%Zr-4%Nb-4%Ta-0.5%Pd-0.2%O	15.82	—	4.40	3.80	0.53	—	—	—	0.020	0.181	0.0059	0.0048	—	Bal.

(0–0.15%)N, Ti–(10–20%)Sn–(4–8%)Nb–(2–4%)Ta–0.2%Pd–(0.05–0.2%)O–(0–0.15%)N, and pure Ti grade 2, Ti–6%Al–4%V ELI, Ti–6%Al–2%Nb–1%Ta and Ti–15%Mo–5%Zr–3%Al alloys were arc-melted in vacuum. After α – β and β forging, the alloys were annealed for 7.2 ks at 973 K. However, for the β type Ti–15%Mo–5%Zr–3%Al alloy, a solution-treated alloy (water cooled after holding at 1058 K for 1.8 ks) was used. Table 1 shows the chemical composition of 100 kg and 0.6 kg ingots to examine the effect of Pd. The chemical compositions of other ingots of 0.6 kg melted by vacuum arc melting and those of about 5 kg melted by plasma electronic beam melting to reduce the amount of impurities are shown elsewhere^{(18)–(22)}.

Block specimens of 10 mm × 10 mm × 5 mm in thickness were cut from the alloys. Anodic polarization tests were conducted using these specimens in 5% HCl, 1% lactic acid (pH=2.5), calf serum, PBS (–) (phosphate-buffered saline solution manufactured by Nissui: containing NaCl: 8 g, KCl: 0.2 g, Na₂HPO₄: 1.15 g, KH₂PO₄: 0.2 g in 1 L of ultra pure water), and Eagle's MEM (minimum essential medium manufactured by Nissui: mainly composed of NaCl: 6.8 g, C₆H₁₂O₆: 1 g, KCl: 0.4 g, CaCl₂: 0.2 g, NaH₂PO₃: 0.115 g containing various inorganic salts, kanamycin, etc. in 1 L of ultra pure water) containing 10% fetal bovine serum and 10% NaHCO₃ at 310 K to evaluate their corrosion resistance. Details of anodic polarization test are reported in references⁽²⁰⁾⁽²²⁾. The calf serum used in the present study contained 6.5 g/L of protein and 14.4 g/L of hemoglobin while the pH number was 6.9.

Block specimens of 10 mm × 10 mm × 5 mm in thickness were cut from the sample alloys. The specimen was ultrasonically cleaned after being finished with waterproof emery paper up to #600. Then 2 × 10^{−4} m³ (200 cm³) of 5% HCl solution was placed in a conical flask and set in a isothermal water bath at 310 K (37°C). After the solution temperature was stabilized at 310 K, the test specimen was placed in the solution to conduct an immersion test by giving it an 8-shaped shake at the rate of 1.33 runs/s (80 runs/min) for 0.2 to 0.6 Ms. The concentra-

tion of Ti ion release into an aerated 5% HCl solution (dissolved oxygen: 7.8 mass ppm) and a 5% HCl solution bubbled with high purity N₂ gas (dissolved oxygen <0.5 mass ppm) was measured with an ICPES (Inductively Coupled Plasma Emission Spectrometer). The immersion time under the aerated condition was mostly 0.6 Ms, and under the N₂ gas bubbling condition was set at 0.4 Ms considering the amount of evaporation during the immersion test. Moreover, a 90%N₂–5%CO₂–5%O₂ mixed gas bubbling was also conducted to examine the effect of dissolved oxygen. The flow rate of N₂ bubbling gas was set at approximately 2 × 10^{−7} m³/s (12 cc/min). The amount of evaporation during bubbling for 0.4 Ms was approximately less than five percent. The rate of Ti ion release was calculated from the mean values of ICPES measurements repeated 3 to 10 times for the different specimens.

The effects of Mo and Pd in passive films were examined with XPS. The sample surfaces were finished by buff-cleaning using the high quality SiO₂ (OP-S) suspension. Anodic polarization tests were carried out at a sweep rate of 6.67 × 10^{−4} V/s (40 mV/min) from −1 to 0.8 V. The XPS measurement was carried out with an X-ray source of Al K α having 200 W output and the X-ray spot size being set at 300 μ m. As the argon ion sputter conditions, an angle of incidence at 30°, 3 kV, 3 mA was set and the sputter shape was a 4 mm × 2 mm ellipse.

III. Results and Discussion

1. Comparison of anodic polarization curves in various pseudo saline solutions

Figures 1 and 2 show the comparison of the anodic polarization curves measured in various physiological saline solutions with high-purity N₂ gas deaerated at 310 K (37°C). Figure 1 summarizes the results in 5% HCl and 1% lactic acid solutions, and Fig. 2 shows the results in PBS (–) and calf serum. Moreover, Figs. 1 and 2 show the anodic polarization curves of SUS316L steel and Co-Cr alloys for comparison. A passivation peak is observed

Fig. 1 Comparison of the anodic polarization curves at a sweep rate of 6.67×10^{-4} V/s (40 mV/min) for implant alloys in deaerated 5 mass% HCl (a) and 1 mass% lactic acid (b) at 310 K.

in the 5% HCl solution. However, in Fig. 2, the curves enter the passivity zone where the current density is low without an obvious passivation peak. The current density in the potential region of 1 V or more increases as the potential increases, and increases rapidly particularly in potentials more than 2 V. In a potential of more than 2 V, Ti-6%Al-4%V ELI alloys has the highest current density followed by pure Ti grade 2, Ti-6%Al-2%Nb-1%Ta, Ti-15%Sn-4%Nb-2%Ta-0.2%Pd-0.2%O and Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N alloys, indicating that the corrosion resistance of Ti-15%Zr alloys is considerably high. Unlike $\alpha + \beta$ type alloys, in the anodic polarization curve of the Ti-15%Mo-5%Zr-3%Al alloy, which is a β type alloy of high Mo content, the current density in the passivity tends to be high. In SUS316L stainless steel and Co-Cr alloys, unlike Ti alloys, passivation peaks in both 1% lactic acid solution and calf serum are seen, but their passivity zone is narrow and the current density increases rapidly at about 400 mV vs. SCE. Consequently, the corrosion resistance of these alloys in the physiological saline solution is considerably lower than that of Ti alloys. Figure 3 shows a comparison of the passive current density ($I_{0.6}$), evaluated by the current density value in +0.6 V vs. SCE in the present study. Variations of $I_{0.6}$ in 1% lactic acid, PBS (-), calf serum and Eagle's MEM + fetal bovine serum are smaller than those in the 5% HCl solutions. The $I_{0.6}$ value of the β type alloy Ti-15%Mo-5%Zr-3%Al tends to be higher as compared to $\alpha + \beta$ type alloys.

Fig. 2 Comparison of the anodic polarization curves at a sweep rate of 6.67×10^{-4} V/s (40 mV/min) for medical implants in deaerated PBS (-) (a) and calf serum (b) at 310 K.

Fig. 3 Comparison of passive current density at 0.6 V vs. SCE ($I_{0.6}$) in the various pseudo physiological solutions.

2. XPS analysis of Mo in passive film

The chemical state of alloying elements in the passive film for the Ti-15%Mo-5%Zr-3%Al alloy which showed a higher passive current density than $\alpha + \beta$ type alloys was investigated by using XPS. Figure 4(a) shows a wide scanning spectra of the passive film formed on Ti-15%Mo-5%Zr-3%Al alloys after the Ar^+ sputtering for 5 s. The figure shows the peaks of electron binding energy of Ti, Mo, Zr and Al. Figures 4(b)–(f) show the

Fig. 4 XPS spectra for surface of passive film formed on β type Ti-15%Mo-5%Zr-3%Al alloy by anodic polarization up to 0.8 V in a deaerated calf serum at 310 K. (a): wide scanning spectra, (b)–(f): narrow scanning spectra.

narrow scanning spectra of each alloying element. Titanium, zirconium and aluminum is present in the passive film as Ti^{4+} , Zr^{4+} and Al^{6+} , respectively. The electron binding values matches with TiO_2 , ZrO_2 , Al_2O_3 oxides given as in the handbook⁽²³⁾. The binding energy of Mo $3d_{5/2}$ electrons for the β stabilization element Mo is 228.7 eV, showing a measured value slightly higher than that for pure Mo $3d_{5/2}$ 227.6 and $3d_{3/2}$ 230.6 eV. The peak of O 1s spectrum can be separated into the peaks of the OH-metal and O-metal bonding. Figure 5 summarizes the variation of the electron binding energy of each alloying element to the direction of the depth of passive film at intervals of 10 s Ar^+ sputtering. The binding energy of titanium oxides tends to decrease as the Ar^+ sputtering time increases, while that of Zr^{4+} $3d_{5/2}$ and Al^{3+} $2p$ remains almost unchanged. The binding energy of Mo $3d_{5/2}$ tends to be slightly higher at the surface of the passive film, but it approaches the value of the bulk Mo binding energy as the sputtering time increases. A similar tendency of the Ti-15%Mo-5%Zr-3%Al alloy was also observed in the 5% HCl solution. Figure 6 shows the depth profile of the passive film formed on the Ti-15%Mo-5%Zr-3%Al alloy anodically polarized up to 0.6 V in the 5% HCl solution where the passive current density is the highest. As the sputtering time increases, the oxygen concentration decreases and the Ti and Mo concentrations increase. The variation in Zr concentration is minor, while the Al concentration tends to be lower at the passive film

Fig. 5 Change in electron binding energy of alloying elements in passive film formed on β type Ti-15%Mo-5%Zr-3%Al alloys by anodic polarization test up to 0.8 V in a deaerated calf serum at 310 K as a function of Ar^+ ion sputtering time.

Fig. 6 XPS sputtering profiles in passive film formed on β type Ti-15%Mo-5%Zr-3%Al alloy by anodic polarization test up to 0.6 V in a deaerated 5% HCl at 310 K.

surface. As the oxygen concentration decreases, the chemical state of the alloying elements changes from oxides to metals. In the vicinity of 80 s, each element approaches the concentration in the metal and becomes constant.

The variation in concentration from the surface of the passive film to the interior of the metal was investigated by depth profiling. Figure 7 shows a comparison of sputtering time for removing the passive film formed on the anodic polarization up to 5 V down to the boundary between the metal/oxide film interface. It shows that the sputtering times for Ti-Zr and Ti-Sn alloys tend to be slightly longer than for Ti-6%Al-4%V ELI alloys. The sputtering time of β type Ti-15%Mo-5%Zr-3%Al alloys

Fig. 7 Comparison of sputtering time for removing passive film formed on implant Ti alloys for anodic polarization up to passivity zone and 5 V in the various pseudo physiological saline solutions at 310 K by Ar^+ ion sputtering.

Fig. 8 Comparison of the rate of Ti ion release measured by ICPES and the rate of mass loss by immersion test in a deaerated 5% HCl and an aerated 5% HCl solutions at 310 K.

is found to be slightly shorter than that of $\alpha + \beta$ type alloys. The sputtering rate of TiO_2 film under the Ar^+ sputtering condition applied to the present study was 0.05 nm/s.

3. Immersion test in 5% HCl solution

Since the effect of Pd addition cannot be well determined by the anodic polarization investigation immersion tests in the aerated and the deaerated 5% HCl solutions were carried out. Figure 8 shows a comparison of the rate of mass loss and the rate of the Ti ion release measured with ICPES by immersing in the N_2 gas bub-

Fig. 9 Change in the quantity of Ti ion release from various Ti alloys for medical implants as a function of immersion time.

Fig. 10 Comparison of the rate of Ti ion release from pure Ti grade 2, Ti-6Al-4V ELI, Ti-6Al-2Nb-1%Ta, Ti-15Sn-4Nb-2%Ta-0.2%Pd-0.2%O, Ti-15Zr-4Nb-4Ta-0.2%Pd-0.2%O-0.05%N, and Ti-15Mo-5Zr-3Al alloys in a 5% HCl solution at 310 K.

bled 5% HCl and aerated 5% HCl solutions at 310 K. A good correlation is observed between the rate of mass loss and the rate of the Ti ion release measured by ICPES. Figure 9 shows the dissolution curve of Ti ions in various Ti alloys immersed for 0.2 Ms to 0.6 Ms. The quantity of the Ti ion release increases linearly with an increase in immersion time except for the Ti-15Sn-4Nb-2%Ta-0.2%Pd-0.2%O alloy under the deaerated condition. The quantity of the Ti ions released from a Ti-15Zr-4Nb-4Ta-0.2%Pd-0.2%Pd-0.2%O-0.05%N alloy is small and coincides with that of the β type Ti-15Mo-5Zr-3Al alloy. The effect of the specimen shape on the rate of Ti ion release is shown in Fig. 10. The influence of the specimen shape on the rate of Ti ion release is small when the specimen shape is changed to a rod or a block. Also, the effect of the surface condition was negligible for specular gloss finished with OP-S suspension or finished with #600 waterproof

Fig. 11 Comparison of SEM micrographs for pure Ti grade 2, Ti-6%Al-4%V ELI, Ti-6%Al-2%Nb-1%Ta, Ti-15%Sn-4%Nb-2%Ta-0.2%Pd-0.2%O, Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N, and Ti-15%Mo-5%Zr-3%Al alloys immersed in a deaerated 5% HCl solution for 0.4 Ms at 310 K.

emery paper. Figure 11 shows the SEM microstructures of the surface immersed in the deaerated 5% HCl solution for 0.4 Ms. For pure Ti grade 2 and Ti-6%Al-4%V ELI alloys, the whole surface is released. But for Ti-6%Al-2%Nb-1%Ta and Ti-15%Sn-4%Nb-2%Ta-0.2%Pd-0.2%O alloys, the α phase is released more as compared to the β phase that appears whitish. Ti-15%Mo-5%Zr-3%Al and Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N alloys retain a specular finish and the sample surfaces are slightly released. The β type alloy with a high Mo concentration shows dissolution of the α phase⁽²²⁾ in the grain boundary and inside the grains.

Figure 12 shows the effect of the alloying elements on the rate of Ti ion release measured by ICPES for Ti-(0–20%)Zr-(0–20%)Sn-(4–8%)Nb-(2–4%)Ta-(0–0.5%)Pd alloys. Even though, other elements like Zr, Sn, Nb, and

Ta were released, in small quantities as compared to Ti, and the effect of the alloying elements on the rate of Ti ion release was measured. The effect of alloying elements on the rate of Ti ion release is greater in the N_2 bubbled HCl solution than in the aerated solution. For Ti-Zr alloys, the rate of Ti ion release decreases as the addition of Pd, Zr and Ta increases. Also the effect of 0.2% Pd is remarkable particularly under the N_2 bubbling condition. On the other hand, the rate of Ti ion release tends to increase in Ti-Sn alloys under the N_2 bubbling condition as the amounts of Sn, Nb and Ta increased. But, the effect of Ta addition is minor for 0.2% Pd-Ti-Zr alloys.

The combined addition of O and N tend to increase the mechanical strength of the alloys⁽¹⁸⁾⁽²⁰⁾. The effect of O and N on the rate of Ti ion release is shown in Fig. 13. Little effect is observed for nitrogen up to 0.15% additions

Fig. 12 Effect of Zr, Sn, Nb, Ta and Pd contents on the rate of Ti ion release from Ti-(0~20%)Zr-(0~20%)Sn-(4~8%)Nb-(2~4%)Ta-(0~0.5%)Pd alloys immersed in the deaerated 5% HCl and an aerated 5% HCl solutions at 310 K.

Fig. 13 Effect of nitrogen and oxygen contents on the rate of Ti ion release from Ti-Zr and Ti-Sn alloys in a deaerated 5% HCl and an aerated 5% HCl solutions at 310 K.

and for oxygen up to 0.3% additions on Ti-Zr alloys with 0.2% Pd under the aerated or deaerated conditions. However, for the Ti-Sn alloys containing 0.2% Pd, the rate of the Ti ion release tends to increase with the addition of 0.05 to 0.15% N irrespective of the bubbling condition.

Figure 14 shows the comparison of the rates of Ti ion release for various Ti alloys immersed in the 5% HCl so-

Fig. 14 Comparison of the rate of Ti ion release in a deaerated 5% HCl and an aerated 5% HCl solutions at 310 K.

Fig. 15 Change in the rate of Ti ion release from various Ti alloys as a function of the critical current density for passivation (I_c).

lution under a high-purity N_2 gas bubbling condition for 0.4 Ms and the aerated 5% HCl solution for 0.6 Ms. Alloys can be classified into three groups according to their type. The first group includes pure Ti grade 2, Ti-6%Al-4%V ELI, and Ti-6%Al-2%Nb-1%Ta alloys which have high rates of Ti ion release even in a solution having a comparatively high concentration of dissolved oxygen, and these rates are equal under both the aerated and deaerated conditions. The second group includes the 0.2% Pd-Ti-Sn alloys and the Pd-free Ti-Zr alloy whose rates of Ti ion release become lower under the aerated condition than under the N_2 gas bubbling condition. The third group includes the 0.2% Pd-Ti-Zr and β type Ti-15%Mo-5%Zr-3%Al alloys. The rate of Ti ion release is considerably low under both the N_2 gas bubbled and aerated conditions. Figure 15 shows the relationship between the rate of Ti ion release and critical current density for passivation (I_c) measured by anodic polarization. It can be

seen from the figure that the release rate of Ti ions for the Pd-free Ti-Zr, 0.2% Pd-Ti-Sn, pure Ti grade 2, Ti-6% Al-4%V ELI, and Ti-6%Al-2%Nb-1%Ta alloys could be shown on the same line. The rate of Ti ion release tends to increase in the 0.2% Pd-Ti-Zr and β type Ti-15%Mo-5%Zr-3%Al alloys as I_c value increases, but the rate of Ti ion release is remarkably reduced compared with the Pd-free alloys. Moreover, it was found that while the I_c value of the Ti-15%Mo-5%Zr-3%Al alloy is higher than the $\alpha + \beta$ type alloys, the rate of Ti ion release tend to decrease.

4. XPS analysis of Pd in passive film

The chemical state of alloying elements in the passive films was investigated by XPS to examine the effect of Pd that remarkably reduces the rate of Ti ion release. Figure 16 show the narrow scanning spectra of the passive film formed on the surface of the Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloy immersed in the aerated 5% HCl solution, and the oxide peaks of Ti^{4+} , Sn^{4+} , Nb^{5+} and Ta^{5+} are observed. As for the Ti-Zr alloy, the peak of Zr^{4+} is observed, but for other alloying elements, the result is the same as the Ti-Sn alloys. For Pd, it is close to the peak of metallic Pd ($3d_{5/2}$ 335.2 and $3d_{3/2}$ 340.4) as shown in Fig. 16(f) and the other peak seems to be close to the value of PdO ($3d_{5/2}$ 336.2–336.5)⁽²³⁾. Also, no major change is observed in the binding energy of Pd after a 20 s Ar^+ sputtering. Figure 17 shows the change in binding energy and intensity of the Pd $3d_{5/2}$ spectrum after Ar^+ sputtering at intervals of 20 s. The binding energy of Pd $3d_{5/2}$ electrons

Fig. 17 Change in intensity and binding energy of Pd $3d_{5/2}$ electron in passive film formed Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloy immersed in an aerated 5% HCl for 0.6 Ms at 310 K as a function of sputtering time.

remains almost constant while the intensity tends to rise in the vicinity of the surface.

IV. Conclusions

Corrosion resistances of Ti-6%Al-2%Nb-1%Ta and Ti-15%Mo-5%Zr-3%Al alloys which are in practical application after clinical experiments and the new Ti alloys for medical implants without V and Al were evaluated electrochemically in various physiological saline solutions. To deduce the effect of Pd on the corrosion resistance, immersion tests were carried out in a 5% HCl solution, and the following conclusions were drawn:

(1) The current density of all the Ti alloys measured in 5% HCl, 1% lactic acid, calf serum, PBS (–) and Eagle's MEM solution with bovine serum increases in the high potential region of 1 V or above. The current density in the high potential region is highest in the Ti-6% Al-4%V ELI alloy followed by pure Ti grade 2, the Ti-6%Al-2%Nb-1%Ta alloy and Ti-15%Sn-4%Nb-2% Ta-0.2%Pd-0.2%O alloy. The Ti-15%Zr-4%Nb-4% Ta-0.2%Pd-0.2%O-0.05% N alloy shows very good corrosion resistance. Unlike $\alpha + \beta$ type alloys, the anodic polarization curve of the β type Ti-15%Mo-5%Zr-3% Al alloy show that the current density tends to increase in the passivity zone.

(2) The rate of Ti ion release in 5% HCl solution decreases with increasing of Pd, Zr, Nb and Ta contents. In particular, the rate of Ti ion release decreases remarkably with the addition of 0.2% Pd. It has also been found that the rate of Ti release increases with an increase of critical current density (I_c) measured by anodic polarization, but the variation of I_c alone cannot explain this remarkable effect of Pd. XPS analysis of Pd in the passive film indicates that the trace amounts of Pd and PdO are present in the passive film.

(3) The rate of Ti ion release from the alloys may be

Fig. 16 XPS narrow scanning spectra for surface of passive film formed on Ti-15%Sn-4%Nb-2%Ta-0.2%Pd alloy immersed in an aerated 5% HCl for 0.6 Ms at 310 K.

classified into the following three groups: pure Ti 2 grade, Ti-6%Al-4%V ELI and Ti-6%Al-2%Nb-1%Ta alloys form the first group whose rates of Ti ions release are the same under both the aerated and deaerated conditions. The second group consists of 0.2% Pd-Ti-Sn alloys and Pd-free Ti-Zr alloys. The rate of release is reduced under the aerated condition than under the deaerated condition. The third group consists of 0.2% Pd-Ti-Zr alloy and β type Ti-15%Mo-5%Zr-3%Al alloys. Their rates of Ti ion release are considerably low in both the aerated and deaerated conditions.

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