

# Corrosion Behavior of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ Amorphous Alloy for Biomedical Use\*

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To evaluate the performance of  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  amorphous alloy for the biomedical use, the effects of chloride ion,  $\text{Cl}^-$ , pH, and dissolved oxygen, DO, on the anodic polarization behavior of the alloy were examined in phosphate buffered solutions. Polarization resistance,  $R_p$ , at open-circuit potential,  $E_{\text{open}}$ , and pitting potential,  $E_{\text{pit}}$ , were determined from the polarization curve. Compositions of passive film generated in a pH-7.5 solution with various concentrations of DO were characterized with X-ray photoelectron spectroscopy. In the solution with pH 7.5, the  $E_{\text{pit}}$  decreased with the increase in logarithm of  $\text{Cl}^-$  concentration,  $[\text{Cl}^-]$ , and showed the highest value with the same DO concentration,  $[\text{DO}]$ , as that *in vivo*. The concentrations of hydroxide group,  $[\text{OH}^-]$ , and phosphate ions,  $[\text{H}_x\text{PO}_4^{(3-x)-}]$ , in the passive film were changed with various  $[\text{DO}]$ s, and the  $E_{\text{pit}}$  decreased with the increase in  $[\text{OH}^-]$  and  $[\text{H}_x\text{PO}_4^{(3-x)-}]$ . In the solution with pH 2.2, the  $E_{\text{pit}}$  was higher than the  $E_{\text{open}}$  with and without DO. Therefore, this alloy may be resistant to the pitting corrosion *in vivo*.

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## 1. Introduction

Metallic biomaterials are used as bone plate, dental implant, wire, electrode, and so on. For the purpose of providing the high quality medical services, improvement of biocompatibility of metallic biomaterials is in progress. The biocompatibility is the ability of material to exist *in vivo* for an acceptable period of time with no detrimental effect on the host;<sup>1)</sup> for example, not to release toxic metal ions and wear debris, to show as low Young's modulus as bone, to be tightly fixed to bone by adhering tissues, to be small and so on.<sup>2)</sup> 316L-type stainless steel, Co-Cr alloy, titanium, and Ti-Al-V alloy are used for biomaterials because of their high corrosion resistance and high strength, however they are sometimes dissolved by corrosion and fractured by corrosion fatigue or fretting corrosion fatigue. Followings are demanded to increase the biocompatibility of the materials; the decrease in Young's modulus, the increase in corrosion resistance and mechanical strength, and downsizing.

Amorphous alloy should be a promising biomaterial because it can show higher strength and corrosion resistance and lower Young's modulus than crystalline alloys. In particular, the high corrosion resistance is the most important property to avoid biological damages, such as allergy and carcinogenicity due to metal ions. Biological environment to which biomaterials directly contact is corrosive to metals. Body fluids and saliva contain  $1.3 \times 10^2 \text{ mol} \cdot \text{m}^{-3}$  NaCl and  $5.0\text{--}20.0 \text{ mol} \cdot \text{m}^{-3}$  NaCl, respectively. The partial pressure of oxygen *in vivo* is one fifth of that of the air.<sup>3)</sup> In addition, the pH of body fluids is usually 7.15 to 7.35, and it decreases to 5.2 by inflammation when materials are implanted.<sup>4)</sup> Therefore, the chemical corrosion factors *in vivo* are concentrations of chloride ion,  $\text{Cl}^-$ , dissolved oxygen, DO, and variation of pH. On the other hand, the mechanical factors are wear and crevice formation, for example, between bone plate and screws.<sup>5)</sup>

Then, zirconium and palladium based amorphous alloys

are probably suitable for the biomedical use for the following reasons. (1) Crystalline zirconium shows high corrosion resistance in acidic and alkaline solutions.<sup>6,7)</sup> (2) Millimeter-sized bulk zirconium based amorphous alloys have been developed and the evaluation of their mechanical properties has been performed.<sup>8-10)</sup> (3) Palladium based amorphous alloy showed high corrosion resistance in an artificial body fluid.<sup>11)</sup> In this study, the corrosion behavior of  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  amorphous alloy ribbon was evaluated in phosphate buffered solutions with various concentrations of  $\text{Cl}^-$ , and DO and various pH, for the purpose of biomedical use.

## 2. Experimental Procedure

### 2.1 Preparation of the amorphous alloy

Master alloy with the composition of  $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$  was prepared by arc melting of pure Zr, Al, Ni, and Cu ( $>99.9 \text{ at}\%$ ) in an argon atmosphere. The alloy was re-melted in a quartz nozzle and rapidly quenched by casting it on the rotating copper roll. Ribbon alloy with 1 mm width and  $50 \mu\text{m}$  thickness was obtained. The structure of the ribbon alloy was determined from X-ray diffraction pattern and was confirmed to be amorphous. The free-side surface was polished with 600 grid silicon carbide paper in distilled water, dried in an ambient for a few days, and kept in a desiccator. The specimen for polarization test was coated with epoxy resin except for a  $0.2 \text{ cm}^2$  measurement area and ultrasonically washed in ethanol. Crystalline pure titanium specimen with  $1.0 \text{ cm}^2$  measurement area was prepared in the same procedure for comparison of corrosion resistance.

### 2.2 Electrolyte

A pH-7.5 phosphate-citric acid buffered solution, PCA, was used to examine the effects of  $\text{Cl}^-$  on polarization behavior of the alloy. The pH-7.5 PCA was prepared with mixing 92 vol%  $0.2 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$   $\text{Na}_2\text{HPO}_4$  and 8 vol%  $0.1 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$  citric acid. The concentration of  $\text{Cl}^-$ ,  $[\text{Cl}^-]$ , was varied  $0$ ,  $3.4 \times 10^1$ ,  $6.8 \times 10^1$ ,  $1.4 \times 10^2$ , and  $1.0 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$  by adding NaCl to pH-7.5 PCA. The  $[\text{Cl}^-]$  *in vivo* is  $1.4 \times 10^2 \text{ mol} \cdot \text{m}^{-3}$ .<sup>2)</sup> The solution was deaerated

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Table 1 Composition of PBS(–).

Composition	NaCl	KCl	Na <sub>2</sub> HPO <sub>4</sub>	KH <sub>2</sub> PO <sub>4</sub>
Concentration/mol·m <sup>–3</sup>	137	2.68	8.10	1.47

with bubbling N<sub>2</sub> at a rate of  $8.3 \times 10^{-7} \text{ m}^3 \cdot \text{s}^{-1}$  for  $3.6 \times 10^3 \text{ s}$ . The bubbling rate and time of gas were the same in all the solutions.

A pH-7.5 phosphate buffered saline solution, PBS(–), and pH-2.2 PCA containing  $1.4 \times 10^2 \text{ mol} \cdot \text{m}^{-3}$  NaCl were prepared to examine the effect of pH and DO. The pH *in vivo* is 7.15–7.35.<sup>4)</sup> The pH-2.2 PCA was prepared with mixing 2 vol%  $0.2 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$  Na<sub>2</sub>HPO<sub>4</sub> and 98 vol%  $0.1 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$  citric acid. Composition of PBS(–) is listed in Table 1. The PBS(–) was aerated with 0, 4, and 20 vol% O<sub>2</sub>/N<sub>2</sub> to vary the concentration of DO, [DO]. The [DO] was measured using a dissolved oxygen meter, and were  $9.4 \times 10^{-3}$ ,  $3.3 \times 10^{-2}$ , and  $1.7 \times 10^{-1} \text{ mol} \cdot \text{m}^{-3}$ , respectively. The [DO] *in vivo* is simulated by aerating 4% O<sub>2</sub>/N<sub>2</sub> because that is one fifth in the ambient.<sup>3)</sup> The pH-2.2 PCA was deaerated and aerated with 4% O<sub>2</sub>/N<sub>2</sub>.

### 2.3 Polarization

The alloy was immersed in the each solution kept at 310 K for  $1.8 \times 10^3 \text{ s}$  until when the  $E_{\text{open}}$  was nearly stabilized and anodically polarized from the  $E_{\text{open}}$  at a rate of  $3.33 \times 10^{-4} \text{ V} \cdot \text{s}^{-1}$ . The crystalline pure titanium was also anodically polarized in deaerated PBS(–). The  $R_p$  was calculated from the slope of the 0.05-V width linear region at  $E_{\text{open}}$  of the polarization curve. The  $E_{\text{pit}}$  was determined from the potential where anodic current density was exceeded the value of  $1 \text{ A} \cdot \text{m}^{-2}$ . Polarization was performed 2–3 times to confirm the change of these values.

### 2.4 Specimen of X-ray photoelectron spectroscopy, XPS

To examine the effect of DO on the composition of passive film, the passive film was generated by polarizing the alloy from  $-0.55$  to  $-0.20 \text{ V}$  in the PBS(–) aerated with 0, 4,

and 20% O<sub>2</sub>/N<sub>2</sub>. The passive film was characterized with XPS (ESCA Quantum 2000). The X-ray source was a monochromatized Al K $\alpha$  line, and the take-off angle of photoelectron was 45°. The concentration of each element in the passive film was calculated from the area of its XPS peak.

## 3. Results

### 3.1 Effect of chloride ion

The  $R_p$ ,  $E_{\text{open}}$ , and  $E_{\text{pit}}$  on the polarization curves of the Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Cu<sub>17.5</sub> amorphous alloy were plotted versus logarithm of [Cl<sup>–</sup>] in Figs. 1(a) and (b), respectively. The  $E_{\text{open}}$  was constant through this concentration range of Cl<sup>–</sup>. On the other hand, the  $R_p$  slightly decreased logarithmically from  $2.5 \times 10^2$  to  $1.0 \times 10^2 \Omega \cdot \text{m}^2$  with the increase in [Cl<sup>–</sup>]. The  $E_{\text{pit}}$  also logarithmically decreased with the increase in [Cl<sup>–</sup>].

The crystalline pure titanium polarized in the deaerated PBS(–) showed  $1.8 \times 10^2 \Omega \cdot \text{m}^2$   $R_p$  at  $E_{\text{open}} = -0.57 \text{ V}$ . The value was also plotted in Fig. 1(a) and was as same as that of the amorphous alloy with the same [Cl<sup>–</sup>].

### 3.2 Effect of pH and dissolved oxygen

The typical polarization curves of the alloy in 4% O<sub>2</sub>/N<sub>2</sub> aerated pH-7.5 and pH-2.2 solutions were shown in Fig. 2. The  $E_{\text{open}}$  and  $E_{\text{pit}}$  with pH 2.2 were higher and lower than those with pH 7.5, respectively. Current density in passive region with pH 2.2 was lower than that with pH 7.5.

The typical polarization curves of the alloy in pH-7.5 solution aerated with N<sub>2</sub> and 20% O<sub>2</sub>/N<sub>2</sub> were shown in Fig. 2. The  $E_{\text{open}}$  and current density in passive region did not change with [DO]. The  $E_{\text{pit}}$  in the pH-7.5 solution aerated with 4% O<sub>2</sub>/N<sub>2</sub> showed the highest  $E_{\text{pit}}$  among those in the pH-7.5 solutions.

The polarization curve of the alloy in the deaerated pH-2.2 solution was also shown in Fig. 2. The  $E_{\text{open}}$  and  $E_{\text{pit}}$  in the deaerated pH-2.2 solution were as same as those in the 4% O<sub>2</sub>/N<sub>2</sub> aerated pH-2.2 solution.

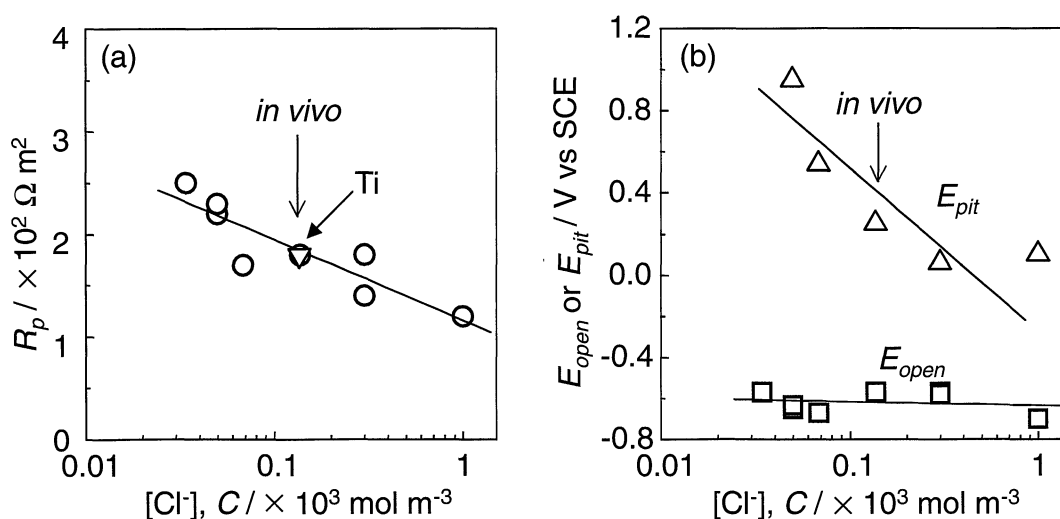


Fig. 1 Dependence of polarization resistance,  $R_p$ , open circuit potential,  $E_{\text{open}}$ , and pitting potential,  $E_{\text{pit}}$ , of the Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Cu<sub>17.5</sub> amorphous alloy on logarithm of chloride ion concentration, [Cl<sup>–</sup>], in PCA. (a)  $R_p$ , (b)  $E_{\text{open}}$  and  $E_{\text{pit}}$ . ○: Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Cu<sub>17.5</sub> amorphous alloy, ▽: crystalline pure titanium.

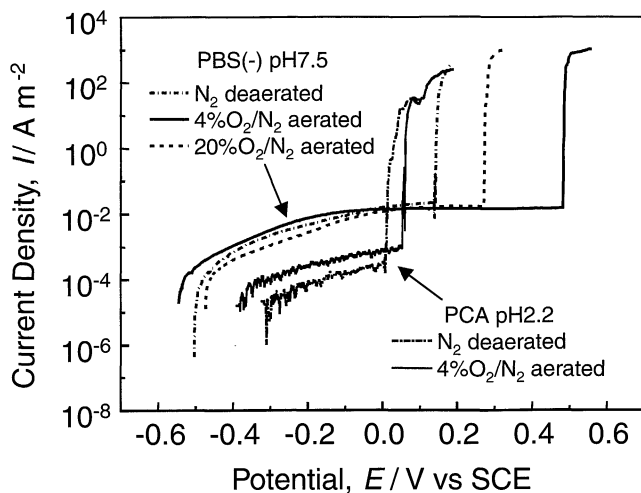


Fig. 2 Polarization curves of the  $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$  amorphous alloy in 0, 4, and 20%  $O_2/N_2$  aerated pH-7.5 PBS(-) and in 0 and 4%  $O_2/N_2$  aerated pH-2.2 PCA.

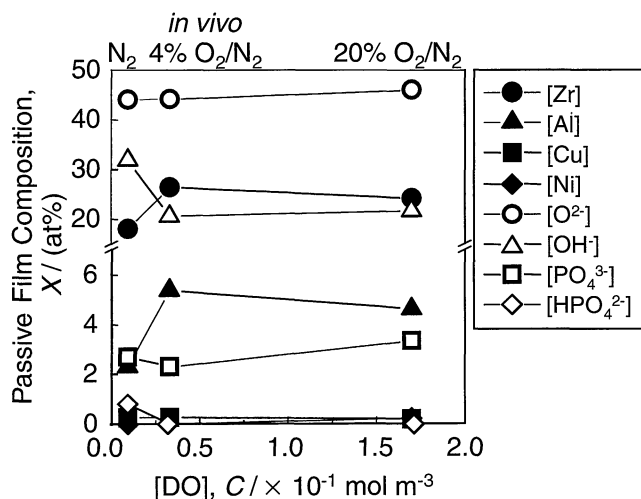


Fig. 3 Passive film composition of the  $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$  amorphous alloy polarized from  $-0.55$  to  $-0.2$  V in PBS(-) aerated with 0, 4, and 20%  $O_2/N_2$ . Zr, Zr oxide; Al, Al oxide; Cu, Cu oxide; Ni, Ni oxide;  $H_xPO_4^{(3-x)-}$ , ( $PO_4^{3-} + HPO_4^{2-}$ ).

### 3.3 Effect of dissolved oxygen on the passive film

The XPS peaks of Zr 3d, Al 2p, Ni 2p, and Cu 2p obtained on the passive film generated in the pH-7.5 solution with various [DO]s were decomposed into two peaks identified as metallic and oxide states according to the published binding energy data.<sup>12)</sup> The decomposition of the peaks of  $Cu^+$  and  $Cu^0$  is difficult, so Cu 2p peak was decomposed into two peaks identified as  $Cu^{2+}$  and ( $Cu^+ + Cu^0$ ) and ( $Cu^+ + Cu^0$ ) was assumed as metallic state in this study. Then, the concentration of metallic Cu was possibly larger than the exact value. O 1s and P 2p peaks were decomposed into two peaks identified as  $O^{2-}$  and hydroxide group,  $OH^-$ , and as  $PO_4^{3-}$  and  $HPO_4^{2-}$ , respectively.<sup>13)</sup>

The peaks of alloying elements identified as metallic state were originated from the substrate alloy and those identified as oxide state from the passive film. The composition of the passive film was plotted versus [DO] in Fig. 3.

In 4%  $O_2/N_2$  aerated solution, concentrations of Zr and Al, [Zr] and [Al], were the highest and concentrations of  $OH^-$ , and ( $PO_4^{3-} + HPO_4^{2-}$ ), [ $OH^-$ ] and [ $H_xPO_4^{(3-x)-}$ ], were the lowest among the tested conditions. The  $O^{2-}$  concentration, [ $O^{2-}$ ], in the solution aerated with 20%  $O_2/N_2$  was slightly higher than that with 4%  $O_2/N_2$ . Low concentration of nickel oxide, [Ni], was measured in the solution aerated with 20%  $O_2/N_2$ .

The  $E_{pit}$  in the PBS(-) with various [DO]s was plotted versus the relative ratios of [ $OH^-$ ] and [ $H_xPO_4^{(3-x)-}$ ] to the total cation concentration of the alloying elements, [TC], as shown in Figs. 4(a) and (b), respectively. The  $E_{pit}$  decreased with the increase in [ $OH^-$ ]/[TC] and [ $H_xPO_4^{(3-x)-}$ ]/[TC]. The [ $OH^-$ ]/[TC] and [ $H_xPO_4^{(3-x)-}$ ]/[TC] showed the lowest value in the solution aerated with 4%  $O_2/N_2$ .

## 4. Discussion

### 4.1 Effect of chloride ion

Zirconium based alloy is sometimes suffered from pitting corrosion in solutions containing  $Cl^-$ .<sup>14)</sup> The pitting corrosion of metallic biomaterial must be avoided not to dissolve large amount of metal ions causing the biological damages to the

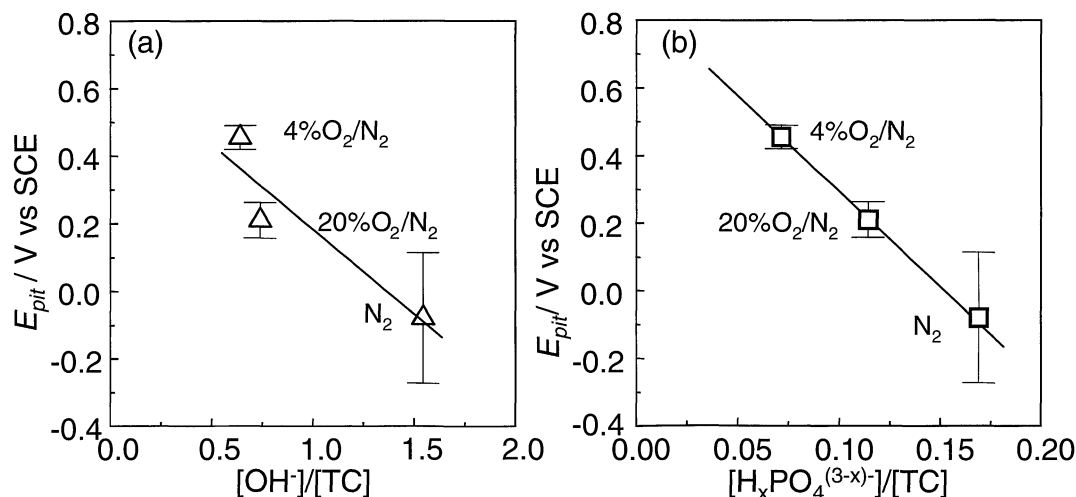


Fig. 4  $E_{pit}$  dependence on [ $OH^-$ ]/[TC] and [ $H_xPO_4^{(3-x)-}$ ]/[TC]. (a) [ $OH^-$ ]/[TC]; (b) [ $H_xPO_4^{(3-x)-}$ ]/[TC].  $H_xPO_4^{(3-x)-}$ , ( $PO_4^{3-} + HPO_4^{2-}$ ); TC, total cation in the passive film.

surrounding tissues.

The decrease in  $E_{\text{pit}}$  with the logarithmic increase in  $[\text{Cl}^-]$  (Fig. 1(b)) indicates that the  $\text{Cl}^-$  causes the pitting corrosion on the Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Cu<sub>17.5</sub> amorphous alloy.<sup>14)</sup> On the other hand, the  $E_{\text{pit}}$  of the amorphous alloy in the solution with  $1 \times 10^3 \text{ mol} \cdot \text{m}^{-3} [\text{Cl}^-]$  was higher than the  $E_{\text{open}}$  (Fig. 1(b)), indicating that the increase of  $[\text{Cl}^-]$  may not individually cause the spontaneous occurrence of pitting corrosion *in vivo*.

The dissolution of the alloy at  $E_{\text{open}}$  may increase with the increase in  $[\text{Cl}^-]$  because the  $R_p$  decreased with the increase in  $[\text{Cl}^-]$ . However the  $R_p$  values,  $(1-2.5) \times 10^2 \Omega \cdot \text{m}^2$ , in this range of  $[\text{Cl}^-]$  were as high as that of the crystalline pure titanium (Fig. 1(a)). Thus, this alloy possibly shows as high corrosion resistance as the crystalline pure titanium *in vivo*.

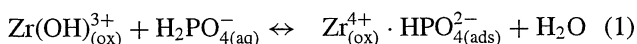
## 4.2 Effect of pH

The pitting corrosion resistance of the alloy decreased by the increase in  $E_{\text{open}}$  with the decrease in pH in both the deaerated and 4%O<sub>2</sub>/N<sub>2</sub> aerated solutions as shown in Fig. 2. The  $E_{\text{open}}$  increases with the decrease in pH on the alloy in the PCA.<sup>15)</sup> However, the  $E_{\text{pit}}$  was higher than the  $E_{\text{open}}$  even in the deaerated pH-2.2 solution. Thus, the decrease in pH may not individually cause the spontaneous pitting corrosion *in vivo*.

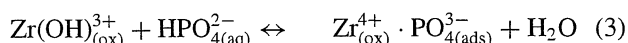
## 4.3 Effect of dissolved oxygen

[Al] in the passive film in the solution aerated with 4%O<sub>2</sub>/N<sub>2</sub> was larger than that in the deaerated solution (Fig. 3), indicating that dissolution of the surface probably decreases with DO. On the other hand, the increase in [Ni] and [O<sup>2-</sup>] with 20%O<sub>2</sub>/N<sub>2</sub> aeration (Fig. 3) indicates the increase in oxidation of the surface with large amount of DO. However, the decrease of [Al] and the increase of [OH<sup>-</sup>] and [H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup>] with 20%O<sub>2</sub>/N<sub>2</sub> aeration (Fig. 3) indicate that the structural defect of the passive film may increase with the enhancement of oxidation.

The [OH<sup>-</sup>] and [H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup>] changed simultaneously with the change of [DO] as shown in Fig. 3, because zirconium adsorbs H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup> to form zirconium phosphate on the passive film as the followings.<sup>13)</sup>



and



The OH<sup>-</sup> and H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup> in the passive film are possibly the target of Cl<sup>-</sup> because the  $E_{\text{pit}}$  decreased with the increase in [OH<sup>-</sup>]/[TC] and [H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup>]/[TC] (Fig. 4).

The  $E_{\text{pit}}$  increased with DO because the oxidation of the surface reduced the [OH<sup>-</sup>] and [H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup>] in the passive film. On the other hand, the enhancement of oxidation with the large amount of DO may prevent the dissolution of nickel and the dehydration of OH<sup>-</sup> in the passive film, so [Ni] and [OH<sup>-</sup>] increased to be targets of Cl<sup>-</sup>. Therefore, the  $E_{\text{pit}}$  was the highest with 4%O<sub>2</sub>/N<sub>2</sub> in this concentration range of DO.

Based on the results of this study, the Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Cu<sub>17.5</sub> amorphous alloy may be resistant to pitting corrosion *in vivo*

and is a promising biomaterial. On the other hand, the investigation of corrosion factors in biological environment is now in progress,<sup>16,17)</sup> so the evaluation of biomedical use of this alloy must be continued more carefully by examining other corrosion factors.

## 5. Conclusions

The biomedical use of Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Cu<sub>17.5</sub> amorphous alloy was evaluated by electrochemical measurement in phosphate buffered solutions with varying [Cl<sup>-</sup>], pH, and [DO]. This alloy possibly shows as high corrosion resistance as that of crystalline pure titanium because the  $R_p$  values in a [Cl<sup>-</sup>] range of this study were as high as that of titanium. On the other hand,  $R_p$  of this alloy and pitting corrosion resistance probably decrease with the increase in [Cl<sup>-</sup>] *in vivo*. The pitting corrosion resistance of the alloy also decrease with the decrease in pH of body fluid, however the alloy showed higher  $E_{\text{pit}}$  than  $E_{\text{open}}$  even in pH-2.2 solutions.

In pH-7.5 solutions with various [DO]s,  $E_{\text{pit}}$  was the highest in the solution aerated with 4%O<sub>2</sub>/N<sub>2</sub>. [Al] in passive film was the highest and [OH<sup>-</sup>] and [H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup>] were the lowest in the solution aerated with 4%O<sub>2</sub>/N<sub>2</sub>. On the other hand, nickel oxide was observed and [OH<sup>-</sup>] and [H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup>] increased in the passive film with 20%O<sub>2</sub>/N<sub>2</sub>, then the  $E_{\text{pit}}$  with 20%O<sub>2</sub>/N<sub>2</sub> was lower than that with 4%O<sub>2</sub>/N<sub>2</sub>. The  $E_{\text{pit}}$  decreased with the increase in [OH<sup>-</sup>] and [H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup>], therefore, the OH<sup>-</sup> and H<sub>x</sub>PO<sub>4</sub><sup>(3-x)-</sup> in the passive film may be the targets of Cl<sup>-</sup> on this alloy.

These results indicate that the Zr<sub>65</sub>Al<sub>7.5</sub>Ni<sub>10</sub>Cu<sub>17.5</sub> amorphous alloy is a promising biomaterial. However, further study must be continued to evaluate the biomedical use of the amorphous alloy.

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