

The Influence of Albumin on Corrosion Resistance of Titanium in Fluoride Solution

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Proteins can interact with corrosion reactions in several ways. In this study, we investigated the effect of albumin on the corrosion resistance of titanium in the presence of fluoride. The effects of the NaF concentration, albumin concentration, and pH on the corrosion characteristics of commercially pure titanium (CP-Ti) were examined by means of electrochemical techniques.

The corrosion resistance of titanium decreased as the NaF concentration increased and as pH decreased. The corrosion resistance of titanium in NaF solutions was improved in the presence of albumin. The natural electrode potential was elevated, and the passive current density was reduced by albumin at a concentration of 0.01%. The polarization resistance rose with increased concentrations of albumin in fluoride solution. These results showed that the albumin in saliva and dental plaque affected the corrosion resistance of CP-Ti in fluoride solution.

Key words: Corrosion resistance, Titanium, Albumin

INTRODUCTION

Strong passive films are formed on the surface of titanium, which provides high corrosion resistance under acidic environments and against various kinds of chemical agents. Thompson *et al.*¹⁾, Speck *et al.*²⁾, Gettleman *et al.*³⁾, Brune *et al.*⁴⁾, and Matsuno⁵⁾ compared the corrosion resistance of titanium with that of other dental alloys, and showed that the corrosion resistance of titanium was superior to those of stainless steel, Co-Cr alloy, Ni-Cr alloy, and gold alloy. However, in the environments where chelate ions of titanium are formed in the presence of fluoride ions, both corrosion⁶⁾ and discoloration⁷⁾ have been reported to occur. Fluorides possess protective effects against dental caries, but Pröbster *et al.*⁸⁾ noted that prophylactic agents containing fluoride must be used with great care on implant materials and crown restorations made of titanium. Ozeki *et al.*⁹⁾ reported that titanium and titanium alloys were resistant to dentifrice containing fluoride up to the concentration of 1,000 ppm but were severely corroded by acidic topical agents containing about 9,000 ppm fluoride. Oda *et al.*¹⁰⁾ reported that the corrosion resistance of titanium was not sufficient in the presence of 0.5% or higher concentrations of sodium fluoride. Nakagawa *et al.*¹¹⁾ also reported that the passive film on the surface of titanium was destroyed under the conditions where 30 ppm or more hydrogen fluoride was generated by electrolytic dissociation of sodium fluoride.

Saliva contains 99.5% water in the oral cavity, and approximately one-third of the remaining 0.5% is organic compounds including salivary protein of 200-500 mg/100 ml¹²⁾. Albumin contains approximately 1% of the salivary protein, and the albumin originating from the blood plasma exists in dental plaque. Compared with other metals, titanium adsorbs plasma protein more rapidly¹³⁻¹⁵⁾, and albumin has been reported to influence the corrosion resistance of dental alloys. However, the effects of albumin on the corrosion resistance of titanium in the presence of fluorides have not been studied.

In the present study, we examined the effects of albumin on corrosion resistance of titanium in various pHs and concentrations of sodium fluoride using several electrochemical measurements, regarding such as natural electrode potential, polarization resistance, and potentiodynamic polarization.

MATERIALS AND METHODS

Materials

1) Samples

Commercial pure titanium boards (KS50, JIS type 2: Kobe Steel, Tokyo, Japan) were cut out square plates measuring 14 mm×14 mm×2 mm, polished successively with water-resistant abrasive papers #180, #400, #600, and then subjected to electrochemical measurements.

2) Preparation of sodium fluoride solutions

To examine the effects of the sodium fluoride (NaF) concentration and pH on the corrosion resistance of titanium, NaF (Wako Pure Chemicals, Osaka, Japan) was dissolved at concentrations of 0.05-1.0 mass%, and the pH of the solution at each concentration was adjusted to 3.5-6.9 with phosphoric acid (H₃PO₄: JIS K9005, Wako Pure Chemicals, Osaka, Japan). The 0.9% NaCl solution was prepared as a control solution.

To examine the effects of albumin on the corrosion of titanium, the 0.2% NaF at pH 5.0 was supplemented with albumin (bovine serum, fatty acid free, pH 7, Wako Pure Chemicals, Osaka, Japan) at final concentrations of 0.01-0.5 mass%.

Measurement

1) Electrochemical measurement

To perform electrochemical measurements, a potentiostat Model 273 and corrosion software M352C (EG & G PARC, Princeton, NJ, USA) were used. The NaF solution described above was filled in an electrochemical corrosion test cell in a water-bath at 37°C and deaerated with nitrogen gas for 30 min. The reference and counter electrodes consisted of a saturated calomel electrode (SCE) and a platinum electrode, respectively.

Polished titanium samples were exposed to air for 1 hour, immersed in the test solution for 5 min using a sample holder (exposed area of a sample: 1 cm²), and then the natural electrode potential and polarization resistance were measured. The linear

polarization resistance was measured by scanning the potential at a rate of 0.1 mV/s within a range of ± 20 mV from the natural electrode potential.

Potentiodynamic polarization curves¹⁶⁻¹⁸⁾ were obtained by plotting the relation between the potential and current density measured by polarization within a range from -1.2 V to +1.0 V at a scanning rate of 0.33 mV/s. The corrosion and passivation potentials, and passive current density¹⁷⁾ at 0.3 V were determined by the potentiodynamic polarization curves. This measurement was performed 3 times. ANOVA and Scheffes test ($\alpha = 0.05$) were used to compare significant differences in the natural electrode potential, polarization resistance and passive current density for the specimen groups.

2) Measurement of the concentration of fluoride ions

The concentration of fluoride ions in 0.2% NaF at various pH values and 0.2% NaF - pH 5.0 which had been supplemented with albumin at the final concentration of 0.01%-0.5% was measured using an ion meter (IM-40S, Toa Denpa, Tokyo, Japan). The measurement was performed 3 times.

3) SEM observation

The surface of each sample after potentiodynamic polarization measurement was observed using a field emission scanning electron microscope (JSM-6340F, JEOL, Akishima, Japan).

RESULTS

Electrochemical measurement

1) Effects of NaF concentration and pH

(1) Natural electrode potential

The natural electrode potential obtained by immersing titanium samples in NaF solutions with different concentrations and pHs are shown in Table 1. The natural elec-

Table 1 Natural electrode potentials of titanium for different concentrations of NaF versus pHs of NaF solution

| | | Potentials (V vs SCE) | | | | | |
|-----------|----|-----------------------|---------|--------|--------|---------|--------|
| mass% | pH | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 | 6.9 |
| 0.05% NaF | | -1.03 | -0.75 | -0.39 | -0.41 | -0.48 | -0.38 |
| | | (0.02) | (0.44) | (0.06) | (0.04) | (0.09) | (0.03) |
| 0.1 " | | -1.05 | -1.16 | -0.62 | -0.46 | -0.36 | -0.43 |
| | | (0.05) | (<0.01) | (0.22) | (0.08) | (0.16) | (0.10) |
| 0.2 " | | -0.97 | -1.14 | -1.17 | -0.63 | -0.49 | -0.46 |
| | | (0.03) | (0.02) | (0.02) | (0.02) | (0.06) | (0.07) |
| 0.5 " | | -1.01 | -1.02 | -1.10 | -0.97 | -0.84 | -0.54 |
| | | (<0.01) | (0.01) | (0.01) | (0.37) | (0.24) | (0.11) |
| 1.0 " | | -1.02 | -1.06 | -1.08 | -1.15 | -1.23 | -0.58 |
| | | (0.01) | (<0.01) | (0.02) | (0.03) | (<0.01) | (0.10) |
| 0.9% NaCl | | -0.48 | | | | | -0.45 |
| | | (0.16) | | | | | (0.02) |

(S.D.)

trode potential varied on the time elapse. The values at 5 min was compared in this study. The natural electrode potential of the titanium samples immersed in 0.9% NaCl as the control was around -0.45 V in different pH solutions at 6.9 and 3.5. The natural electrode potential of the titanium sample immersed in NaF solutions was markedly affected by their pH and concentration. In the 0.05% NaF at pHs 6.9-4.5, the natural electrode potential was not significantly different from that in the control solution (0.9% NaCl, pH 6.9), but the natural electrode potential was reduced to -1.03 ± 0.02 V (mean \pm SD) in the 0.05% NaF at pH 3.5, which was significantly lower than that in the control solution ($p < 0.01$). The natural electrode potential was significantly lower in the 0.1% NaF solution at a pH less than 4.5. In addition it was significantly lower in the 1.0% NaF at a pH of 5.5 and less ($p < 0.01$). The natural electrode potential was examined in NaF solutions at several fixed pH values. At pH 6.9, the natural electrode potential was -0.58 ± 0.10 V in the 1.0% NaF which was significantly lower than -0.38 ± 0.03 V in the 0.05% NaF at same pH ($p < 0.01$). At pH 4.5, the natural electrode potential was -0.62 V in the 0.1% NaF which was significantly lower than -0.39 V in the 0.05% NaF at the same pH ($p < 0.01$). The decreased rate was more rapid at pH 4.5 than at pH 6.9. At pH 3.5, the natural electrode potential was markedly reduced to -1.03 ± 0.02 V in the 0.05% NaF.

(2) Polarization resistance

Table 2 shows the polarization resistance obtained by immersing the titanium sample in NaF solutions at different concentrations and pHs. The maximal polarization resistance was 277 ± 121 $k\Omega \cdot cm^2$ in 0.9% NaCl (pH 6.9) as the control. The polarization resistance of the titanium samples immersed in 0.05% NaF was 91 ± 18 $k\Omega \cdot cm^2$ at pH 6.9, 25 ± 18 $k\Omega \cdot cm^2$ at pH 5.5, 10 ± 6 $k\Omega \cdot cm^2$ at pH 4.5, and 0.3 ± 0.1 $k\Omega \cdot cm^2$ at pH 3.5, showing decreases in the polarization resistance with decreases in pH. The polarization resistance in NaF solutions at fixed pHs was as follows. At pH 6.9, the polarization resistance was 88 ± 42 $k\Omega \cdot cm^2$ in the 0.1% NaF, 22 ± 17 $k\Omega \cdot cm^2$ in the

Table 2 Polarization resistances of titanium for different concentrations of NaF versus pHs of NaF solution

| pH mass% | | Resistances ($k\Omega \cdot cm^2$) | | | | | |
|-------------|---|--------------------------------------|-----------------|-----------------|------------------|------------------|--------------------|
| | | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 | 6.9 |
| 0.05%NaF | | 0.33 (0.11) | 1.41 (2.03) | 10.01 (5.91) | 51.40 (25.31) | 25.12 (18.45) | 90.95 (18.45) |
| 0.1 | " | 0.28 (0.04) | 0.47 (0.18) | 3.79 (3.42) | 13.79 (16.39) | 9.65 (2.83) | 88.42 (42.47) |
| 0.2 | " | 0.11 (0.07) | 0.14 (0.04) | 0.23 (0.07) | 10.29 (1.97) | 14.51 (9.51) | 21.61 (16.78) |
| 0.5 | " | 0.03 (0.01) | 0.03 (<0.01) | 0.08 (<0.01) | 0.25 (0.14) | 1.11 (1.66) | 33.96 (17.68) |
| 1.0 | " | 0.01 (0.01) | 0.02 (<0.01) | 0.05 (0.05) | 0.11 (0.11) | 0.19 (0.16) | 4.11 (3.25) |
| 0.9%NaCl | | 55.62 (49.48) | | | | | 276.73 (121.38) |

(S.D.)

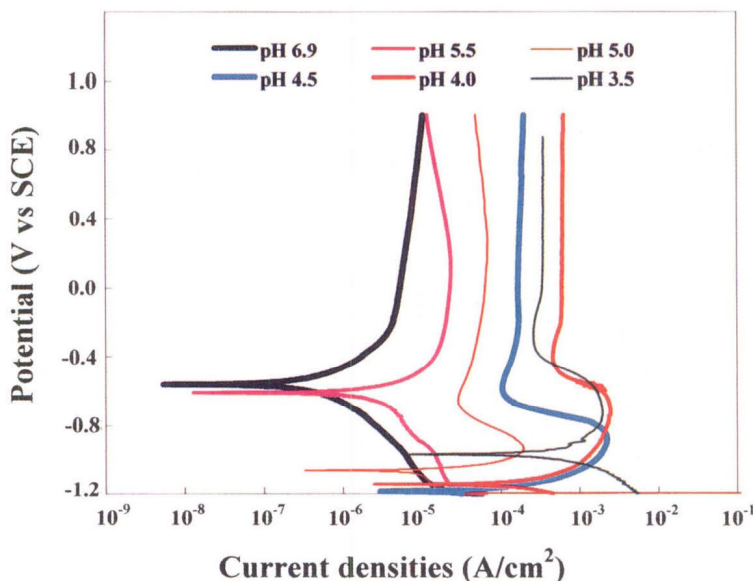


Fig.1 Typical potentiodynamic polarization profiles of titanium in 0.2% NaF at different pH.

0.2% NaF solution, and $4 \pm 3 \text{ k}\Omega \cdot \text{cm}^2$ in the 1.0% NaF, showing decreases in the polarization resistance with increases in the concentration.

(3) Potentiodynamic polarization curve

Typical potentiodynamic polarization profiles in 0.2% NaF are shown in Fig. 1. The corrosion potential was less than -1.0 V at pHs lower than 5.0 in the NaF solutions. At pH 5.0, the current density was approximately $50 \mu\text{A}/\text{cm}^2$ at a potential above -0.4 V , while the current density increased to more than $350 \mu\text{A}/\text{cm}^2$ at pH 4.5. With changes in pH to the neutral level, the corrosion potential increased, showing approximately -0.4 V at pH 6.9. The current density remained at an almost constant level (about $10 \mu\text{A}/\text{cm}^2$) until the 1.0 V of the potential. Similar findings were observed in the NaF solutions at other concentrations. With increases in the NaF concentration, the pH at which titanium maintained a passive current density less than $100 \mu\text{A}/\text{cm}^2$ tended to shift from the acidic range to the neutral range.

2) Effects of albumin on electrochemical properties

(1) Natural electrode potential and polarization resistance

The natural electrode potential and polarization resistance of the titanium samples immersed in 0.2% NaF (pH 5.0) to which albumin had been added at the final concentration of 0.01-0.5% are shown Fig. 2. The natural electrode potential increased from $-0.63 \pm 0.02 \text{ V}$ to $-0.23 \pm 0.07 \text{ V}$ by the addition of albumin to 0.01%. When additional albumin was increased the natural electrode potential remained stable at approximately -0.25 V . With an increase in the amount of added albumin, the polarization resistance increased. The addition of albumin to a concentration of

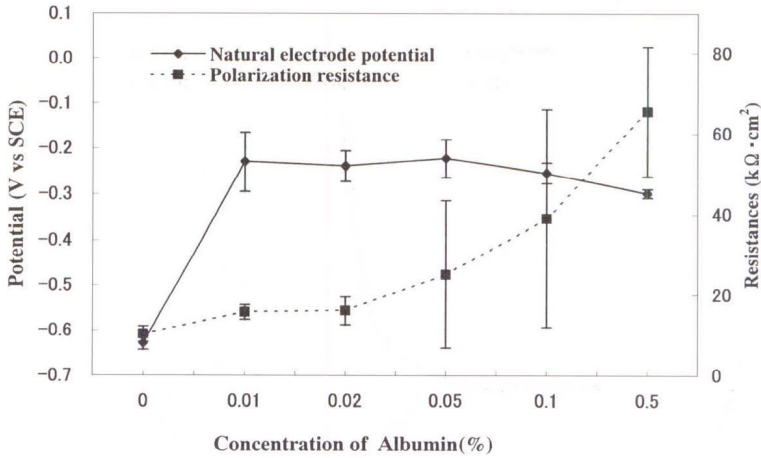


Fig. 2 Natural electrode potentials and polarization resistances versus concentration of albumin in 0.2% NaF at pH 5.0. (Vertical lines reveal the standard deviation)

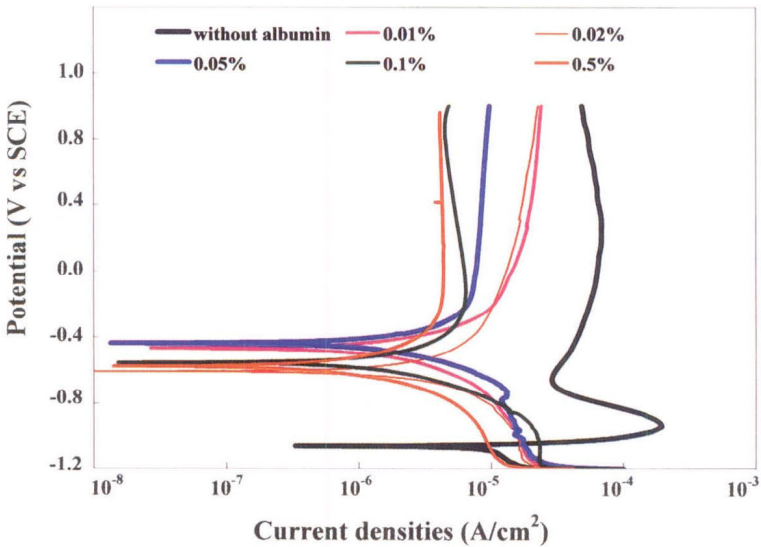


Fig. 3 Typical potentiodynamic polarization profiles of titanium in 0.2% NaF (pH 5.0) with various concentrations of albumin.

0.5% increased the polarization resistance from $10 \pm 2 \text{ k}\Omega \cdot \text{cm}^2$ to $65 \pm 16 \text{ k}\Omega \cdot \text{cm}^2$.

(2) Potentiodynamic polarization curve

Fig. 3 shows the potentiodynamic polarization curves of the titanium sample immersed in 0.2% NaF (pH 5.0) to which albumin had been added at 0.01-0.5%. Without the addition of albumin, the passive current density at a potential of about -0.4 V was approximately $50 \mu\text{A}/\text{cm}^2$, and the value decreased as albumin was added. At

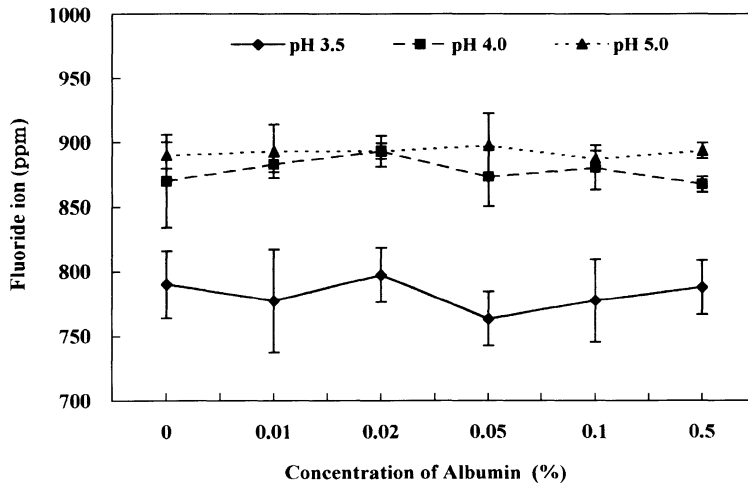


Fig. 4 Concentration of fluoride ion in 0.2% NaF including various concentrations of albumin. (Vertical lines reveal the standard deviation)

a concentration of 0.05% albumin, the passive current density remained less than $10 \mu\text{A}/\text{cm}^2$.

Measurement of the concentration of fluoride ions

The effects of albumin on the concentration of fluoride ion in 0.2% NaF are shown in Fig. 4. The concentration of fluoride ions ranged from 850 to 890 ppm at a pH greater than 4.0, but less than 800 ppm at pH 3.5, the difference was significant ($p < 0.01$). The concentration of fluoride ions remained almost unchanged by adding various amounts of albumin (0-0.5%) to the 0.2% NaF, suggesting that there were no significant effects of albumin on the concentration of fluoride ions in the NaF.

SEM observation

The surface morphology of the samples after potentiodynamic polarization measurement was quite different with and without albumin. The surface of the titanium samples immersed in the 0.2% NaF (pH 4.0) without albumin was rough (Fig. 5 (a)), and that in the 0.2% NaF (pH 4.0) with 0.5% albumin was smooth (Fig. 5 (b)). No marked difference was recognized for both samples with 0.5% albumin (Fig. 5 (b)) and that before measurement (Fig. 5 (c)).

DISCUSSION

Effects of NaF concentration and pH

The position of titanium in the electrochemical series is less noble, with the theoretical value of the standard potential of $\text{Ti}^{2+} + 2e^- \rightleftharpoons \text{Ti}$ at -1.63 V , and Ti is dissolved in the form of Ti^{3+} under an activated state¹⁹⁾. However, it readily becomes the passive

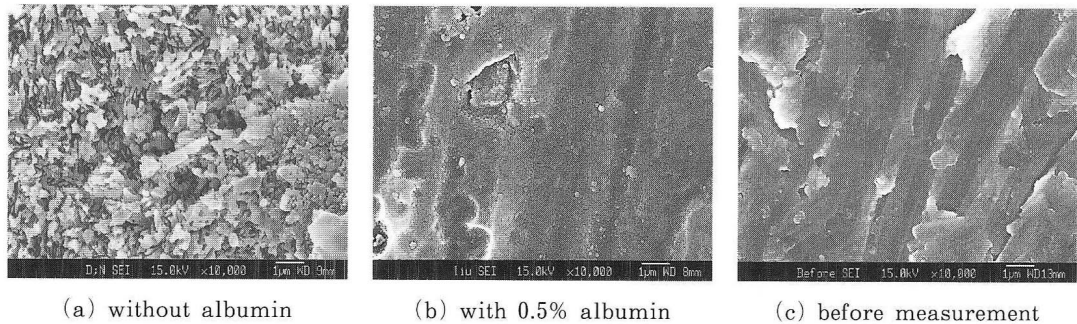


Fig. 5 SEM images of the surface of titanium specimen after electrochemical measurement in 0.2% NaF at pH 4.0.

state in aerated solutions of dilute acid or alkali, and was covered with nonstoichiometric oxide film. Therefore, titanium is noble in seawater, and shows excellent corrosion resistance without pitting and crevice corrosion in oxidizing environments and even in environments with Cl^- ion such as seawater and the control solution used in this study¹⁹⁾. Matsuno⁵⁾ reported that the corrosion resistance of titanium and titanium alloys as dental materials were higher than those of dental gold alloys accompanied by weight and color in artificial saliva in addition electrochemical findings. In the present study, the natural electrode potential of the titanium sample immersed in 0.9% NaCl at a pH range of 6.9 and 3.5 was stable (-0.45 V and -0.48 V), showing no significant differences (Table 1).

It is also known that the corrosion resistance of titanium is poor in non-oxidized environments such as in HF solution, fluoride, HCl and H_2SO_4 ^{9,19)}. In the NaF solutions used for immersing the titanium sample in the present study, the natural electrode potential varied with the pH. The natural electrode potential was decreased by acidifying the NaF solution, and the reactivity increased slightly (Table 1). These results suggested that the concentration and pH of NaF solution affected the reactivity of titanium, and the natural electrode potential was decreased by an increase in NaF concentration or an acidification of NaF solution. The results of the polarization resistance were similar to those of the natural electrode potential. With increases in the NaF concentration and with decreases in pH, the polarization resistance decreased, showing that the corrosion reaction readily occurred in the immersion solution. The passive current density determined at 0.3 V from the potentiodynamic polarization curves showed similar results. The passive current density was higher than $100 \mu\text{A}/\text{cm}^2$ at concentrations of NaF higher than 1.0% and 0.1% at pH 6.9 and pH 3.5, respectively, showing that titanium corrodes easily in environments severer than these conditions. Nakagawa *et al.*¹¹⁾ clarified that the natural electrode potential changes markedly at pH 3.7-3.8 in 0.05% NaF solution and at pH 4.7-4.8 in 0.2% NaF, and suggested that there are limit values for the corrosion resistance. The present study showed similar results, but no marked differences in the corrosion resistance were detected around the limit value by measurement of the polarization

resistance and the findings of polarization. The present results showing that the corrosion resistance was gradually reduced regardless of the limit value.

Effects of albumin on corrosion resistance of titanium

Titanium is covered with a passive film, titanium used as restoration and implant materials in the mouth is likely to adsorb plasma protein. Many suggested have indicated that a large amount of albumin exists in saliva and dental plaque, and that albumin is particularly well adsorbed by titanium¹³⁻¹⁵. Topical fluoride agents and fluoride mouth-rinsing agents are recommended for the prevention of dental caries in patients who undergo orthodontic treatment²⁰. The standard prescription of fluoride mouth-rinsing agents is 0.2% NaF (F⁻: 900 ppm) for weekly rinsing or 0.05% NaF (F⁻: 225 ppm) for daily rinsing. In the present study, the effects of albumin, which is present in saliva, dental plaque and blood, were examined by adding albumin to 0.2% NaF solution (pH 5.0). Bovine serum albumin, which is commonly used in *in vitro* examinations, was used^{21,22}. With an increase in the amount of added albumin, the natural electrode potential and the polarization resistance increased (Fig. 2), the passive current density on the potentiodynamic polarization curves decreased significantly ($p < 0.01$). At different NaF concentrations (0.05%-1.0%) and pHs (6.9-3.5), the natural electrode potential was examined. The natural electrode potential was higher under all conditions added with albumin than those without albumin. The passive current density at 0.3 V (Fig. 3), which was determined on the potentiodynamic polarization curves, was higher than $50 \mu\text{A}/\text{cm}^2$ without albumin, but significantly reduced to less than $20 \mu\text{A}/\text{cm}^2$ by the addition of albumin to 0.01% ($p < 0.05$). The passive current density obtained by the addition of albumin to 0.5% was approximately $10 \mu\text{A}/\text{cm}^2$, which was less than 1/6 of that without albumin. This suggested that the dissolution of titanium was reduced. Titanium is suggested to be less affected in the presence of albumin and salivary protein by fluoride at low concentrations such as in fluoride mouth-rinsing agents.

The effects of protein on the corrosion of alloys, of which passive film prevents corrosion as in titanium have been studied. Brown *et al.*²³ reported that protein enhanced dissolution of stainless steel by means of measurement of elemental release. Williams *et al.*²⁴ also reported that protein enhanced the corrosion of stainless steel and titanium. Isami²⁵ reported that dissolution of nickel was enhanced by the addition of albumin by means of measurement of elemental release, while Wataha *et al.*²⁶ reported that dissolution of nickel from Ni-Cr alloy was decreased by 3% of BSA. The effects of albumin on the corrosion resistance of metals are controversial, with different results being reported depending on sample conditions and environments. In the present study, it was shown that albumin reduced the reactivity of titanium to NaF.

Nakagawa *et al.*¹¹ examined the relation between the concentration of fluoride ion or HF, and corrosion of titanium, and reported that titanium was dissolved by HF. To elucidate the effects of added albumin on the concentration of fluoride ion or HF, we examined the relation between the concentration of fluoride ion in the NaF

and the concentration of added albumin (Fig. 4). The concentration of fluoride ion in NaF depend on the pH, because F^- is easy to change to HF at a pH less than 4 via reactions such as $HF \rightleftharpoons F^- + H^+$. The concentration of fluoride ion was constant, irrespective of the concentration of added albumin (Fig. 4), showing that the added albumin did not affect the concentration of fluoride ion in the NaF solution.

Since pH might be altered by the addition of albumin, the pH of 0.2% NaF was adjusted to 5.0 and measured after the addition of albumin. The pH was 5.02 in the presence of 0.01% albumin, 5.07 in the presence of 0.02% albumin, 5.12 in the presence of 0.05% albumin, 5.21 in the presence of 0.1% albumin, and 5.61 in the presence of 0.5% albumin, showing a gradual shift to the neutral range. Therefore, the possibility that the buffer action of albumin was involved in the improvement of the corrosion resistance of titanium samples could not be excluded. However, the passive current density at 0.3 V in the 0.2% NaF at pH 5.0 was reduced from 52 to $8 \mu A/cm^2$ by the addition of albumin to 0.5% (Fig. 3). This current density shows a higher corrosion resistance than $17 \mu A/cm^2$ of the passive current density in the 0.2% NaF at pH 5.5, which was equivalent to that after the addition of albumin. The changes in the polarization resistance caused by adding albumin were larger. The polarization resistance improved from 10 to $65 k\Omega \cdot cm^2$ (Fig. 2). This was significantly higher than $14.5 k\Omega \cdot cm^2$ (Table 2) in the 0.2% NaF at pH 5.5, which was equal to the value after adding albumin, showing that the corrosion resistance of titanium was improved by other mechanisms rather than by the buffering action of albumin.

The surface configuration was markedly different depending on whether albumin existed. There was no marked difference between the sample of with albumin and that of before potentiodynamic polarization measurement (Fig. 5). Since albumin is easily adsorbed on the surface of titanium, the corrosion resistance of titanium would be improved by adsorption of albumin. Since it is clear that the corrosion of titanium by NaF was improved by adding albumin, the presence of protein should be considered when evaluating the corrosion resistance of titanium in the presence of fluoride.

CONCLUSIONS

In this study, we examined the effects of the concentration of sodium fluoride and pH on the electrochemical properties of titanium. We also evaluated the effects of albumin under these conditions. The results are summarized as follows.

1. The corrosion resistance of titanium decreased as the NaF concentration increased and pH decreased. The corrosion resistance could not be maintained in 0.05% NaF at a pH less than 4.5, and in 0.2% NaF at a pH less than 5.0. Under the neutral condition (pH 6.9), the corrosion resistance of titanium could also not be maintained in the NaF with a concentration higher than 0.5%.

2. The corrosion resistance of titanium in NaF solutions was improved in the presence of albumin. The natural electrode potential was elevated, and the passive current density was reduced by albumin at a concentration of 0.01%. The polarization

resistances gradually increased with the concentration of albumin in fluoride solution.

These results showed that the presence of albumin is important when evaluating the corrosion resistance of titanium.

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