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Effect of Fluoride Concentration and pH on Corrosion Behavior of Titanium for Dental Use

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Abstract. Titanium is used as a metal for biocompatible materials such as dental implants or restorations because of its excellent chemical stability. However, the corrosion of Ti in the prophylactic fluoride-containing environment can become problematic. To clarify the effects of fluoride concentration and pH on the corrosion behavior of Ti, we conducted anodic polarization and immersion tests in NaF solution of various concentrations and pH values. The concentrations of dissolved Ti in the test solutions were analyzed by inductively coupled plasma mass spectroscopy. There were obvious limits of fluoride concentration and the pH value at which the corrosion behavior of Ti changed. The corrosion of Ti in the solution containing fluoride depended on the concentration of hydrofluoric acid (HF). When the HF concentration in the solution was higher than about 30 ppm, the passivation film of the Ti was destroyed. The results of this study revealed a relation between the fluoride concentrations and pH values at which Ti corrosion occurred and provided data on such corrosion in environments where the fluoride concentration and pH value are known.

Key words: titanium, corrosion, fluoride.

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Introduction

Titanium is a very active metal with a standard reduction potential approaching that of aluminum. On the other hand, titanium has an excellent chemical stability, generates a highly protective oxide film on its surface, and becomes passive. Therefore, titanium shows excellent corrosion resistance in various test solutions, such as artificial saliva, Ringer's solution, 0.9% NaCl solution, or physiological saline solution. Because of these and other characteristics, titanium is used for dental implants and restorations. However, it has been reported that the corrosion resistance of titanium was lost in solution which contained fluoride (Lausmaa *et al.*, 1985; Probster *et al.*, 1992). Pure titanium (CP titanium) and titanium alloy cannot withstand exposure to NaF solution exceeding a concentration of 0.5% (Oda *et al.*, 1996). Titanium was not considered to be corrosion-resistant in a solution containing 500 ppm F (Mimura and Miyagawa, 1996). The commercial dental gels and rinses containing fluoride from 1000 to 10000 ppm, with a pH between about 3.5 and neutral, are frequently used for caries-preventive prophylactic applications. The use of fluoride-containing rinses or gels might be harmful to titanium devices if the pH of these prophylactic materials is below neutral (Boere, 1995; Toumelin-Chemla *et al.*, 1996). Thus, the corrosion of titanium seems to depend not only on fluoride concentration but also on pH. There should be a close relation between those factors. However, the above-cited studies have not elucidated how fluoride and pH affect the corrosion behavior of titanium. The aim of the present study was to clarify the relation between the fluoride concentrations and pH values at which titanium corrosion occurred.

Materials and methods

Materials

A commercially pure titanium (CP titanium) plate (JIS grade 2) was embedded in epoxy resin. The specimen was polished to #1500 with waterproof grinding paper and washed by ethanol. The exposed surface area of the titanium specimen was 0.4 to 0.6 cm^2.

Test solutions

As test solutions, we used 0.02 to 2.0% NaF (90.5 to 9048 ppm F) solutions and artificial saliva (NaCl, 0.4 g; KCl, 0.4 g; $CaCl_2 \cdot 2H_2O$, 0.795 g; $NaH_2PO_4 \cdot 2H_2O$, 0.78 g; $Na_2S \cdot 9H_2O$, 0.005 g; NH_2CONH_2, 1.0 g; distilled water, 1000 mL). To examine the effect of pH, we varied the acidity of the electrolyte within the range of pH 3.0 to 7.0 by adding H_3PO_4. The temperature of the test solution was maintained at 37 ± 0.1°C; the solution was stirred at 200 rpm by means of a magnetic stirrer.

Corrosion test

The counter and reference electrodes were platinum and KCl-saturated Ag/AgCl electrodes, respectively. The potential of the reference electrode (E) is denoted by E(Ag/AgCl) = E (saturated calomel electrode [SCE]) + 48.4 mV. The test solutions were de-aerated with pure nitrogen gas ($N_2 \geq 99.999$ vol%) at a flow rate of 150 mL/min. Cathodic treatment was performed at - 1.0 V for 300 sec in the test solution. After the specimens were left for 20 min at the natural potential, the anodic polarization curves were obtained (Potentiostat HA-301 and Function generator HB-104, Hokuto Denko, Osaka, Japan). Potential was scanned from natural potential (corrosion potential) to +2000 mV (*vs.* KCl-saturated Ag/AgCl electrode) at the scanning rate of 1 mV/sec. We conducted a series of immersion tests to measure the changes in the natural electrode (open circuit) potential of titanium compared with immersion time in the test solution without de-aeration.

Analysis of dissolved titanium and fluoride concentrations

The concentrations of titanium dissolved in the test solution after polarization and immersion tests were analyzed by inductively coupled plasma mass (ICP-MS) spectroscopy (PMS 2000, Yokogawa, Tokyo, Japan). The concentrations of fluoride ion in the original test solutions were analyzed by means of an ion meter (Microprocessor Ionalyzer/901, Orion Research, USA) with a combination of fluoride electrodes (9609BN, Orion Research, Boston, MA, USA). Each measurement was repeated five times under the same conditions. Results were statistically analyzed by ANOVA with Scheffé's test at a significance level of 1%.

Results

Anodic polarization test

The anodic polarization curves in 0.1% NaF solution at pH 4.0 and 7.1 are shown in Fig. 1. The anodic polarization curve in artificial saliva is shown for comparison.

The anodic polarization curves in 0.1% NaF solution with pH values between 3.0 and 5.0 are shown in Fig. 2a. There is a difference in the corrosion potentials between pH below 4.2 and pH above 4.3. A similar difference also exists between pH 5.4 and 5.5 in 0.5% NaF solution (Fig. 2b).

Immersion test

Changes in the natural electrode (open circuit) potentials with immersion time in 0.05% NaF solution are shown in Fig. 3a. There is a marked difference in the natural electrode potential on both sides of the boundary between pH 3.8 and 3.7. A similar difference also exists between pH 4.8 and 4.7 in 0.2% NaF solution (Fig. 3b).

Analysis of dissolved titanium

Fig. 4 shows the amounts of titanium dissolved in the solution after anodic polarization from corrosion potential to +2000 mV (a) and immersion for 24 hrs (b) in 0.05% and 0.1% NaF solutions at various pH values. The amounts of titanium dissolved from the specimens decreased significantly ($p < 0.01$) as the values of pH increased.

Analysis of fluoride ion concentrations

Concentrations of fluoride ion and hydrofluoric acid (HF) in 0.05% and 0.1% NaF at various pH values are shown in the Table. The concentration of the fluoride ion decreased significantly ($p < 0.01$) as the value of pH decreased. We calculated the HF concentrations by assuming that the amount of F^- ion, which was the difference between the nominal F^- ion concentration and the measured one, was consumed to form HF. In the last column of the Table, "H" and "L" symbolize the test solution in which the corrosion potential was low (approximately -1000 mV) and high (approximately -500 mV), respectively, in the anodic polarization test (Fig. 2).

Discussion

From the results of this study, it is clear that the corrosion behavior of titanium is affected not only by fluoride concentration but also by pH. It was reported that a tarnish of titanium alloys was recognized in 30 ppm NaF solution (Lausmaa *et al.*, 1985). In this study, corrosion of titanium was not recognized in the solution of 0.1% NaF (1000 ppm NaF) at

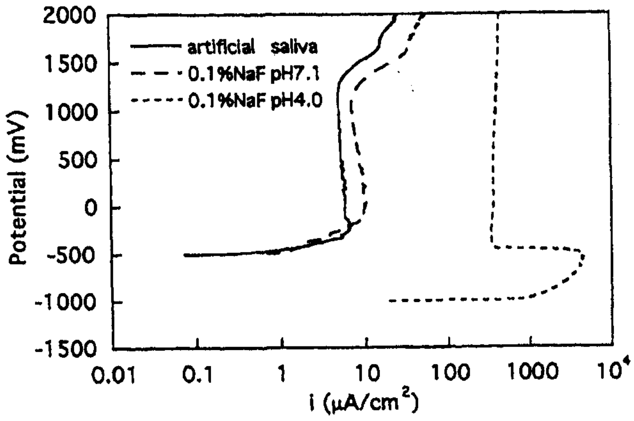

Figure 1. Anodic polarization curves of titanium in 0.1% NaF at pH 4.0 and 7.1 and in artificial saliva at 37°C.

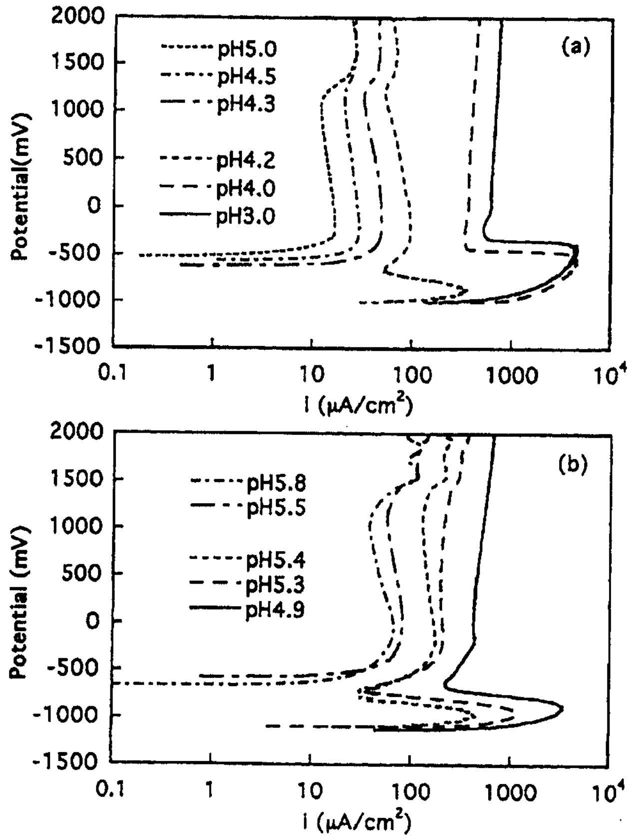

Figure 2. Anodic polarization curves of titanium in 0.1% NaF (a) and 0.5% NaF (b) at various pH values.

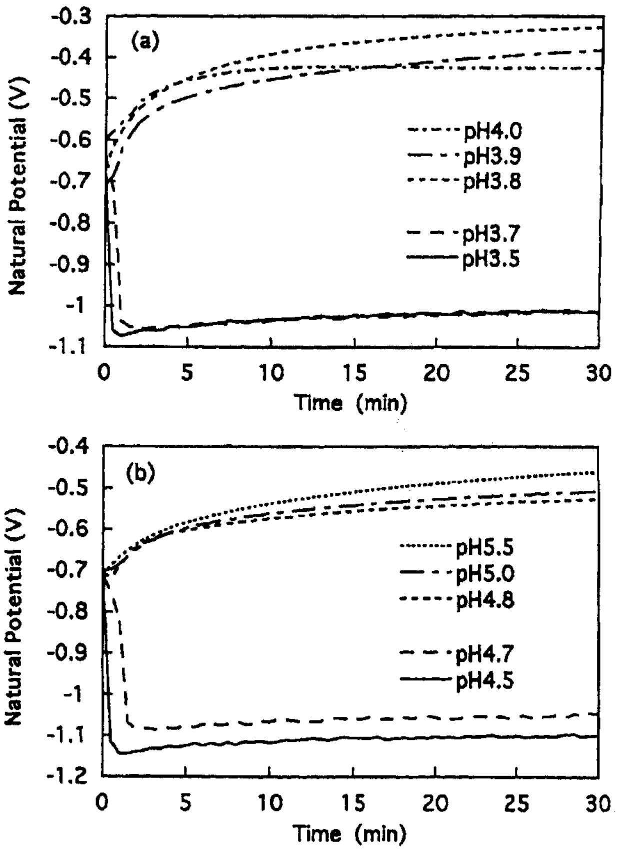

Figure 3. Changes in natural potential of titanium with time in 0.05% NaF (a) and 0.2% NaF (b).

pH 7.1, because the anodic polarization curve was similar to that in artificial saliva and indicated the passivation of titanium. Therefore, it was thought that a tarnish of titanium did not occur if the pH value of the solution was neutral or higher than neutral. In prophylactic gels or solutions containing 400 to 9000 ppm F, corrosion of titanium was often recognized (Probster *et al.*, 1992), because the pH of these gels and solutions was usually lower than neutral. In this study, corrosion of titanium also took place in the acidic solution containing 0.05% NaF (226.2 ppm F) to 2% NaF (9048.8 ppm F). It was reported that titanium was not considered to be corrosion-resistant in the solution containing 500 ppm F at pH 4 (Mimura and Miyagawa, 1996). This agrees with the results of the present study, in that the corrosion resistance of titanium was lost in the 0.1% NaF (452.4 ppm F) solution at pH 4.2.

The results obtained by the present anodic polarization and immersion experiments in solutions of various NaF concentrations and various pH values revealed that there were obvious limits of NaF concentrations and pH values at which the corrosion behavior of titanium changed drastically (Figs. 2, 3). Fig. 5 shows the value limits obtained by anodic polarization and immersion experiments in solutions of various NaF concentrations and various pH values. The horizontal axis represents the total amount of fluoride (ppm) contained in the test solution. The pH limit values shifted to the high pH side as the fluoride concentration increased. Logarithmic least-squares fitting led to the following linear relations between the pH limit values and the logarithm of fluoride concentration limits:

$$\mathrm{pH} = 1.49 \log(\mathrm{F}) + 0.422 \text{ (anodic polarization experiment)}$$

$$\mathrm{pH} = 1.51 \log(\mathrm{F}) + 0.237 \text{ (immersion experiment)}$$

The multiple correlation coefficients R^2 of results obtained by anodic polarization and immersion experiments were 0.998 and 0.999, respectively, and good correlations were obtained.

The results of ICP-MS analysis (Fig. 4) indicate that the amounts of titanium dissolved in the solution with fluoride concentration and pH value in the corrosive region in Fig. 5 were remarkably large. Therefore, it is reasonable to consider that the corrosion resistance of titanium is maintained in a solution with fluoride concentration and pH in the non-corrosive region, whereas titanium corrosion occurs in a solution with fluoride concentration and pH in the corrosive region (Fig. 5). Moreover, it was revealed that titanium was corroded by the existence of a small amount of NaF if the value of pH was considerably low, and that titanium was corroded even at high pH if the NaF concentration was considerably high. This means that titanium in a dental prosthesis is easily corroded in the oral environment after the use of an odontologic gel, rinse, or toothpaste containing an acidic fluoride.

The presence of F^- ions in a neutral solution (10,000 ppm F at pH 6.75) does not hinder the formation of a protective

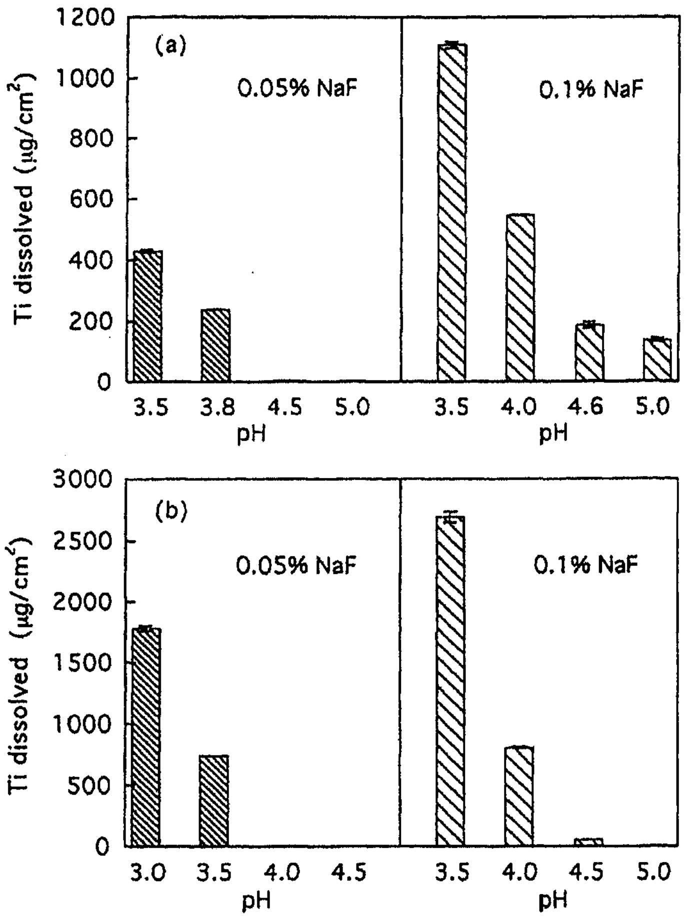

Figure 4. Amount of Ti dissolved after anodic polarization from corrosion potential to +2000 mV at the scanning speed of 1 mV/sec (a) and 24 hr of immersion (b) in NaF solutions at various pH values. Bars show means (n = 5); error bars show standard deviations. Levels of significance in each mean were calculated by Scheffé's test at 1%.

Table. F^- ion and HF concentrations in solutions of various pH (means [n = 5] and standard deviations [SD])

		F^- (ppm)			
	pH	Mean	SD	HF (ppm)	H/L[a]
0.05% NaF	5.0	228.6	1.62	0.0	H
	4.5	224.9	2.16	3.9	H
	4.0	208.9	1.23	21.0	H
	3.8	197.3	1.98	33.0	L
	3.6	182.5	1.52	49.0	L
0.1% NaF	5.0	455.0	0.92	0.0	H
	4.5	444.0	1.36	12.0	H
	4.4	442.2	2.18	13.0	H
	4.3	435.0	1.15	21.0	H
	4.2	429.7	1.95	27.0	L

[a] H, high corrosion potential; L, low corrosion potential.

layer, but the protective oxide film has been degraded in the acidic and fluoridated environments (Toumelin-Chemla *et al.*, 1996). In this study, corrosion resistance of titanium was maintained in the 2.0% NaF (9048.8 ppm F) solution at pH higher than 6.2, but the titanium corroded in a solution at pH less than 6.2, indicating that the protective oxide film of the titanium was destroyed by the presence of F^- ions.

It is known that the oxide film on the surface of titanium is destroyed by hydrofluoric acid (Bard, 1976). Hydrofluoric acid is known to dissolve the surface oxide layer by the following reactions:

$Ti_2O_3 + 6HF \rightarrow 2TiF_3 + 3H_2O$,

$TiO_2 + 4HF \rightarrow TiF_4 + 2H_2O$ (Boere, 1995), or

$TiO_2 + 2HF \rightarrow TiOF_2 + H_2O$ (Oda *et al.*, 1996).

Among these titanium fluorides or titanium oxyfluoride, titanium (IV) fluoride (TiF_4) is a soluble compound. It is thought that titanium dissolves in the solution as a complex ion containing fluoride or as a trivalent titanium ion: $Ti \rightarrow Ti^{3+} + 3e$. The corrosion of titanium is enhanced in an acidic environment, because F^- ion in the solution combines with H^+ ion to form HF, even if the NaF concentration is low (Boere, 1995; Oda *et al.*, 1996). The Table shows analyzed free F^- ion and calculated HF concentrations at each pH in 0.05% NaF and 0.1% NaF solutions. The F^- ion concentrations at pH 5.0 were 228.6 ppm in 0.05% NaF and 455.0 ppm in 0.1% NaF. These values were very close to nominal values of 226.2 ppm (0.05% NaF) and 452.4 ppm (0.1% NaF), which we calculated by assuming that NaF was fully dissociated into Na^+ ion and F^- ion. The free F^- ion concentration decreased to form HF as the pH of the solution decreased. The limit values of pH at which the corrosion resistance of titanium could be maintained were 4.0 in 0.05% NaF and 4.3 in 0.1% NaF, respectively. The F^- ion concentrations at the limit values of pH were 208.9 ppm in 0.05% NaF and 435.0 in 0.1% NaF. However, the HF concentration was the same (21 ppm) at the limit pH in both cases. At higher HF concentrations than the value, corrosion of the titanium seemed to occur easily, as denoted by "L" in the last column of the Table. This suggested that the corrosion resistance of titanium was affected by the HF concentrations in the solutions. Therefore, we also performed anodic polarization experiments of titanium in solutions containing only hydrofluoric acid, to confirm the influence of hydrofluoric acid concentration (Fig. 6). The anodic polarization curve of titanium in 20 ppm HF solution indicated the passivation of titanium. However, the corrosion resistance of titanium was lost in the solution containing more than 30 ppm HF. The result of this polarization test proved the calculated upper limit HF concentration to be 21 ppm where the corrosion resistance of titanium was maintained. An acid dissociation constant of HF is reported to be 5.18×10^{-4} at 37°C (Sillen and Martell, 1970). About 97.7% of HF molecules are undissociated in the HF solution. Therefore, the nominal concentration of HF could be regarded as the undissociated HF concentration. The HF concentration of 21 ppm well agreed with the calculated value, which corresponds to a limiting value of titanium corrosion in the polarization test in NaF solution. It was concluded that the corrosion resistance of titanium was controlled by the HF concentration and depended on the pH value and the total fluoride concentration in the solution.

The results of this study provide valuable information for

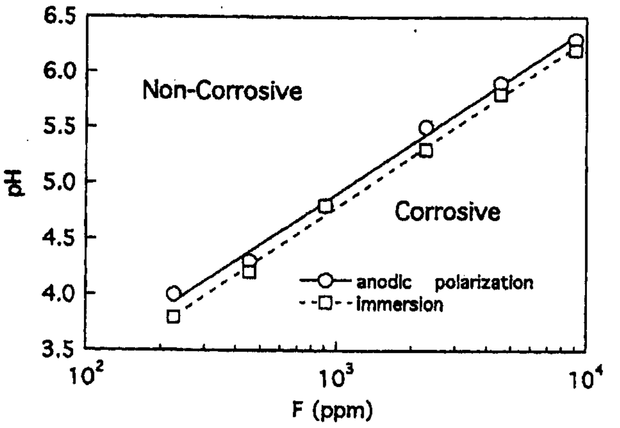

Figure 5. Limit values of F concentration and pH obtained by anodic polarization (○) and immersion (□) tests, at which the corrosion behavior of titanium changes.

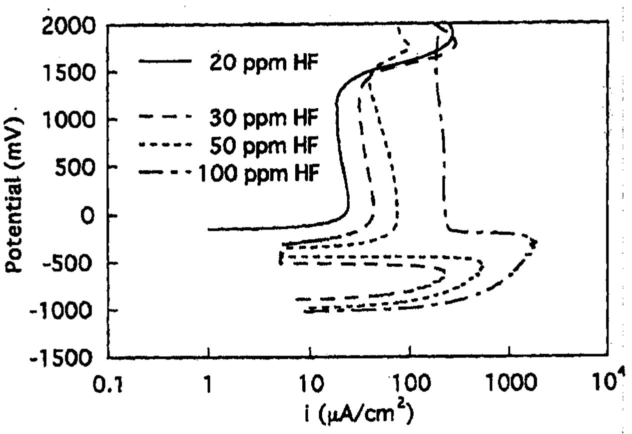

Figure 6. Anodic polarization curves of titanium in hydrofluoric acid solution.

predicting whether titanium will corrode when an acidic fluoride-containing dental-caries-preventive material is used in tooth-surface embrocations or fluoride-containing dental pastes, if the fluoride concentration and pH in the environment involved are known.

Acknowledgments

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The measurement of dissolved Ti was made by means of ICP-MS at the Center of Advanced Instrumental Analysis, Kyushu University, Japan.

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