Effect of Corrosion Behavior of Pure Titanium and Titanium Alloy on Fluoride Addition in Acidic Environment by *Streptococcus mutans* (Corrosion Behavior of Titanium by Fluoride and *Streptococcus mutans*)

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**Clinical significance**

This study evaluated corrosion behavior of pure titanium and titanium alloy in the pseudo oral environment. It was suggested that pure titanium and titanium alloys were corroded by acid which produced by *streptococcus mutans* in oral biofilms with 500ppm fluoride on the titanium prosthetic appliance.

**Abstract**

**Purpose:** As for commercially pure titanium (CP-Ti) and titanium alloys (Ti-6Al-4V, Ti-6Al-7Nb), when fluoride exists in an acidic environment, it is known to corrode from recent research. However, it is also reported that the corrosion resistance improves when small amount of platinum is added to pure titanium. The purpose of this study is to examine the corrosion behavior of CP-Ti, Ti-6Al-4V, Ti-6Al-7Nb, and high corrosion Ti-0.5Pt alloy when a fluoride added to the acidic environment produced by *streptococcus mutans*.

**Methods:** The specimen (CP-Ti, Ti-6Al-4V, Ti-6Al-7Nb, and experimentally produced Ti-0.5Pt alloy) were polished like a mirror. *Streptococcus mutans* was cultured for 24 hours with brain heart infusion (BHI) medium adding sucrose on the specimen, and then 1000ppm fluoride solution of same medium volume was added (that is, fluoride concentration becomes 500 ppm). After 10 min, all the solutions were removed and new culture for 24 hours started again. These cycles of 3, 5, 7, and 10 times were repeated and the surfaces of the specimens were observed by scanning electron microscope (SEM).

**Results:** The CP-Ti and Ti-6Al-4V, Ti-6Al-7Nb alloys were observed the typically metallographical structure by adding fluoride solution repeatedly. The surface of Ti-0.5Pt alloy was no change by adding fluoride solution. 

**Conclusion:** When a fluoride with less than 500 ppm concentration was added to the acid biofilm which was produced by *Streptococcus mutans*, as for CP-Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys the possibility to corrode was suggested. The Ti-0.5Pt alloy had a high corrosion resistance in the same condition.

**Key words:** corrosion, titanium, *streptococcus mutans*

**Introduction**

Titanium (Ti) and its alloys are clinically used for dental implants and denture bases because of their superior corrosion resistance and biocompatibility. CP-Ti and its alloys have a high corrosion resistance of these alloys depend on a passive film on their surfaces. However, it is known that the corrosion resistance of titanium decreases remarkably in the presence of fluoride using for the dental caries prevention. In fact, we observed the presence of metallographic structure on the neck area of the implant removed from the mouth of the patient after several years of implantation and we revealed that this metallographic structure was due to corrosion (Fig. 1).

In our previous study, we reported that Ti, Ti-6Al-4V, and Ti-6Al-7Nb alloys, which are both commercially available as dental implants, were prone to suffer corrosion in the presence of a small amount of fluoride (about 250 ppm) with a low dissolved oxygen concentration below 0.1 ppm. In the oral environment, the low dissolved-
Corrosion Behavior of Titanium on Fluoride Addition in Acidic Environment

oxygen situation seems fairly common. Mettraux et al.\textsuperscript{11} reported that the oxygen partial pressure in a human subgingival pocket near a dental restoration such as an implant, crown, or bridge fell to about 0.8 ppm. We reported that the addition of a small amount of Pt or Pd to pure Ti was very effective in improving the corrosion resistance of Ti in various concentrations NaF solutions. In particular, the Ti-0.5Pt (Ti-0.5 wt% Pt) alloy most effectively improved (keeping the highest corrosion potential) the corrosion resistance of Ti (Fig. 2).\textsuperscript{12}

After taking sugars (sucrose), a plaque (biofilm) on tooth becomes more acidic with low pH value. This response was demonstrated by Stephan,\textsuperscript{13,14} the pH value decreased rapidly to 4.3 and the pH value rises gradually to the original pH of 6.8 or 7.0. According to the Stephan curve, plaque pH rapidly decreased to around 4.3 after sucrose rinse has been added. The decrease of pH is mainly due to acid produced by the \textit{streptococcus mutans}.

In this study, we examined the corrosion behaviors of CP-Ti, Ti-6Al-4V, Ti-6Al-7Nb, and Ti-0.5Pt alloys (experimentally produced), when the acid produced by \textit{streptococcus mutans} coexists with fluoride in the biofilm on the specimens.

\textbf{Materials and methods}

\textbf{Preparation of specimens}

In this study, we examined commercially pure titanium (CP-Ti, Kobe Steel Co. Ltd., Kobe, Japan), the Ti-6Al-4V (Daido Steel Co. Ltd., Nagoya, Japan) and Ti-6Al-7Nb (GC Co. Ltd., Tokyo, Japan) alloys, which are presently used in clinical practice, and the experimental Ti-0.5 wt% Pt with a high corrosion resistance. The specimens of pure titanium, Ti-6Al-4V and Ti-6Al-7Nb alloys were made from as-received materials which were supplied from each manufacturer using an argon–arc casting machine (Cyclarc II, J. Morita Co., Kyoto, Japan). The Ti-0.5 wt%Pt alloy was made from pure titanium and 99.95% Pt using the Cyclarc II. All specimens were melted by the argon arc and kept for 60 sec in a melted condition in the Cyclarc II. They were twice melted by changing the top and bottom in the crucible and were then cast into the mold (Titavest CB, Morita Co., Kyoto, Japan). We polished the specimens to a luster using aluminum powder (particle size less than 0.3 \(\mu m\)).

\textbf{Experimental technique}

The specimens are set up in the 12-well tissue culture plate and 25 \(\mu L\) \textit{streptococcus mutans} (S. mutans) strain UA-159 were seeded to each well. S. mutans were grown in 2 mL of brain heart infusion (BHI) broth (Difco, Japan Becton Dickinson Co. Ltd., Tokyo, Japan) with the addition of 2% sucrose at 37°C overnight under 5% \(CO_2\). The pH of culture medium was measured by the pH meter (TPX-90, Toko Chemical Co., Tokyo, Japan). After 24 h, 2 mL of 1000 ppm fluoride solution was added to the culture medium for 10 min. Since the addition volume of fluoride...
solution is the same as the culture medium, the concentration of fluoride becomes 500 ppm. This operation corresponds to tooth brushing for 10 min using the commercial toothpaste containing fluoride. After 10 min all the fluid included fluoride (BHI+2% sucrose +F) were removed from the culture wells and replaced by new 2 mL BHI+2% sucrose culture medium. Samples were again exposed to culture medium for 24 hrs. After that, 2 mL of 1000 ppm fluoride solution was added to the culture medium for 10 min. The cycle of the addition of such a fluoride was repeated. A fluoride was added to CP-Ti and Ti-0.5Pt alloy in 3, 5, 7 and 10 cycles. A fluoride was added to Ti-6Al-7Nb and Ti-6Al-4V alloy in 5 and 10 cycles.

**Surface observation**

The specimens which were added with fluoride for the prescribed number of times were taken out from the culture wells. The pseudo biofilms which adhered to the surface of specimens were washed away with distilled water, immersed in the ethanol and cleaned ultrasonically. Five specimens of each alloy were used for the experiment. We observed the surface of a specimen by naked eyes and by scanning electron microscope (SEM) of JEOL JSM-5400LV (JEOL Ltd., Tokyo, Japan).

**Results**

Changes in the macroscopic and microscopic surface morphologies

Figure 3 shows macroscopic (naked eyes) observation of (a) CP-Ti which was added fluoride by 10 cycles, (b) Ti-6Al-7Nb which was added fluoride by 10 cycles, and (c) Ti-6Al-4V which was added fluoride by 10 cycles. On visual inspection, the surfaces of CP-Ti, Ti-6Al-7Nb, and Ti-6Al-4V remained mirror-like after added fluoride by 10 cycles.

Figure 4 shows the SEM images of CP-Ti which was polished like a mirror and which were added fluoride by 3, 5, 7, and 10 cycles. CP-Ti which added fluoride by 3 cycles did not typically change (Fig. 4(b)), but CP-Ti which was added fluoride by 5 cycles had a number of holes on the surface (Fig. 4(c)). The specimen which was added fluoride by 10 cycles had bigger holes on the surface (Fig. 4(e)). Figure 5 shows the SEM images of Ti-6Al-7Nb alloy which was polished like a mirror and which were added fluoride by 5 and 10 cycles. After fluoride addition specimens were mirror-like surface by macroscopic observation, but the metallurgical structure was observed by SEM observation. For the specimen which was added fluoride by 5 and 10 cycles, presence of white strips by corrosion were observed (Figs. 5(b) and (c)). Figure 6 shows the SEM images of Ti-6Al-4V alloy which was polished like a mir-
Corrosion Behavior of Titanium on Fluoride Addition in Acidic Environment

The surface of the specimen which added fluoride by 5 and 10 cycles were observed white spots (Figs. 6(b) and (c)). Figure 7 shows the SEM images of Ti-0.5Pt alloy which was polished like a mirror and which were added fluoride by 3, 5, 7, and 10 cycles. Although the specimen which was addition of fluoride by 10 cycles showed slightly small pits, the other specimens surface maintained a smooth surface which was the same as the polished one.

The SEM and naked eyes observation images showed typical one but as for 5 specimens of the same conditions, the all tendencies were same.

Discussion

This study qualitatively evaluated corrosion behavior of pure titanium and titanium alloy in the pseudo oral environment by SEM observation. The demineralization of dental tissue at low pH caused by the production of lactic acid in dental plaque is generally acknowledged as the primary factor in the mechanism of caries. The pH value had been reported to decrease to approximately 4.0 when sucrose was taken. A small degree of dissolution by titanium ions and weight loss of the titanium specimens has been reported to be observed at pH between 1.0 and 8.5 in lactic acid. The amount of lactic acid produced by dental plaque after consuming sugar became five times higher than that before sugar consumption. However, the decline of oral pH by drinking and eating is not considered to persist for a prolonged period because of the buffering action of other factors such as saliva.

In this study, CP-Ti, Ti-6Al-7Nb, and Ti-6Al-4V alloys showed surface changes due to corrosion when fluoride was added more than 5 cycles (Figs. 4, 5, and 6). The pH of the culture media before addition of fluoride decreased to about pH 4.1, which closely corresponded to the pH value reported by Imfeld Th. The pH of the culture medium after the addition of fluoride was about 4.2. In addition, the actual concentration of fluoride to which the surface of the specimen was exposed is critical.
has been exposed was about 500 ppm. This was also found in the study which showed a border line between the non-corrosive and corrosive regions of CP-Ti, Ti-6Al-7Nb, and Ti-6Al-4V alloy immersed in fluoride solution with various concentrations and pH. According to our study, Ti-6Al-4V was in the corrosion area completely in this acidic fluoride-containing environment. CP-Ti and Ti-6Al-7Nb located on the border line between the non-corrosive and corrosive regions. In addition, the existence of lactic acid and formic acid may affect the corrosion behavior of pure Ti, Ti-6Al-4V and Ti-6Al-7Nb alloys. The increase of the pH by the buffer action of saliva is thought to be an actual oral environment. Mettraux et al reported that the oxygen partial pressure in a human subgingival pocket near dental restorations, such as an implant, crown, or bridge, reached about 15 mmHg. Moreover, Ti and its alloy have been reported to corrode easily in an environment with a low concentration of oxygen. An intra-oral subgingival pocket is an area to which biofilm can easily adhere. Corrosion is thus thought to easily occur in this area.

As shown in Figures 4, 5, 6 and 7, even if the surface of Ti and Ti-6Al-7Nb, and Ti-6Al-4V alloys seemed like the mirror by macroscopic observation, the possibility that the corrosion by intraoral acidic biofilm and fluoride has been progressing by the SEM observation was suggested. In contrast, Ti-0.5Pt which was developed in our laboratory hardly showed any corrosion in the same environments. Ti has an extremely low electronegativity, electrons moved toward the region of Pt atoms in the alloy. Thus, the Ti matrix becomes anodic and the region around the Pt atoms becomes cathodic. This will cause an enhancement of hydrogen evolution in the acidic media or an oxygen reduction in the neutral media at the cathodic area around the Pt atoms. The enhanced cathodic reaction would accelerate spontaneous passivation of the Ti surface at the anodic area by forming a TiO2 layer. Therefore, Ti added Pt alloy shows high corrosion resistance. Moreover, it was reported that the mechanical strengths (maximum tensile strengths) of Ti-0.5Pt alloy was equal to or higher than those of pure Ti. It is thought that this newly developed Ti-0.5Pt alloy is useful as a dental implant or denture base alloy with a high corrosion resistance property.

### Conclusion

1. When biofilm forms on the surface of CP-Ti, Ti-6Al-7Nb and Ti-6Al-4V alloys, the evidence of corrosion was observed even when the fluoride concentration of the culture medium was as low as 500 ppm, due to the acid produced by S. mutans in the biofilm.
2. Even though macroscopically the surface maintained a mirror like condition, there is still a possibility of corrosion.
3. The Ti-0.5Pt alloy had a high corrosion resistance even in fluoride containing an (500 ppm) acidic environment (approximately pH 4.0).

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### References