

Title	EQCM analysis of titanium corrosion in peroxide- or fluoride-containing solutions.
Author(s)	Hattori, M; Oda, Y
Journal	Bulletin of Tokyo Dental College, 54(3): 135-140
URL	<a href="http://hdl.handle.net/10130/3738">http://hdl.handle.net/10130/3738</a>
Right	

Original Article

## EQCM Analysis of Titanium Corrosion in Peroxide- or Fluoride-Containing Solutions

Masayuki Hattori and Yutaka Oda

Department of Dental Materials Science, Tokyo Dental College,  
2-9-18 Misaki-cho, Chiyoda-ku, Tokyo 101-0061, Japan

Received 16 January, 2013/Accepted for publication 25 February, 2013

### Abstract

Although offering superior resistance to corrosion, titanium is unable to withstand discoloration with exposure to peroxide or fluoride. The mechanism of this discoloration, however, remains to be clarified. The purpose of this study was to investigate the mechanism underlying discoloration of titanium with immersion in peroxide- or fluoride-containing solutions based on electrochemical quartz crystal microbalance (EQCM) analysis. A 9-MHz titanium-deposited quartz crystal was used as for the electrodes. Four test solutions were prepared for immersion of the electrodes: 154 mM (0.9%) NaCl; 150 mM H<sub>2</sub>O<sub>2</sub> + 154 mM NaCl (pH = 4 by addition of lactic acid); 150 mM H<sub>2</sub>O<sub>2</sub> + 154 mM NaCl (pH = 8 by addition of sodium hydroxide solution); and 48 mM (0.2%) NaF + 154 mM NaCl (pH = 5.0 by addition of lactic acid). A WinEchem electrochemistry software-controlled quartz crystal analyzer (QCA922) and the Potentiostat/Galvanostat (Princeton Applied Research) on Windows XP were used to measure concurrently the resonance frequency and potential of the electrodes. The EQCM data differed among solutions. In the acidulated fluoride-containing solution, the electrode showed lower open circuit potential and a gradual increase in electrode frequency, indicating a loss of mass by titanium dissolution. In the peroxide-containing solution, although open circuit potential showed no marked difference, electrode frequency showed a gentle decrease in acidic solution, indicating a gain in mass by oxidation; but an increase in alkaline solution, indicating a loss of mass by dissolution. These results confirmed that exposure to acidulated fluoride- or alkaline peroxide-containing solutions causes dissolution-induced discoloration, while that to acidulated peroxide-containing solutions resulted in the formation of an oxide film together with discoloration.

Key words: Corrosion—Electrochemical quartz crystal microbalance—Titanium—Fluoride—Peroxide

### Introduction

Titanium implants and prostheses are widely used in clinical dentistry. However, some studies have reported pigmentation

and discoloration occurring in titanium implants and denture bases<sup>3,15,16</sup>.

Although titanium offers superior resistance to corrosion, it is still prone to corrosion on exposure to fluoride. Pröbster *et al.* noted

that prophylactic agents containing fluoride must be used with great care on implant materials and crown restorations made of titanium<sup>15</sup>. Ozeki *et al.* reported that titanium and titanium alloys were resistant to dentifrices containing fluoride up to a concentration of 1,000 ppm, but were severely corroded by acidic topical agents containing approximately 9,000 ppm of fluoride<sup>10</sup>. Oda *et al.* also reported that titanium began to show signs of corrosion in solutions containing 0.5% or higher concentrations of sodium fluoride<sup>6</sup>. Moreover, Nakagawa *et al.* reported that the passive film on titanium surfaces was destroyed under conditions where 30 ppm or more hydrofluoric acid was generated by dissociation of sodium fluoride<sup>9</sup>. In summary, these reports indicate fluoride as a possible cause of discoloration in titanium prostheses.

Pan *et al.* reported that peroxide was produced by bacteria and leukocytes during inflammatory reactions and that it attacked titanium surfaces<sup>11,12</sup>. *In vitro* studies have reported a decrease in resistance to corrosion and signs of pitting in titanium in the presence of hydrogen peroxide<sup>2,4</sup>. Furthermore, Abe *et al.* noted severe discoloration with highly alkaline, peroxide-containing denture cleaners<sup>1</sup>.

Taken together, these reports suggest that peroxide produced by inflammatory cells and fluoride-containing prophylactic agents cause discoloration in titanium. Therefore, although the mechanical properties and biocompatibility of titanium are excellent, discoloration resistance in an oral environment remains a major challenge. However, information regarding the corrosion behavior of titanium in a fluoride- or peroxide-containing environment is relatively limited. The scientific and clinical importance of this phenomenon, though, demands further investigation.

An Electrochemical Quartz Crystal Microbalance (EQCM) is a versatile instrument which can be used to simultaneously monitor electrochemical behavior while detecting changes in mass on the ng/cm<sup>2</sup> scale, which makes it a useful tool in the clarification of discoloration of titanium by exposure to per-

oxide or fluoride.

The purpose of this study was to elucidate the underlying mechanism of discoloration and dissolution of titanium with immersion in peroxide- or fluoride-containing solutions using EQCM-based analysis.

## Materials and Methods

### 1. Test solutions

Four test solutions were prepared for immersion of titanium electrodes. A saline solution (154 mM (0.9%) NaCl; code NaCl) was prepared as a control. An acidulated fluoride solution was also prepared containing 0.2% NaF (48 mM NaF + 154 mM NaCl, pH 5.0 by addition of lactic acid; code NaF), in which the concentration of fluoride was similar to that found in dental prophylactic agents used for mouth rinses. Two peroxide-containing solutions with different pHs were used: one with 150 mM H<sub>2</sub>O<sub>2</sub> + 154 mM NaCl (pH=4 by addition of lactic acid; code 4H<sub>2</sub>O<sub>2</sub>); and another with 150 mM H<sub>2</sub>O<sub>2</sub> + 154 mM NaCl (pH=8 by addition of sodium hydroxide solution; code 8H<sub>2</sub>O<sub>2</sub>), whereby the concentration of peroxide was similar to that found in body fluids during an inflammatory response<sup>12</sup>. Analytical grade reagents (Wako Chem., Japan) were used for the preparation of these test solutions.

### 2. Electrochemical quartz crystal microbalance analysis

A titanium-deposited quartz crystal with a fundamental frequency of 9 MHz (QA-A9M-TI, Ø5 mm, 400 nmTi, Seiko EG&G, Japan) was used as a working electrode. A corrosion cell comprising a saturated calomel electrode (SCE) as a reference electrode and a platinum plate as a counter electrode was maintained at a constant temperature of 35 ± 0.5°C in a thermostatic chamber. The EQCM measurements were performed by using a quartz crystal analyzer (QCA922) and the Potentiostat/Galvanostat 263A (EG&G, USA) driven by the WinEchem electrochemistry software package (EG&G, USA) on Windows

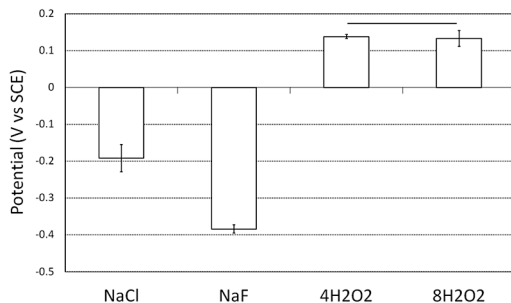


Fig. 1 Average OCP at 16 hrs after immersion in each solution

Open circuit potentials (V) were measured versus saturated calomel electrode (SCE). Horizontal lines above bars indicate groups that did not differ statistically from each other.

XP. The open circuit potential (OCP) and resonance frequency of the electrodes in each solution were simultaneously monitored over a 16 hrs period. Variation in frequency is linked to variation in mass at the electrode surface. Frequency sensitivity according to the Sauerbrey equation is  $1 \text{ ng Hz}^{-1}$  in this electrode<sup>14</sup>). Five specimens were tested under each condition.

### 3. Scanning electron microscopy

Following EQCM analysis, the surface of each sample was observed using a field emission scanning electron microscope (JSM-6340F, JEOL, Japan).

### 4. Statistical analysis

A one-way ANOVA and the Scheffé test ( $\alpha=0.05$ ) were used for a comparison and to determine significant differences in OCP and changes in frequency between groups.

## Results

Figure 1 shows the average OCP at 16 hrs after immersion in each solution. The OCP ranged from  $-0.4$  to  $0.15\text{V}$  and differed among solutions. In the NaF solution, it was approximately  $-0.4\text{V}$ , which was significantly lower than that in the other solutions. In the

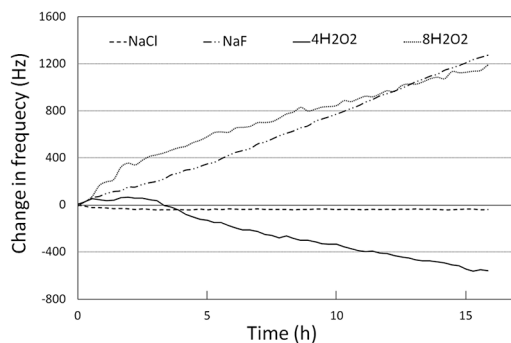


Fig. 2 Time-dependent frequency change in each solution

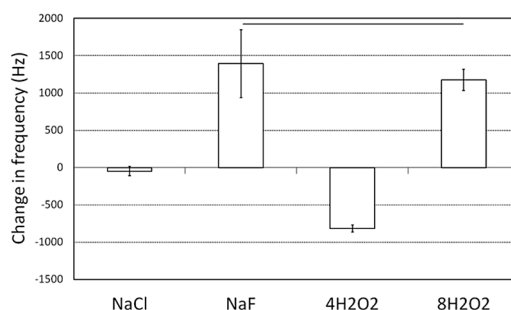


Fig. 3 Average frequency change at 16 hrs after immersion

Horizontal lines above bars indicate no statistically significant difference.

hydrogen peroxide-containing solution, it was approximately  $0.15\text{V}$ , which was not significantly different from that in the acidic (4H<sub>2</sub>O<sub>2</sub>) or alkaline (8H<sub>2</sub>O<sub>2</sub>) solutions.

Figure 2 shows change over time in each solution. In the NaCl solution, no marked change was observed over the 16 hrs. In the NaF- or H<sub>2</sub>O<sub>2</sub>-containing alkaline (8H<sub>2</sub>O<sub>2</sub>) solutions, electrode frequency showed an increase, whereas in the H<sub>2</sub>O<sub>2</sub>-containing acidic (4H<sub>2</sub>O<sub>2</sub>) solution showed a decrease.

Figure 3 shows the average frequency change at 16 hrs after immersion. The change in frequency ranged from  $-800$  to  $1,400\text{Hz}$  and differed among solutions. No remarkable change was observed in the NaCl solution. In the NaF- or H<sub>2</sub>O<sub>2</sub>-containing alkaline (8H<sub>2</sub>O<sub>2</sub>)

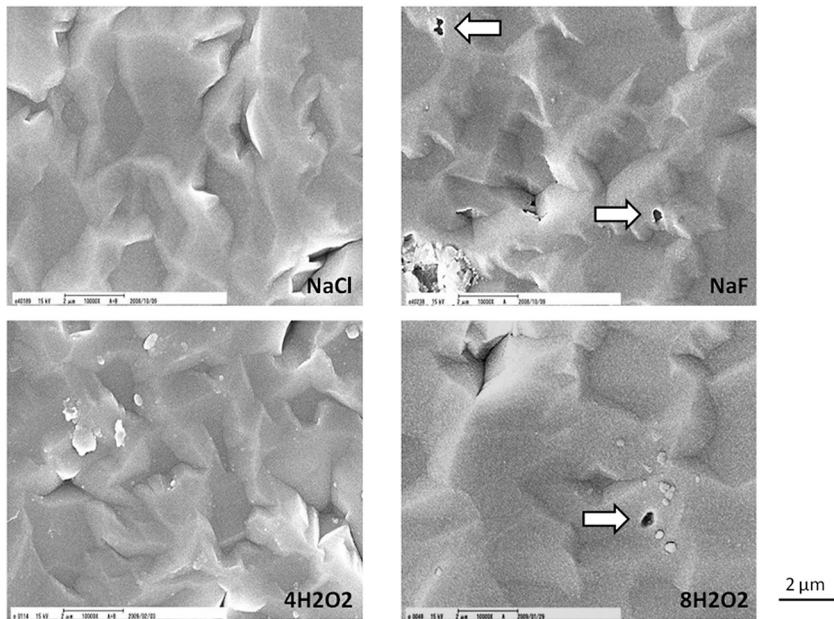


Fig. 4 Typical surface morphologies of titanium electrodes immersed in each solution for 16 hrs  
White arrows indicate pitting.

solutions, the frequency change reached more than 1,000 Hz at 16 hrs. This suggests that more than 1 microgram of dissolution occurred, as 1 Hz frequency difference corresponds to 1 ng. In the  $\text{H}_2\text{O}_2$ -containing acidic solution (4H $\text{H}_2\text{O}_2$ ), frequency decreased to  $-800$  Hz at 16 hrs, indicating a 800 ng increase in mass.

Figure 4 shows the typical surface morphologies of the titanium electrodes after immersion in each solution for 16 hrs. The morphologies of the samples immersed in NaCl- or  $\text{H}_2\text{O}_2$ -containing acidic solutions were similar to those prior to immersion. However, pitting was observed on the surface of the samples immersed in the NaF- or  $\text{H}_2\text{O}_2$ -containing alkaline solutions.

### Discussion

Studies on the corrosion resistance of titanium are generally performed by incubating Ti in saline or artificial saliva. In such solutions, titanium exhibits superior corrosion

resistance due to the presence of a stable and dense titanium oxide film that spontaneously covers the metal surface. However, titanium has been reported to be sensitive to fluoride<sup>3,5,6,13,16</sup> and peroxide<sup>2,11,12</sup>. Corrosion or discoloration behavior is related to the concentration of fluoride or peroxide. The standard prescription for fluoride mouth-rinsing agents is 0.2% NaF ( $\text{F}^-$ : 905 ppm) for home use. In the present study, we selected sodium fluoride solution at a concentration of 0.2% NaF. Small amounts of peroxide are produced by bacteria and leukocytes during inflammatory reactions. Several authors have investigated the effects of hydrogen peroxide on titanium corrosion at a concentration range of 0.05–0.15 mol/liter<sup>2,11</sup>. In the present study, a solution with the maximum concentration of 0.15 mol/liter hydrogen peroxide (pH = 4.0 or 8.0) was selected.

The OCP and rate of frequency change differed among the solutions. This may have been due to the formation of a thick oxide film or dissolution due to corrosion. The data

Table 1 Data comparison of OCP, frequency change, and color difference in each solution

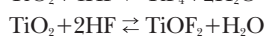
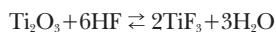
Solution	Potential (V)	Frequency ( $\Delta$ Hz)	Color difference ( $\Delta E^*ab$ )#
NaCl	-0.192	-49	2
NaF	-0.384	1,393	13
4H <sub>2</sub> O <sub>2</sub>	0.138	-816	33
8H <sub>2</sub> O <sub>2</sub>	0.133	1,177	25

#: data quoted from previous reports 6), 7), and 8)

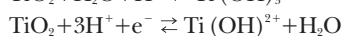
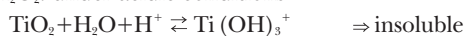
were compared with those obtained from polished titanium specimens in earlier studies<sup>6-9)</sup>. Table 1 shows a comparison of these data for OCP, frequency change and color difference in various solutions. When polished titanium was immersed in saline solution, there was no detectable change in color or dissolution. However, pure titanium was discolored in sodium fluoride- or hydrogen peroxide-containing solution. The color difference value was  $\Delta E^*ab = 13$  in NaF,  $\Delta E^*ab = 33$  in hydrogen peroxide-containing acidic solution and  $\Delta E^*ab = 25$  in alkaline solutions. In the hydrogen peroxide-containing solution, color change in titanium was remarkable in both solutions, but electrode frequency showed inverse results. In the present study, frequency decreased in acidic solution, indicating a gain in mass, and increased in alkaline solutions, indicating a loss in mass. Consequently, in hydrogen peroxide-containing acidic solution, titanium showed a marked increase in mass and discoloration, suggesting that discoloration of titanium alloys in acidic hydrogen peroxide-containing solutions is mainly due to hydrogen peroxide-induced oxidation. On the other hand, the increased electrode frequency in H<sub>2</sub>O<sub>2</sub>-containing alkaline solution indicated a loss of mass by dissolution. In the fluoride-containing solution, however, titanium showed medium discoloration while electrode frequency showed an increase, indicating a loss of mass by dissolution. Frequency change showed a similar tendency in NaF- or hydrogen peroxide-containing alkaline solutions.

The following is a summary of some of the reactions which we believe may have occurred in the present experiments: in the acidic NaF solution, titanium reacted with HF, making a soluble complex compound (1); introduction of H<sub>2</sub>O<sub>2</sub> into acidic solution promoted oxidation, probably due to the formation of an insoluble complex compound (2), resulting in the total oxide film reaching a thickness corresponding to a large color difference; under alkaline conditions, a soluble complex compound was formed (3), resulting in increased dissolution of the titanium.

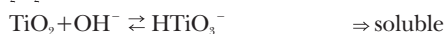
(1) NaF: under acidic conditions



(2) H<sub>2</sub>O<sub>2</sub>: under acidic conditions



(3) H<sub>2</sub>O<sub>2</sub>: under alkaline conditions



These results indicate that EQCM analysis is a useful tool in elucidating the corrosion and discoloration of titanium with immersion in peroxide- or fluoride-containing solutions.

## Conclusion

Electrochemical quartz crystal microbalance-based analysis was employed to clarify the mechanism underlying discoloration of titanium with exposure to fluoride- or peroxide-containing solutions.

In acidulated fluoride-containing solution, titanium showed a lower OCP and a gradual increase in electrode frequency. In H<sub>2</sub>O<sub>2</sub>-containing solution, although no marked difference was observed in OCP, electrode frequency showed a gentle decrease in acidic solution; but an increase in alkaline solution.

These results confirmed that exposure to acidulated fluoride- or alkaline peroxide-containing solutions causes corrosion in titanium, and that oxide film formation occurred simultaneously with discoloration in acidulated peroxide-containing solution.

### Acknowledgements

This study was supported in part by a Grant-in-aid for Developmental Scientific Research from the Ministry of Education, Science, Culture and Sports, Japan. The authors would like to thank Associate Professor Jeremy Williams, Tokyo Dental College, for his assistance with the English of the manuscript.

### References

- 1) Abe T, Matsumoto M, Hattori M, Hasegawa K, Yoshinari M, Kawada E, Oda Y (2001) Discoloration of titanium induced by denture cleaner. *Jpn J Dent Mater* 20:366–371.
- 2) Fonseca C, Barbosa MA (2001) Corrosion behavior of titanium in biofluids containing H<sub>2</sub>O<sub>2</sub> studied by electrochemical impedance spectroscopy. *Corros Sci* 43:547–559.
- 3) Lausmaa J, Kasemo B, Hansson S (1985) Accelerated oxide growth on titanium implants during autoclaving caused by fluorine contamination. *Biomaterials* 6:23–27.
- 4) Mabilieu G, Bourdon S, Joly-Guillou ML, Filmon R, Basle MF, Chappard D (2006) Influence of fluoride, hydrogen peroxide and lactic acid on the corrosion resistance of commercially pure titanium. *Acta Biomater* 2:121–129.
- 5) Nakagawa M, Shiraishi T, Ohta M (1999) Effect of fluoride concentration and pH on corrosion behavior of titanium for dental use. *J Dent Res* 78:1568–1572.
- 6) Oda Y, Kawada E, Yoshinari M, Hasegawa K, Okabe T (1996) The influence of fluoride concentration on the corrosion of titanium and titanium alloys. *Jpn J Dent Mater* 15:317–322. (in Japanese)
- 7) Oda Y, Takemoto S, Hattori M, Yoshinari M, Kawada E (2008) Discoloration of titanium-based alloys in alkaline peroxide-containing solution. 86th General Session & Exhibition of the IADR #2376.
- 8) Oda Y, Takemoto S, Hattori M, Yoshinari M, Kawada E (2007) Influence of pH on discoloration of titanium-based alloys in solutions containing hydrogen peroxide, Proceedings of the International Dental Materials Congress, 163.
- 9) Oda Y, Takemoto S, Hattori M, Yoshinari M, Kawada E (2004) Influence of pH on the titanium-based alloys corrosion with fluoride containing saline. 82th General Session of the IADR #0630.
- 10) Ozeki K, Oda Y, Sumii T (1996) The influence of fluoride prophylactic agents on the corrosion of titanium and titanium alloys. *The Shikwa Gakuho* 96:293–304. (in Japanese)
- 11) Pan J, Liao H, Leygraf C, Thierry D, Li J (1998) Variation of oxide films on titanium induced by osteoblast-like cell culture and the influence of an H<sub>2</sub>O<sub>2</sub> pretreatment. *J Biomed Mater Res* 40:244–256.
- 12) Pan J, Thierry D, Leygraf C (1996) Hydrogen peroxide toward enhanced oxide growth on titanium in PBS solution: blue coloration and clinical relevance. *J Biomed Mater Res* 30:393–402.
- 13) Pröbster L, Lin W, Hüttemann H (1992) Effect of fluoride prophylactic agents on titanium surface. *Int J Oral Maxillofac Implants* 7:390–394.
- 14) Sauerbrey G (1959) Verwendung von schwingquarzen zur wägung dünner schichten und mikrowägung. *Z Phys* 155:206.
- 15) Soma H, Imamura Y (2001) The circumstances of cast titanium prosthesis. *Quintessence Dent Tech* 26:462–473. (in Japanese)
- 16) Sutton AJ, Rogers PM (2001) Discoloration of a titanium alloy removable partial denture: A clinical report. *J Prosthodont* 10:102–104.

### Reprint requests to:

Dr. Masayuki Hattori  
Department of Dental Materials  
Science,  
Tokyo Dental College,  
2-9-18 Misaki-cho, Chiyoda-ku,  
Tokyo 101-0061, Japan  
E-mail: hattori@tdc.ac.jp