



Effect of fluoride from glass ionomer on discoloration and corrosion of titanium

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ABSTRACT

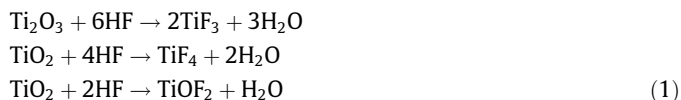
The objective of the study was to examine the effects that fluoride ions released from different dental glass ionomer cements may have on titanium. The study included determination of the amounts of released ions and measurement of the color changes on titanium plates cemented with four kinds of commercial glass ionomer cements due to immersion of such “sandwich specimens” in 1% saline (NaCl) solution. The discoloration of titanium in the presence of glass ionomer cements was observed. In addition, for specimens cemented with two of the cements titanium ions were found in the solution after immersion. The results of the present study show that a low concentration of released fluoride ions and other elements from glass ionomer cements may cause aesthetic problems of discoloration of titanium restorations and appliances.

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1. Introduction

In dental practice it is often necessary to place more than one type of man-made material into the oral cavity for restorative purposes, including metals and other inorganic as well as organic materials, and the mutual interaction of these material must be considered.

Titanium and titanium alloys are a group of more recent materials used for dental implants and restorations. Although titanium is thermodynamically active in reactions with air and water, it behaves like a noble metal due to the formation of a highly protective oxide film, and it is highly biocompatible. However, the oxide film on the surface of titanium can be destroyed by hydrofluoric acid shown by the following reaction [1]:



Although the natural oral environment is not an aggressive electrolyte for titanium, when fluoride ions are introduced they tend to destabilize the passive film on titanium and thus increase the corrosion susceptibility [2].

In previously published work [1,3–12], the effect of fluoride ions has been investigated using mostly relatively high fluoride concen-

trations, and it was concluded that the use of fluoride-containing rinses or gels might be harmful to titanium. For example, it was reported that exposure to NaF (sodium fluoride) solution exceeding a concentration of 0.5% was harmful to pure titanium and titanium alloys [3]. In an acidic environment, corrosion of titanium and titanium alloys easily occurred at 226 ppm fluoride concentration [4]. Under low dissolved-oxygen concentration conditions the boundary pH values, at which the corrosion behavior of titanium and titanium alloys changed, shifted to higher pH values than at high dissolved-oxygen concentration [5]. Albumin-containing NaF solution has been found harmful to a titanium alloy at a concentration of 0.1% [6,7]. Another study showed that the passive film of titanium and titanium alloys suffered destruction in an acidic solution containing 100–150 ppm fluoride [8–10]. Titanium alloys have been reported to tarnish in a 30 ppm NaF solution [1,11,12].

Fluorides are used to prevent caries and secondary caries. In addition to fluoridated drinking water, sources of fluoride ions may include toothpaste (usually 900–1000 ppm), topical applications (9000 ppm), mouth rinse (450–500 ppm) and glass ionomer cements (less than 50 ppm). In the first three sources the concentration of fluoride ions is high, but their presence in the oral cavity is short.

Glass ionomer cements are translucent materials, with optical properties similar to enamel, adhering to both enamel and dentine. They are used for both filling cavities and cementing fixed prosthesis. Glass ionomer cements release fluoride ions, and the effect of the released fluorides on bacteria metabolism has been reported [13–15]. In view of the susceptibility of titanium to fluoride ions, the possible effect of the release from glass ionomer cements on

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the clinical longevity of restorations is of some concern. Although the concentration of fluoride ions caused by the release from the glass ionomer cements in the oral cavity is low, the release continues for a long time, and its effect on titanium is not yet fully understood. The objective of the present study was to examine the effect that fluoride ions released from different dental glass ionomer cements may have on titanium.

2. Materials and methods

2.1. Experimental design

The study included determination of pH and of the amounts of released ions in 1% saline (NaCl), and a measurement of the color changes on titanium plates cemented with glass ionomer cements due to immersion in this solution.

2.2. Materials

The luting cements were two conventional glass ionomer cements, GFI (Fuji Slow Set, GC Co., Ltd., Tokyo, Japan) and HGX (HY-Bond Glass Ionomer CX, Shofu Inc., Kyoto, Japan), and two resin-modified glass ionomer cements, GFL (Fuji Lute, GC Co., Ltd., Tokyo, Japan) and 3MV (Vitremmer, 3M Dental Product, St. Paul, MN, USA). The design of the specimens as titanium–cement–titanium “sandwiches” simulated therapeutic cementing of prostheses, except that titanium rather than dentine or enamel was used adjacent to titanium.

2.3. Specimens

Commercially pure titanium plates (JIS Grade II, size $15 \times 20 \times 1$ mm, Selec, Osaka, Japan) were ground through 600 grit SiC, and washed in distilled water and acetone using an ultrasonic cleaner. Grade II titanium was selected as the most common grade of unalloyed titanium used in dentistry. These specimens were prepared by cementing two titanium plates together with glass ionomer cement, mixed in a ratio suggested by the manufacturer. The titanium plates were cemented for 5 min at a load of 5 kg, following which they were placed for 30 min in water bath (Yamato, Tokyo, Japan) at 37 °C. When the thickness of the cement line after cementing was measured, it was between 0.02 and 0.05 mm (20–50 µm). Eighteen “sandwich” specimens were prepared for each cement.

2.4. Immersion tests

After 30 min in the water bath the specimens were removed and the immersion test was performed. Each set of “sandwich specimens” ($n = 3$) was suspended, using a cotton thread, in a polypropylene immersion bottle containing 50 ml of 1% saline (NaCl) maintained at 37 °C. The immersion test periods were 1, 4, 8, 12, 16 and 24 weeks, using new test specimens for each period.

2.5. pH measurements

The pH value of the 1% saline was measured using a pH-meter (Beckman Coulter Inc., Fullerton, CA, USA) during each immersion period and before the quantitative analysis for the fluoride ions.

2.6. Measurement of the color vector change

The measurements were performed using a color sensor MCR-A (MINOLTA, Tokyo, Japan). Prior to each set of measurements the color sensor was calibrated according to the manufacturer's

instructions by using the supplied white calibration standard. The color vectors L^* (light–dark), a^* (red–green) and b^* (yellow–blue) of the surface of the specimens were measured before and after immersion. The specimens were placed under the measuring head of the color sensor, and a fluorescent lamp was used for illumination. Three measurements were taken at the central region of the specimen. The average value of these three readings was automatically calculated by the color sensor and recorded. The total color change vector (ΔE_{ab}^*) was calculated using the following equation [16]:

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (2)$$

2.7. Analysis for released chemical species

Following the immersion test period, the solution was analyzed for fluoride ions using an ion meter IM-40S (TOA, Tokyo, Japan) and a fluoride electrode (TOA, Tokyo, Japan). The concentrations of Ti (titanium), Ca (calcium), Al (aluminum), Si (silicon) and P (phosphorus) ions were measured by means of an inductively coupled plasma emission spectrometer (ICPV-1012, Shimadzu, Kyoto, Japan). The results for calcium, aluminum, silicon and phosphorus were expressed as concentrations, as well of the species as the mass of the element released per unit cement line surface area of the glass ionomer (mg cm^{-2}). The results for titanium were expressed as the mass of the released element per unit area considering both surfaces of the sandwich specimen ($\mu\text{g cm}^{-2}$).

2.8. Statistical analysis

Following the immersion test, the amounts of released chemical species, the color vector change and the pH value for each test were analyzed, as appropriate, either by two-way analysis of variance (ANOVA) and Tukey's test, or Student's *t*-test at $p = 0.01$ or $p = 0.05$, as indicated in the results, using a statistical package (Excel Statistics, SRI, Tokyo, Japan).

3. Results

3.1. Amounts of released fluoride ions

The results of the analyses for released fluoride ions are presented in Fig. 1, which shows the concentration found in the solution at the end of each immersion period. For all specimens, there was some fluoride release, the concentrations being significantly higher than for blank samples (1% saline), which ranged from

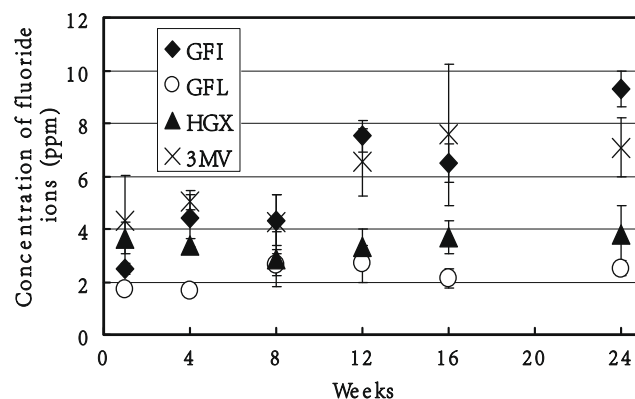


Fig. 1. Concentration of released fluoride ions from glass ionomer cement of sandwich specimens with immersion time in 1% saline at 37 °C. Bars represent means ($n = 3$), error bars show ± 1 standard deviation.

0.026 to 0.046 ppm for weeks 1–24. It remained low (about 2–5 ppm) for immersion periods of 4 and 8 weeks. The fluoride concentration was slightly higher for GFI and 3MV than for HGX and GFL. For an immersion period of 12 weeks and longer, the fluoride ion concentration increased substantially for GFI and 3MV, while it remained relatively stable for HGX and GFL. Two-way ANOVA showed significant differences ($p < 0.01$) between the two groups.

3.2. pH values

Fig. 2 shows the solution pH values for each of the four glass ionomer cements after each immersion period. The solution with the HGX cement exhibited a stable pH, while the pH of the solutions with the GFL, GFI and 3MV cements increased during the 1 week immersion period by a little less than one pH unit and then remained relatively stable. The pH values of the blanks varied within very narrow limits (5.27–5.43).

3.3. Discoloration and color change vector results

Following the immersion tests the surfaces of the “sandwich specimens” were first examined by naked eye. The specimens cemented with GFI lost luster but no discoloration was observed. The specimens cemented with the other three cements exhibited discoloration apparent in the naked eye examination.

The results of the total color change vector (ΔE_{ab}^*) are shown in Fig. 3. Generally, the evaluation of ΔE_{ab}^* values used the following nomenclature [16]: $\Delta E_{ab}^* = 0.5$ –1.5, slight change; $\Delta E_{ab}^* = 1.5$ –3.0, noticeable change; $\Delta E_{ab}^* = 3.0$ –6.0, applicable change; $\Delta E_{ab}^* = 6.0$ –12.0, much change; $\Delta E_{ab}^* > 12$, very much change.

Except for weeks 1, 12, 16 and 24 for GFI and weeks 1 and 4 for GFL, the value of ΔE_{ab}^* was higher than two. The ΔE_{ab}^* was the highest for HGX, followed by GFL, 3MV and GFI. The maximum color change for HGX showed $\Delta E_{ab}^* > 10$. The ΔE_{ab}^* for GFL, HGX and 3MV increased with increasing immersion time (Fig. 3). The differences between 3MV and GFL were not statistically significant ($p < 0.05$). A positive correlation was found between the fluoride release and total color change vector for GFL ($r = 0.7478$) and HGX ($r = 0.9667$). The ΔE_{ab}^* of a control (a titanium plate without cement immersed into 1% saline) remained stable (1.03–1.39).

3.4. Released titanium ions

Fig. 4 shows the results for the release of titanium. A small amount of titanium ions was released from the plates cemented with GFI and 3MV, the trend being similar to that for the fluoride

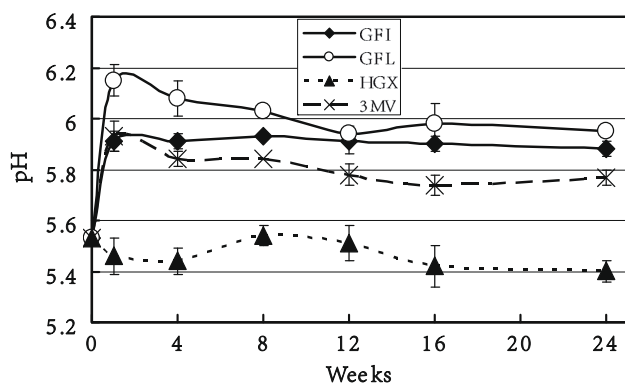


Fig. 2. pH value changes in 1% saline with time of immersion of from titanium/glass ionomer sandwich specimens. Bars represent means ($n = 3$), error bars show ± 1 standard deviation.

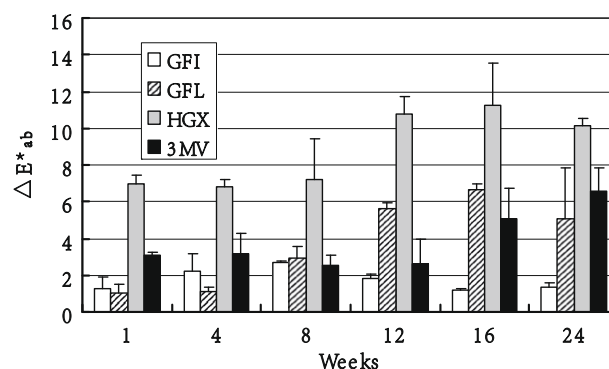


Fig. 3. Total color change vector on the surface of titanium cemented with glass ionomer cements in 1% saline at 37 °C. Bars represent means ($n = 3$), error bars show ± 1 standard deviation.

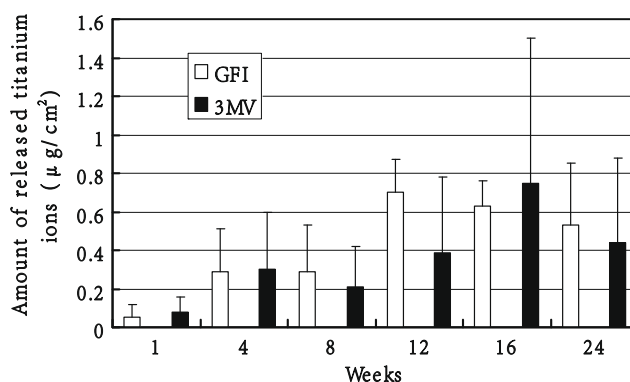


Fig. 4. Amounts of released titanium from titanium/glass ionomer sandwich specimens in 1% saline at 37 °C. Bars represent means ($n = 3$), error bars show ± 1 standard deviation.

ions. The differences between the results for 3MV and GFI were not statistically significant ($p < 0.05$). A positive correlation was found between the amounts of released fluoride and titanium ions for GFI ($r = 0.8837$) and 3MV ($r = 0.7151$).

3.5. Other released metal ions

Fig. 5 shows the results of the analyses for the four other released ions (A, Si; B, Al; C, Ca; and D, P). The four kinds of glass ionomer cements released different proportions of silicon, aluminum, calcium and phosphorus. The accumulated amount of the four released elements (Si, Al, Ca, P) was highest for 3MV.

4. Discussion

One of the few weaknesses of titanium is the susceptibility of the metal and its oxide to fluoride ions. Fluoride ions are released from glass ionomer cements, but the concentration due to this source is low, typically 50 ppm, and there is little effect on the pH value [13]. In this study, for samples cemented with the four kinds of cements and immersed in 1% saline solution the pH value varied in a relatively moderate range (5.40–6.15) during the 24 weeks immersion period, the general tendency being for a small increase in the pH value.

In previous works using a solution of neutral pH titanium was reported to maintain a smooth metallic appearance [17]. The fluoride ions apparently did not cause significant damage in the form of excessive dissolution or localized corrosion attack. In this study titanium was found in the solution after immersion for specimens

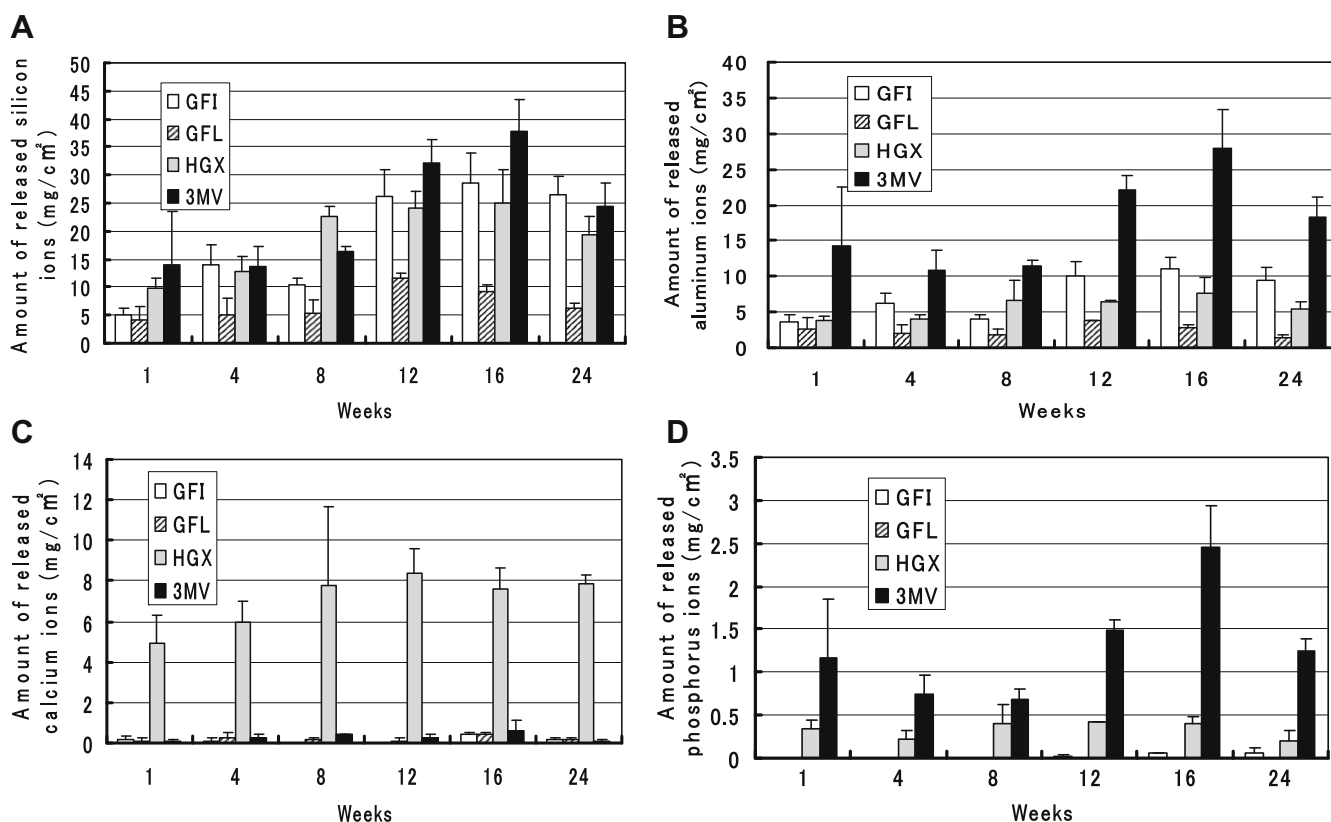


Fig. 5. Amounts of other ions (A, silicon; B, aluminum; C, calcium; D, phosphorus) released from titanium/glass ionomer sandwich specimens in 1% saline at 37 °C. Bars represent means ($n = 3$), error bars show ± 1 standard deviation.

cemented with GFI and 3MV (Fig. 4), which also released the highest amounts of fluoride ions (Fig. 1), and a positive correlation was found between the fluoride concentration and the concentration of released titanium ions, indicating that dissolution of titanium oxide had occurred. However, the release was still too low to correspond to a significant mass loss and only indicated that dissolution of titanium oxide was enhanced by the released fluoride ions. Halides, such as chlorides and fluorides, generally increase the dissolution rate of oxide passive films [18,19]. According to Uhlig's theory, halides compete with dissolved oxygen or OH^- , enhance hydration of metal ions and thus increase the dissolution rate [18]. The results of this study were consistent with this theory, but also showed that the release of titanium ions occurred only when the release of fluoride ions was relatively high, as for glass ionomer cements GFI and 3MV.

Apart from possible general or localized dissolution, the interaction with the oral environment may cause a loss of aesthetic quality of dental restorations and appliances by discoloration (tarnishing) related to surface changes [20]. In the present study, discoloration of titanium in the presence of glass ionomer cements was observed for three of the four glass ionomer cements. One form of discoloration is related to the changes in the oxide thickness, which results in changes in light interference in the oxide and thus changes in the observed coloration, different colors corresponding to different thicknesses of the oxide [11]. The effect of fluorides on titanium oxide thickness thus appears to be highly dependent on the fluoride ion concentration [11,21]. At low concentrations fluoride ions have been reported to enhance titanium oxide growth [11,21], which would result in oxide thickening. The effect may be attributed to an increase in the oxide conductivity due to the incorporation of fluoride ions, resulting in a promotion of oxide growth [11,21]. At higher fluoride concentrations

oxide dissolution is dominant, resulting in oxide thinning and, in the absence of other tarnishing factors, retention of a metallic luster. In this study, a positive correlation between the fluoride concentration and the total color change vector was found for specimens with GFL and HGX cements, for which a release of titanium ions was not observed, indicating that the enhancement of the oxide film growth by the ions was at least in part responsible for the observed change in color. On the other hand, the lower values of the discoloration parameter for the specimens cemented with GFI and the initially low discoloration for 3MV can be attributed to a thinning of the oxide resulting from a higher fluoride release than from GFL and HGX.

The causes and mechanisms of tarnishing may be quite complex, however. In addition to the released fluoride ions and their effect on the titanium oxide thickness, glass ionomer cements also release other ions [22,23], which may play important roles in the observed tarnishing. Metal ions in the solution may cause visible changes by deposition on the surface in the form of insoluble salts, or could be incorporated in the film and change its optical characteristics. Especially calcium ions have been reported to be easily adsorbed and incorporated into titanium oxide films [24]. The specimens cemented with HGX exhibited strongest discoloration while releasing the highest amounts of calcium ions, indicating that deposition of calcium may have been a contributor to the tarnishing of those specimens. In the case of 3MV, some of the discoloration could be attributed to a deposition of a phosphorus salt. For both HGX and GFL, there was an indication that this element may also have contributed to discoloration. The results have shown various other positive correlations between the total color change vector and concentrations of released metal ions. The existence of a correlation, however, is not conclusive evidence of the effect of any particular element.

In this study, the longest immersion time was 6 months. It has been reported that the release of fluoride ions from glass ionomer cements continued for longer than a year [25]. Furthermore, the fluoride-releasing ability of glass ionomer cements may be regenerated or recharged by the use of solutions of high fluoride concentration, such as mouth rinses and topical applications [26–29], and the discoloration effect thus may last a long time.

5. Conclusions

The interaction between glass ionomer cements and titanium has received little attention, because of the stronger effects of other sources of higher fluoride concentrations. The results of the present study show, however, that a low concentration of released fluoride ions and other elements from glass ionomer cements may cause aesthetic problems of discoloration of titanium restorations and appliances. The results also show that there are significant differences between different commercial cements in their ability to cause discoloration.

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