Effects of fluoride-contained oral rinses on the corrosion resistance of titanium alloy (Ti-6Al-4V)

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Effects of fluoride-contained oral rinses on the corrosion resistance of titanium alloy (Ti-6Al-4V)

A Dissertation Thesis

Submitted to the Department of Dentistry

And the Graduate School of Yonsei University

In partial fulfillment of the

Requirements for the degree of

Master of Dental Science

Gui-Yue Huang

December 2015

This certifies that the dissertation thesis of Gui-Yue Huang is approved.

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December 2015

감사의 글

논문의 시작부터 완성되기까지 세심한 배려와 가르침으로 이끌어 주시고 부족한 저에게 항상 따뜻한 조언을 아끼지 않으시는 황충주 지도 교수님께 진심으로 감사 드립니다. 그리고 바쁘신 가운데 논문 심사를 맡아주셔서 많은 관심과 조언으로 도움을 주셨던 차정열 교수님, 김광만 교수님께도 깊은 감사의 말씀을 올립니다.

또한 제가 교정학에 대한 학문적 소양을 기를 수 있도록 많은 가르침을 주신 박영철 교수님, 백형선 교수님, 김경호 교수님, 유형석 교수님, 이기준 교수님, 정주령 교수님, 최윤정 교수님께 감사를 드립니다.

논문의 통계적 부분에 대하여 많은 도움과 조언을 주신 정회인 교수님께도 진심으로 감사 드리며, 실험적인 방면에서 많은 도움을 주신 강형파 선배님께도 감사 드립니다.

석사 과정 동안 저에게 많은 도움을 주었던 실험실 동료 선생님들을 비롯한 모든 분들에게 이 지면을 빌어 감사의 마음을 전합니다.

마지막으로 언제나 변함없는 사랑으로 아낌없이 지원해주시는 존경하는 부모님과 사랑하는 가족들에게 감사의 마음을 전합니다.

2015년 12월 저자 씀

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Abstract

Effects of fluoride-contained oral rinses on the corrosion resistance of titanium alloy (Ti-6Al-4V)

A fluoride-contained adhesive, paste, and oral rinse are commonly used to prevent dental caries and tooth demineralization in orthodontic treatment. According to many findings, the presence of fluoride had been reported to cause corrosion of the titanium which can lead to fracture of the implant due to stress corrosion. When the metal corrosion occurred, it can not only cause the reduction of mechanical strength but also cause the inflammation and toxicity to the surrounding tissue by release of metal ions which can stimulate carcinogenic reactions. The purpose of this study is to examine the effects of commercially available fluoride-contained oral rinses on the corrosion behaviors of titanium alloys which are main component of orthodontic miniscrew implant. Four oral rinses [Listerine® (IDS Manufacturing Ltd. Thailand) Natural Green Tea (Solution A: pH 4.46/ 260 ppm F), Listerine® Teeth & Gum Defence (Solution B: pH 4.41/ 178 ppm F), Listerine® Tartar Control (Solution D: pH 4.17/ 3.92 ppm F) and Garglin® Regular Solution (Dong-A Pharm. Korea) (Solution C:pH 6.30/ 117 ppm F)] were tested on titanium alloys (Ti-6Al-4V) circular plates TC4® (Sheng Xinyuan Titanium Industry Co., LTD. Baoji City. China) and saline Klenzo® (JW Pharmaceutical. Korea; pH 6.24/ 3.56 ppm F) was used as control group. Electrochemical corrosion tests such as Open circuit potential measurements and Potentiodynamic polarization measurements were conducted for these materials, using four oral rinses and saline as the electrolytes. After the electrochemical measurements, all the samples were evaluated by examining the specimens using a scanning electron microscope.

1. In the tested oral rinses except solution D, corrosion potential of titanium alloy samples exposured in the solution containing more fluoride showed more obvious downtrend.

2. In the tested oral rinses except solution D, the more fluoride a solution contained, the significantly lower corrosion resistance the titanium alloy sample showed ($P < 0.05$).

3. Observed the surface morphology of titanium alloy samples by SEM, all the samples showed some defects, crevices or pittings in the 4 oral rinses compared with the sample before being tested, especially the samples in the solution A showed the most changes.

As a result of this, it was confirmed that commercially available fluoride treatment oral rinses could reduce the corrosion resistance of titanium alloy after using them more than 6 months (40 seconds use per day).

Although fluoride is useful to prevent caries, if patients use high concentration of fluoride-contained oral rinses during orthodontic treatment, the corrosion resistance of titanium alloy devices such as miniscrew implant could be affected.

Key words: Fluoride, corrosion resistance, titanium alloy, oral rinses

Effects of fluoride-contained oral rinses on the corrosion resistance of titanium alloy (Ti-6Al-4V)

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(Directed by Prof. Chung Ju Hwang, D.D.S., M.S., Ph.D.)

I. Introduction

Titanium or its alloy is regarded as a good metallic implant material because of its high corrosion resistance, excellent biocompatibility with oral tissues and great mechanical strength (Anusavice et al., 2012; Hey et al., 2014). Due to many advantages such as the lower cost, simple implant procedure, small trauma during removal and less Foreign Body Sensation, titanium implants are widely used as a skeletal anchorage in orthodontic treatment (Kuroda et al., 2007; Miyawaki et al., 2003).

Recently, with the increasingly widespread use of mini-implants in orthodontic treatment, much research has been conducted on their impact factors for success. According to the reported literature, failure rate was as high as 6% to 30%. One of the reported complications is fracture phenomena that occur in the course of a mini-implant placement or removal, the incidence of fracture in clinical studies and animal studies is approximately 4-5% (Buchter et al., 2005; Chen et al., 2006; Park et al., 2006).

A fluoride-contained adhesive, paste, and oral rinse are commonly used to prevent dental caries and tooth demineralization in orthodontic treatment (Mellberg and Ripa, 1983; Schiff et al., 2005; Sudjalim et al., 2007). However, according to many findings, the presence of fluoride has been reported to cause corrosion of the titanium which can lead to fracture of the implant due to stress corrosion (Boere, 1995; Könönen et al., 1995; Lausmaa et al., 1985; Toumelin-Chemla et al., 1996). A solution containing hydrofluoric acid (HF) more than 30 ppm was reported to cause corrosion by destroying the oxidation film of titanium (Nakagawa et al., 1999; Oshida et al., 2005; Souza et al., 2012). When the metal corrosion occurred, it can not only cause the reduction of mechanical strength but also cause the inflammation and toxicity to the surrounding tissue by release of metal ions which can stimulate carcinogenic reactions (Broggini et al., 2003; Case et al., 1994; Goodman, 2007; Guindy et al., 2003; Manaranche and Hornberger, 2007; Manda et al., 2009; Urban et al., 2000; Wang et al., 2007).

The purpose of this study is to examine the effects of commercially available fluoride-contained oral rinses on the corrosion behaviors of titanium alloys which are main component of orthodontic miniscrew implant. The null hypothesis of this study is that there is no significant difference regarding the corrosion behavior between titanium alloys in oral rinses containing different levels of fluoride.

II. Materials and Methods

1. Materials

Twenty commercial titanium alloys (Ti-6Al-4V) circular plates TC4® (Sheng Xinyuan Titanium Industry Co., LTD. Baoji City. China) were examined under each set of test conditions in this study (n=20). The alloy specimens (diameter 15 mm, 2 mm thick) were used for corrosion test and surface characteristics determination. They were mirror polished using 1 micron diamond grinding paste and washed with ethanol.

2. Test solutions

The 4 commercially available oral rinses used as the test solution (400mL) and saline used as the control solution were given in Table 1. All the products were carried out the pH measurement and F^{-} ion concentration test. The temperature of the test solution was kept at (37±0.1) ℃ during electrochemical analysis of Titanium alloys.

3. Open circuit potential measurements (OCP)

The counter and reference electrodes were graphite and KCl saturated Ag/AgCl electrode, respectively. The potential of this reference electrode was denoted by

E (Ag/AgCl) = E (saturated hydrogen electrode:SHE)+197 mV. The test samples were connected as working electrode (WE) and immersed for 2 hours in the test solution. The 2 hours of immersion used in this study would correspond approximately to the use of oral rinse for 6 months (40 seconds use per day), which is similar to the normal orthodontic treatment time with the fixed miniscrew appliance (Muguruma et al., 2011). The exposure area of the working electrode was 0.95 mm^2.

4. Potentiodynamic polarization measurements

After OCP was monitored for 2 hours, the potentiodynamic polarization measurement was conducted. Because of the low OCP value measured on Titanium in the test solutions, the potentiodynamic polarization was started up at -1.5 V, and performed till 0.5 V at a scan rate of 10 mV/s (Souza et al., 2015). Subsequently, it was subjected to the Tafel tests arranged from E_{ocp} (open circuit/natural electrode potential) -250 mV to +250 mV, to identify the I_{corr} (corrosion current density), E_{corr} (corrosion potential at I_{corr}) and R_{corr} (corrosion rate at I_{corr}) (Oshida et al., 2005). Results were statistically analyzed by one-way ANOVA with Tukey HSD at a significance level of 0.05.

5. Surface analysis

After the electrochemical measurements, all the samples were evaluated by examining the surface using a scanning electron microscope.

Table 1. The 4 commercially available oral rinses and saline

Code No.	Oral rinse product	pH	F^{-} ion Concentration(mg/L)
A	Listerine® Natural Green Tea	4.46	260
B	Listerine® Teeth &Gum Defence	4.41	178
C	Garglin® Regular Solution	6.30	117
D	Listerine® Tartar Control	4.17	3.92
S	Klenzo®	6.24	3.56

Listerine® (IDS Manufacturing Ltd. Thailand)

Garglin® (Dong-A Pharm. Korea)

Klenzo® (JW Pharmaceutical. Korea)

III. Results

1. Open circuit potential measurements

The changes of the open circuit potential (OCP) versus time in 4 oral rinses containing different amounts of fluoride ions and in saline was shown in Figure 1. Under the open-air condition, it was noticed that the OCP values decrease significantly in solution A and B with the time. The curve of Solution A decreased more rapidly than solution B. The curves of solution B and C revealed stability OCP values (approximate to 0. 2 V) in 2 hours. The OCP value of saline increased quickly during the first few minutes, later gradually built up to close to 0.2 V in the remaining time.

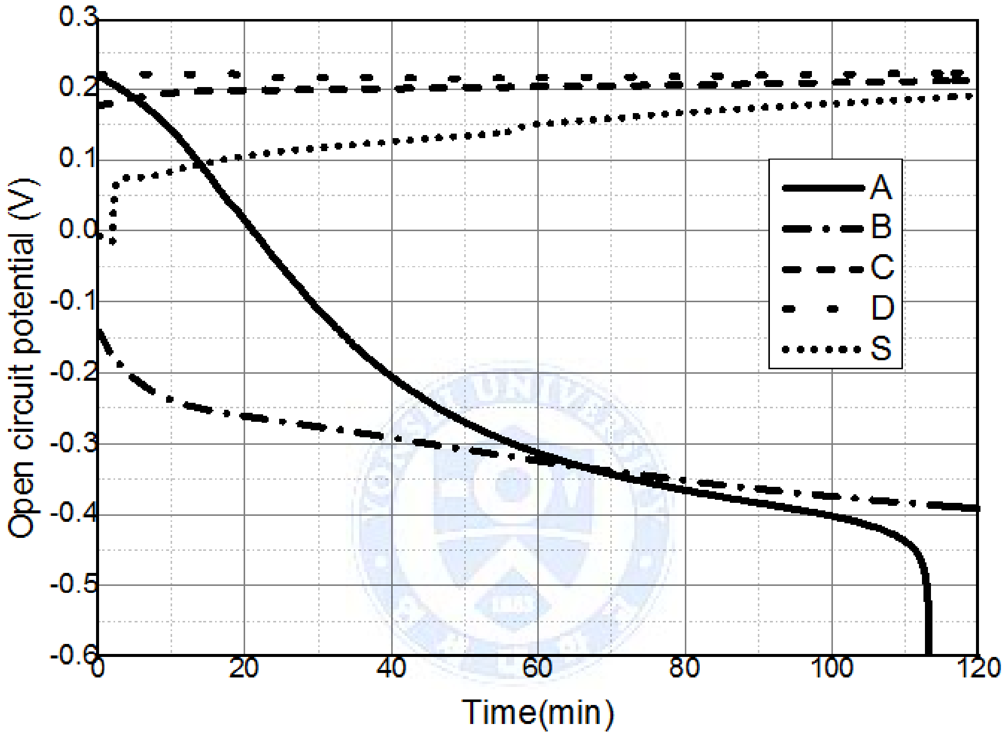

Figure 1. Representative open circuit potential plot: Variation of titanium alloy open circuit potential in 4 oral rinses containing 260 ppm F (A), 178 ppm F (B), 117 ppm F (C) and 3.92 ppm F (D) respectively, and in saline.

2. Potentiodynamic polarization measurements

Potentiodynamic polarization curves recorded in this study on titanium alloy in saline and 4 oral rinses containing different concentrations of fluoride and pH's, were shown in Figure 2. The graph was drawn with the minimums in each group.

There was a marked difference in the corrosion potential between the 5 solutions. It could be observed that the corrosion potential in sequence from high to low was: solution C, saline, solution B, solution D and solution A.

When the stable passive current plateau appeared, the values of current density in solution A and B was higher than solution C and D. Meanwhile the values of solution A was higher than solution B. And the values of current density in solution C, D and saline were approximately similar.

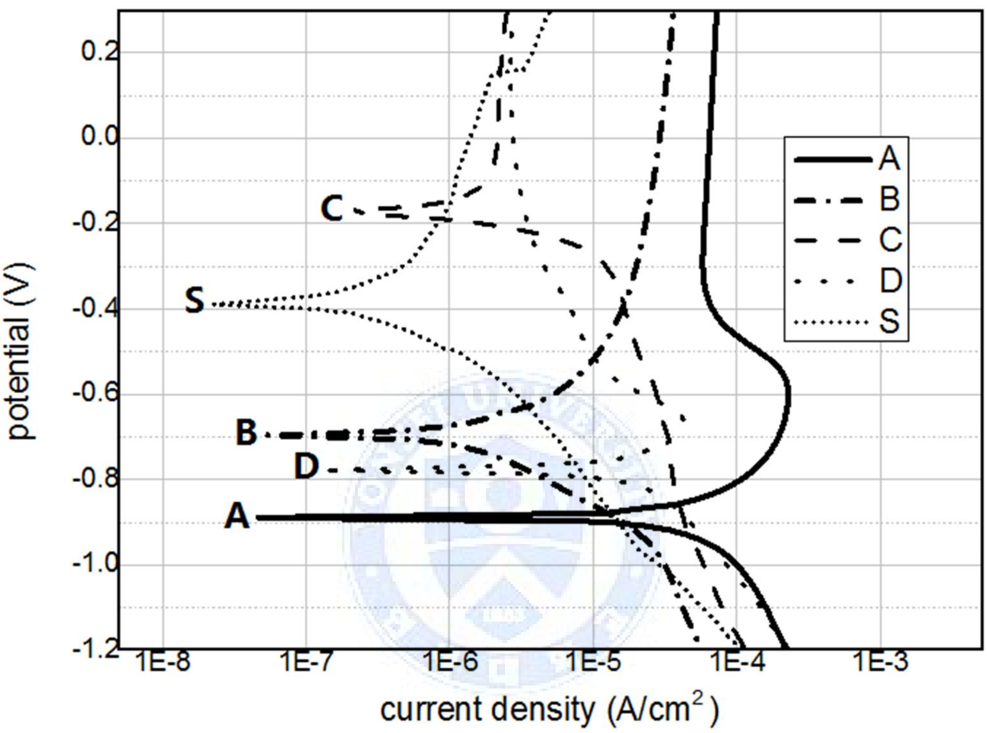

Figure 2. Representative potentiodynamic polarization plot: Titanium alloy in 4 oral rinses containing 260 ppm F (A), 178 ppm F (B), 117 ppm F (C) and 3.92 ppm F (D) respectively, and in saline. Potential scan rate was 10 mV/s.

Five samples in each solution were tested. Means and standard deviations of I_{corr} (corrosion current density), E_{corr} (corrosion potential at I_{corr}) and R_{corr} (corrosion rate at I_{corr}) were shown in Table 2. There were statistically significant difference in I_{corr}, E_{corr} and R_{corr} between the five solutions ($P < 0.05$).

Regarding on the I_{corr}, there were statistically significant difference between solution A and B, A and C, A and saline ($P < 0.05$). Regarding on the E_{corr}, there was no statistically significant difference between solution A and D, B and saline. Regarding on the R_{corr}, there were statistically significant difference between solution A and B, A and C, A and saline ($P < 0.05$).

Table 2. Means and standard deviations of I_{corr}, E_{corr} and R_{corr} in 4 oral rinses and saline with ANOVA

		Mean	SD
I_{corr} (uA/cm^2)	A	64.6^{b}	40.5
	B	10.6^{a}	6.2
	C	7.2^{a}	2.1
	D	29.4^{ab}	23.5
	S	1.3^{a}	0.6
E_{corr} (mV)	A	-808.4^{c}	97.7
	B	-516.1^{b}	106.9
	C	-148.4^{a}	19.4
	D	-695.0^{c}	115.5
	S	-367.5^{b}	15.8
R_{corr} (mpy)	A	23.7^{b}	14.9
	B	3.9^{a}	2.3
	C	2.6^{a}	0.8
	D	10.8^{ab}	8.6
	S	0.5^{a}	0.2

The same superscript letters indicate no statistically significant difference between the groups ($P > 0.05$). Increasing group mean values were expressed in ascending alphabetical order.

I_{corr} (corrosion current density), E_{corr} (corrosion potential at I_{corr}) and R_{corr} (corrosion rate at I_{corr}).

4 oral rinses containing 260 ppm F (A), 178 ppm F (B), 117 ppm F (C) and 3.92 ppm F (D) respectively, and saline (S).

3. Surface analysis

The surface morphology of titanium samples observed by SEM (scanning electron microscope) after electrochemical corrosion tests (OCP and Potentiodynamic polarization) were shown in Figure 3. It could be observed that sample A revealed mainly scratches and defects originating from the grinding and polishing operation done as pre-test. There was no clear signs of any general or localized corrosion on the surface. However, samples in 4 oral rinses and saline have revealed localized corrosion compared with the sample A. The sample in solution A revealed much more defects, crevice corrosion and pitting than the other samples. Then the sample in solution B also revealed some defects and pittings, but not as much as solution A had done. The samples in solution C, D and saline had revealed more slight pittings compared with A and B.

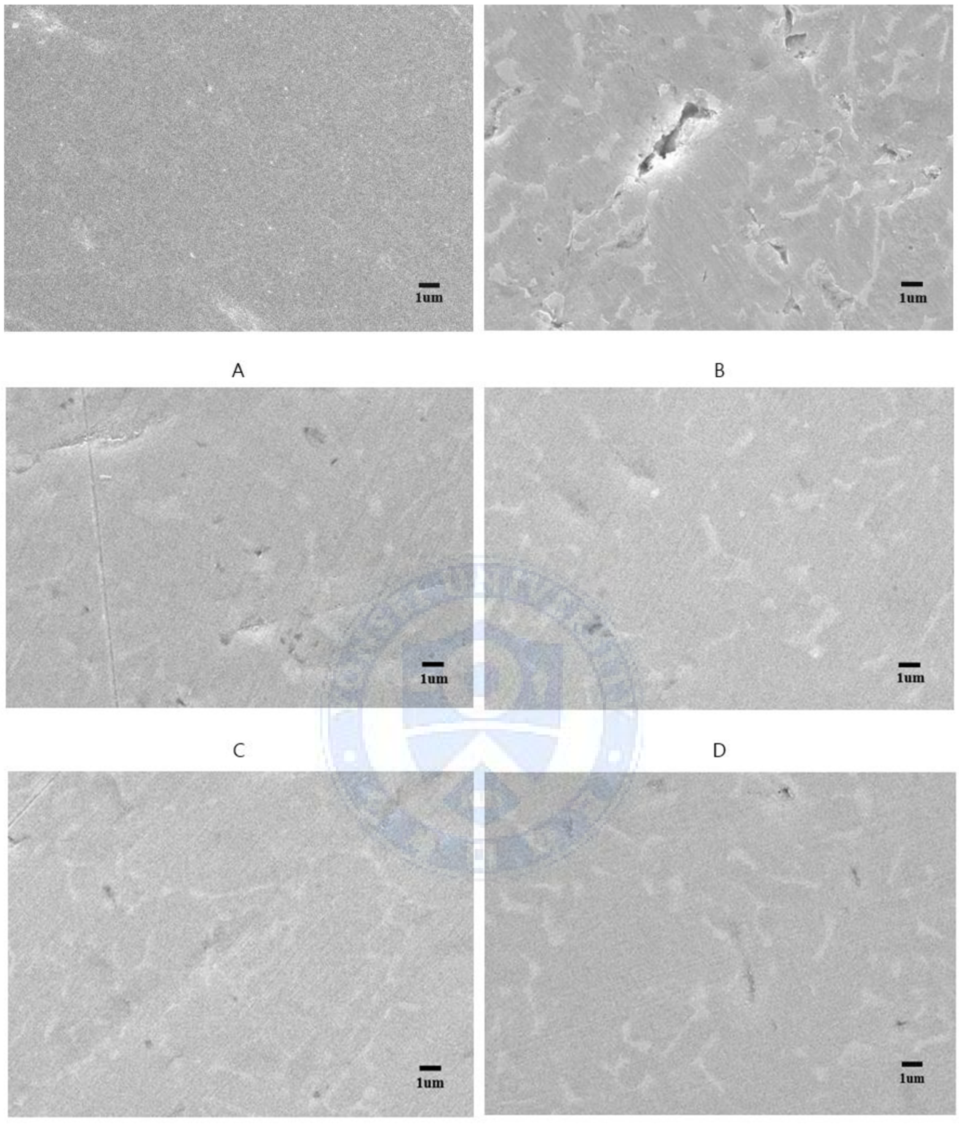

Figure 3. Surface morphology of titanium samples observed by SEM after electrochemical corrosion test (magnification, X 5000). A represents the sample before electrochemical test. B, C, D, E and F represent the samples in solution A,B,C,D and saline, respectively.

IV. Discussion

In order to be more closer to the clinical, present study used some commercially available oral rinses as the experiment solutions and used saline as the control solution. Many researches have investigated the influence of sodium fluoride containing solution on the titanium and titanium alloy which are widely used as implant materials in dental treatment.

In a previous study, it was reported that in an acidic environment, corrosion of pure Ti and titanium alloys might easily occur even in low fluoride concentrations (Nakagawa et al., 2001).

The results obtained from the present Open circuit potential and Potentiodynamic polarization experiments in saline and 4 oral rinses containing different concentrations of fluorides revealed that the corrosion behavior of titanium alloy samples changed obviously as shown in Figure 1. and Figure 2. A decrease of the OCP of a metallic material in contact with a certain environment revealed an increase of its chemical reactivity, and a subsequent predisposition to corrosion (Blackwood et al., 1988). As shown in Figure 1, the OCP values of titanium in solution A and B decreased obviously, especially in solution A. OCP curves recorded in this study confirmed a noticeable increase of the chemical reactivity of Titanium alloy at solution A and solution B with a probable change of the properties of the titanium oxide surface film. While, alloy samples in solution C and D revealed a similar and relatively stable chemical reactivity at a noble potential. The corrosion potential gradually increased with time in saline, this suggested that alloy samples maintained a good corrosion resistance in this solution.

As it shown in anodic polarization curve, when the stable passive current plateau appeared, the values of current density in solution A, B and C become decreased in sequence with increasing fluoride concentration (Figure 2). Due to the higher current density, the more dissolution of metallic ions, it could indicate that the corrosion resistance of titanium alloy turned to be inferior when fluoride concentration increased.

Based on the result of E_{corr} values in Potentiodynamic polarization test, there were statistically significant difference between each two solution, excepted between solution A and D, B and saline ($P < 0.05$). In solution A, B and C, the mean E_{corr} values decreased in sequence with increasing fluoride concentration (Table 2). This indicated reduction in corrosion resistance of titanium alloy and in the stability of its passive film when fluoride concentration increased.

Regarding on R_{corr}, the mean value also increased along with increasing fluoride concentration except in solution D. It could suggest that the corrosion rates of titanium alloy in solution A, B and C increased with the increasing fluoride concentration.

Although the mean E_{corr} in solution C was higher than it in saline, the mean I_{corr} and mean R_{corr} in saline was much lower than it in solution C. It could be interpreted that the actual corrosion rate in solution C was higher than it in saline. The pH values of solution A and B were similar to each other, both were approximately 4.4 (Table 1). When compared the solution A and B, with the increasing of fluoride concentration, the corrosion resistance of Titanium alloy decreased. In the previous study, it also has been reported that the decrease of corrosion resistance of titanium alloy was more significant in the solution containing more fluoride at a same pH condition (Souza et al., 2015).

As to the solution D, which was informed to have no fluoride by manufacturer, there might be several reasons to reduce the corrosion resistance of Titanium alloy. It might be that there had a little fluoride in solution D, just did not be informed. Because the pH value in solution D was the lowest among the 4 oral rinses. Although, there was no statistically significant difference between solution A and D, comparing the mean E_{corr}, the sample in solution D had a higher value than sample in solution A. Based on the previous study, it has been reported that a solution had a lower pH value, lead the lower corrosion resistance of titanium alloy in a same fluoride concentration (Nakagawa et al., 2001). In spite of the solution D had a lower pH value than solution A, the corrosion resistance of alloy sample in solution D was higher than sample in solution A containing more fluoride. This result might be related to the concentration of fluoride contained in oral rinses. The other probability might be that there had some other compositions which could cause the reduction of corrosion resistance.

On the whole, comparing the polarization curves in four oral rinses, it was found that none of the solutions could establish a stable passive film formation in oral environment after they exposured to 4 oral rinses, indicating a continuous anodic dissolution of metallic ions.

Based on the surface morphology of titanium samples observed by SEM (scanning electron microscope) after electrochemical corrosion tests (OCP and Potentiodynamic polarization) in Figure 3, the sample in solution A revealed much more defects, crevice corrosion and pitting corrosion than other samples. It was well known that the more pitting corrosion and crevice corrosion on the surfaces of samples, the more corrosion occurred. In spite of the surface of alloy in saline also seemingly revealed some slight crevice corrosion and pitting corrosion, it might be caused by the autocatalytic reaction of chloride ion. When there has a pit or crevice on the surface of metal, due to the lack of oxygen inside it compared with other parts, the quantity of metal cation increased. In order to maintain charge balance, the more chloride ions move to the pit or crevice and lead to the autocatalytic reaction. This process can cause the metal corrosion. Thus, the result in Figure 3. could be explained that the more fluoride, caused the more corrosion on the samples.

Based on the results of the present study, they partially supported the rejection of the null hypothesis. They showed significant differences in the corrosion behavior between titanium alloys in oral rinses containing different levels of fluoride.

V. Conclusion

This study of the corrosion behaviors of titanium alloy samples in saline and commercially available 4 oral rinses (A: PH 4.46/ 260ppm F, B: PH 4.41/ 178ppm F, C: PH 6.30/ 117ppm F and D: PH 4.17/ 3.92ppm), based on Open circuit potential measurements, Potentiodynamic polarization measurments and surface analysis with Scanning electron microscope showed that:

1. In the tested oral rinses except solution D, corrosion potential of Titanium alloy samples exposured in the solution containing more fluoride showed more obvious downtrend.

2. In the tested oral rinses except solution D, the more fluoride a solution contained, the significantly higher I_{corr}, lower E_{corr} and higher R_{corr} the titanium alloy sample showed.

3. Observed the surface morphology of titanium alloy samples by SEM, all the samples showed some defects, crevices or pittings in the 4 oral rinses compared with the sample before being tested, especially the samples in the solution A showed the most changes.

As a result of this, it was confirmed that commercially available fluoride treatment oral rinses could reduce the corrosion resistance of titanium alloy after using them more than 6 months (40 seconds use per day).

Although fluoride is useful to prevent caries, if patients use high concentration of fluoride-contained oral rinses during orthodontic treatment, the corrosion resistance of titanium alloy devices such as miniscrew implant could be affected.

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국 문 요 약

불소를 함유한 구강청결제의 사용이 티타늄 합금(Ti-6Al-4V)의 내부식성에 미치는 영향

(지도교수 황충주)

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불소를 함유한 접착제, 치약 및 구강청결제들은 치아 우식 및 탈회를 예방하기 위하여 교정치료 과정에서 많이 사용되고 있다. 그러나 이전의 연구들에 의하면 불소의 존재는 티타늄 금속의 부식을 일으키는데 이는 응력부식에 의한 티타늄 재질 임플란트의 파절을 일으킬 수 있다고 보고 되었다. 금속의 부식은 기계적 강도의 저하를 일으킬 뿐만 아니라 주위 조직에 금속 이온을 유리함으로써 염증 및 독성 반응을 일으키며 나아가서 암을 유발할 수도 있다고 보고 되었다. 본 연구의 목적은 시판되고 있는 불소를 함유한 구강청결제의 사용이 티타늄 합금의 내부식성에 미치는 영향을 조사하는데 있다.

구강청결제로는 Listerine® (IDS Manufacturing Ltd. Thailand) 시리즈 중의 내츄럴 그린 티 (Solution A: pH 4.46/ 260 ppm F), 티스 앤드 검 디펜스 (Solution B: pH 4.41/ 178 ppm F), 타르타르 (Solution D: pH 4.17/ 3.92 ppm F), Garglin® (Dong-A Pharm. Korea)시리즈 중의 레귤러액 (Solution C: pH 6.30/ 117 ppm F) 등 4가지 제품을 사용하였고 대조군으로는 생

리 식염수 Klenzo® (JW Pharmaceutical. Korea; pH 6.24/ 3.56 ppm F)를 사용하였으며, 시편으로는 티타늄 합금(Ti-6Al-4V) 원형시편 TC4® (Sheng Xinyuan Titanium Industry Co., LTD. Baoji City. China)를 본 실험에 사용 하였다. 전기화학 부식 실험으로는 Open circuit potential measurements 와 Potentiodynamic polarization measurements 를 진행하였으며 부식 실험후의 시편 표면 상태를 scanning electron microscope (SEM)를 통하여 관찰하였다. 본 실험 결과는 아래와 같다:

1. D용액을 제외한 모든 실험군에서, 불소 농도가 높을수록 용액 속에 노출된 티타늄 합금 시편의 부식전위는 현저한 하강추세를 나타내었다.

2. D용액을 제외한 모든 실험군에서, 불소 함유량이 높은 용액일수록 티타늄 합금 시편의 내부식성이 유의하게 감소하였다 ($P < 0.05$).

3. SEM상에서, 실험 전의 티타늄 합금 시편과 비교하였을 때 실험 후의 모든 시편표면에서 결손, 틈 부식 혹은 공식을 관찰하였으며, 특히 불소 농도가 가장 높은 A용액 속에 노출된 시편에서 결손이 가장 많이 관찰 되었다.

이상의 연구결과, 시판되고 있는 불소가 함유된 구강청결제를 6개월 이상 사용시 (40초/일), 티타늄 합금의 내부식성을 저하 시킬 수 있을 것으로 생각된다. 그러므로, 교정치료과정에서 환자들이 불소 함유량이 높은 구강청결제를 사용시 미니스크류 임플란트와 같은 티타늄 합금 재질 제품의 내부식성에 영향을 미칠 것으로 판단된다.

핵심되는 말: 불화물, 내부식성, 티타늄 합금, 구강청결제