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Author(s) Alternative	Noguchi, T; Takemoto, S; Hattori, M; Yoshinari, M; Kawada, E; Oda, Y
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Discoloration and Dissolution of Titanium and Titanium Alloys with Immersion in Peroxide- or Fluoride-Containing Solutions

Tatsumi NOGUCHI, Shinji TAKEMOTO, Masayuki HATTORI, Masao YOSHINARI, Eiji KAWADA and Yutaka ODA

Department of Dental Materials Science, Tokyo Dental College, 1-2-2 Masago, Mihama-ku, Chiba 261-8502, Japan

Corresponding author: Yutaka Oda

E-mail: yoda@tdc.ac.jp

Tel: 043-270-3778

Fax: 043-270-3780

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SYNOPSIS

This study compared differences in discoloration and dissolution in several titanium alloys with immersion in peroxide- or fluoride-containing solution. Commercially pure titanium (CP-Ti) and six titanium-based alloys were used: Ti-0.15Pd, Ti-6Al-4V, Ti-7Nb-6Al, Ti-55Ni, Ti-10Cu, and Ti-20Cr. Two test solutions were prepared for immersion of polished titanium and titanium alloys: one consisting of 0.2% NaF + 0.9% NaCl (pH 3.8 with lactic acid) and the other of 0.1 mol/l H₂O₂ + 0.9% NaCl (pH 5.5). Following immersion, color changes were determined with a color meter and released elements were measured using ICP-OES. Discoloration and dissolution rates differed between the two solutions. In the hydrogen peroxide-containing solution, color difference was higher in Ti-55Ni and Ti-6Al-4V than in any of the other alloys, and that Ti-55Ni showed the highest degree of dissolution. In the acidulated fluoride-containing solution, CP-Ti, Ti-0.15Pd, Ti-6Al-4V, Ti-7Nb-6Al, and Ti-10Cu alloys showed remarkable discoloration and dissolution with immersion. On the contrary, Ti-20Cr alloy showed very little discoloration and dissolution in either solution.

INTRODUCTION

In recent years, titanium implants and prostheses have come into wide use in clinical dentistry. However, there have been reports of pigmentation and discoloration occurring with the practical application of titanium implants and denture bases¹⁻³).

Although titanium is well known for its superior corrosion resistance, it is not strongly resistant to corrosion caused by fluoride. Probst *et al.* noted that prophylactic agents containing fluoride must be used with great care on implant materials and crown restorations made of titanium⁴). 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 fluoride⁵). Oda *et al.* also reported that the corrosion resistance of titanium was insufficient in the presence of 0.5% or higher concentrations of sodium fluoride⁶). Moreover, Nakagawa *et al.* reported that the passive film on titanium surface was destroyed under conditions where 30 ppm or more hydrofluoric acid was generated by dissociation of sodium fluoride⁷). In summary, these reports indicated fluoride as a possible cause of discoloration in titanium prostheses.

Separately, Pan *et al.* reported that peroxide was produced by bacteria and leukocytes during inflammatory reactions, and that it attacked titanium surfaces^{8,9)}. In the same vein, *in vitro* studies have reported on decrease in resistance to corrosion and signs of pitting corrosion in titanium in the presence of hydrogen peroxide^{10,11)}. Furthermore, Abe *et al.* noted severe discoloration with highly alkaline, peroxide-containing denture cleaners¹²⁾.

Taken together, these reports⁴⁻¹²⁾ suggested that peroxide produced by inflammatory cells and fluoride-containing prophylactic agents caused discoloration in titanium and titanium alloys. Therefore, although the mechanical properties and biocompatibility of titanium and titanium alloys are excellent, discoloration resistance in an oral environment remains a major challenge.

In view of the discoloration problem plaguing titanium alloys in practical application, this study was undertaken with two-fold aims: (1) to compare metal release and discoloration in several titanium alloys with exposure to peroxide- and acidulated fluoride-containing solutions; and (2) to determine whether there was any association between discoloration and oxide film formation or dissolution.

MATERIALS AND METHODS

Alloy specimens

Commercially available pure titanium (KS50, JIS type 2, Kobe Steel Industry; TI) and four titanium-based alloys were used, together with two experimental alloys (Table. 1). Pd-containing titanium alloy (TPD) is a corrosion-resistant titanium used in industry. Ti-6Al-4V (TAV) and Ti-7Nb-6Al (TNB) alloys are widely used for denture bases. Ti-Ni (TNI) alloy is used for orthodontic appliances. Copper- or chromium-containing alloys (TCU, TCR) were experimental alloys used in the development of dental casting alloys. These experimental copper- and chromium-containing alloys were made by melting titanium sponge (99.8% or above, Sumitomo Titanium, Amagasaki, Japan), copper (99.99% minimum purity, Research Institute for Electric and Magnetic Materials, Sendai, Japan) and chromium (99.99%, JMC New Materials Inc., Tokyo, Japan) into 20-g buttons in an argon-arc melting furnace (ACM-01, Diavac, Chiba, Japan). Obtained alloy buttons were arc-melted and cast in an alumina-magnesia mold (Titavest CB, J. Morita, Kyoto, Japan) using an argon-arc melting/pressure casting machine (Cyclarc II, J. Morita, Kyoto, Japan).

Table 1

Specimens of 14×14×1 mm or f20×1 mm size were cut from a sheet or rod of commercially available titanium or titanium alloy, while experimental titanium alloy specimens were cast using a wax pattern of the same size. Each specimen was embedded in epoxy resin (1-inch EX-ring, Refine Tech Co., Yokohama, Japan), and the alloy surface was polished with abrasive paper according to the standard metallurgical procedure. Polishing was completed with 0.02-μm colloidal silica particles and ultrasonic washing in distilled water for 10 minutes.

Test solutions

Two solutions were prepared for the discoloration and dissolution tests. An acidulated fluoride solution containing 0.2% NaF with 0.9% NaCl (pH 3.8 with lactic acid; NF), whereby its concentration was similar to that of fluoride in dental prophylactic agents used for mouth rinses. The low pH was intended to accelerate the effect on titanium. The other test solution consisted of 0.1 mol/l H₂O₂ with 0.9% NaCl (pH 5.5; HO), whereby its concentration was similar to that of peroxide in body fluids with inflammatory response⁸⁾. Analytical grade reagents (Wako Chem., Osaka, Japan) were used for the preparation of these two test solutions.

Discoloration measurement

Polished titanium and titanium alloy specimens were mounted on an immersion device and dipped in the test solution for 15 seconds per one-minute block, with the temperature controlled at 23±1°C according to ISO 10271¹³⁾. With the NF solution, the immersion period was one hour. With the HO solution, specimens were immersed for periods of 24, 72, and 168 hours in consideration of the slowness of color change. Following immersion, color changes were determined with a color meter (MCR-A, Minolta, Japan). Color values and amounts of color change were determined according to the CIE L*a*b* color coordinator system. Color difference was calculated using the following equation:

$$\Delta E_{ab}^* = [(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2]^{1/2}$$

where L₀^{*}, a₀^{*}, b₀^{*} were values before immersion, while L^{*}, a^{*}, b^{*} were values after immersion.

Dissolution measurement

Polished titanium and titanium alloy specimens were immersed in 20 ml of each test solution in a glass vial. The polished surface was exposed to NF solution for one hour and HO solution for 168 hours. Following immersion, the released elements were measured using ICP-OES (Vista-MPX, SII, Japan). Detection limit was below 0.01 ppm.

SEM observation

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

Statistical analysis

Color difference in, and the quantity of each metal released from, each alloy were statistically analyzed with two-way analysis of variance (ANOVA, $p < 0.05$) to determine the effects of alloy type and solution type. One-way ANOVA and Scheffé's test ($\alpha = 0.05$) were used to compare the specimen groups for significant differences in the color difference and total amount of released elements.

RESULTS

Discoloration

Change in color with time of immersion in the HO solution is shown in Fig. 1. TNI and TAV alloys showed a distinct increase in color difference with time. The other alloys showed a color change of less than 5 units, indicating that visual detection of discoloration would be difficult.

A pink rectangular box containing the text "Fig. 1".

Figure 2 shows the color difference in the titanium alloys in both solutions. The given values represented changes in color after 168 hours in HO solution and one hour in NF solution. TAV and TNI alloys showed a remarkable change in color in the HO solution. TI, TPD, TAV, TNB, and TCU alloys showed similar degrees of color change in the NF solution, with color difference values ranging around 20. On the contrary, TCR alloy showed the least color difference in both solutions.

A pink rectangular box containing the text "Fig. 2".

Dissolution

Table 2 shows the detected elements in HO and NF solutions after immersion of titanium and titanium alloy specimens. Titanium was detected in both HO and NF solutions for every alloy. In the HO solution, release of almost all the constituent elements of each alloy was detected, while Cu and Cr were under the detection limit in the NF solution.

Table 2

Figure 3 shows the total amounts of released elements in both solutions. TNI alloy showed remarkable dissolution in the HO solution, whereas TCU alloy showed the least dissolution in HO solution. TI, TPD, and TNB alloys showed higher dissolution than the other alloys in the NF solution. On the contrary, TCR alloy showed the least dissolution in NF solution.

Fig. 3

SEM observation

Figure 4 shows the typical surface morphologies of the samples following immersion in HO solution. TNI alloy showed some pitting and holes on the surface. As for the other alloys in HO solution (such as TAV and TCR in Fig. 4), no remarkable changes in their surface morphology were observed.

Fig. 4

In terms of surface morphology after immersion in NF solution, Fig. 5 shows that those of TI, TNI, TCU, and TCR differed from each other. TI showed a rough and porous profile, whereas TNI showed a minute granular profile. TCU showed a moderately rough and porous profile, whereas TCR showed a smooth surface. As for TPD, TAV, and TNB alloys, they showed a surface morphology similar to that of TI samples.

Fig. 5

DISCUSSION

Over the last few decades, the increasing use of titanium and titanium alloy dental implants has raised hopes for the treatment of partially or completely edentulous patients. Studies on the corrosion resistance of titanium are generally performed by incubating Ti in saline or artificial saliva. In such solutions, titanium exhibits a superior corrosion resistance due to the presence of a stable and dense titanium oxide film that spontaneously covers the metal surface. However, despite its excellent corrosion resistance when tested *in vitro*, titanium has been reported to be sensitive to sodium fluoride^{1,3-6} and hydrogen peroxide⁷⁻¹¹. Against this background, this study sought to investigate the effects of peroxide- and fluoride-containing

solutions on discoloration and metal release in several titanium alloys. Generally, the corrosion resistance behaviors of titanium-based alloys do not differ much in artificial saliva¹⁴). In this connection, the null hypotheses in this study were that the amount of metal elements released does not differ among titanium-based alloys, and that discoloration correlates with dissolution.

The sodium fluoride content of commercially fluoridated mouth rinses and topical application gels is between 0.1% and 2%. The standard prescription for fluoride mouth-rinsing agents is 0.2% NaF (F^- : 905 ppm) for weekly rinsing. *In vitro* studies have reported that corrosion of CP-Ti can occur at a concentration of 0.2% NaF, and that an acid medium can enhance fluoride activity and accelerate corrosion rate⁴⁻⁶). In the present study, we selected acidulated sodium fluoride solution at a concentration of 0.2% NaF to induce corrosion. Apart from fluoride, hydrogen peroxide — produced by bacteria and leukocytes during inflammatory reactions — has been shown to attack titanium surfaces. Several authors have investigated the effects of hydrogen peroxide on titanium corrosion at a concentration range of 0.05–0.15 mol/l^{7,9}). In the present study, a solution with a concentration of 0.1 mol/l H_2O_2 with 0.9% NaCl (pH 5.5) was selected to induce corrosion.

Color differences were classified into six ranks: $\Delta E_{ab}^* = 0.5-1.5$, slight; $\Delta E_{ab}^* = 1.5-3.0$, noticeable; $\Delta E_{ab}^* = 3.0-6.0$, appreciable; $\Delta E_{ab}^* = 6.0-12.0$, much; $\Delta E_{ab}^* = 12.0-$, very much¹⁵). TNI and TAV alloys showed a remarkable color difference of more than 12.0 in HO solution. TI, TPD, TAV, TNB, and TCU alloys also showed remarkable color difference of more than 12.0 in NF solution. A plausible explanation for the remarkable color difference observed in this experiment pointed to the formation of a thick oxide film or increased surface roughness due to corrosion. Color difference was calculated from differences in L^* , a^* , and b^* values. The formation of an oxide film would contribute substantially to differences in a^* and b^* values, while surface roughness would contribute substantially to differences in L^* value. In the case of TAV that showed much color difference in HO solution, it was the difference in b^* value that accounted for much of the color difference. On the contrary, when TNI showed much color difference in HO solution, it was the difference in L^* value that accounted for much of the color difference.

The surfaces of titanium and titanium alloys consist of a thin oxide layer (2–6 nm). This oxide layer is amorphous or poorly crystalline, and is composed of a slightly oxygen-deficient titanium oxide^{16,17}). When titanium is brought into contact with hydrogen

peroxide, a phenomenon will take place at the metal interface. Titanium decomposes the hydrogen peroxide, and oxide film is formed by oxidation reaction. In other words, the hydrogen peroxide behaves as an oxidizing agent and catalyzes the formation of a titanium oxide film^{18,19)}. This oxide film is far thicker than the one obtained by simple immersion of the metal in saline solutions for similar periods¹³⁾. When the oxide layer develops to a thickness in the order of 40 nm, interference with color occurs⁷⁾.

Conversion of fluoride ions into hydrofluoric acid partially depends on the pH of the solution. Hydrofluoric acid attacks passive films on the titanium surface^{6,20)}. This attack is preferentially targeted toward loosely packed atoms, thus revealing grain boundaries and increasing surface roughness. Consequently, a high degree of color difference occurs.

Dissolution is the most obvious indicator of corrosion. The correlation between color difference and the total amount of released elements in the hydrogen peroxide-containing solution is shown in Fig. 6. TNI alloy showed a high degree of dissolution and color difference. SEM observation of the same disks also recognized signs of roughness. This implied that the main reason for this discoloration was corrosion. As for the TAV alloy, a high degree of color difference was observed despite its lower dissolution. This implied that the main reason for this discoloration was the formation of a thick oxide film. Titanium-nickel alloy is potentially susceptible to release of Ni ions in NaCl solution²¹⁻²³⁾. Although the mechanism of titanium-nickel alloy corrosion in hydrogen peroxide-containing solution remained to be fully clarified, its dissolution rate seemed to be accelerated by the presence of hydrogen peroxide.

Fig. 6

The correlation between color difference and the total amount of released elements in the fluoride-containing solution is shown in Fig. 7. Evidently, almost all of the discoloration was caused by dissolution, especially in TI, TPD, TAV, TNB, and TCU alloys. However, TCR alloy showed no distinct changes. It appeared that the titanium alloys were chemically attacked in the presence of sodium fluoride, releasing Ti ions into the solution, except for titanium alloy containing chromium.

Fig. 7

The corrosion resistance of a titanium alloy is related to its composition. For example, the greatest increase in corrosion resistance is obtained when titanium is alloyed with cathodic additions capable of shifting the corrosion potential of the alloy in the noble direction (for instance, by palladium) and also by metals which increase the tendency of titanium to passivate²⁴⁾. It was also noted that, when the aluminum content increased in

titanium alloy, the passive potential region extended with a concomitant decrease in titanium corrosion rate²⁵⁾. Conversely, the addition of copper and nickel decreased the breakdown potential of titanium alloy with a subsequent decrease in corrosion resistance^{21,26)}. From these viewpoints, it would seem that palladium- or aluminum-containing alloys would show excellent corrosion resistance in fluoride-containing solution. However, in this study, TPD alloy showed no remarkable difference from pure titanium. It should be noted that all the abovementioned observations were based on exposure to near-neutral chloride solutions. Brossia and Cragnolino²⁷⁾ reported that although palladium addition significantly affected the localized corrosion resistance of titanium, palladium did not appear to influence the passive corrosion rate nor mitigate the deleterious effects of fluoride. Our results in the present study were generally in line with those of Brossia and Cragnolino²⁷⁾.

On the other hand, TCR alloy exhibited superior corrosion resistance in both solutions. It was presumed that chromium oxide on the TCR alloy played a significant role in the latter's high corrosion resistance to fluoride. Titanium oxides on the TCR alloy dissolved in the fluoride-containing solution, whereas chromium oxide barely dissolved. Consequently, a chromium-rich oxide film formed on the TCR alloy, suppressing dissolution of titanium and preventing fluoride attack²⁸⁾. It is noteworthy that in this study, ion leakage from the titanium alloys was higher in acidic sodium fluoride solution — except with TCR alloy. This exception thus highlighted the role of additive chromium in corrosion resistance in titanium alloys.

One of our null hypotheses was that the amount of metal elements released does not differ among the titanium-based alloys. However, the total amount of released elements differed not only with difference in solution type, but also with difference in the constituent elements of the alloys. Consequently, this null hypothesis was rejected. Indeed, it was clearly shown that additive elements of titanium alloys played an important role in corrosion resistance.

The other null hypothesis was that discoloration correlates with dissolution. Although the TAV alloy showed a remarkable color difference in the hydrogen peroxide-containing solution, it hardly showed any dissolution. In other words, the discoloration of titanium alloys stemmed from a variety of causes, with the most likely candidates being oxide film formation and dissolution.

CONCLUSIONS

We investigated the discoloration and dissolution of several titanium alloys with exposure to hydrogen peroxide- or acidulated sodium fluoride-containing solution.

The degrees of discoloration and dissolution differed between the two solutions. In the hydrogen peroxide-containing solution, the degree of discoloration was higher in Ti-Ni and Ti-Al-V alloys than in any of the other alloys. In the acidulated sodium fluoride-containing solution, Ti, Ti-Pd, Ti-Al-V, Ti-Nb-Al, and Ti-Cu alloys showed remarkable discoloration and dissolution. As for Ti-Cr alloy, it showed very little discoloration and dissolution in either solution.

Taken together, these results implied that the mechanism of discoloration in titanium alloys differed according to solution type — whether it contained peroxide or fluoride.

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LIST OF FIGURE CAPTIONS

- Figure 1** Change in color in titanium alloys in HO solution.
- Figure 2** Color difference in titanium alloys in both solutions. Means with the same superscript letter are not significantly different at $p < 0.05$.
- Figure 3** Total amount of released elements in each solution. Means with the same superscript letter are not significantly different at $p < 0.05$.
- Figure 4** SEM images of alloy surface after immersion in HO solution.
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- Figure 6** Total amount of released elements vs color difference in HO solution.
- Figure 7** Total amount of released elements vs color difference in NF solution.

LIST OF TABLE CAPTIONS

- Table 1** Titanium and titanium alloys used.
- Table 2** Amounts of detected elements in hydrogen peroxide- and fluoride-containing solutions after immersion of titanium and titanium alloys.

Color print

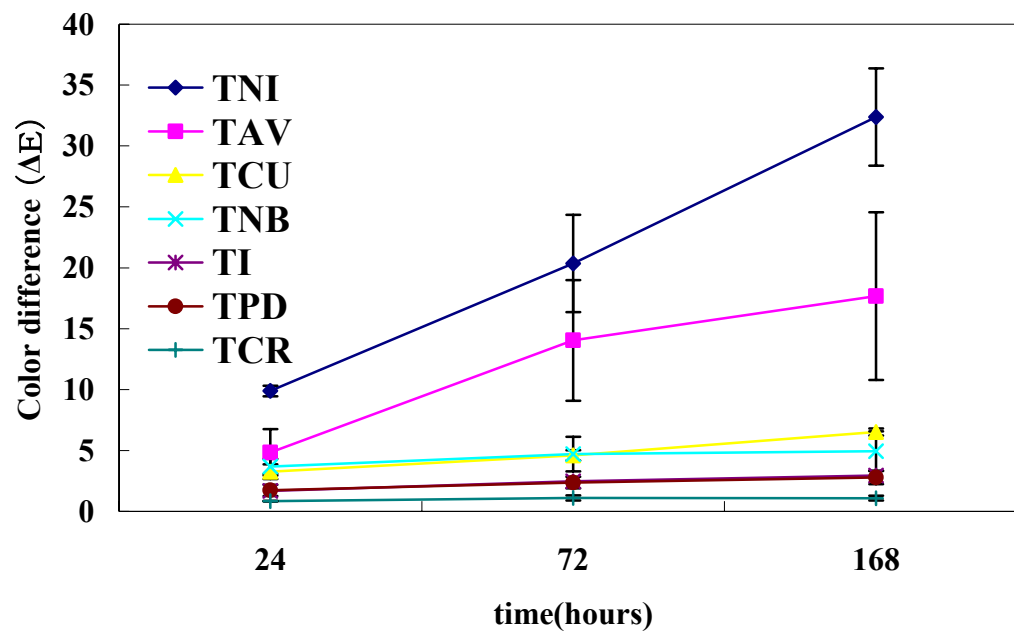


Fig.1 Change in color in titanium alloys in HO solution.

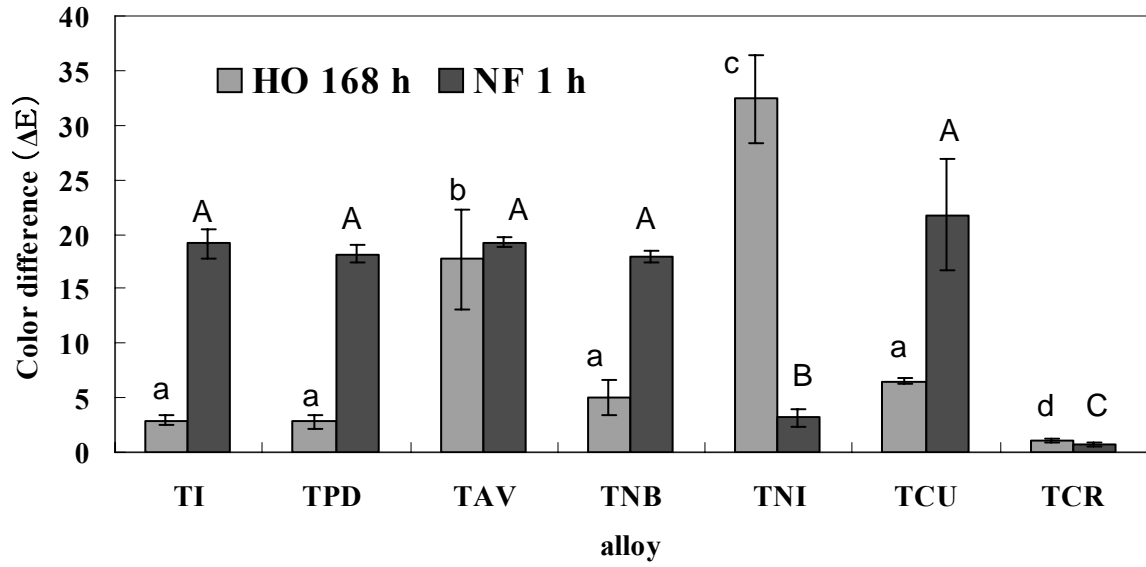


Fig.2 Color difference in titanium alloys in both solutions. Means with the same superscript letter are not significantly different at $p < 0.05$.

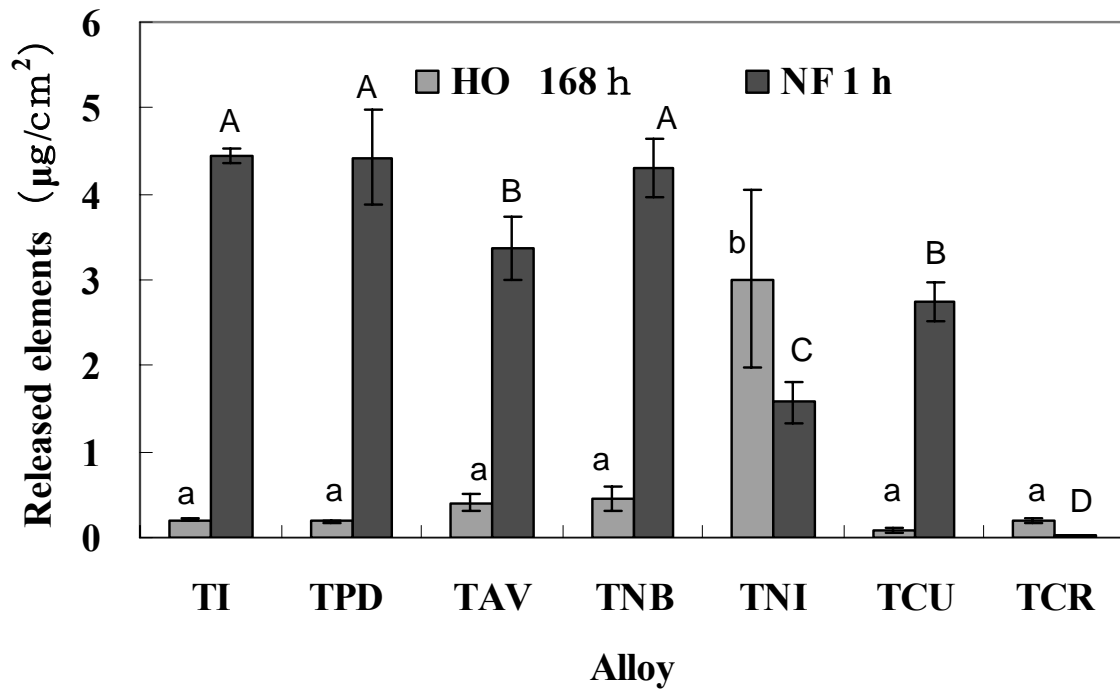
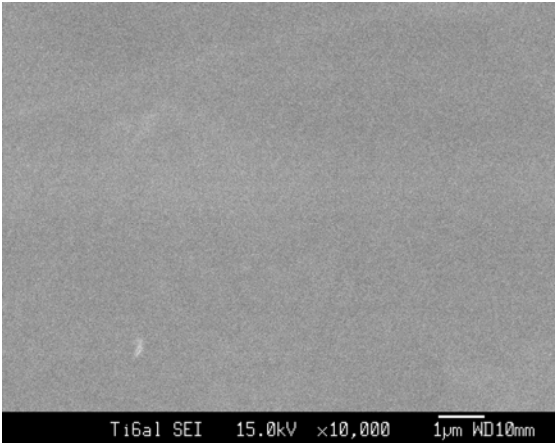
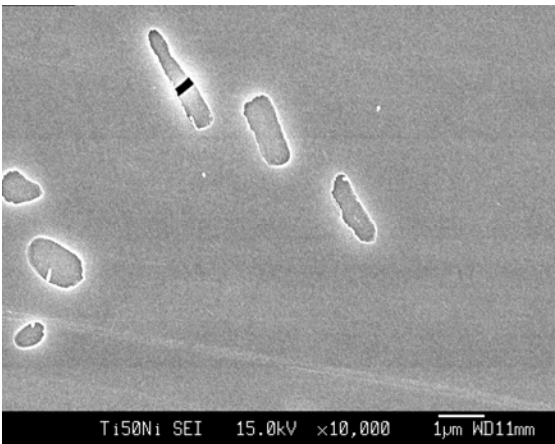


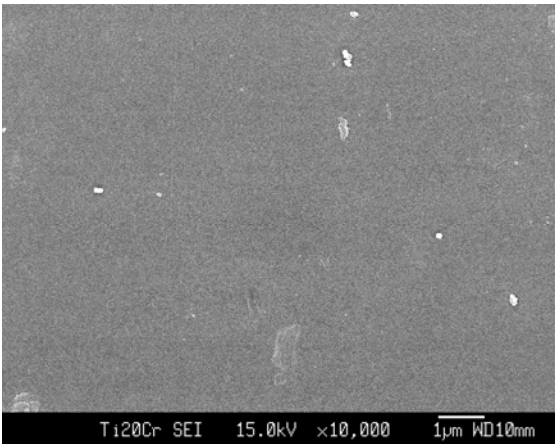
Fig.3 Total amount of released elements in each solution. Means with the same superscript letter are not significantly different at $p < 0.05$.



TAV

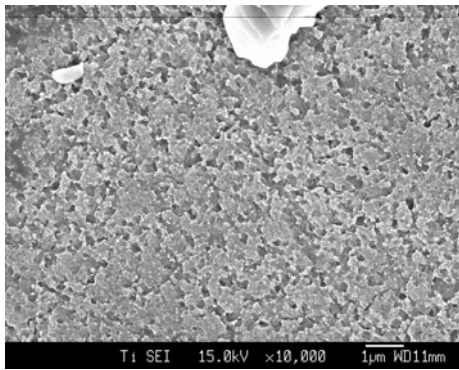


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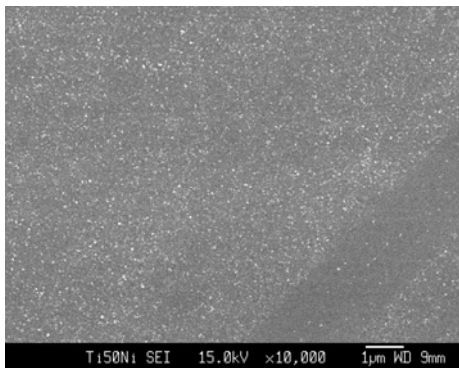


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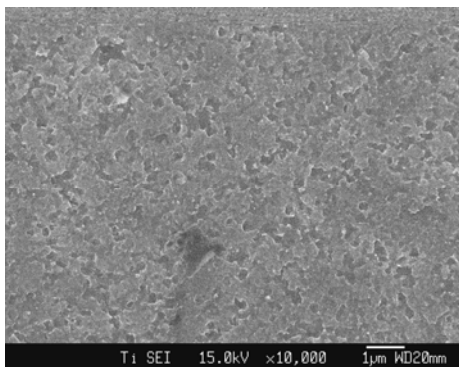
Fig. 4 SEM images of alloy surface after immersion in HO solution



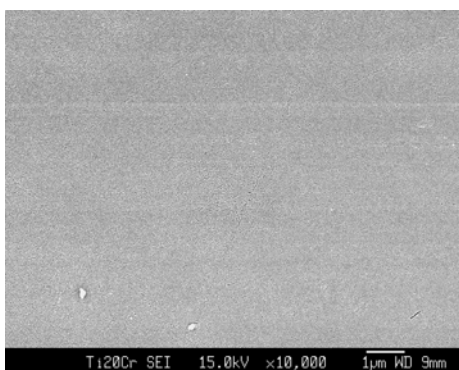
TI



TNI



TCU



TCR

Fig. 5 SEM images of alloy surface after immersion in NF solution

Color print

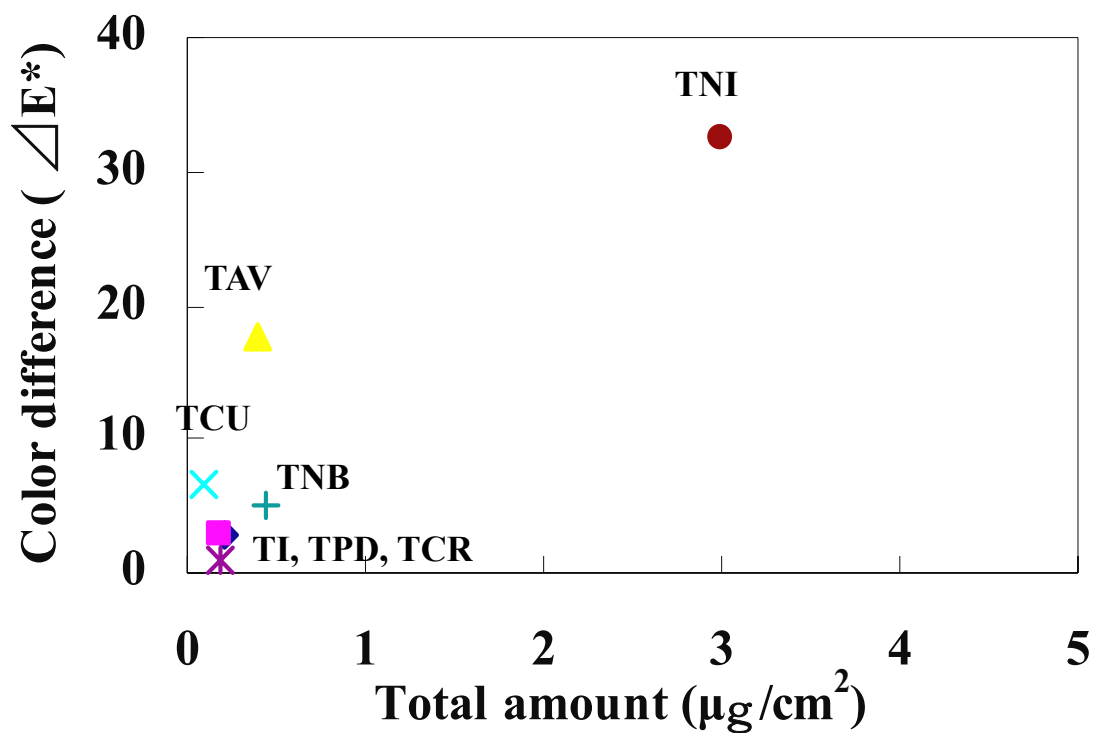


Fig.6 Total amount of released elements vs color difference in HO solution.

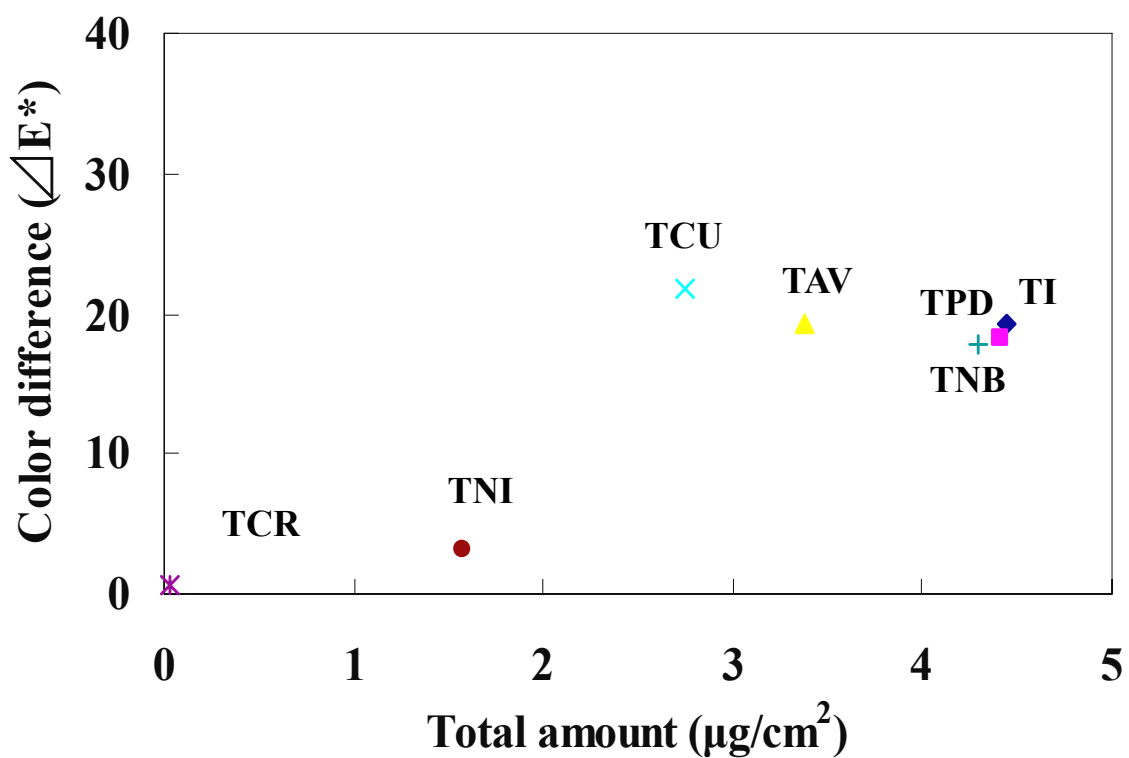


Fig.7 Total amount of released elements vs color difference in NF solution