

Title	Corrosion mechanism of Ti-Cr alloys in solution containing fluoride
Author(s) Alternative	Takemoto, S; Hattori, M; Yoshinari, M; Kawada, E; Asami, K; Oda, Y
Journal	Dental materials, 25(4): 467-472
URL	http://hdl.handle.net/10130/832
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Corrosion Mechanism of Ti-Cr Alloys in Solution Containing Fluoride

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[Short Title]

Corrosion mechanism of Ti-Cr alloys

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Introduction

The good resistance to corrosion and biocompatibility of titanium and its alloys have led to an increase in their use as restorative and prosthodontic dental materials in clinical dentistry. The passive films of these materials allow them to maintain resistance to corrosion¹⁻³). Although titanium and its alloys are well-known for their good corrosion resistance in the body, titanium appliances do occasionally show discoloration or corrosion in an oral environment^{4,5}). One reason for this is the presence of fluoride in prophylactic agents used to help prevent dental caries^{6,7}). Fluoride has been reported to compromise the passive film in an oral environment⁸⁻¹³). Therefore, high resistance to fluoride-induced corrosion would further enhance the suitability of titanium alloys for clinical use.

Recently, in discoloration experiments on titanium alloys, we found that an experimental titanium alloy containing 20 mass% chromium (Ti-20Cr alloy) showed the least discoloration and superior corrosion resistance in a fluoride-containing saline solution^{14,15}). This particular alloy has been reported to show greater corrosion resistance in an acidic saline solution containing fluoride than commercially pure titanium¹⁶). Furthermore, the chromium content of Ti-Cr alloy has been suggested to be related to its mechanical properties¹⁷), and resistance to fluoride-induced corrosion. However, how surface reaction to fluoride affects the chromium content of such alloys, and whether the chromium itself is responsible for the enhanced resistance to fluoride-induced corrosion, remains to be clarified. Therefore, it is important to determine the role of chromium in Ti-Cr alloys when discussing surface reaction.

The purpose of the present study was to clarify the corrosion mechanism of Ti-Cr alloys in acidic saline solution containing fluoride by investigating the surface structure

of the oxide films on those Ti-Cr alloys.

Materials and Methods

Specimens

Experimental Ti-5, 10, 15 and 20 mass% Cr alloys (denoted as CR5, CR10, CR15 and CR20, respectively) were made by melting sponge titanium (>99.8%, Sumitomo Titanium, Japan) and pure chromium (99.99% JMC New Materials Inc., Japan) in an argon-arc melting furnace (ACM-01, Daivac Limited, Japan) to produce 30-g button alloys. To make the castings, a sheet-type wax pattern 14 mm in diameter and 1.5 mm in thickness was invested. Each alloy was arc-melted and cast in an alumina-magnesia mold (Titavest CB, J. Morita, Japan) using an argon-arc melting/pressure casting machine (Cyclarc II, J. Morita, Japan). The specimen for XPS measurement was polished with No. 600 silicon carbide paper, and that for AES measurement was finally mirror-polished with buff and colloidal silica. As reference specimens, titanium plates (TI) were cut from a sheet of commercially available pure titanium (TI, grade 2, Kobe Steel, Japan).

The immersion solution contained 0.154 mol NaCl and 0.0476 mol NaF (905 mg F) in 1 L distilled water (NAF solution). The NAF solution was adjusted to a pH of 5.0 using lactic acid at 37°C. The specimens were immersed in 36 mL test solution at 37°C. They were then removed from the solutions after a 3-day immersion and gently rinsed with distilled water.

Dissolution of metal elements

Three specimens of each alloy were prepared for each condition to determine the

amount of dissolved metal. The amount of dissolved metal in the test solution after immersion was determined with an inductively coupled plasma emission spectrometer (ICP; Vista-MPX, SII, Japan). Amount of dissolution was calculated per unit metal area in contact with the solution. Area was determined by the image analysis system HC-2500/OL (Olympus, Japan) and Image-Pro PLUS software (Media Cybernetics Inc., USA). Amount of dissolved metal was statistically analyzed using a one-way analysis of variance (ANOVA) at a significance level of 95%. The specimens were then compared using the Scheffe test at a significance level of 95%.

XPS analysis

XPS measurement was performed by means of an SSX-100 photoelectron spectrometer (SSI, USA) with monochromatized Al K α radiation (1486.6 eV). The take-off angle for photoelectron detection was set at 35° for the specimen surface. The vacuum level of the analyzing chamber during measurement was of the order of 10⁻⁸ Pa. The binding energy was normalized to the C 1s peak (285.0 eV) of hydrocarbon on the specimen. At least 3 specimens of each alloy were prepared. The composition of the surface oxide film was quantitatively calculated according to the method of Asami et al.^{18,19)}. Empirical data¹⁸⁻²²⁾ and theoretically calculated data²³⁾ on the relative photoionization cross-sections were used for quantification.

AES analysis

AES measurement was performed by means of a JAMP-7100 electron spectrometer (JEOL, Japan) with argon-ion-sputter etching. The vacuum level of the analyzing chamber during measurement was of the order of 5 × 10⁻⁷ Pa. The differential Auger

electron spectra were measured, and their peak-to-peak intensities were used for quantification. Argon-ion-sputter was applied under 3 kV and 3 $\mu\text{A}/\text{cm}^2$ in 7×10^{-2} Pa, and the etching rate for the SiO_2 on silicon substrate was 0.15 nm/s. Thickness of oxide layer was determined as the oxygen signal in the oxide at the point halfway between its initial intensity and the background noise²⁴). Two specimens of each alloy were prepared.

Results

Dissolution of metal elements

Fig. 1 shows the total amounts of dissolved metal from the Ti-Cr alloys in NAF solution following a 3-day immersion. Titanium showed the highest level of dissolution, and the amount of dissolved chromium was around 4 $\mu\text{g}/\text{cm}^2$. Total amounts of dissolved metal showed a significant decrease with increase in chromium content in the alloys. A significant difference was observed in total amount of elements released from each alloy ($p < 0.05$).

XPS analysis

Chemical states

Figs. 2(a) ~ (c) show the typical *Ti 2p*, *Cr 2p* and *O 1s* XPS spectra of CR5 and CR20 before and after immersion in NAF solution. The *Ti 2p* XPS spectrum before immersion included $2p_{1/2}$ and $2p_{3/2}$ electron peaks that decomposed into Ti^0 , Ti^{2+} , Ti^{3+} , and Ti^{4+} , indicating the presence of both metal and oxide. Although the Ti^0 peak was clearly visible in the *Ti 2p* spectrum of both CR5 and CR20 before immersion in NAF solution, both these specimens showed a smaller peak or shoulder after immersion. In

Fig. 2(b), the *Cr 2p* XPS spectrum included $2p_{1/2}$ and $2p_{3/2}$ electron peaks. The *Cr 2p_{3/2}* peak decomposed into two peaks, indicating a metallic, Cr^0 , and oxide, Cr^{3+} , state. The Cr^0 peak in the *Cr 2p_{3/2}* spectrum of both CR5 and CR20 decreased with immersion in NAF solution. The O *1s* XPS spectra shown in Fig. 2(c) decomposed into three peaks indicating metal oxide, O^{2-} , hydroxide or hydroxyl groups, OH^- , and hydrate and/or adsorbed water, H_2O . The oxide films on all the Ti-Cr alloys consisted of oxide, hydroxide, and hydrate. The decomposed peak, O^{2-} , in the CR5 and CR20 spectra after immersion was slightly larger than that before immersion.

Composition

All as-polished Ti-Cr alloys consisted of carbon, oxygen, titanium, chromium, and trace nitrogen. The carbon and nitrogen were removed from the composition calculation because they originated in a contaminant layer. Chromium concentration of as-polished CR5, CR10, CR15, and CR20 was 2.0, 3.3, 3.8, and 4.7 atomic%, respectively, and titanium concentration was 22.7, 22.7, 21.3, and 21.2 in atomic%. Furthermore, oxygen concentration was approximately 74 atomic% and constant in the oxide films, regardless of chromium content. Table 1 lists the composition of the surface oxide films on the Ti-Cr alloys after immersion as determined by XPS. Fluorine was detected on all specimens. An increase in chromium ratio was found in the oxide films with increase in chromium content.

The fraction in Fig. 3 shows the proportion of chromium to chromium and titanium in the surface oxide films of the Ti-Cr alloys before and after immersion. The $[Cr]/([Ti]+[Cr])$ values in CR5, CR10, CR15, and CR20 before immersion were 0.08, 0.13, 0.16, and 0.19, respectively. These values were close to the nominal values.

After immersion, the $[\text{Cr}]/([\text{Ti}]+[\text{Cr}])$ value increased with increase in chromium content. Furthermore, the Ti-Cr alloys showed larger $[\text{Cr}]/([\text{Ti}]+[\text{Cr}])$ values after immersion.

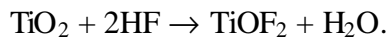
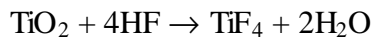
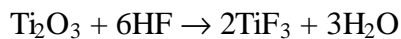
AES analysis

Fig. 4 shows the typical AES depth profiles of relative concentration of each element in the surface oxide layer of TI and CR5 before and after immersion. In Fig. 4(a), the AES depth profile of as-polished TI indicated that carbon concentration abruptly decreased, and then remained constant after 30 s Ar^+ etching. Oxygen concentration increased with decrease in carbon concentration, and then abruptly decreased. Titanium concentration increased with decrease in oxygen concentration. Relative concentrations of carbon and oxygen gradually decreased, whereas that of titanium increased after immersion, as seen in Fig. 4(b). The profile of the relative concentration of fluorine showed an abrupt decrease.

The AES depth profiles for CR5 and CR10 were similar to that for TI; that is, the relative concentrations of titanium and chromium increased with decrease in carbon and oxygen concentrations, as shown in Figs. 4(c), (d), (e) and (f). Furthermore, fluorine concentration in CR5 after immersion indicated a decrease with 100 s Ar^+ etching, as shown in Fig. 4(d). The thickness of oxide film in as-polished TI was 30 nm, whereas that in CR5 was about 15 nm. After immersion in acidic fluoride-containing saline solution, TI and CR5 showed a thicker oxide layer than as-polished alloys. Furthermore, higher chromium content in the Ti-Cr alloy, as shown in Figs. 4(e) and (f), yielded a thinner oxide layer on the alloy after immersion.

Discussion

Titanium and its alloys were corroded by fluoride in solutions^{8,10,25}). It was suggested that sodium fluoride and monofluoro phosphoric acid in prophylactic agents electrically dissociate, with subsequent generation of fluoride ions, and that the degree to which these electrical-dissociated fluoride ions become hydrofluoric acid partially depends on the pH of the solution^{10,25}). It was also found that hydrofluoric acid attacked the passive film on the titanium surface, with subsequent formation of corrosion products, titanium-fluorine compounds, which were degraded in solution as follows:



In this study, too, the metal elements of Ti-Cr alloys showed dissolution after immersion in an acidic saline solution containing fluoride. This dissolution of titanium and chromium was confirmed in all the Ti-Cr alloys tested. However, the amount of chromium dissolved was small, and showed no correlation with chromium content. On the other hand, amount of titanium dissolved was lower than that in Ti, with rate of dissolution decreasing with increase in chromium content in all alloys. These results agree with those of earlier studies showing greater corrosion resistance to fluoride and lower discoloration in fluoride-containing saline solution in Ti-20Cr alloy than in commercially pure titanium¹⁴⁻¹⁶).

Chromium oxide films on cobalt-chromium alloys and stainless steel on dental alloys show consistently good corrosion resistance in an oral environment²⁶⁻²⁹). According to the electrochemical corrosion test, cobalt-chromium alloys in an acidic

saline solution containing 0.1% sodium fluoride were reported to show good corrosion resistance, equal to that exhibited by gold alloys²⁶⁾. Furthermore, stainless steel wire was found to show low reactivity, low discoloration, and low dissolution in fluoride-containing solutions^{27,28)}. This suggests that chromium oxide has good resistance to fluoride-induced corrosion, and that corrosion resistance to fluoride differs between titanium oxide and chromium oxide, with corrosion occurring in titanium oxide, but being resisted in chromium oxide.

The $[\text{Cr}]/([\text{Ti}]+[\text{Cr}])$ values in the oxide films reflected the compositional rate of the as-polished Ti-Cr alloys. Also, the chemical state in O 1s XPS spectra suggested that the titanium and chromium oxides consisted of oxide, hydroxide, and hydrate, indicating that the titanate and chromate species in oxide films were contained. After immersion, the Ti-Cr alloys mainly consisted of Ti^{4+} and Cr^{3+} , indicating progression in oxidation of the titanium and chromium and subsequent increase in thickness of the oxide film. Furthermore, the oxide films on the Ti-Cr alloys showed larger $[\text{Cr}]/([\text{Ti}]+[\text{Cr}])$ values after immersion. These results suggest selective fluoride-induced corrosion of the titanium oxide in the oxide film, although both titanium and chromium were re-passivated in the solutions. This selective dissolution of titanium oxide indicated microscopic localized corrosion. This corrosion induced a rough surface on the alloys, after which, the alloys were re-passivated by greater exposure to access by water. Viewed from the outermost surface, a thick oxide film appeared to have formed.

The thickness of oxide films on alloys as determined by AES analysis depends on the Ar^+ etching rate, which depends on the elements of those alloys. Therefore, difference in thickness among alloys can not be discussed within this context.

However, increase or decrease in thickness of oxide films on alloys before and after immersion in solution can be.. AES analysis indicated that the thicknesses of the oxide films on TI and CR5 were approximately 30 and 15 nm (calculated from SiO₂ on Si), respectively, before immersion in saline solution. After immersion, the thicknesses of the oxide films on TI and CR5 showed an increase. These findings agreed with the XPS results indicating an increase in the thickness of the oxide films after immersion in fluoride-containing solution. Furthermore, the oxide film in CR5 was thinner than that in TI, indicating that titanium alloy containing chromium exhibited lower oxidation in fluoride-containing solution than commercially pure titanium. On the other hand, the profiles of TI and CR5 revealed fluorine on the outermost surface of the oxide films. These data suggest that corrosion resulted from contact between fluoride and the outermost surface of the specimens.

Corrosion resistance to fluoride has been reported in Ti-Cr alloys. As-polished Ti-Cr alloys exhibited chromium and titanium oxide films with a thickness of less than 3 nm. With immersion in an acidic saline solution containing fluoride, the surface oxide films of these alloys was attacked by hydrofluoric acid partially arising from fluoride ions^{8,10,25}). Titanium oxide film was selectively dissolved in solution, with a chromium oxide film remaining due to greater resistance to fluoride. On exposure of titanium or chromium by dissolution of oxide film, these metals are then rapidly repassivated by contact with H₂O. In this study, rate of chromium oxide formation increased as chromium content increased, with subsequent formation of a chromium oxide-rich layer in the Ti-Cr alloys. Increase in chromium oxide on Ti-Cr alloys would decrease the potential for contact between titanium oxide and fluoride in the solution. This suggests that addition of chromium to titanium is effective in enhancing resistance

to corrosion by fluoride.

Conclusion

Four Ti-Cr alloys were characterized in terms of corrosion resistance in fluoride-containing saline solution and surface structure. Amount of chromium oxide in the oxide films was correlated with chromium content in the Ti-Cr alloys, with increase in chromium oxide depending on chromium content of the alloy. Formation of a chromium oxide-rich surface film improved corrosion resistance to fluoride in Ti-Cr alloys.

Acknowledgements

This study was supported in part by a Grant-in Aid for Scientific Research (No. 15791140, No. 16390564, No. 17791413) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors would like to thank Mr. S. Okano and Mr. Y. Kitazawa of the Oral Health Science Center of Tokyo Dental College for their invaluable support in the experiments. The XPS and AES measurements were performed under an inter-university cooperative research program run by the Advanced Research Center of Metallic Glasses, Institute for Materials Research, Tohoku University. The authors wish to thank Associate Professor H. Kimura, Mr. N. Ohtsu and Mr. Y. Murakami of the Institute of Materials Research of Tohoku University for the XPS and AES measurements. Finally, we would like to thank Associate Prof. Williams J. of Tokyo Dental College, for assistance with the English of this manuscript.

References

1. Hanawa T, Ota M. Characterization of surface film formed on titanium in electrolyte using XPS. *Appl Surf Sci* 1992; 55: 269-276.
2. Ong JL, Lucas LC, Raikar GN, Connatser R, Gregory JC. Spectroscopic characterization of passivated titanium in a physiologic solution. *J Mater Sci Mater Med* 1995; 6: 113-119.
3. Hanawa T, Asami K, Asaoka K. Repassivation of titanium and surface oxide film regenerated in simulated bioliquid. *J Biomed Mater Res* 1998; 40: 530-538.
4. Bergman B, Bessing C, Ericson G, Lundquist P, Nilson H, Andersson M. A 2-year follow-up study of titanium crowns. *Acta Odontol Scand* 1990; 48: 113-117.
5. Sutton AJ, Rogers PM. Discoloration of a titanium alloy removable partial denture: A Clinical Report. *J Prosthodont* 2001; 10: 102-104.
6. Pröbster L, Lin W, Hüttemann H. Effect of fluoride prophylactic agents on titanium surfaces. *Int J Oral Maxillofac Implants* 1992; 7: 390-394.
7. Ozeki K, Oda Y, Sumii T. The influence of fluoride prophylactic agents on the corrosion of titanium and titanium alloy. *Shikwa Gakuho* 1996; 96: 293-304.
8. Oda Y, Kawada E, Yoshinari M, Hasegawa K, Okabe T. The influence of fluoride concentration on the corrosion of titanium and titanium alloys. *J J Dent Mater* 1996; 15: 317-322.
9. Reclaru L, Meyer J-M. Effects of fluorides on titanium and other dental alloys in dentistry. *Biomaterials* 1998; 19: 85-92.
10. Nakagawa M, Matsuya S, Shiraishi T, Ohta M. Effect of fluoride concentration and pH on corrosion behavior of titanium for dental use. *J Dent Res* 1999; 78: 1568-1572.

11. Nakagawa M, Matsuya S, Udoh K. Corrosion behavior of pure titanium and titanium alloys in fluoride-containing solutions. *Dent Mater J* 2001; 20: 305-314.
12. Nakagawa M, Matsuya S, Udoh K. Effect of fluoride and dissolved oxygen concentrations on the corrosion behavior of pure titanium and titanium alloys. *Dent Mater J* 2002; 21: 83-92.
13. Schiff N, Grosogeat B, Lissac M, Dalard F. Influence of fluoride content and pH on the corrosion resistance of titanium and its alloys. *Biomaterials* 2002; 23: 1995-2002.
14. Noguchi T, Takemoto S, Hattori M, Yoshinari M, Kawada E, Oda Y. Discoloration and dissolution of titanium and titanium alloys with immersion in peroxide- or fluoride-containing solutions. *Dent Mater J* 2008; 27: 117-123.
15. Oda Y, Hattori M, Yoshinari M, Kawada E. Discoloration of titanium and titanium alloys with peroxide and fluoride solution. *J Dent Res (Spec Iss B)* 2003; 82: 308. Abstract No. 2380.
16. Takemoto S, Hattori M, Yoshinari M, Kawada E, Oda Y. Corrosion behavior and surface characterization of Ti-20Cr alloy in a solution containing fluoride. *Dental Mater J* 2004; 23: 379-386.
17. Koike M, Ito M, Okuno O, Kimura K, Takeda O, Okabe TH, Okabe T. Evaluation of Ti-Cr-Cu alloys for dental applications. *J Mater Eng Perform* 2005; 14: 778-783.
18. Asami K, Hashimoto K. X-ray photoelectron spectra of several oxides of iron and chromium. *Corros Sci* 1977; 17: 559-570.
19. Asami K, Hashimoto K, Shimodaira S. XPS determination of compositions of alloy surfaces and surface oxides on mechanically polished iron-chromium alloys. *Corros Sci* 1977; 17: 713-723.

20. Asami K, Chen SC, Habazaki H, Kawashima A, Hashimoto K. A photoelectrochemical and ESCA study of passivity of amorphous nickel-valve metal alloys. *Corros Sci* 1990; 31: 727-732.
21. Asami K, Chen SC, Habazaki H, Hashimoto K. The surface characterization of titanium and titanium-nickel alloys in sulfuric-acid. *Corros Sci* 1993; 35: 43-49.
22. Scofield JH. Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV. *J. Electron Spectrosc Relat Phenom* 1976; 8: 129-137.
23. Hanawa T. Characterization of surface films formed on titanium in electrolytic solutions. *J J Dent Mater* 1989; 8: 832-844.
24. Trepanier C, Tabrizian M, Yahia L'H, Bilodeau L, Piron DL. Effect of modification of oxide layer on NiTi stent corrosion resistance. *J Biomed Mater Res (Appl Biomater)* 1999; 43: 433-440.
25. Wilhelmssen W, Grande AP. The influence of hydrofluoric acid and fluoride ion on the corrosion and passive behavior of titanium. *Electrochimica Acta* 1987; 32: 1469-1472.
26. Takemoto S, Hattori M, Yoshinari M, Kawada E, Oda Y. Corrosion resistance of dental alloys in gargle solutions. *J J Soc Dent Mater Dev* 2005; 24: 31-38.
27. Jang HS, Son WS, Park SB, Kim HI, Kwon YH. Effect of acetic NaF solution on the corrosion behavior of stainless steel orthodontic brackets. *Dent Mater J* 2006; 25: 339-344.
28. Kao CT, Ding SJ, Wang Ck, He H, Chou MY, Huang TH. Comparison of frictional resistance after immersion of metal brackets and orthodontic wires in a fluoride-containing prophylactic agent. *Am J Orthod Dentofacial Orthop* 2006;130:568.e1-568.e9.

29. Li X-Y, Akiyama E, Habazaki H, Kawashima A, Asami K, Hashimoto K. Spontaneously passivated films on sputter-deposited Cr-Ti alloys in 6 M HCl solution. *Corros Sci* 1997; 39: 935-948.

Figure and Table Caption

Figure 1 Total amount of dissolved elements (chromium and titanium) from TI and Ti-Cr casting alloys immersed in acidic saline solution containing fluoride for 3 days.

Figure 2 Typical XPS spectra of CR5 and CR20 before and after immersion in acidic saline solution containing fluoride. (a) Ti 2p, (b) Cr 2p, (c) O 1s

Figure 3 Fraction showing proportion of chromium to constituted metals (chromium and titanium) in surface oxide films on Ti-Cr casting alloys before and after immersion in acidic saline solution containing fluoride. "Nominal" indicates composition when making of ingot.

Figure 4 AES depth profiles of the relative concentrations of elements at the surface oxide of TI, CR5 and CR10 before and after immersion in an acidic saline solution containing fluoride. The horizontal axis of TI indicates twice that of CR5 and CR10.

(a) TI before immersion, (b) TI after immersion in NAF, (c) CR5 before immersion, (d) CR5 after immersion in NAF, (e) CR10 before immersion, (f) CR10 after immersion NAF

Table 1 Composition of surface oxide films on Ti-Cr casting alloys after immersion in acidic fluoride-containing saline solution determined by XPS (n=3)

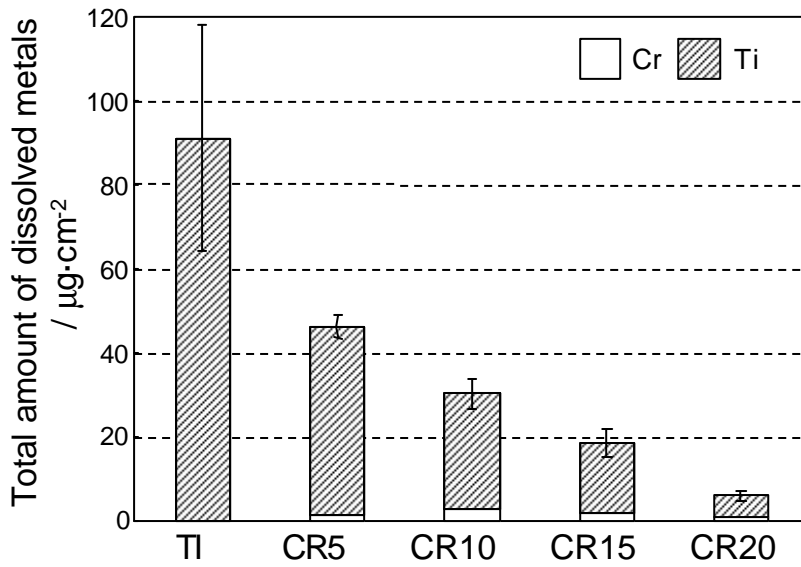


Figure 1 Total amount of dissolved elements (chromium and titanium) from TI and Ti-Cr casting alloys immersed in an acidic saline solution containing fluoride for 3 days.

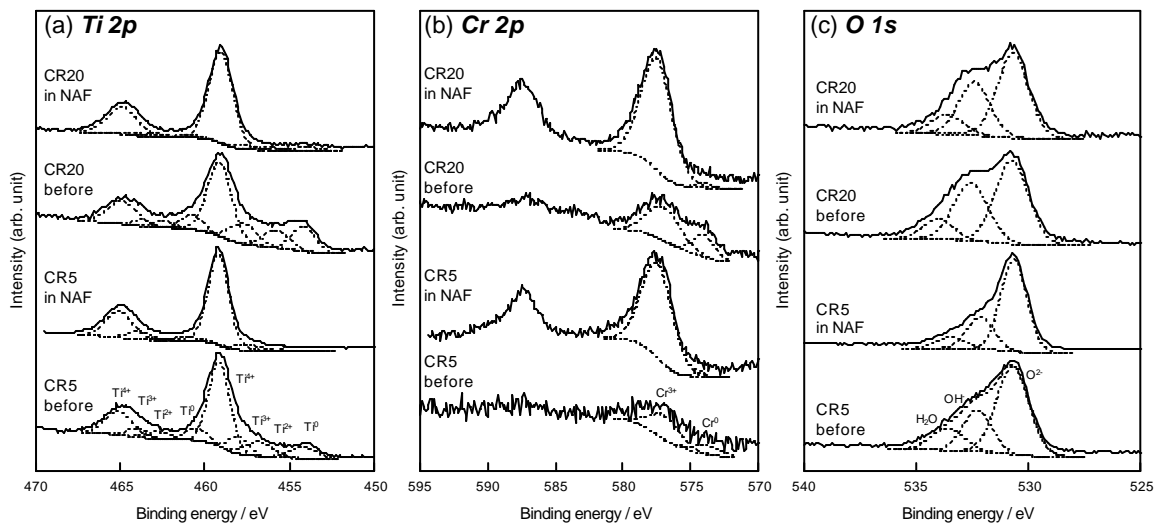


Figure 2 Typical XPS spectra of CR5 and CR20 before and after immersion in an acidic saline solution containing fluoride. (a) Ti 2p, (b) Cr 2p, (c) O 1s

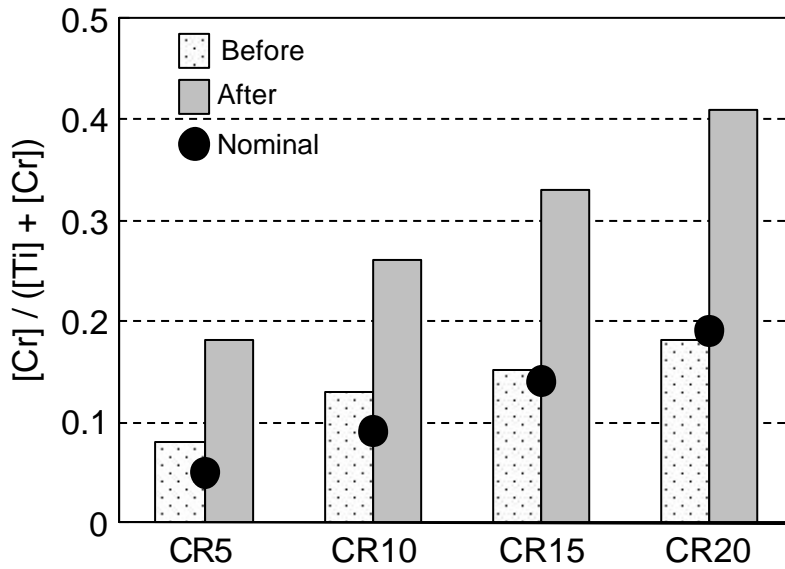


Figure 3 Fraction of proportional chromium to constituted metals (chromium and titanium) in the surface oxide films on Ti-Cr casting alloys before and after immersion in an acidic saline solution containing fluoride. "Nominal" indicates the composition when making of an ingot.

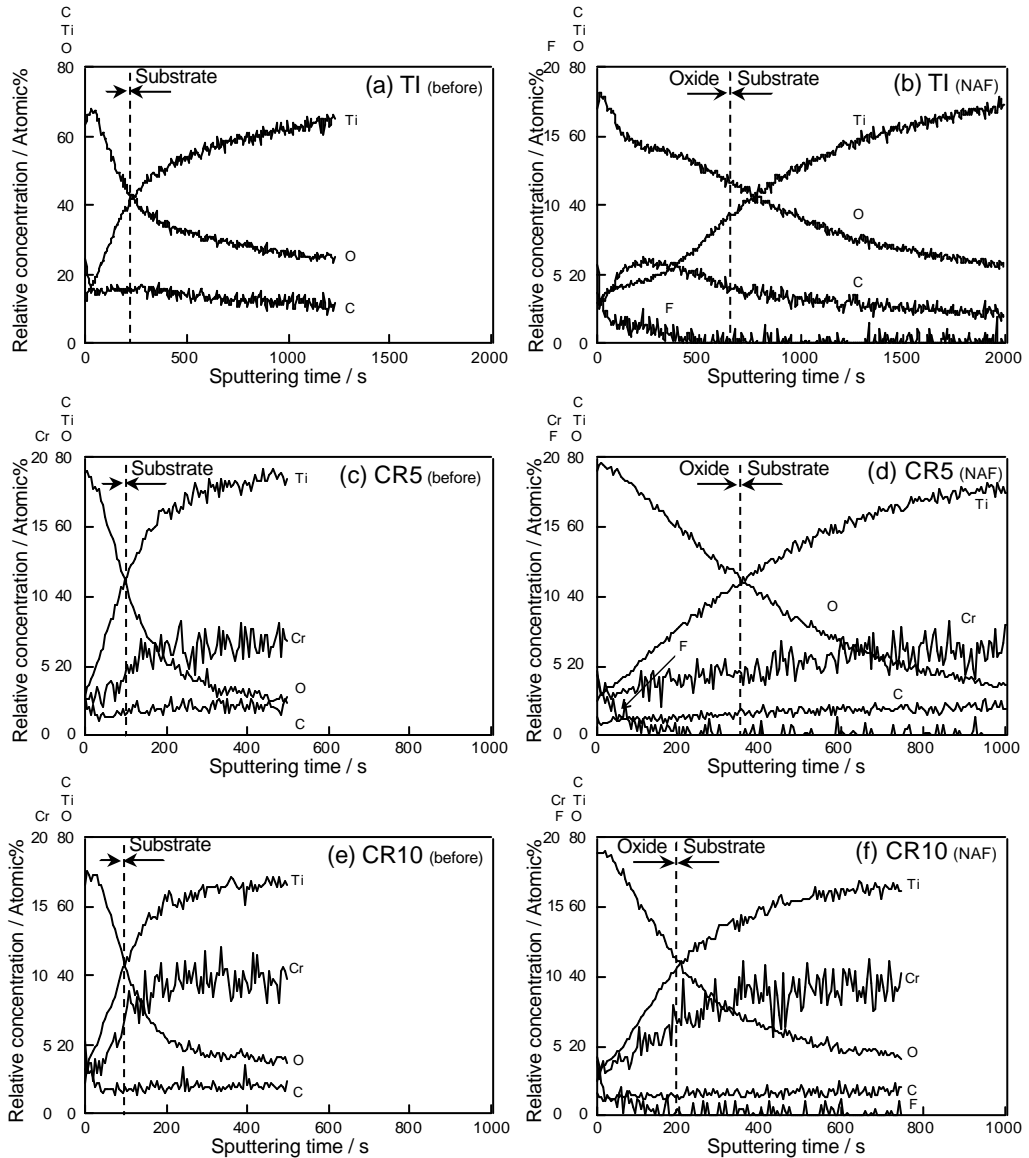


Figure 4 AES depth profiles of the relative concentrations of elements at the surface oxide of TI, CR5 and CR10 before and after immersion in an acidic saline solution containing fluoride. The horizontal axis of TI indicates twice that of CR5 and CR10.

(a) TI before immersion, (b) TI after immersion in NAF, (c) CR5 before immersion, (d) CR5 after immersion in NAF, (e) CR10 before immersion, (f) CR10 after immersion NAF

Table 1 Composition of surface oxide films on Ti-Cr casting alloys after immersion in acidic fluoride-containing saline solution determined by XPS (n=3)

Specimen	Composition (atomic%)			
	Ti	Cr	O	F
CR5	26.0 ± 0.2	5.8 ± 0.9	63.9 ± 2.4	4.2 ± 2.2
CR10	22.1 ± 0.8	7.9 ± 1.1	63.7 ± 2.1	6.4 ± 1.7
CR15	18.7 ± 0.2	9.2 ± 1.0	65.6 ± 1.7	6.5 ± 1.4
CR20	16.8 ± 0.8	11.6 ± 0.5	67.4 ± 0.6	4.3 ± 0.2
Average ± Standard deviation				