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RESEARCH AND EDUCATION

Surface properties of Ti-35Nb-7Zr-5Ta: Effects of long-term immersion in artificial saliva and fluoride solution

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ABSTRACT

Statement of problem. The mechanical properties of new titanium alloys with an elastic modulus closest to cortical bone have been studied. However, potentially damaging conditions experienced in the oral cavity, such as fluoride ions, can initiate a localized or crevice process of corrosive degradation in the alloy surfaces.

Purpose. The purpose of this in vitro study was to evaluate the effects of long-term immersion in artificial saliva or in fluoride solution on mean roughness (R_a), Vickers hardness, and topography of the new titanium alloy Ti-35Nb-7Zr-5Ta (TNZT) compared with those of cp Ti and Ti-6Al-4V (TAV).

Material and methods. Disks (N=210) were divided into cp Ti, TAV, and TNZT and subdivided according to the following treatments: no immersion (N^-, control), immersion in artificial saliva (S), and immersion in fluoride (F) during periods equivalent to 5, 10, 15, and 20 years. The R_a and Vickers hardness were measured with a profilometer and a hardness tester. The topography was analyzed by scanning electronic microscopy. Data were compared using the Kruskal-Wallis and Dunn tests (α=.05).

Results. Values of R_a and hardness were significantly different among the metals (R_a: TAV<TNZT<cp Ti; P<.05); and hardness (cp Ti<TNZT<TAV; P<.05); with a tendency for R_a to increase for TAV after 20 years of fluoride immersion and changes in hardness values of TAV and TNZT after immersion. TAV surfaces showed a heterogeneous appearance.

Conclusions. Long-term immersion in NaF did not change the roughness of Ti-35Nb-7Zr-5Ta. However, the hardness of the alloys increased with immersion. (J Prosthet Dent 2016;116:102-111)

Titanium and its alloys are used in dentistry for the fabrication of implants, prostheses, and prosthetic components because of their favorable combination of mechanical, physical, and chemical properties, including low density, high mechanical strength, good corrosion resistance, and biocompatibility.[1] Although commercially pure titanium (cp Ti) offers better corrosion resistance and better biocompatibility and is used to manufacture implants, the Ti-6Al-4V (TAV) alloy is the most frequently applied biomaterial in the manufacturing of prosthetic components[2] because of its much greater strength, including fatigue strength.

However, concerns regarding toxicity and biomechanical mismatching between TAV and the surrounding tissues have encouraged development of new alloys. The release of vanadium and aluminum ions is associated with cytotoxic reactions and neuron damage,[3] and evaluations of mechanical properties have demonstrated that the differences between the elastic modulus of TAV ($\cong$ 110 GPa) and cortical bone ($\cong$ 10-30 GPa)[4] may compromise the load transfer to the surrounding bone, leading to eventual failure of the implant. As a result, research of biomaterials has been focused both on the development of new alloys and on the surface treatments that improve implant/bone interaction.

A new generation of alloys without aluminum or vanadium and with improved biological (no toxicity) and mechanical (lower elastic modulus) compatibility has been studied.[5] Currently, there is considerable interest in the development of β titanium alloys[6-8] because of their combination of high strength and toughness.[9,10] Those alloys with the addition of niobium (Nb), zirconium (Zr),

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Clinical Implications

The new titanium alloy Ti-35Nb-7Zr-5Ta exhibits a better elastic modulus than that of Ti-6Al-4V and could be an alternative for patients with allergies because it does not have Al and V ions and appears to be less susceptible to surface changes when exposed to a fluoridated solution.

and/or tantalum (Ta) are considered the most promising.[9-12] These elements provide chemical properties similar to those of titanium[13] because they tend to stabilize the β phase, improving mechanical properties, in addition to their effects as solid solution hardeners.[14,15] Ternary Ti-Nb-Zr alloys have been studied for use in dentistry,[16] whereas the quaternary Ti-35Nb-7Zr-5Ta (TNZT) alloy has been evaluated only in the medical field.[17-19]

With development of these new alloys comes the need to simulate the conditions that are often found in the oral environment.[18-22] The long-term success of implants and prosthetic structures will depend on their resistance to the forces resulting from mastication and chemical and electrochemical reactions occurring on the surface.[23-25] The infiltration of saliva between implants and implant-supported structures creates galvanic cells between the dental alloys,[26] favoring crevice corrosion[27,28] and ion release. Moreover, fluoride ions can attack the oxide layer on the surface of titanium and its alloys, decreasing the corrosion resistance of these metals.[29]

In relation to implants and prosthetic components, the interaction between the metals used as raw material and the fluoride ions is interesting because of the growing use of compounds containing high levels of fluoride to prevent dental caries. When these compounds are present in toothpastes, gels, and/or mouth rinses,[30] the possible products of corrosion can induce inflammatory reactions and periprosthetic bone loss.[31] Accordingly, the purpose of this study was to evaluate the surface properties of TAV, TNZT, and cp Ti after long-term immersion in artificial saliva and fluoride solution. The null hypothesis was that no difference would be found among the surface properties of TAV, TNZT, and cp Ti after long-term immersion in artificial saliva and fluoride solution.

MATERIAL AND METHODS

Disks (8-mm diameter, 2-mm length) of commercial TAV alloy (Realum Industry and Commerce Pure Metals and Alloys Ltd), cp Ti grade II (Realum Industry and Commerce Pure Metals and Alloys Ltd), and arc-vacuum–melted TNZT were used in this study. To obtain TNZT alloy, the starting materials Ti (Realum Industry and Commerce Pure Metals and Alloys Ltd), Nb (CBMM Companhia Brasileira de Metalurgia e Mineração), Zr (Sigma-Aldrich Co), and Ta (Sigma-Aldrich Co), with a degree of purity greater than or equal to 99.00%, were arc melted using a water-cooled copper hearth in an argon atmosphere.[32] Ingots of 30 g were flipped and remelted 3 to 5 times. These ingots were heat treated at 1000°C for 8 hours in an argon atmosphere and furnace cooled. They were then hot forged as bars, machined as disks, and subjected to another heat treatment (1000°C, 1 hour, air cooled) to relieve stresses.

All disks were mechanically polished consecutively using 320, 600, 800 (for 30 seconds), 1200, 1500, and 2500 (for 40 seconds) grade silicon carbide (Hermes Schleifmittel GmbH & Co). Disks were then ultrasonically cleaned in isopropyl alcohol for 10 minutes and in distilled water for a further 10 minutes. Disks were etched with Kroll reagent (distilled water, nitric acid, and hydrofluoric acid (1:1:1, vol) to remove the original passive film and then ultrasonically cleaned again. Specimens were assigned to 27 groups (Table 1).

Control specimens (N^{-}) remained in storage for 730 hours, whereas the other specimens were immersed in

Table 1. Characteristics of experimental subgroups

Description	Metal	Subgroup
Control, without immersion	Ti-6Al-4V	TAV N^{-}
	Ti-35Nb-7Zr-5Ta	TNZT N^{-}
	cp Ti	T N^{-}
Immersion in artificial saliva, 5 y	Ti-6Al-4V	TAV S5
	Ti-35Nb-7Zr-5Ta	TNZT S5
	cp Ti	T S5
Immersion in artificial saliva, 10 y	Ti-6Al-4V	TAV S10
	Ti-35Nb-7Zr-5Ta	TNZT S10
	cp Ti	T S10
Immersion in artificial saliva, 15 y	Ti-6Al-4V	TAV S15
	Ti-35Nb-7Zr-5Ta	TNZT S15
	cp Ti	T S15
Immersion in artificial saliva, 20 y	Ti-6Al-4V	TAV S20
	Ti-35Nb-7Zr-5Ta	TNZT S20
	cp Ti	T S20
Immersion in sodium fluoride, 5 y	Ti-6Al-4V	TAV F5
	Ti-35Nb-7Zr-5Ta	TNZT F5
	cp Ti	T F5
Immersion in sodium fluoride, 10 y	Ti-6Al-4V	TAV F10
	Ti-35Nb-7Zr-5Ta	TNZT F10
	cp Ti	T F10
Immersion in sodium fluoride, 15 y	Ti-6Al-4V	TAV F15
	Ti-35Nb-7Zr-5Ta	TNZT F15
	cp Ti	T F15
Immersion in sodium fluoride, 20 y	Ti-6Al-4V	TAV F20
	Ti-35Nb-7Zr-5Ta	TNZT F20
	cp Ti	T F20

cp, commercially pure; F, fluoride; S, (artificial) saliva; TAV, cp Ti and Ti-6Al-4V; TNZT, Ti-35Nb-7Zr-5Ta.

Table 2. Chemical composition of artificial Fusayama saliva solution (g/L)

NaCl	KCl	$CaCl_2.2H_2O$	$Na_2S.9H_2O$	$NaH_2PO_4.2H_2O$	Urea
0.4	0.4	0.795	0.005	0.69	1

artificial saliva or in sodium fluoride (NaF) with 1500 ppm F^- NaF at pH 5.5 (Reactive Pharmacy Ltd). This concentration was established by considering the commonly found levels of fluoride in commercial mouth rinses (225 ppm) and toothpastes (500 ppm).[33] The composition of the artificial saliva Fusayama (pH 5.25) used in this study is given in Table 2.

For immersion in artificial saliva (S5, S10, S15, and S20) or in NaF (F5, F10, F15, and F20), the disks remained statically submerged in well plates containing 2 mL of each solution for 182.5 hours, 365 hours, 547.5 hours, or 730 hours, periods that simulated 5, 10, 15, and 20 years. This time estimate was based on 3 tooth brushings a day, with an average time of 2 minutes each.[29,30] The solution was changed every 12 hours.[34,35] At the end of the immersion tests, the disks were ultrasonically cleaned in isopropyl alcohol for 10 minutes and in distilled water for a further 10 minutes.

The mean roughness (R_a), Vickers hardness, and surface topography were used to verify the effects of fluoride ions on TAV, TNZT, and cp Ti. R_a was measured with a profilometer (Mitutoyo S; Mitutoyo Corp); 2 readings with an accuracy of 0.01 μm, a read length of 2.5 mm, and a speed of 0.5 mm/s were made for each specimen. Vickers hardness was measured in a hardness tester (Micromet 2100; Buehler) with 6 measurements per disk, 4.9 N for 15 seconds.[36] Overall surface topography was characterized with scanning electron microscopy (SEM) (JEOL JSM-6610LV; JEOL) equipped with energy-dispersive x-ray spectroscopy (EDS) with an overall analytic accuracy of ±2%. The distribution of chemical elements on the surfaces was determined through the spectra and mapping EDS attached to the SEM. Disks were placed directly onto the stub and examined without any preparation or manipulation. Each property was analyzed before (baseline) and after (final) the experimental treatments.

Data were statistically analyzed using the Kruskal-Wallis and Dunn tests (α=.05) to compare R_a and Vickers hardness among the experimental groups.

RESULTS

Mean R_a and Vickers hardness values for TAV, TNZT, and cp Ti are shown in Tables 3 and 4. Table 3 shows that significant differences in R_a were found among the studied metals. TAV showed the lowest value of R_a ($\cong$ 0.15 μm), TNZT had intermediate values ($\cong$ 0.27 μm) of R_a, and cpTi ($\cong$ 1.00 μm) had the highest values of R_a. Different behaviors were found for the specimens after immersion. Although cp Ti and the TNZT alloy did not exhibit changes in R_a after simulated long-term immersion (5-20 years) in artificial saliva and fluoride solution, the disks of TAV showed statistically significant variation, resulting in higher roughness in F20. However, all immersed specimens of TAV were statistically equivalent to those of the control group.

Table 3. Mean roughness (R_a, in μm) according to experimental groups

Solution	Immersion Period	TAV	TNZT	cp Ti[a]	*P*
NA	N (control)	0.165^{Aabc}	0.235^{Ba}	0.1035^{Ca}	<.05
Artificial saliva	S5	0.170^{Ac}	0.235^{Ba}	0.985^{Ca}	<.05
	S10	0.150^{Aabc}	0.245^{Ba}	1.080^{Ca}	<.05
	S15	0.150^{Aab}	0.255^{Ba}	0.980^{Ca}	<.05
	S20	0.150^{Aa}	0.240^{Ba}	0.930^{Ca}	<.05
NaF	F5	0.150^{Aa}	0.270^{Ba}	0.975^{Ca}	<.05
	F10	0.145^{Aa}	0.285^{Ba}	1.050^{Ca}	<.05
	F15	0.150^{Aa}	0.330^{Ba}	1.100^{Ca}	<.05
	F20	0.170^{Aabc}	0.370^{Ba}	0.970^{Ca}	<.05
P		<.001	.331	.097	

F, fluoride; NA, not applicable; S, saliva. [a]Different superscript uppercase letters indicate statistically significant differences between columns; different superscript lowercase letters indicate statistically significant differences between rows.

Table 4. Median Vickers hardness values according to experimental group

Solution	Immersion Period	TAV	TNZT	cp Ti[a]	*P*
Artificial saliva	N (control)	335.45^{Cabc}	197.15^{Bf}	133.85^{Aa}	<.05
	S5	319.90^{Ca}	173.60^{Bef}	129.45^{Aa}	<.05
	S10	352.60^{Cbcd}	182.75^{Ba}	130.40^{Aa}	<.05
	S15	370.30^{Cg}	193.90^{Bab}	132.75^{Aa}	<.05
	S20	356.05^{Ccdeg}	194.20^{Bbcd}	132.95^{Aa}	<.05
NaF	F5	334.00^{Cab}	187.10^{Ba}	137.10^{Aa}	<.05
	F10	342.90^{Cbc}	192.20^{Bab}	134.15^{Aa}	<.05
	F15	352.75^{Ccd}	193.80^{Babc}	131.15^{Aa}	<.05
	F20	354.75^{Ccde}	203.10^{Bef}	136.80^{Aa}	<.05
P		.001	.001	.683	

[a]Different superscript uppercase letters indicate statistically significant differences between columns; different superscript lowercase letters indicate statistically significant differences between rows.

In terms of Vickers hardness (Table 4), statistically significant differences were found among the metals (*P*<.05), with increased values as follows: cp Ti ($\cong$ 133 VHN) < TNZT ($\cong$ 192 VHN) < TAV alloy ($\cong$ 348 VHN). The Vickers hardness of cp Ti was unchanged after simulated long-term immersion in both artificial saliva and fluoride solution (*P*=.068). In contrast, the TAV (*P*=.001) and TNZT (*P*=.001) alloys varied in Vickers hardness values.

Figures 1 to 4 show micrographs of cp Ti, TAV, and TNZT. Small differences are evident among Figures 1 through 4, with no evidence of corrosion pits after exposure to fluorides (Figs. 2E-H, 3E-H, and 4E-H). Supporting the R_a findings for the TAV groups, the topography in Figures 3E-H show a more heterogeneous surface after NaF exposure. Figure 5 emphasizes the

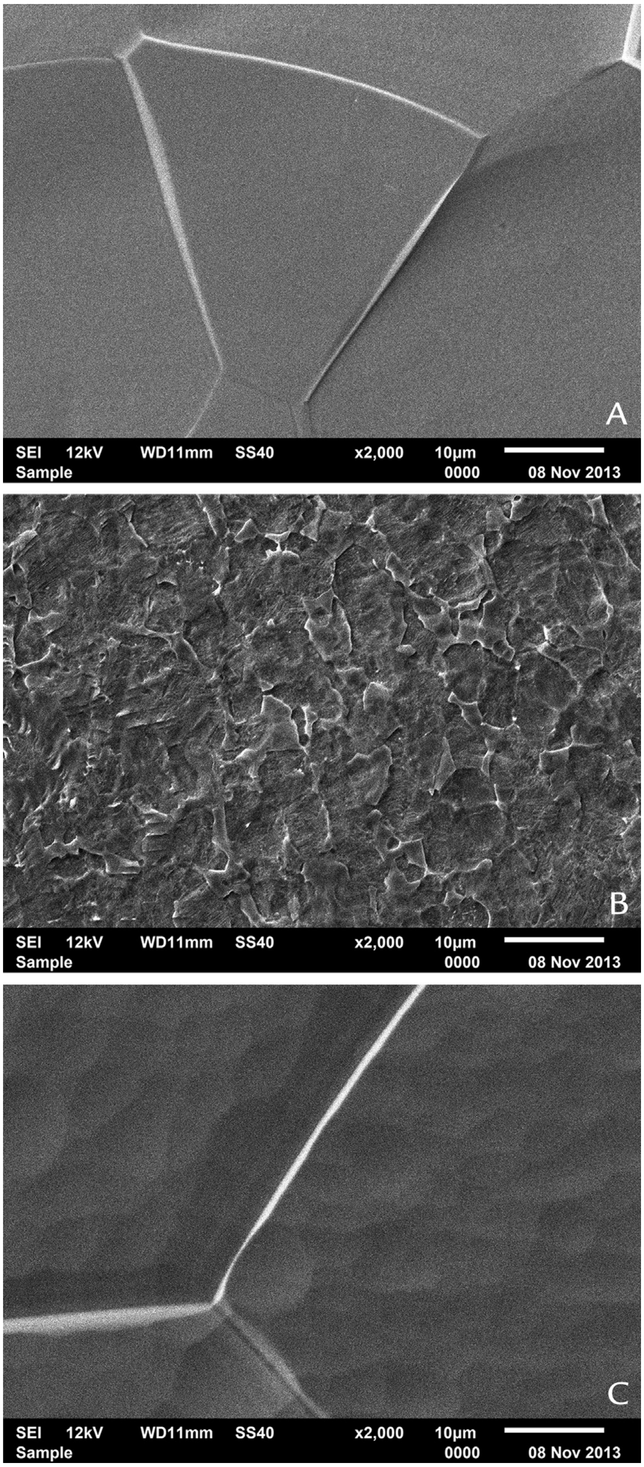

Figure 1. Control specimen surfaces (×2000 magnification). A, cp Ti (N^-). B, TAV alloy (N^-). C, TNZT alloy (N^-).

detection of fluoride and sodium ions on the surfaces of the TAV F10 and TAV F15 specimens. Arrows in Figure 2A indicate the particles where Ca and P ions, the main compounds in the artificial saliva that was used in this study (Table 2), were identified by EDS (Fig. 6).

DISCUSSION

In the oral environment, implants and implant-supported structures are constantly exposed to saliva, and their secreted electrolytes, for example, sodium, potassium, chloride, calcium, phosphate, bicarbonate, fluoride, thiocyanate, magnesium, sulfate, and iodide.[28] The presence of fluoride ions can initiate a localized or crevice process of corrosive degradation in titanium.[27,28] As a result, an increase in roughness associated with the adhesion of more microrganisms[27] and even the torque loss of abutments[25] can occur. This study evaluated the surface properties of TAV, TNZT, and cp Ti after long-term immersion in fluoride solution. The null hypothesis was rejected because some changes were found in the surface properties of TAV, TNZT, and cp Ti after long-term immersion in artificial saliva or fluoride solution.

Muguruma et al[24] stated that NaF dissociates into fluoride ions and sodium ions by starting chain reactions with the surface of the titanium. The fluoride ions react with hydrogen ions and are partially converted into hydrofluoric acid (HF), which reacts with the oxide layer and begins to degrade the titanium. In the case of severe levels of corrosion, the HF forms deposits of titanium oxide fluoride, titanium fluoride, and/or sodium fluorotitanate on the surface of the titanium.[24] Furthermore, the integrity of the oxide layer could influence the effects of fluorides. When the fluoride concentration increases from zero to a value lower than the critical value, the film is partially damaged but still protective; then, interactions between fluorides and titanium can only occur in the outer layer, and the inner layer is still resistant to corrosion. However, if the fluoride concentration exceeds the critical value, the fluoride ion can interact with the entire film, causing it to break down or preventing it from forming again, resulting in a porous and nonprotective film.[29]

In this study, significant differences were found among the R_a values of cp Ti, TAV, and TNZT alloys. The higher R_a values of cp Ti surfaces could be a result of the "purer" oxide layer, composed only of TiO_2, that was revealed more clearly by Kroll etching, thereby generating higher surface irregularities and, consequently, higher values of R_a. The R_a of most marketed implants can be divided into the following 4 categories: smooth surfaces with R_a values <0.5 µm; minimally rough surfaces with R_a values of 0.5 to 1 µm; moderately rough surfaces with R_a values of 1 to 2 µm; and rough surfaces with R_a values greater than 2 µm. Thus, the TAV and TNZT alloys were in the same category, namely, smooth surfaces, whereas cp Ti was in a different category (minimal roughness).[23]

Differences between TAV and TNZT after NaF immersion may be explained as follows. It is plausible that the small amount of titanium in the experimental alloy associated[30] with the presence of Zr and Ta[12] facilitated

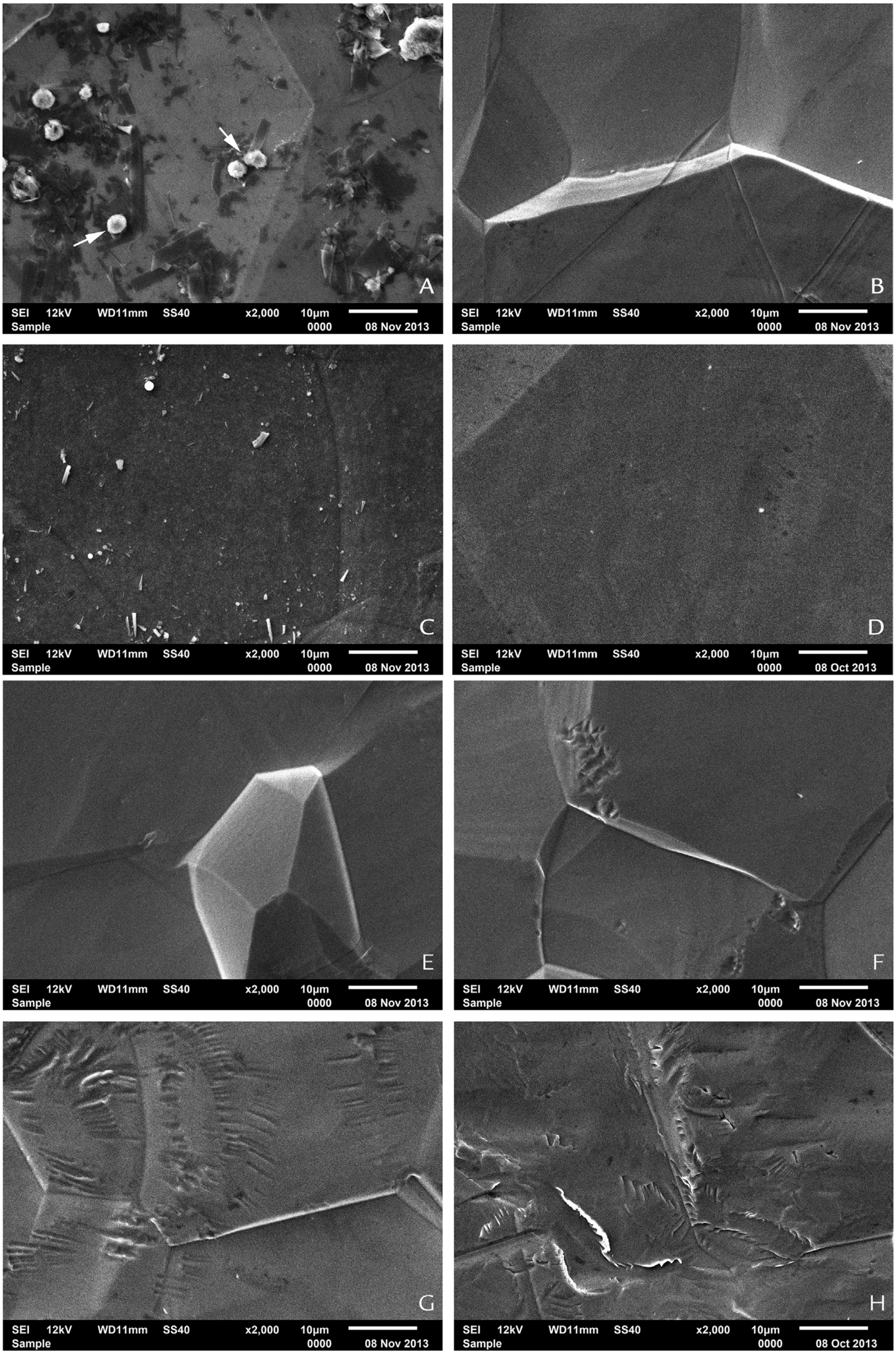

Figure 2. Electron micrographs of cp Ti (×2000 magnification) after immersion. A, Artificial saliva, 5 years (S5). B, Artificial saliva, 10 years (S10). C, Artificial saliva, 15 years (S15). D, Artificial saliva, 20 years (S20). E, NaF, 5 years (F5). F, NaF, 10 years (F10). G, NaF, 15 years (F15). H, NaF, 20 years (F20). Arrows indicate particles with Ca and P according to EDS results. EDS, energy-dispersive x-ray spectroscopy.

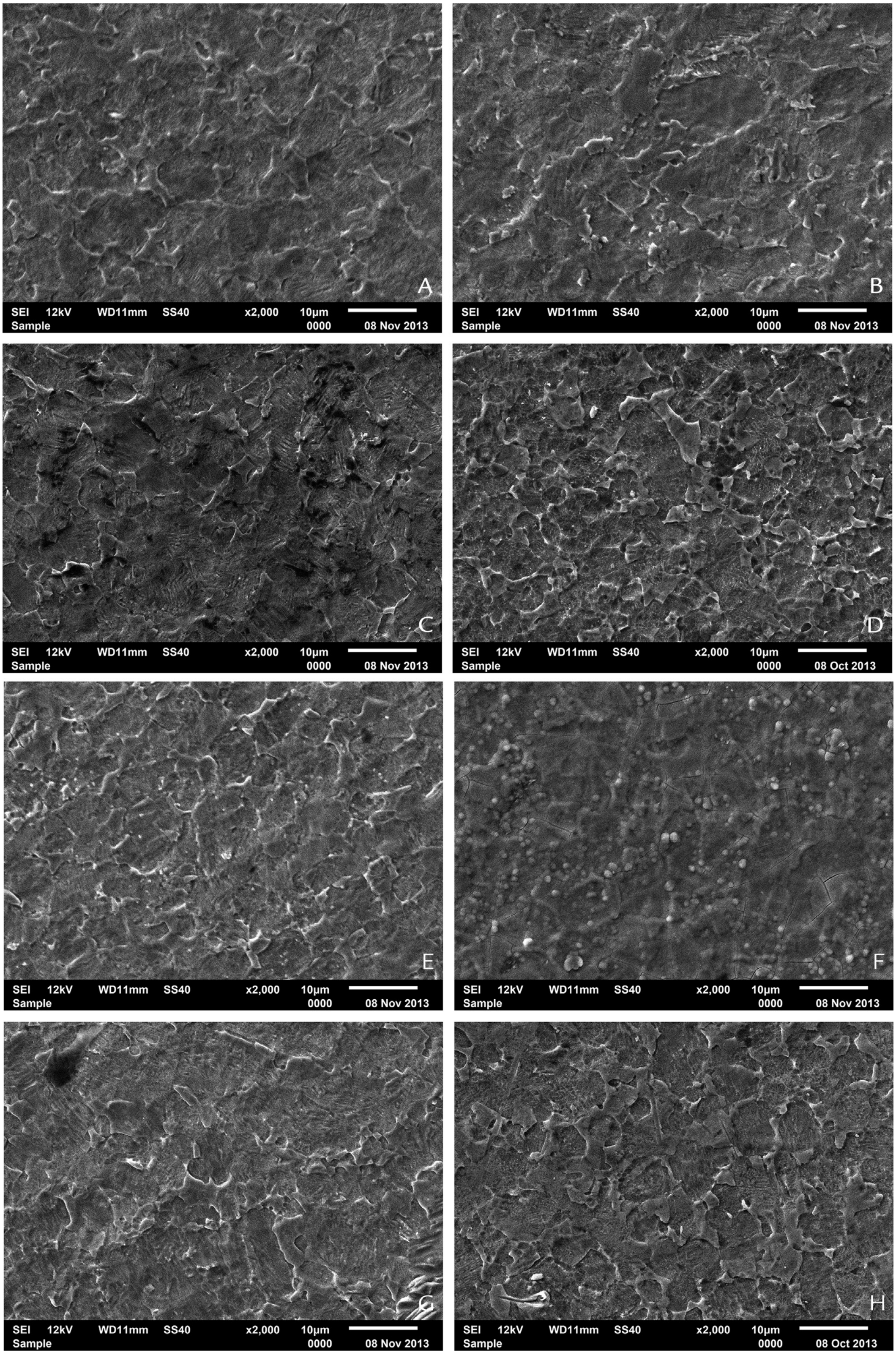

Figure 3. Electron micrographs of TAV alloy (×2000 magnification) after immersion. A, Artificial saliva, 5 years (S5). B, Artificial saliva, 10 years (S10). C, Artificial saliva, 15 years (S15). D, Artificial saliva, 20 years (S20). E, NaF, 5 years (F5). F, NaF, 10 years (F10). G, NaF, 15 years (F15). H, NaF, 20 years (F20). F, fluoride; S, saliva.

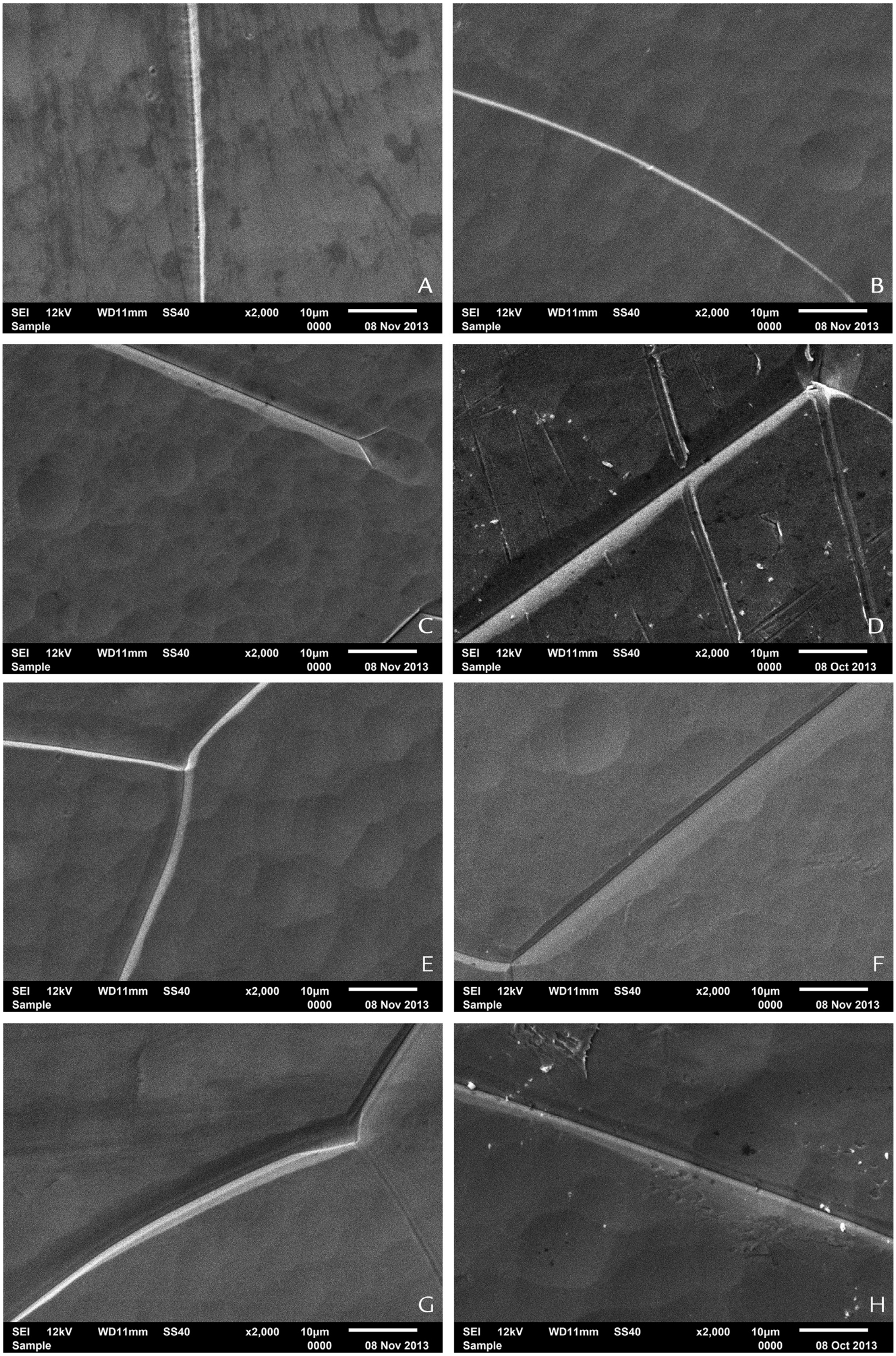

Figure 4. Electron micrographs of TNZT alloy (×2000 magnification) after immersion. A, Artificial saliva, 5 years (S5). B, Artificial saliva, 10 years (S10). C, Artificial saliva, 15 years (S15). D, Artificial saliva, 20 years (S20). E, NaF, 5 years (F5). F, NaF, 10 years (F10). G, NaF, 15 years (F15). H, NaF, 20 years (F20). F, fluoride; S, saliva.

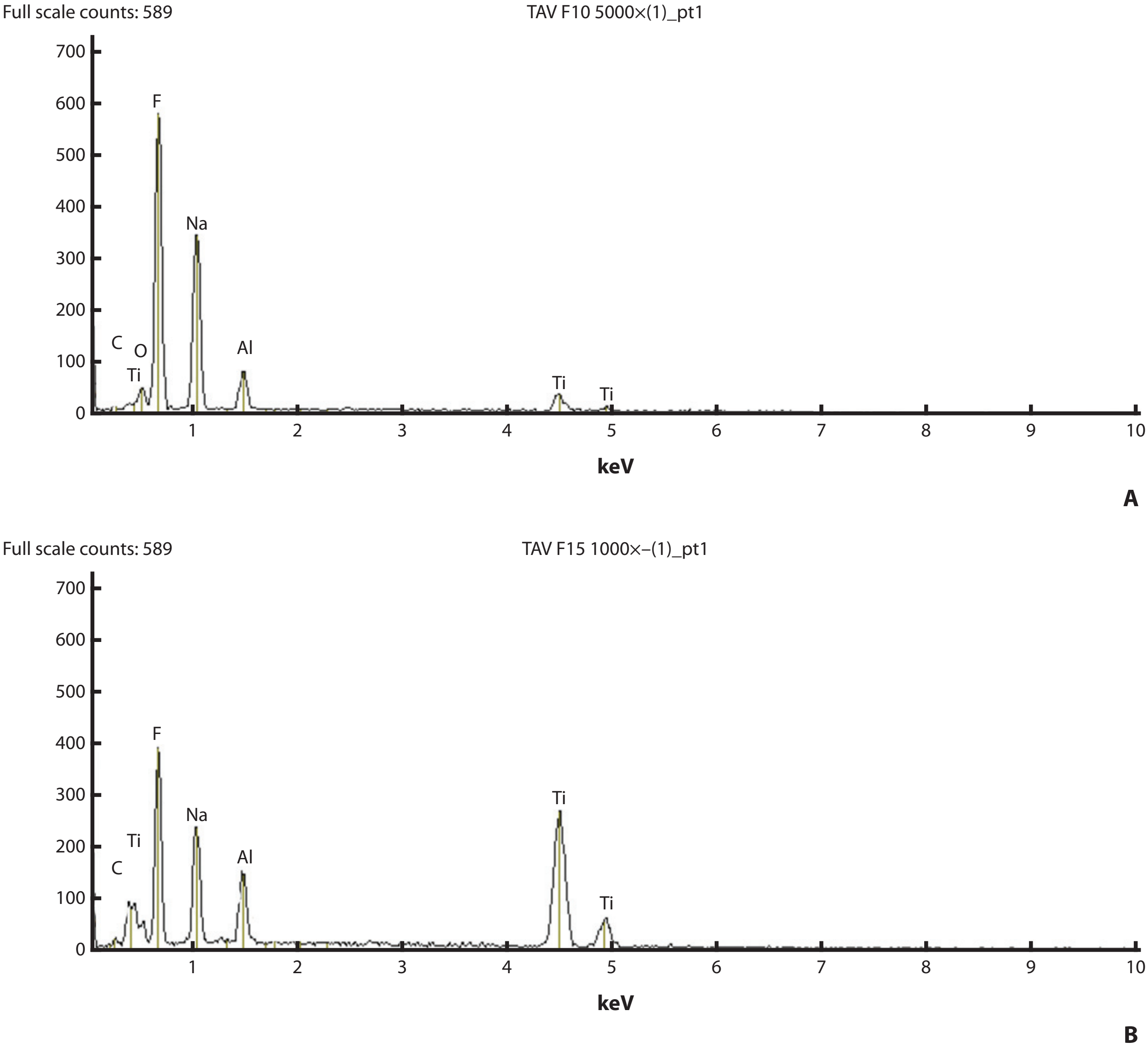

Figure 5. Qualitative composition of TAV surface after immersion in NaF. A, 10 years (F10). B, 15 years (F15). F, fluoride; TAV, cp Ti and Ti-6Al-4V.

greater protection against the action of HF, preventing possible scaling of the surface, corrosive pitting, and changes in the values of R_a, as observed for the TAV alloy. Nakagawa et al[26] determined important parameters that characterize the relationship among the concentration of NaF, the pH value, and the corrosion of cp Ti and TAV. According to Nkagawa et al,[26] an F^- concentration of 1500 ppm induced corrosive processes in TAV only if the pH was less than 5.1. Popa et al[21] found topographical changes and an increase in the average roughness of the TAV after 500 hours of immersion in artificial saliva, with 0.01 M F^- and pH equal to 5. Al-Mayouf et al[20] correlated the concentration of fluoride with an increase in porosity in the layer of oxides of cpTi and TAV, demonstrating that 0.01 M and 0.05 M NaF reduce the level of corrosion protection.

The quaternary alloy Ti-Nb-Zr-Ta can be classified as a metastable β-alloy.[13] This alloy can develop a variety of microstructures and phases depending on the composition and heat treatment. Unlike the cp Ti (α) and TAV (α + β), the TNZT alloy can contribute to better load transfer to the adjacent bone because it is a type β alloy, with lower values of the elastic modulus. In the last 2 decades, development of β-type titanium alloys has increased because they can avoid stress shielding when used in biomedical[8] applications. This is a result of their low Young moduli (40 to 60 GPa),[6,7] close to that of bone (≅ 10 to 30 GPa),[4] which allows it to be effective both in preventing bone resorption and in promoting good bone remodeling.[10]

According to Niinomi,[4] the presence of the α phase or precipitates of the α phase increases the Vickers hardness

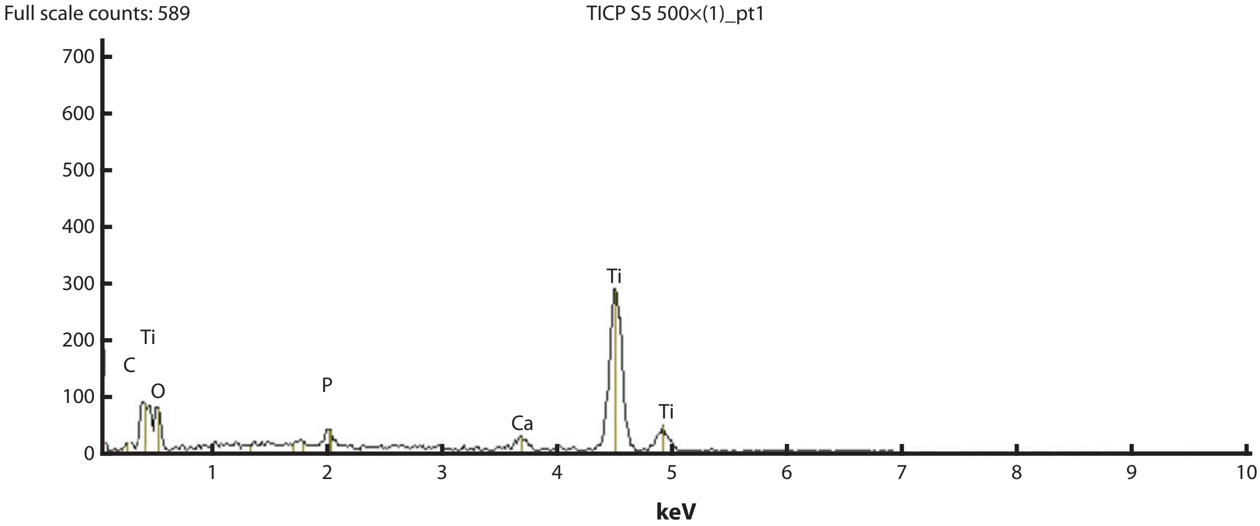

Figure 6. Qualitative composition of cp Ti surface after immersion in saliva, 5 years (S5). S, saliva.

of titanium alloys. This property may explain the higher values measured in TAV. Thus, although the hardness of TNZT was lower than that found by other authors,[11,18,32] this value is closer to cp Ti, in agreement with the values found by Elias et al[17] and similar to that of a Ti-Ta alloy.[14] These findings may be related to the absence of α phase precipitation, the presence/amount of Nb in the TNZT alloy, and primarily to the heat treatment performed in this study; heat treatment also affects the hardness values of cp Ti and other alloys.[11,18]

Although the results of this study suggest that the experimental TNZT alloy may have been protected after long-term immersion in fluorides, the study is an in vitro study with several limitations related to the oral environment. These limitations include the possible effects of variables such as the presence of proteins, oscillations in fluoride concentration, pH, and temperature. As the metal ions released from metallic biomaterials could compromise biocompatibility, future studies should compare the ion release from cp Ti, Ti-6Al-4V, and TNZT in other mediums such as physiological NaCl solution, physiological Hanks' Balanced Salt Solution (HBSS), and saliva. TNZT alloy surfaces should also be described before and after ion release.

CONCLUSIONS

Based on the results of this in vitro study, it was concluded that the long-term immersion of cp Ti, TAV, and TNZT in artificial saliva or fluoride solution did not change the roughness of TNZT or cp Ti, whereas the TAV alloy tended to increase in R_a after a simulated 20 years of exposure to NaF and showed a heterogeneous surface. The Vickers hardness of TNZT was similar to that of cp Ti; however, the results compared with those found for TAV, with increasing values as a function of immersion periods (both in fluoride solution and in artificial saliva).

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