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Surface Characterization of Titanium Implants Treated in Hydrofluoric Acid

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ABSTRACT

The results of XPS measurements of commercially pure titanium (*cp*-Ti) before and after chemical treatment are presented. We have measured XPS spectra of core levels (Ti 2*p*, O 1*s*, C 1*s*, F 1*s*) and valence bands of coarse-grained *cp*-Ti before and after standard acid treatment accepted in dentistry (in 1% HF and 40% HF for 1 min). It is found, that acid treatment of *cp*-Ti reduces the content of hydrocarbons increasing the surface energy and bio-compatibility of Ti-implants. On the other hand, it is fixed that oxygen concentration on the surface of the acid treated *cp*-Ti is much higher than for the untreated sample, because the acid treatment removes the contaminated surface layers, increases their reactivity, provides a better passivation and formation of thick protecting TiO_2 layer.

Keywords: Commercially Pure Titanium; Surface Composition; Hydrofluoric Acid; Surface Characterization; Biocompatibility

1. Introduction

The materials for medical implants are required to be biocompatible, not toxic and also should not cause allergic reactions. They must have high ultimate strength and yield points with desirable low density and low modulus of elasticity. Commercially pure Ti (*cp*-Ti) (99.85% Ti) meets all these requirements and is considered to be one of the most biocompatible and corrosion resistant metals available for medical applications.

The reaction of biological tissue to biomaterial surfaces and the formation of bonds between implant surfaces and biological tissues are largely dependant on the existence of a high surface energy on the implant surface. Contamination of biomaterial surfaces with hydrocarbons, molecules and elements can reduce the surface energy and, thereby, also the potential bio-to create these components, incorporating the applicable criteria that follow compatibility of an implant. It is known, that commercially pure titanium is highly reactive and its surface composition is substantially different from the bulk [1] and forms spontaneously, within seconds, several oxides when exposed to air, water, or an aqueous biological environment among which TiO_2 is the most common one [2].

The interaction of the implant with its biological environment, the formation of material-tissue interface and the long-term success or failure of the integration in the body is now realized to be strongly connected with the surface properties of the implant device. Even within one type of material, such as *cp*-Ti, the degree of integration depends on the quality of the surface. It is found, that fluoride-modification of titanium medical (dental) implants (performed by chemical treatment in HF-hydrofluoric acid) provides the better implant attachment and improves bone response [3], reduces the healing time needed before loading, as well as significantly improves the bone-to-implant contact [4]. In the present paper the results of surface characterization of *cp*-Ti after chemical treatment in the hydrofluoric acid (HF) are presented. We have measured XPS core levels (Ti 2*p*, O 1*s*, C 1*s*, F 1*s*) and valence band spectra before and after standard chemical treatment (in 1% HF, 1 min and in 40% HF, 1 min) which is used in the dentistry before implantation. For each set of measurement the ion etching (with Ar$^+$ ions) was performed in a step by step mode with etching intervals of few minutes (from 1 to 10 min). In this way, the detailed study of composition and chemical state of titanium and oxygen (as well as carbon and fluorine) is performed, what gives us the full information about the surface and the near-surface layers of *cp*-Ti before and after chemical treatment.

2. Experimental

Commercially pure titanium *cp*-Ti Grade 4 (Ti: base, C: 0.052%, O: 0.34%, Fe: 0%, N: 0.015% (wt%)) was employed to conduct the research (**Figure 1**). The coarse grained *cp*-Ti in the form of discs (10 mm dia and 1 mm thick) was annealed at 950˚C for 1 hr and then etched in hydrofluoric acid (1% HF and 40% HF) during 1 min. The XPS measurements were performed on initial and etched *cp*-Ti samples using a Perkin Elmer PHI 5600 ci Multitechnique System with monochromatized Al Kα radiation (FWHM = 0.3 eV). The XPS binding energies of untreated *cp*-Ti, given in **Table 1**, were determined using the Au $4f_{7/2}$ core level (E_b (Au $4f_{7/2}$) = 84.0 eV) as a reference. For each set of XPS measurements the ion etching (with Ar^+ ions) was performed step by step with intervals of few minutes (from 1 min to 10 min).

3. Results and Discussion

XPS wide scans of coarse-grained *cp*-Ti before and after chemical treatment in hydrofluoric acid (1% and 40% HF) are presented in **Figure 2**. The XPS analysis shows, that dental implant surfaces consist of titanium, oxygen and carbon. As can be seen (**Figure 2** and **Table 2**), C/Ti intensity ratio estimated from XPS survey spectra decreased from 6.3 to 5.3 after treatment in 1% HF (for 1 min) and from 6.3 to 2.9 after treatment in 40% HF (for 1 min). Therefore, the acid treatment reduces the contamination of *cp*-Ti surface with hydrocarbons, and increases the surface energy and potential bio-compatibility of the Ti-implant.

The concentration profiles of carbon, oxygen and titanium on the surface of untreated and chemically treated *cp*-Ti (**Figure 3**) show, that the acid etched surface is much cleaner than the untreated surface. The carbon contamination for the acid etched surface is much lower and the oxygen concentration is much higher than for the untreated sample. The curves of the acid etched surface are much flatter than those of the untreated surface, what means that the oxide in the near-surface region is much more homogeneous than in the untreated sample. The surface contamination of the acid treated sample can practically be removed within very few sputter cycles, whereas for the untreated sample the contamination reaches deeper into the bulk.

According to XPS measurements of high-energy resolved Ti $2p_{3/2, 1/2}$ spectra (**Figure 4**), the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks are located at 459.2 eV and 464.9 eV both before and after acid treatment and can be attributed to Ti^{4+} [5]. No Ti^{3+} shoulder at lower binding energy on the Ti $2p_{3/2}$ peak is detected, suggesting that all samples have a stoichiometric TiO_2 surface. As can be seen, XPS Ti $2p$ spectra consist of high-energy shake up satellites at 477.8 eV and 472.4 eV which are typical for TiO_2 [6]. It is in
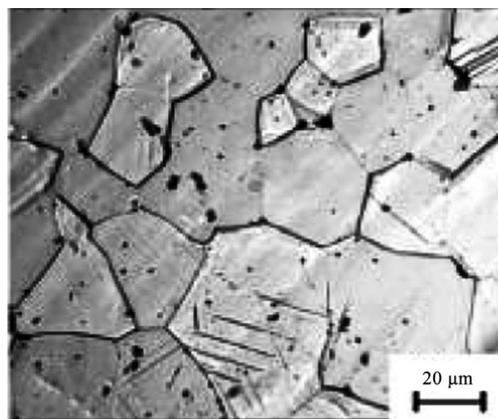

Figure 1. Microstructure of the initial coarse grained *cp*-Ti.

Table 1. XPS binding energies of untreated *cp*-Ti.

Core level	Binding energy[a] (eV)	FWHM(eV)
Ti 2*s*	561.4	
Ti 2*p*$_{1/2}$	460.8	1.3
Ti 2*p*$_{3/2}$	454.7	2.0
Ti 3*s*	59.1	
Ti 3*p*	34.0	
O 1*s*	531.4	1.1
O 2*s*	23.5	

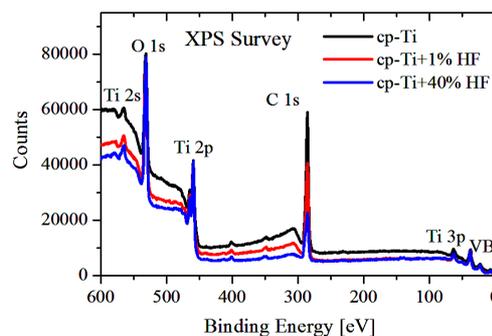[a]Reference: E_B(Au $4f_{7/2}$) = 84.0 eV.

Figure 2. XPS wide scans of coarse-grained *cp*-Ti before and after chemical treatment in hydrofluoric acid (1% and 40% HF).

Table 2. Concentration of Ti, C and O estimated from high-energy resolved XPS spectra.

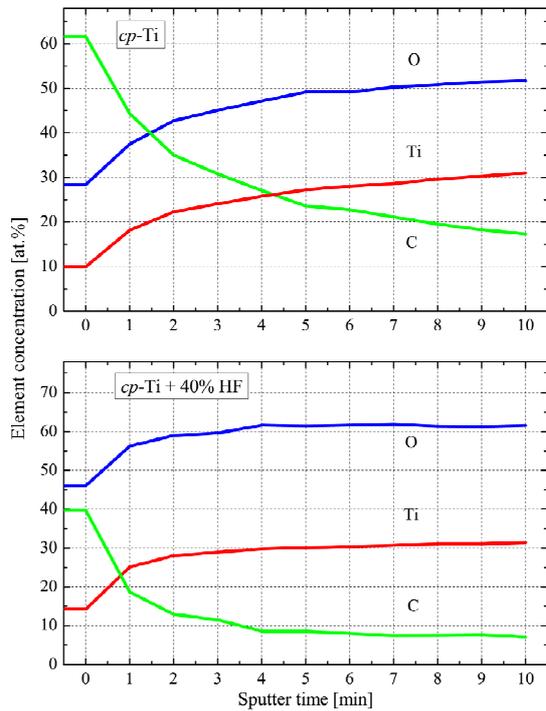| Sample	Ti (at%)	O (at%)	C (at%)	O/Ti ratio (at%)
cp-Ti, without treatment	9.8	28.2 (13.4/14.8) (shoulder/peak)	62.0	14.8/9.8 = 1.51
cp-Ti, 1% HF, 1 min	10.7	32.5 (14.3/18.2) (shoulder/peak)	56.8	18.2/10.7 = 1.70
cp-Ti, 40% HF, 1 min	13.8	46.3 (23.2/23.1) (shoulder/peak)	39.9	23.1/13.8 = 1.67

Figure 3. The concentration profiles of carbon, oxygen and titanium on the surface of untreated and chemically treated *cp*-Ti.
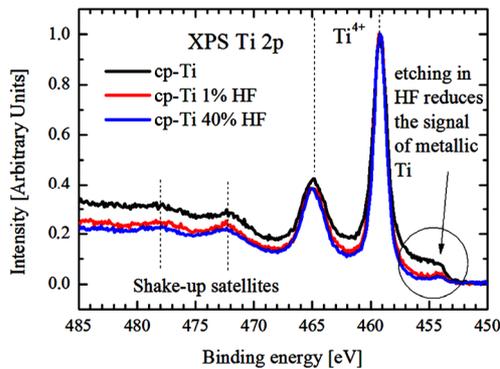

Figure 4. XPS Ti 2*p*-spectra of initial and acid treated *cp*-Ti.

agreement with the theoretical thermodynamics, which specify, that the free energy of formation of TiO_2 is favored over other titanium oxides [7]. XPS Ti 2*p* spectra of untreated and chemically treated *cp*-Ti measured depending on time of Ar^+-ion etching (1 min - 10 min) are found to be quite different (**Figure 5**). One can see, that the near- surface region of untreated *cp*-Ti is composed by superposition of TiO_2, Ti_2O_3, TiO and Ti-metal, whereas the contributions of Ti_2O_3, TiO and Ti-metal are strongly reduced for chemically treated sample. It means that the TiO_2 concentration in the surface region of the acid treated sample is significantly higher than in the untreated sample.

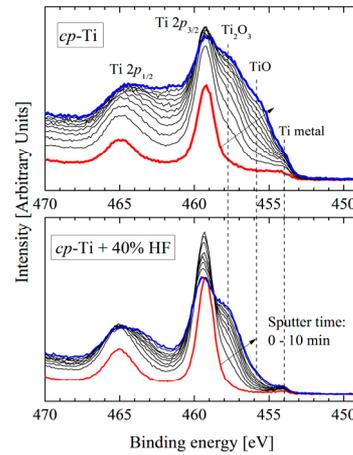**Figures 6** and **7** display the high-resolution XPS C 1*s*

Figure 5. XPS Ti 2*p*-spectra of untreated (upper panel) and chemically treated (lower panel) *cp*-Ti in dependence of etching time.
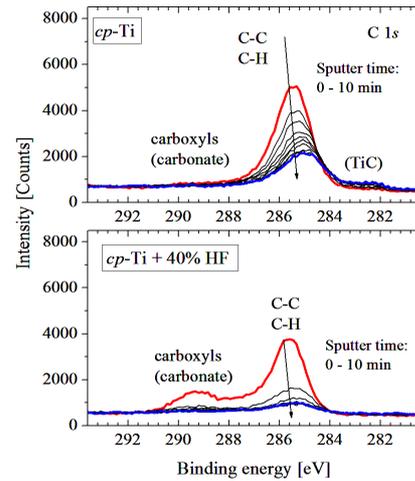

Figure 6. XPS C 1*s* spectra of initial (upper panel) and acid treated (lower panel) *cp*-Ti in dependence of time etching.
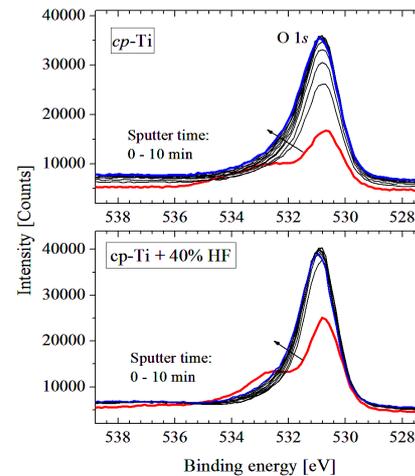

Figure 7. XPS O 1*s* spectra of untreated (upper panel) and chemically treated (lower panel) *cp*-Ti in dependence of time etching.

and O 1*s* core levels spectra of initial and chemically treated *cp*-Ti in dependence of Ar$^+$-ion etching. One can see that the hydrocarbons (C-C, C-H) give the main contribution to the C 1*s* peak, while the less intensive high energy shoulder is formed by carboxyl/carbonate groups [8] (**Figure 6**). Chemical treatment strongly reduces carbon contamination especially in the near-surface region.

Both initial and treated *cp*-Ti samples show an intensive O 1*s* peak from Ti-O bonds at 530.6 eV and a shoulder at higher energy which can be attributed to the contributions of OH and H$_2$O species [9], the content of which is not strongly changed after chemical treatment (**Figure 7**). One can see, that O 1*s* signal is not practically reduced with the ion etching giving additional evidence of formation of thick TiO$_2$ layer on the surface of chemically treated *cp*-Ti. It has been suggested, that the hydroxyl groups contribute to bone growth because calcium ions bind with the acidic groups and phosphate molecules bind with the basic groups of hydroxyapatite [8].

XPS F 1*s* spectra of *cp*-Ti after chemical treatment in HF (not shown) are found to be very similar to those of Ti immersed in solution containing fluoride [10]. The formation of titanium fluoride (TiF$_4$) on the surface of *cp*-Ti after acid treatment is not clearly detected.

In **Figure 8** the XPS valence bands of initial and chemically treated *cp*-Ti are presented. They consist of four peaks located at 14.5 eV, 7.4 eV, 5.5 eV and 0.9 eV. In agreement with previous studies we assign the feature located at 7.4 eV to O 2*p*-Ti 3*d* hybridized states, while the 5.5 eV feature has mainly O 2*p* character [11]. One can see, that the ratio of the two peaks located at 7.4 and 5.5 eV is found to be very similar to that of TiO$_2$ [5]. C 2*s*-states are fixed at E = 14.5 eV and are seen mainly in the spectrum of untreated *cp*-Ti where the contribution of carbon contamination is the highest (see **Figures 1** and **5**). The peak at 0.9 eV can be attributed to a contribution of 3*d*-states of metallic Ti [12]; the relative intensity of this peak is not changed after etching which is consistent with XPS Ti 2*p*-measurements (see **Figure 3**).
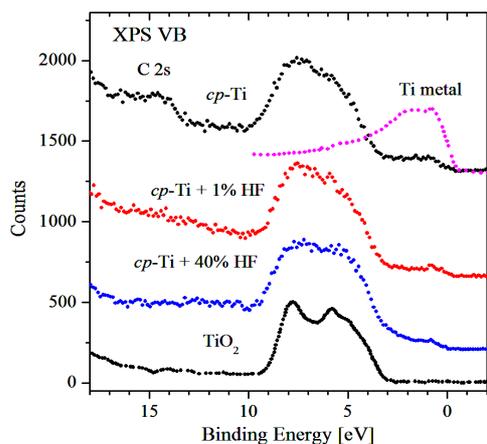

Figure 8. XPS valence bands of initial and acid treated *cp*-Ti.

4. Conclusion

To conclude, we have performed a full surface characterization of commercially pure Ti (*cp*-Ti) before and after chemical treatment in hydrofluoric acid with help of the XPS measurements of core levels and valence bands. It is found, that after acid treatment the content of hydrocarbons is reduced, what increases the surface energy and potential of bio-acceptability of a Ti-implant. According to our measurements, the acid treatment reduces the level of surface contaminations and induces the formation of thick TiO$_2$ oxide layer.

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