Chemical and Morphologic Analysis of Titanium Dental Implants: X-ray Photoemission Techniques (XPS) and Scanning Electron Microscopy (SEM) with EDX Analysis

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Nowadays the implants rehabilitations are used deeply by clinicians. The importance to technological improvement is working to find the best surface of the fixture to obtain a good and stable osteointegration. By the use of the Energy Dispersive X-ray (EDX) analysis and the X-ray Photoemission Spectroscopy (XPS) evaluate the surface quality of commercial implants. The XPS analysis was made to evaluate the chemical elements that compose the material surface of the implant and determine the state of atomical connections. The EDX analysis was performed to evaluate the characteristic qualitative and quantitative of the metallic alloys of the fixtures to determinate the pureness of the metals under the surfaces. The major difference found between the samples is the amount of surface aluminum (in oxidized state, alumina), which in the samples 2 appears to be more than an order of magnitude greater (12 times). In Sample 2 there are traces of P, Na and Cl not present in Sample 1. The presence of C, O, N, Si and Ca are similar on both samples (1 and 2). Now, in the market there are many different dental implants. All the producers are working hard on micro and macro design of the fixtures, but not so many attentions is spent on the type of the alloy composing the implant. From this analysis, it is observed that different Type 4 dental implant are not so similar by composition. Moreover, the pure Titanium is well tolerated by biological tissues, on the other hand is not well known if the presence of other materials can influence the biological reaction. The samples of the fixture analyzed present different composition of the alloy, although both classified as Type 5 Titanium. Further studies on this topic are needed to understand if these differences of alloy composition can influence the clinical outcome.

Keywords: Energy Dispersive X-ray (EDX), X-ray Photoemission Spectroscopy (XPS), dental implants

Implantology is one of the branch in dentistry in which we are going to observe the highest level of improvements along the years. Clinical aim is to obtain a good osteointegration, in order to load with a prosthetic, manufacture the fixture in the bone tissue [1]. To guarantee effective bone integration the following rules were applied: biocompatibility, form of the implant, macro-microscopic surface of the implant, loading conditions applied, state of the site where the implant is destined and the surgical technique [2-5]. Moreover, related to the atomic composition of the implants there are not so many studies [6]. It is demonstrated that a roof implant surface is able to improve the secondary stability (biological stability) and to reduce the healing time between the interface boneimplant surface [7]. In fact, the roof complex surfaces prove to a better coagulum retention instead of the smooth surfaces [8]. The beginner coagulum is very important to the formation of a scaffold to obtain an early cellular migration. During the healing phase the hematoma is transforming in new bone, whereas the damaged bone tissue recovery through the revascularization, the demineralization [9]. Many of the previous studies of PEO have been carried out on titanium under a relatively wide range of conditions for the preparation of the coatings. They are: different electrical regimes, treatment times and electrolyte compositions [10]. The most common electrolytes used for plasma electrolytic oxidation of titanium are: phosphoric and sulfuric acids, sodium metasilicate pentahydrate, silicon acetate within Ca-

Experimental part

Materials and methods

The morphology and the composition of both samples was done through a Scanning Electronic Microscopy (SEM) coupled to a spectrometer EDX (Energy Dispersive X-ray) and XPS (X-Ray Photoemission) by Dr. Cinzia Cepek (Istituto Officina dei Materiali Sede di Istituto Trieste: Area Science Park, Basovizza S.S.14 Km 163.5 – 34149 Trieste, Italy). The analyse was performed on two implants group: group 1- BIOMET 3I (sample 1) and group 2-MYIMPLANT (sample2). The chemical composition of the 1 and 2 (table 1) has been studied via XPS.

glycerophosphate and NaOH, Ca--glycerophosphate and calcium acetate, potassium phosphate with potassium hydroxide, potassium pyrophosphate and potassium hydroxide, calcium glycerophosphate with calcium acetate, tripotassium phosphate and potassium hydroxide with and without monoclinic zirconia powder, sodium silicate with phosphoric acid and potassium hydroxide, tungstosilicic acid, ethylene diamine tetraacetic acid disodium with calcium oxide and calcium dihydrogen phosphate and sodium metasilicate nonahydrate, sodium phosphate with hydrated sodium borate and sodium tungstate dihydrate and iron(III) oxalate, sodium hydroxide with monosodium dihydrogen orthophosphate with and without Cu nanoparticles, glycerophosphate disodium salt pentahydrate with calcium acetate hydrate, calcium acetate hydrate with disodium hydrogen phosphate anhydrous^[10].

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Table 1 MANUFACTURING SPECIFICATION OF THE SAMPLES 1 AND 2.

| SAMPLE NUMBER | MANUFACTURE | LOT | REF. | STATUS |
|------------------|-------------|--------|----------|--------|
| 1 | BIOMET | 971352 | IOSS585 | NEW |
| 2 | MYIMPLANT | S90142 | EI400100 | NEW |

The samples have been removed from their original sterile packaging and immediately introduced into the XPS experimental chamber. They have been touched only with clean stainless-steel tweezers and during all the mounting operations gloves were always used in order to avoid any kind of external contamination. At the end of the analysis, the samples were re-stored in their original packaging. All XPS spectra were acquired in ultra-high vacuum at room temperature using a conventional Mg X-ray source (hv =1253.6 eV) and a hemispherical electron energy analyzer (total energy resolution $\sim 0.8 \text{eV}$). The binding energy (BE) has been calibrated using a gold polycrystalline foil in electric contact with the analyzed sample. For all samples, a survey spectra have been first acquired to individuate all the elements present on the surface. The most relevant XPS core level of each detected elements was measured in detail to evaluate precisely the sample's stoichiometry. All spectra were normalized to the incident photon flux and analyzed by calculating the peaks intensity (area) after the subtraction of a linear background in the BE region of interest. The stoichiometry of all samples has been evaluated by supposing a homogeneous distribution of the elements in all samples.

X-ray Photoemission Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surfacesensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analyzed. XPS is a surface chemical analysis technique that can be used to analyse the surface chemistry of a material in its as-received state. The X-ray Photoemission Spectroscopy (XPS) was effected using the Analytic section laboratory of the TASC-IOM-CNR (base pressure 10-11mbar). We used a hemispheric energy analyzer of electrons (120mm, PSP)

and a conventional non monochromatized Mg x-ray source. All the spectrum was normalized at the photons number and the bond energy was calibrated using a sample of polycrystalline gold. In presence of chargement phenomenon's the bond energy was attributed putting the Ti 2p3/2 a 459.1eV. (fig.1 a and b).

Energy-Dispersive X-ray Spectroscopy (EDX) Energy-dispersive X-ray spectroscopy (EDX), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis, is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a specific set of peaks on its Xray emission spectrum. Morphology and composition of all sample were studied by using a Scanning Electronic Microscopy (SEM) coupled with an EDX spectrometer (Energy Dispersive X-ray). It was not necessary to put the samples on a metallic film, because was not observed a deep charging effects on them. The device is made from Zeiss factory, model Supra 40 (energetic range 0.1-30 KeV, lateral resolution until 2nm). The experimental conditions are summarized on every single picture. Every EDX spectrum were acquired using a spatial resolution of the SEM image bounded by a rectangle (fig. 3 A and B, fig. 4) previously showed by EDX spectrum.

Concentration obtained by EDX spectroscopy were calculated using the standard program of the device.

Results and discussions

To better underline the presence of contaminants due to clearing processes of implants (for example aluminum and\or silicate) the results will be presented according with type of implants. Table 2 presentes the distribution of the chemical elements and in the table 3 ishows the same values but after normalization of all concentrations referred to titanium concentration value.

Following two spectrums (fig. 1), measured in an energetic region where are present some peaks of numerous elements detected, are linked to two samples examined (number 1 in red and number 2 in blue) and they were normalized to titanium intensity to facilitate comparison between the two samples. Furthermore, the distribution of the chemical elements is according with



Fig. 2. The behavior of the ions presents on the implant surface (BIOMET) during XPS treatment (a) . The behavior of the ions presents on the implant surface (MYIMPLANT) during XPS treatment (b)



Fig. 3A: Binding Energy for sample no.1; B Binding energy for sample no.2 Table 2

THE DISTRIBUTION OF THE CHEMICAL ELEMENTS ACCORDING WITH TYPE OF IMPLANTS

| | Sample number | C% | 0% | Ti% | Al% | N% | Si% | Ca% | P% | Na% | Mg% | Cl% |
|-----------|------------------|------|------|------|------|-----|-----|-----|-----|-----|-----|-----|
| BIOMET | 1 | 47.9 | 34.2 | 12.3 | 1.4 | 0.6 | 2.9 | 0.6 | ſ | 1 | / | / |
| MYIMPLANT | 2 | 23.4 | 52.7 | 8.9 | 10.6 | 1.0 | 1.4 | 0.4 | 0.7 | 0.8 | / | 0.2 |

Table 3

THE NORMALIZATION OF ALL CONCENTRATIONS REFERRED TO TITANIUM CONCENTRATION VALUE

| | Sample number | C/Ti | O/Ti | Ti/Ti | Al/Ti | N/Ti | Si/Ti | Ca/Ti | P/Ti | Na/Ti | Mg/Ti | C1/Ti |
|-----------|------------------|------|------|-------|-------|------|-------|-------|------|-------|-------|-------|
| BIOMET | 1 | 3.9 | 2.8 | 1.0 | 0.1 | 0.05 | 0.2 | 0.05 | / | / | / | / |
| MYIMPLANT | 2 | 2.6 | 5.0 | 1.0 | 1.2 | 0.1 | 0.1 | 0.04 | 0.08 | 0.9 | / | 0.02 |

| Table 4 | | | | | | | | | | |
|---|--|--|--|--|--|--|--|--|--|--|
| VALUES IN PERCENTAGE OF THE IONS CONCENTRATION INTO SAMPLE no.1 | | | | | | | | | | |

| | C% | 0% | Ti% | N% | Ca% | Si% | P% | Al% | Na% | |
|--------|------|------|------|-----|-----|-----|----|-----|-----|--------|
| Biomet | 47.9 | 34.2 | 12.3 | 0.6 | 0.6 | 2.9 | 1 | 1.4 | / | Tarces |

| Tabl | le ¦ |
|------|------|
| | |

VALUES IN PERCENTAGES OF THE IONS CONCENTRATIONS INTO SAMPLE no.2

| | C% | 0% | Ti% | N% | Ca% | Si% | P% | Al% | Na% | S% |
|-----------|------|------|-----|-----|-----|------|-----|------|-----|-----|
| MYIMPLANT | 23.4 | 52.7 | 8.9 | 1.0 | 0.4 | 1.40 | 0.7 | 10.6 | 0.8 | 0.2 |

the implants type and this are presented in the table 2. Figure 1 shows the XPS survey spectra of the two samples (a) and the enlarged region in the BE range between 240eV and -1eV (b), where some of the elements present in the samples are better visualized. The sample's stoichiometry, extracted by measuring the most significant spectra of each detected element (spectra not shown), are reported in table 2 and has been measured supposing a homogeneous composition of the sample, as already mentioned in the previous section.

The following obtained values reports the experimental XPS data of all measurements made on the 2 samples. The percentage values of the ions concentration into sample n.1 are presented in table 4. The figure 2 (a) shows

the behavior of the ions presents on the implant surface (BIOMET) during XPS treatment are identify.

The same analyze was made on sample 2 identifying the ion concentration percentage (table 5) and the behavior of the ions presents on the implant surface (MYIMPLANT) during XPS treatment (fig. 2 b).

None of the samples needed a metallic film, because it has not been observed dramatic effects of the change. The device used is produced by the Zeiss company, Supra 40 models (energetic range 0.1-30 KeV, lateral resolution till to 2nm). The concentration obtained from the spectroscopy EDX was calculated using the program in the device's equipment. The concentration values obtained through EDX and XPS are different. This is due to the

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Fig. 4. SEM images measured on Sample 1 (a, c, e) and Sample 2 (b, d, f) acquired

different sensibility in depth of the two-experimental technique: in case of XPS few nanometers, whereas about a hundred nanometers for EDX. The comparison between the values obtained from the two techniques can afford to characterize better which are the surface contamination elements due to the surfaces preparation process before their use. After the XPS analysis, the samples were measured in a scanning electron microscopy SEM coupled with an energy dispersive X-ray (EDX) spectrometer. The instrument used is by Zeiss, model SUPRA 40 (energy range: 0.1-30KeV, lateral resolution up to \sim 2nm). The energy of the electron beam used in all measurements is 10keV. We remark that concentration values obtained by EDX and XPS are significantly different. This is due to different sensitivity in the deep layers of the 2 experimental techniques: XPS can penetrate few nanometers, otherwise EDX technique can penetrate hundreds of nanometers, so much deeper.

To put in evidence the presence of possible contaminants due to the cleaning process of the fixtures (Aluminum, Silicium), the table $\tilde{2}$ show the same values of the table 1 after normalization of Titanium value to 1.0. The major difference found between the samples not used by the company's products analyzed is the amount of surface aluminum (in oxidized state, alumina), which in the sample MYIMPLANT appears to be more than an order of magnitude greater (12 times). We note that the amount of aluminum compared to titanium in the sample MYIMPLANT (1.2) is significantly higher than that found in titanium alloys typically used for dental implants (between 0 and about 0.06), while in the sample BIOMET (0.1) approaches and is compatible with these values within the experimental errors. A number of in vivo studies have reported that the sur-face chemistry of titanium implants plays an important role for osteointegration [11]. The study importance of manufacturer in implant market is focused on the micro and macro design of the fixtures [12-16]. Related to the composition of the alloy of the fixtures, the researcher does not give a great importance, furthermore almost all products are classified as Type 5 Titanium. This classification is not so strict, as we observed after our results. The chemical composition of the alloy is different from different products, and in some of these (My Implant product) we find a great amount of Carbonic and Oxygen. These products are probably to be considered as contamination of the surface during the production procedures, and are not present in other products (3i Biomet) that represent some of the top-quality product on

the market. There are no studies on the interaction of these contamination with the process of osteointegration of the implant. No literature studies were found on the biological tissue reaction with this kind of alloy detected by our study. All the osteointegration studies are based on the interaction of living tissues and pure titanium, no other contaminant material is considered on this topic [17,18]. The implants present in the market can be really different from one to the other, although both of them are classified as Type 5 Titanium.

Conclusions

Nowadays in the market there are many different products in implant dental field. Some of them come from well-known manufacturers and with a high probability of quality control. Many of them are made by little manufactures and not always the alloy composition is so well defined. The presence on contaminant of this surfaces may drive to a problem with the osteointegration process, that is evaluated on the interaction between pure titanium and tissue. We think that we need more studies on the interaction of the contamination materials and the tissues, and especially a better knowledge of the alloy compositions of implant on the market with a better control of them. Therefore, from the point of view of the clinician is impossible to analyze the real implant composition that he uses. The only outcome that the clinician has is the percentage of success obtained in the practice.

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