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REPORT ON SURFACE ANALYSIS OF

TITANMED DENTAL IMPLANTS

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Tests performed by:

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Aims of this work

The aim of this work was the analysis of the surface of titanium dental implants produced by Titanmed and subjected to a SLA-like surface treatment. In particular, the scope was to evaluate the cleanliness of the surface by X-ray Photolectron Spectroscopy (XPS) analysis, and to confirm the SLA-nature of surface topography by Scanning Electron Microscope (SEM) and roughness analysis by Stereo SEM measurement.

Methods and materials

Samples were supplied by Titanmed as reported in D.d.t. n. 1867 issued on 26.06.2012. They were subjected to surface treatment by large grit sandblasting followed by double acid etching.

Surface characterisation was performed by XPS (X-ray Photoelectron Spectroscopy) to evaluate surface chemistry and SEM (Scanning Electron Microscopy) to evaluate surface topography, as described in the following sections.

Surface chemistry

XPS analysis was performed using a Perkin Elmer PHI 5400 ESCA spectrometer. This is equipped with an X-ray source with a Mg anode, maintained at 20 kV with a nominal power rating of 200 W. The depth analysed is approx. 5 nm. The pressure inside the analysis chamber has been maintained at approx. 10^{-9} Torr. The analysis results are expressed in atomic percentages.

Surface topography

The surface topography of the implants was evaluated by scanning electron microscope. Analysis was conducted using an EVO MA 10 SEM (Zeiss). The electron acceleration voltage was maintained at 15 kV, the working distance between 12,5 and 13,0 mm, depending on the specific requirements of the analysis. These parameters are reported in the images, along with the level of magnification (MAG) and the kind of detector utilised (Signal A= SE1 or CZ BSD).

Images were acquired in both conventional mode (Signal A= SE1) and in backscattered electron mode (Signal A= CZ BSD), allowing improved contrast between different chemical elements.

Roughness was evaluated quantitatively by Stereo-SEM (SSEM),using a dedicated software to convert conventional SEM images into three-dimensional data (Mex 4.2, Alicona Imaging). In particular, this evaluation exploits the basic principle of stereo vision. Basically, two images of the same field of view are acquired after eucentric rotation by a given angle. This is obtained by changing the angle between the sample and the electrons, by tilting the table that holds the sample. The tilting angle is set and controlled by the instrument control software. The couple of images obtained (stereopair), the size of the field of view and the tilting angle are the incoming data, that the software converts into a single three-dimensional image, where each data point is characterized by the values of the x, y, z coordinates. The image obtained by this process allows then to measure height profiles (roughness profiles) and to calculate the different roughness parameters defined by relevant literature and standards. More details on this topic will be provided in the section on results.

Results

As to evaluation of the surface composition, the table below reports the data obtained by XPS analysis. The table reports, as a comparison, data obtained on a reference Straumann SLA sample, using the same technique and instrument

Surface composition (atomic percentage)

Sample	**O**	**Ti**	**C**	**N**	**Si**	**Cl**
Titanmed SLA treatment	42.4	18.4	38.1	0.9	0.2	
Straumann, Standard Plus Implant, 3.3x 10 Lot J4827	39.0	16.6	41.5	1.9	0.8	0.1

In order to better understand these data, some preliminary consideration on the peculiarities of surface analysis is important. As a general remark, it should be remembered that in the surface analysis of Ti, the presence of at least 3 elements is to be expected: Ti, oxygen (because titanium oxide is present on the surface) and carbon. The latter element is due to the presence of carbon-containing molecules (CO_2 or hydrocarbon-type compounds) unavoidably present in the atmosphere.

Metal surfaces combine with these carbon-containing species (the technical term is “absorption”) which are then detected by specific surface analysis techniques, such as XPS, but are not detected by more traditional analytical methods, which consider the material in its entirety. Carbon can also be derived from much “heavier” forms of contamination, such as contact with oil or grease during processing. In order to distinguish between “natural” C and C from contamination, it is essential to take the quantitative aspects into consideration. Percentage values of 30-40% are physiological, and may be considered normal. Higher percentages suggest the presence of contamination. It should still be remembered that the maximum percentage of Ti that may be theoretically observed by surface analysis is approx. 33% (because TiO_2 is present on the surface). The unavoidable presence of C (explained previously) lowers this theoretical limit even further.

It is here important to remark that no regulation-defined quantitative standard exists to set acceptance limits for “clean” Ti implant surfaces. International standards just suggest that implant surfaces should be as clean as possible and should avoid risks for the patient and the intended use. Based on our experience regarding surface analysis of implants and data from the literature, we set “good practice” standards that allow to define limits of concentration for the various elements that can be found on implant surfaces. In particular, the max. concentration of Ti that may be observed by XPS analysis is 14-19%. A Ti percentage greater than 12% may be considered satisfactory.

Besides the usual O, Ti and C, other elements such as P, Ca, Si, N, Cl and others are often frequently observed by XPS. These are normally present in low percentages, a few units at most, and may be derived from the washing, or in any case, some of the processing steps.

Considering present data, a few remarks can be made: first, the overall carbon content (and related Ti concentration) are good, for all samples tested. Then the other elements detected are in agreement with what commonly found on implant surfaces and they are within the expected concentration form a quantitative point of view (incidentally, our internal standard put an upper limit of 4% to Si and other non-toxic elements). Finally, no aluminium from blasting residual is detected, suggesting that all residuals were removed in processing and cleaning steps.

Shortly, present data show that both Titanmed and Straumann implants surface chemistry is in agreement with expectation for clean implant surfaces; and that there's no significant difference between Titanmed and Straumann surface chemistry. Incidentally, these are the composition limits we put for NBR treated implants, as evaluated by internal control by XPS, in our normal production:

Surface composition (as evaluated by XPS analysis)

C	**O**	**Ti**	**Other common elements**
< 45	> 36	>12	<4

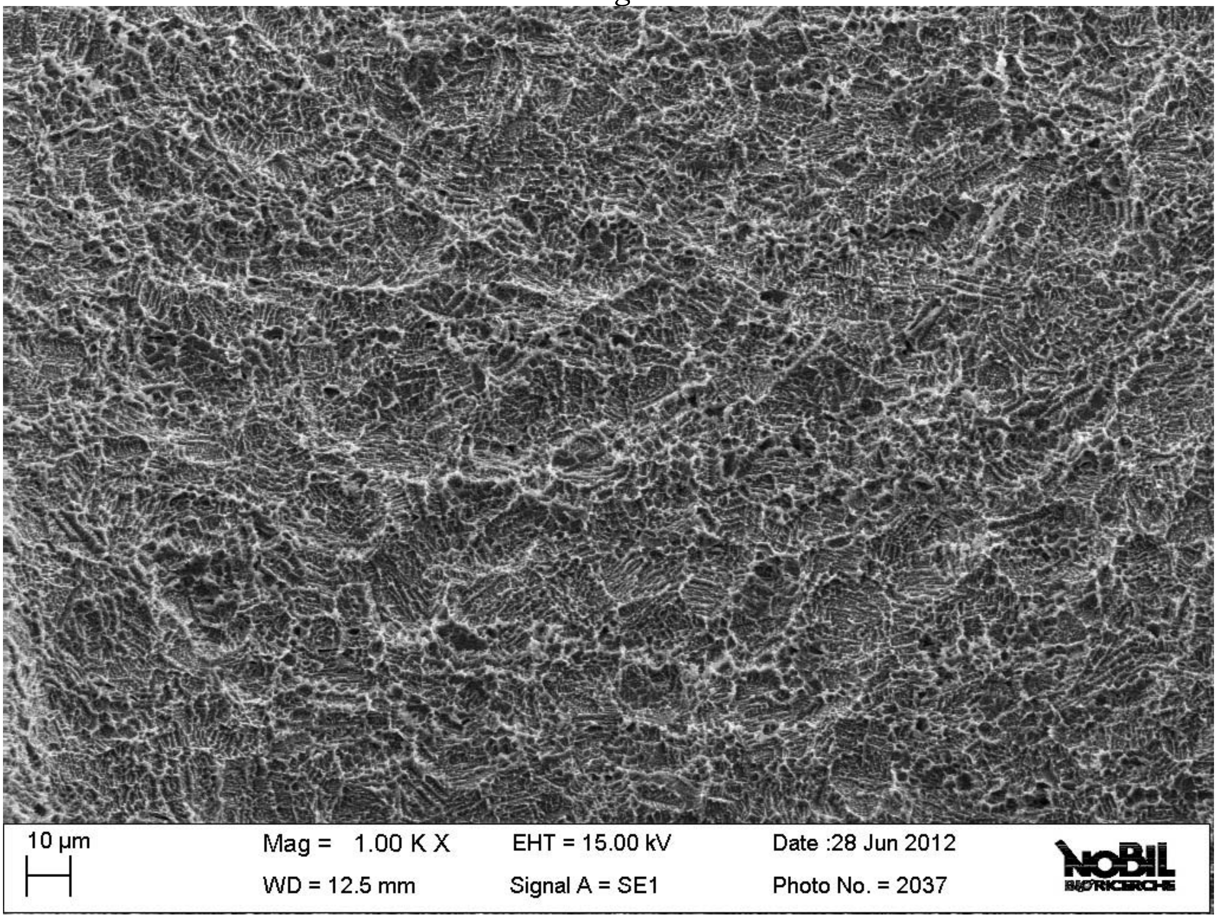
The "Other common elements" entry includes the elements commonly observed on the surfaces of implants, such as Ca, Mg, N, S, P, Na, Cl and Si. Generally, traces of other elements (Fe, Cu, Ni, Cr, Co, Pb) must be completely absent, while traces (< 0.2%) of F and other non-toxic elements, whose presence may be justified by the process, may be tolerated.

Tested samples comply to these criteria.

Surface topography

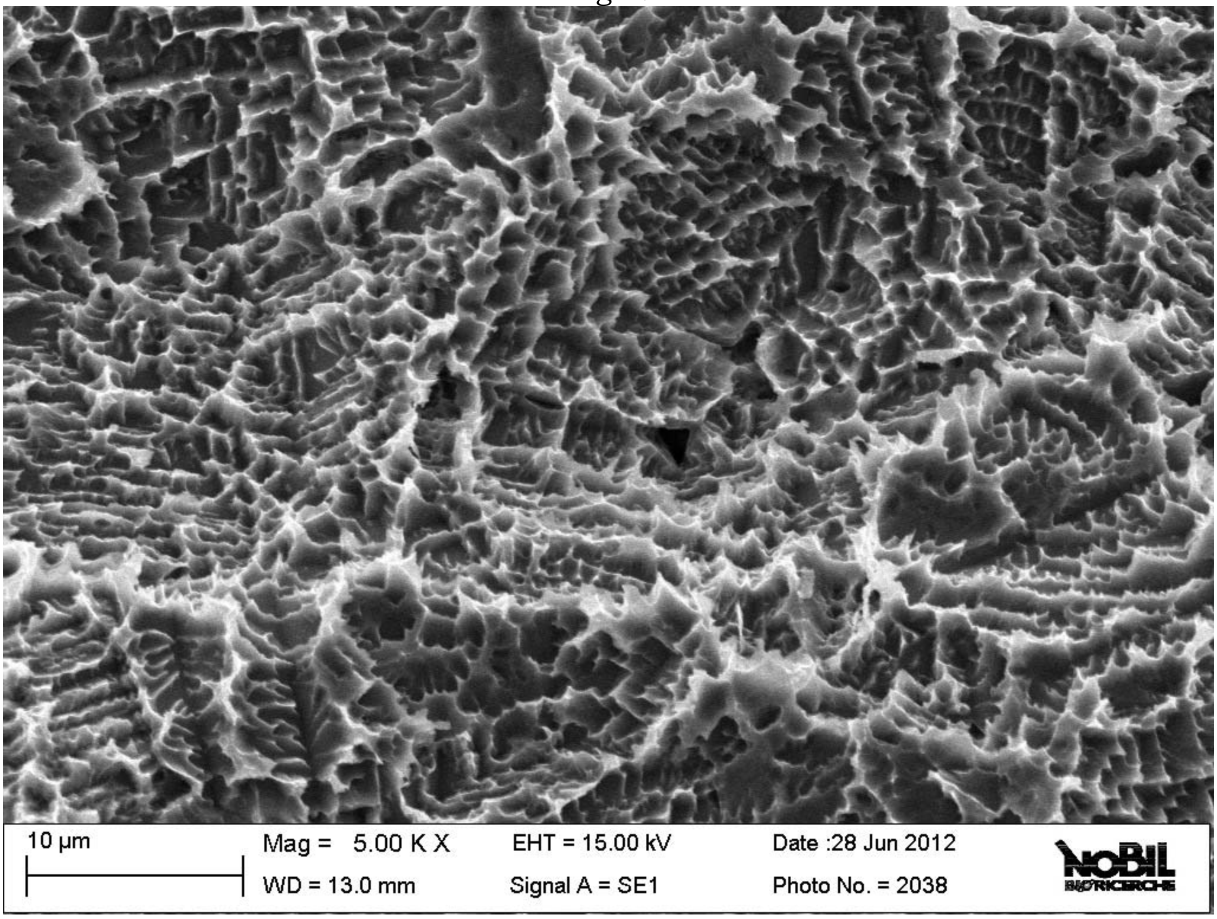
As to the evaluation of surface topography, Fig. 1 and 2 below show microscopic views of the Titanmed SLA-treated implant Surface. Namely, Fig. 1 is a low-magnification image (1000 x) that highlights the double-range roughness typical of the SLA treatment, that contains both big “holes” due to large-grit sandblasting on which the microroughness due to acid etching is superimposed.

Fig. 1



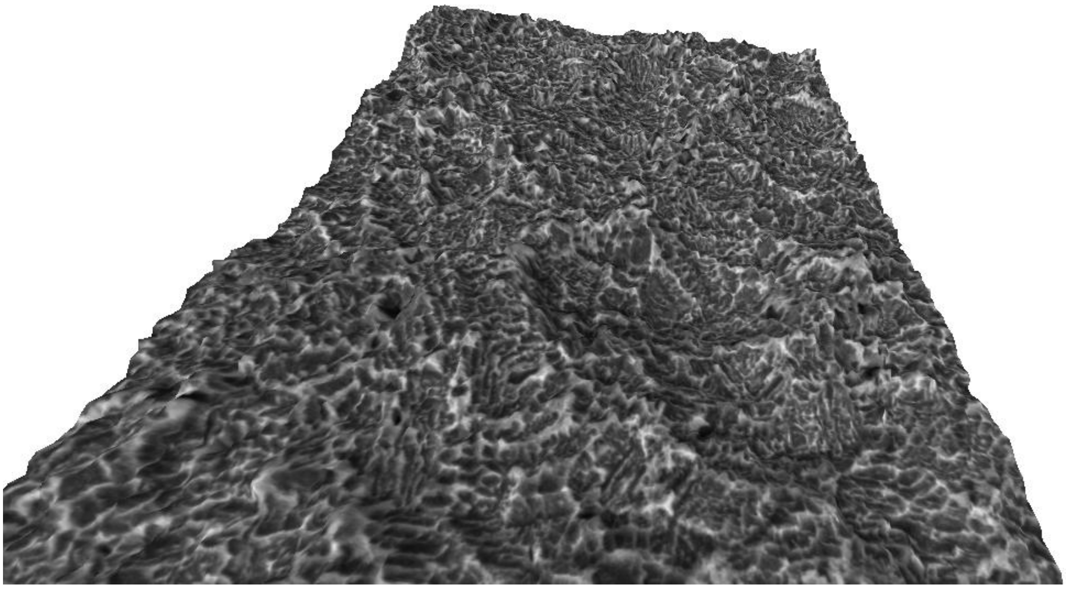
The latter is clearly seen in Fig. 2 (5000 x) that shows the typical nice tri-dimensional topography, that imparts to these surfaces spongy-like characteristics that are at the basis of their excellent clinical performances. In fact, both the short peak-to-peak distance, of the order of about one micrometer, stimulates osteogenic cell activity, and the capillary penetration of blood into the surface structure, are very favourable to stimulate bone healing and new bone formation, as described in many papers on this topic. This unique combination of long- range (large grit sandblasting) and short range (acid etching) roughness is the typical feature of SLA surfaces and it has been successfully replicated on Titanmed implants.

Fig. 2



Quantitative evaluation of surface roughness has been conducted in accordance with ISO 4287, providing values for all the parameters defined in the standard. As described before, data were obtained by StereoSEM, generating three dimensional images from a stereo pair made up by two SEM images of the same field of view, obtained at 2000 x with a tilting angle of 5 degrees. A typical three-dimensional view of the Titanmed implant surface in shown in Fig. 3, that once again shows the co-existence of long-range and short range roughness:

Fig 3



Roughness data were calculated from 800 micrometers path length, as shown in Fig. 4, while Fig. 5 shows a typical height profile:

Fig 4

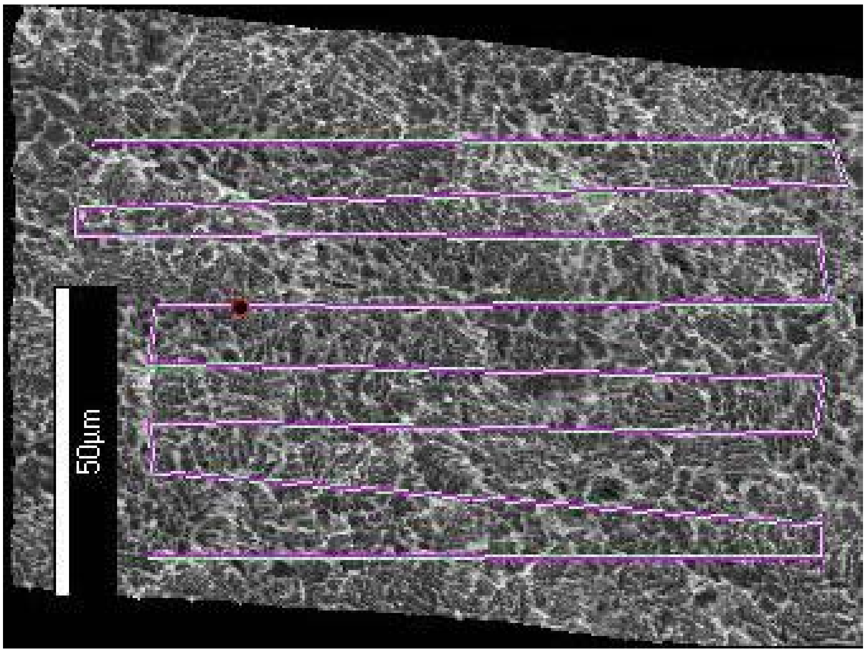
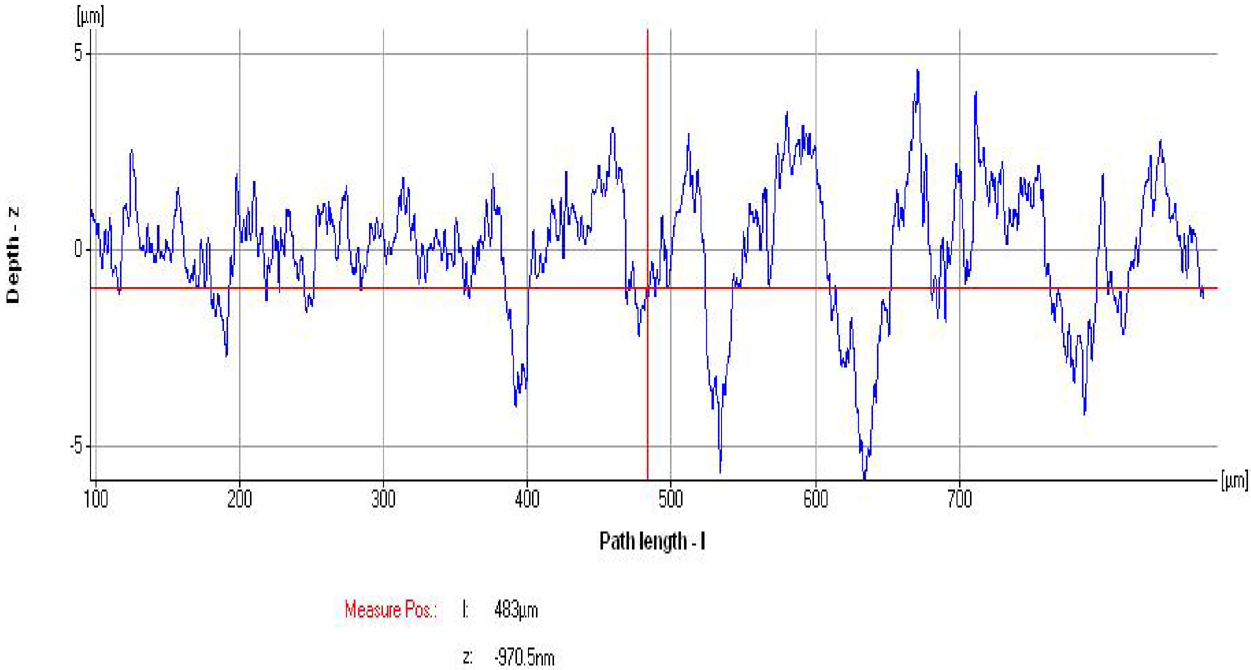


Fig. 5



Quantitative roughness data are reported in the table below, together with measurements performed on the SLA reference sample and data obtained from the literature (data are expressed in micrometers, as the mean and standard deviation for three independent measurements):

Parameter	SLA Titanmed (average from 3)	SLA Straumann, our measurement	SLA Straumann, literature(1)	SLA Straumann, literature(2)
Ra	1.62 ± 0.21	1.72 ± 0.19	1.53 ± 0.11	1.19 ± 0.04
Rq	1.81 ± 0.34	1.90 ± 0.41	nr	nr
Rz	9.58 ± 0.51	10.54 ± 0.44	9.19 ± 0.47	10.53± 0.72
Rp	5.46 ± 0.42	6.40 ± 0.65	nr	nr
Rv	4.02 ± 0.91	4.13 ± 0.43	nr	nr
Rc	5.25 ± 0.31	5.63 ± 0.67	nr	nr

Where the definitions of the various parameters are as follows:

Parameter	**Definition**
Ra	Average roughness of profile
Rq	Root-Mean-Square roughness of profile
Rz	Maximum height of roughness profile
Rp	Maximum peak height of roughness profile
Rv	Maximum valley depth of roughness profile
Rc	Mean height of profile irregularities of roughness

1 = Biological Properties of Acid Etched Titanium Implants: Effect of Sandblasting on Bone Anchorage

S. Szmukler-Moncler, D. Perrin, V. Ahossi, G. Magnin, J. P. Bernard J Biomed Mater Res Part B: Appl Biomater 68B: 149–159, 2004

2 = The biocompatibility of SLA-treated titanium implants, Kim H, Choi SH, Ryu JJ, Koh SY, Park JL, Lee IS, Biomedical Materials, 1, 3, 2008

nr = not reported in the quoted paper

Conclusions

In conclusion, this report provides surface characterization data on Titanmed titanium dental implants. SEM images show that the surface topography is the expected one, made-up by long-range macroroughness due to sandblasting and short-range microroughness due to acid etching. Quantitative surface roughness evaluation shows good agreement between parameters measured on Titanmed and control Straumann implants, and good agreement with literature data.

Surface chemistry evaluation by XPS provides data that shows an excellent surface chemistry, fully complying to acceptance limits for clean implant surfaces.