New micro- and nanoscaled titanium surface structures textured by electrochemical methods

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E·MRS

May 29th - June 2nd, 2006
Nice, France

INTRODUCTION

Titanium and Titanium alloys have been used widely and successfully for various types of load bearing bone-anchored implants. It has revealed that the surface topography has a great importance thereby. Also the properties of oxide films covering these implant surfaces are important for the osseointegration [1]. An interesting way to produce such oxide films are micro-arc or micro-plasma processes [2,3]. A lot of manufacturers are interested in turning away from the standard surface refinements and in implementing new surface treatments for further filigree surface structures.

The aim of our investigations here was to texture the implant surface at the micro- and nanoscale and to test various methods and processes with respect to their desired surface effects.

In our project we used chemical etching to remove corundum particles remaining on the surface after blasting process - because of their possibly negative influence on osteointegration [4] - and electrolytic plasma processes to create new surface structures. The formation of covering by micro-plasma processes gives also the possibility to integrate any helpful ions. We tested it by variation of electrolyte composition.

MATERIAL PREPARATION

General pre-treatment (CB-->CE). Titanium (Ti) samples of technical purity (grade 2) with 30mm in diameter were used for all investigations. In the first step all samples were blasted with corundum (Al_2O_3) particles (3.5 bar) for producing of a coarse surface structure (CB). Then all samples were chemically etched (CE) in an etching solution (37% HCl; 98% H_2SO_4; H_2O; 2:1:1) for 5 min at 80 °C to remove the remaining corundum particles from blasting process and to cause a basic fine structure. In the next step the samples were treated in different ways as described below:

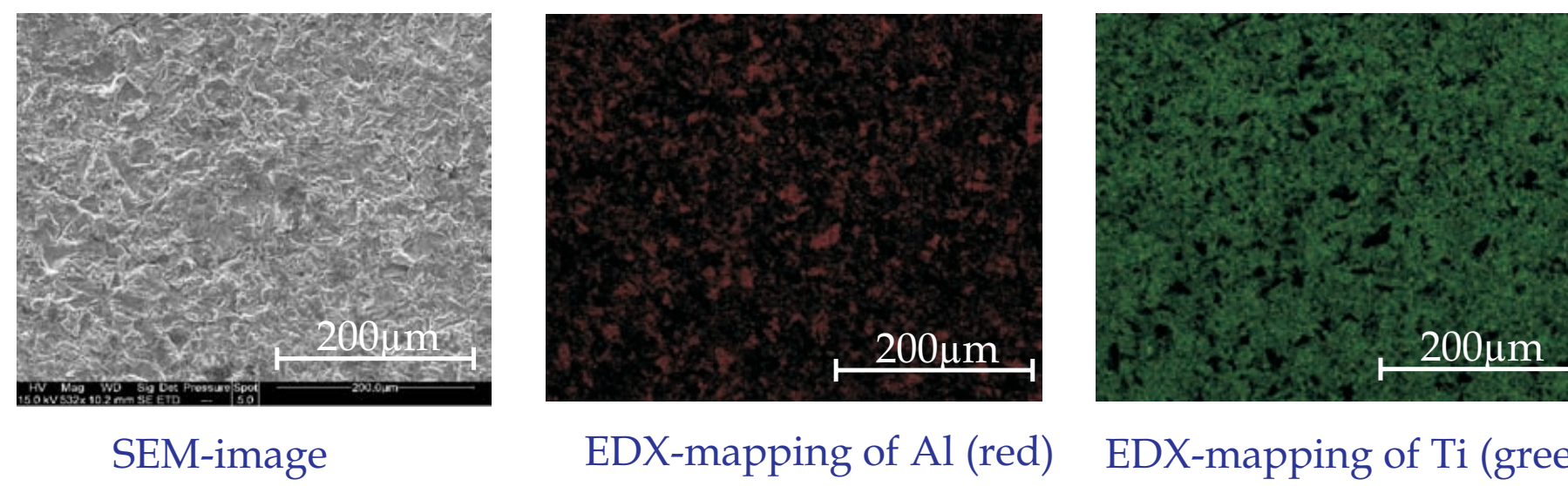MP1 - Micro-plasma treatment Version 1

MP2 - Micro-plasma treatment Version 2
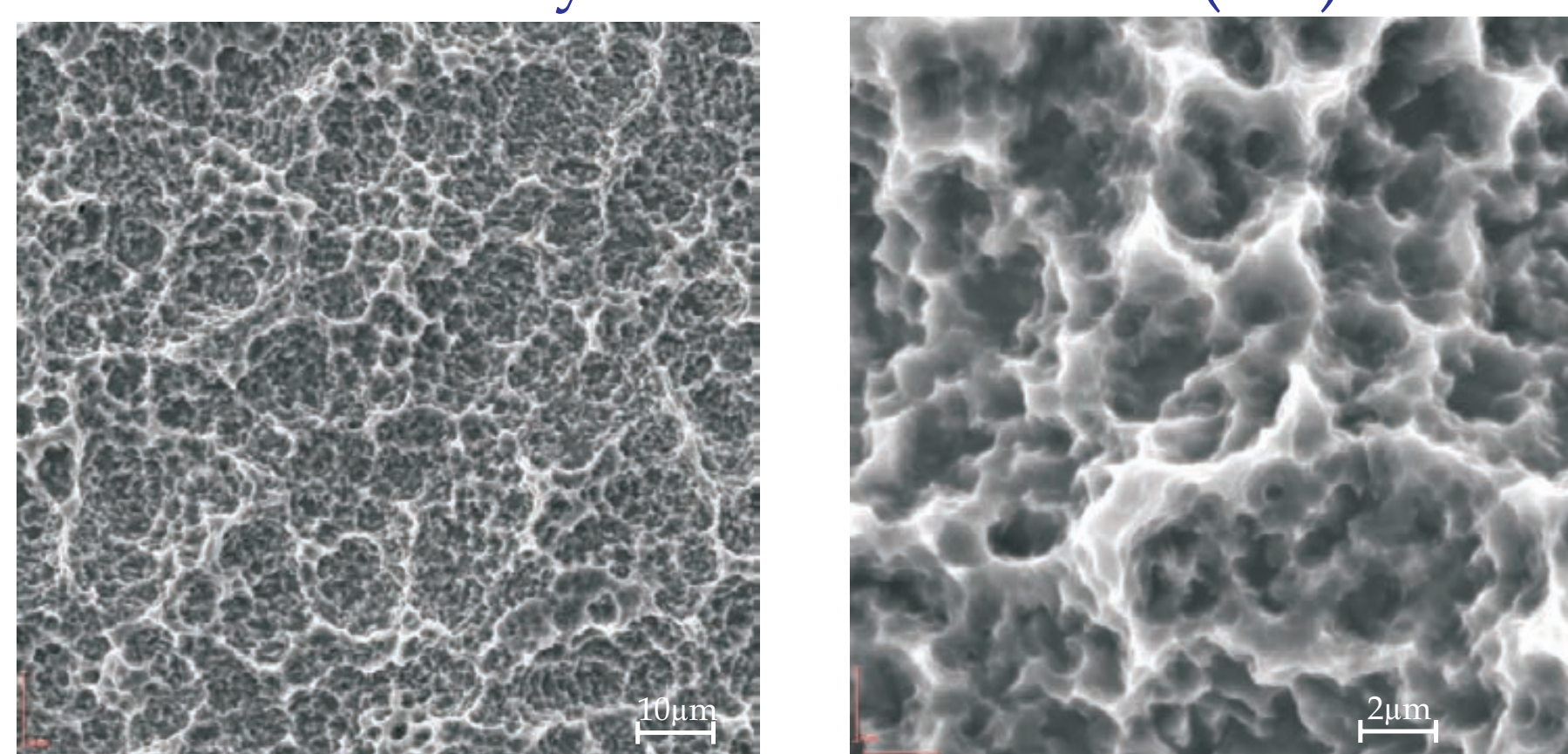
General pre-treatment
corundum blasted Ti-surface (CB)
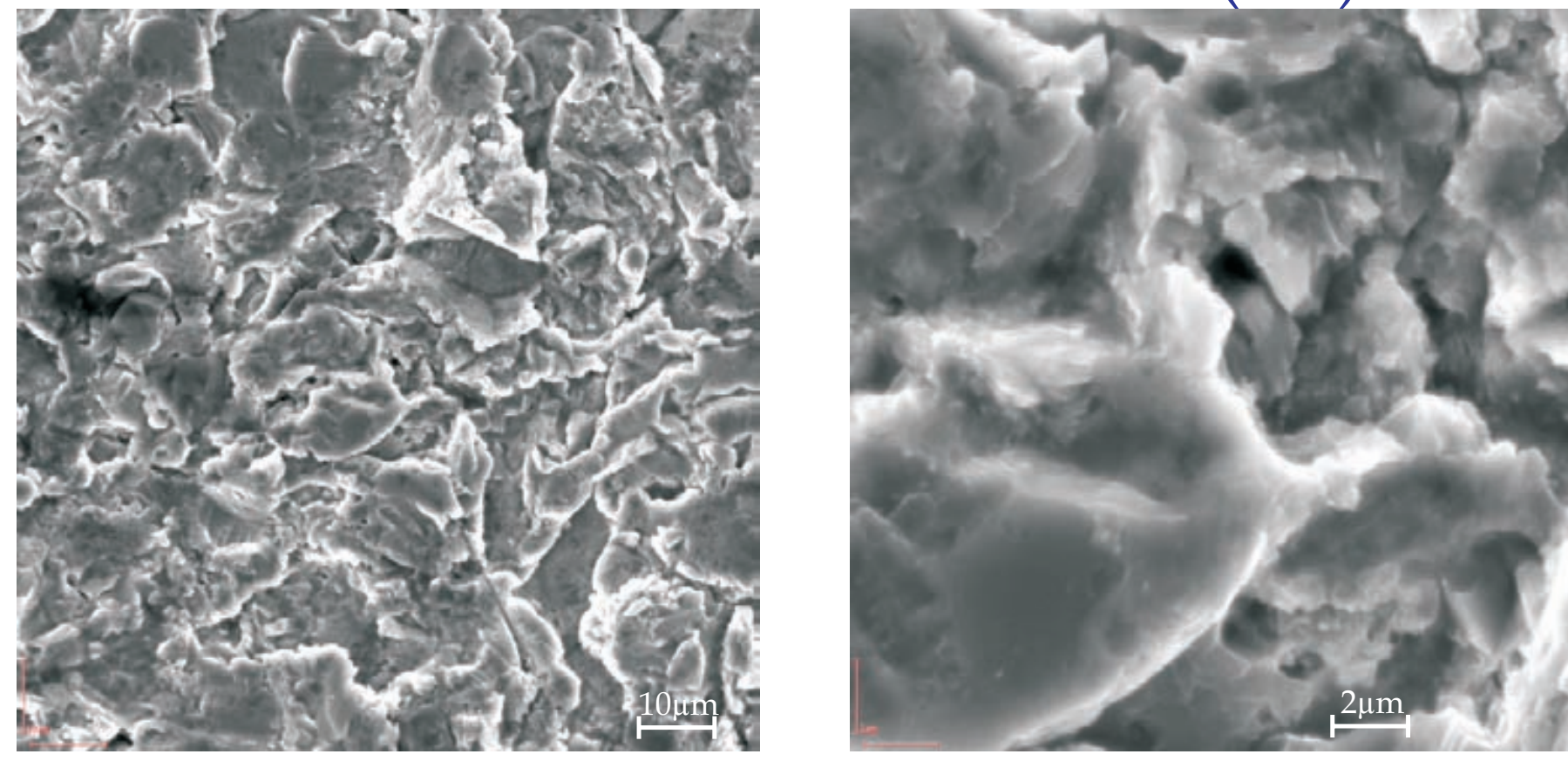
EDX-analysis of a corundum blasted Ti-surface

SEM-image | EDX-mapping of Al (red) | EDX-mapping of Ti (green)

chemically etched Ti-surface (CE)

MATERIAL CHARACTERISATION

Mechanical/Optical characterisation. For measurement of the roughness a surface profiler (T8000, Hommelwerke VS, Germany) was used. All surface profiles were measured over the same sample length l_m of 4.8 mm with a scan rate of 0.15 mm/s. The average roughness (R_a) and other roughness parameters (ISO 4287/1) were calculated from the primary profile. All samples were optically examined by scanning electron microscopy (SEM) (S360, LEO, Germany) to get an impression of the material surface before and after the consecutive preparation steps. The samples also were investigated with EDX (Quanta 400 with EDAX, FEI, USA) to get information about residua of the blasting material on the sample surface and also about the composition of a possibly existent covering layer.

Electrochemical Measurements. All electrochemical experiments were performed with 3-electrode-technique in PBS (pH 7.2) not deaerated electrolyte solution. A geometrical area of 2.27 cm^2 of the Ti specimen served as working electrode. As reference system a saturated calomel electrode (SCE) KE-10 (Sensortechnik Meinsberg GmbH, Germany) was used. The counter electrode consisted of a platinum sheet (4.67 cm^2) placed in a 30 mm distance vis-à-vis to the working electrode. Measurements were performed at room temperature.

Electrochemical DC-Measurements. After measuring of the open circuit potential (E_{ocp}) for 30 min a voltammetric experiment was performed from -0.5 V to 0 V vs. SCE in anodic direction with a scan rate of 0.5 mV/s (IM6e, ZAHNER-elektrik GmbH & Co. KG, Germany) to get a quasi-stationary current-voltage (CV)-characteristic. Values for corrosion potential (E_{corr}), corrosion current (I_{corr}), corrosion resistance (R_{corr}) and cathodic Tafel-slope were obtained by classical Tafel-analysis of the cathodic branch of the CV-characteristic.

A chronoamperometric experiment with a potential jump of 300 mV in anodic direction was used to determine the electrical displacement flux Q in the double layer capacity as a measure for surface area changing (AUTOLAB, Eco Chemie B.V., Netherlands).

Electrochemical AC-Measurements. Electrochemical impedance spectroscopy (EIS) was performed in single sine mode (f=1 mHz…10 kHz, ΔE=10mV) with respect to E_{OCP} (ZAHNER IM6e). The EIS data were analysed with THALES software from ZAHNER. The spectra were fitted with a suitable equivalent circuit (EQC) for the determination of surface capacities C (like electrochemical double layer, coating layer or space charge capacity) and the polarisation resistance R_p.

Micro-plasma process

The samples were treated anodic by a so-called electrolytic micro-plasma process which takes place at the interface between a solid (metals like Al or Ti) and a liquid electrode. After a pulsed DC voltage is applied to the electrochemical cell a series of thermal and chemical-thermal processes proceed. Because of the water electrolysis firstly a thin film of steam is produced at the cell interface and then the ohmic resistance of the interface increases. Afterwards the aqueous electrolyte begins to boil caused by faraday-current. As result of electrical arc discharge the ionic plasma (about 1027 ions in 1s/m^2) will be generated. Due to the local stochastic distribution of the ohmic resistance and electric field strength at the interface the plasma occurs as a local micro-plasma. Therefore the metal surface is textured and coated also locally. After the plasma process the samples were blasted with a wet stream of $NaHCO_3$ at 3…4 bar.
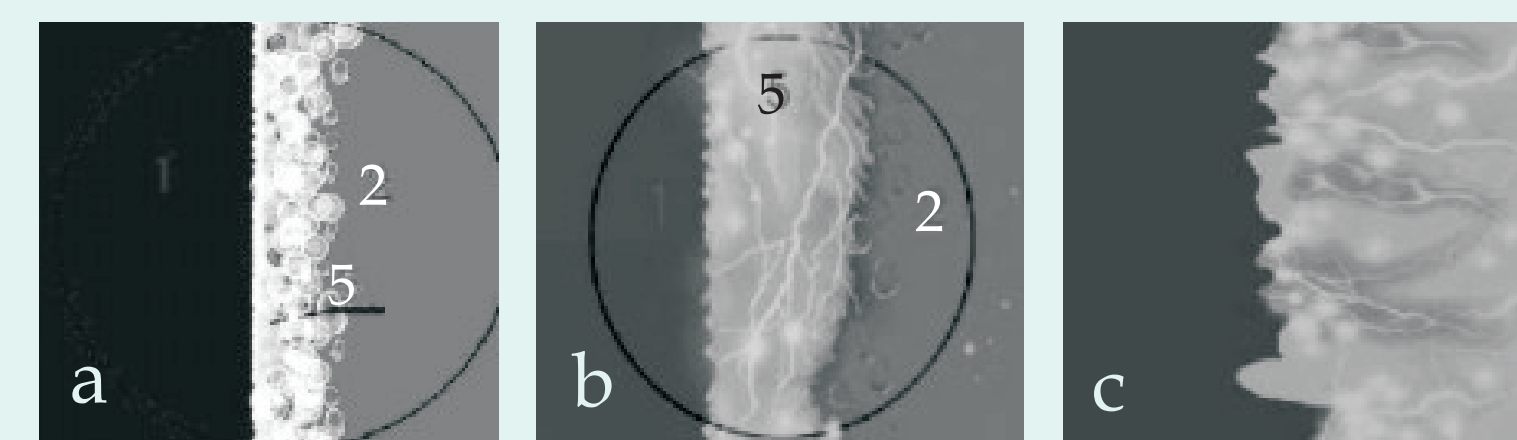

Schematic pictures of the interface between a Ti-electrode (dark at the left side) and a liquid electrode (2- aqueous electrolyte) during the plasma process:
(a) steam film at the metal surface and boiling aqueous electrolyte (5),
(b) beginning of discharge process at the interface (5),
(c) surface structuring produced by plasma process

source: Steklovac Company brochure

Micro-plasma treatment Version 1 (MP1)

electrolyte: 37% HCl; 98% H_2SO_4; H_2O --> 2:1:1   **process parameters:** 20°C, 100V, 1 min.

Characteristic electrochemical parameters


- I corr [nA]
- Q [µAs]
- C [µF]

CB | CE | MP1
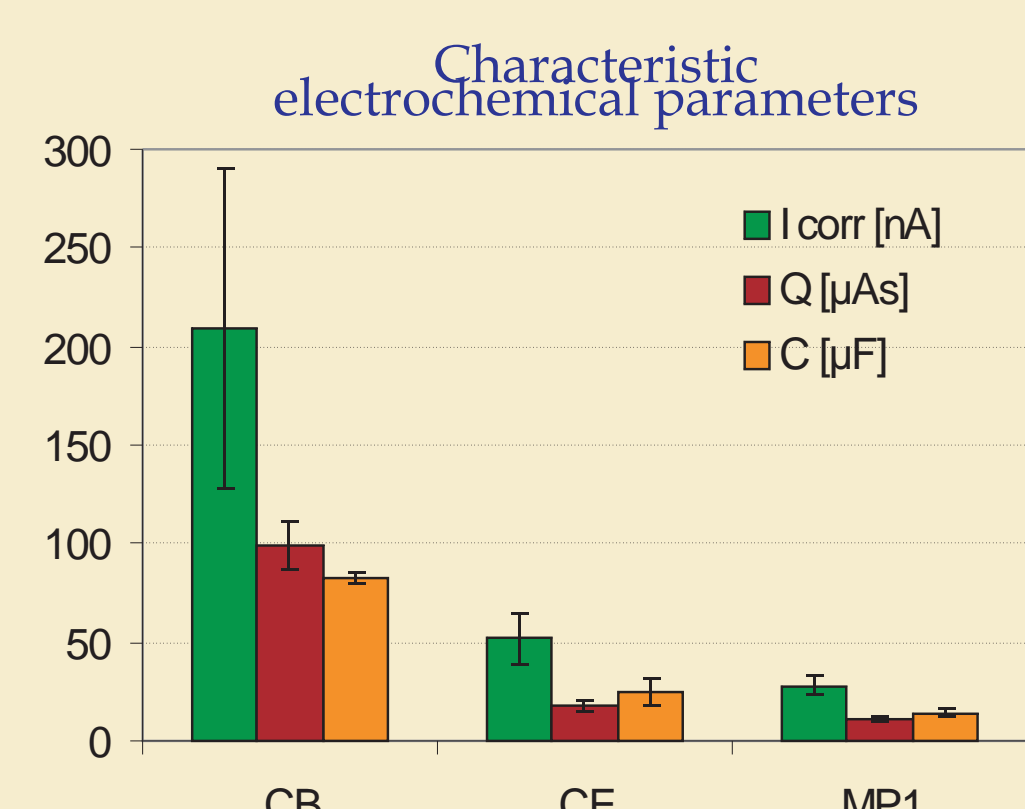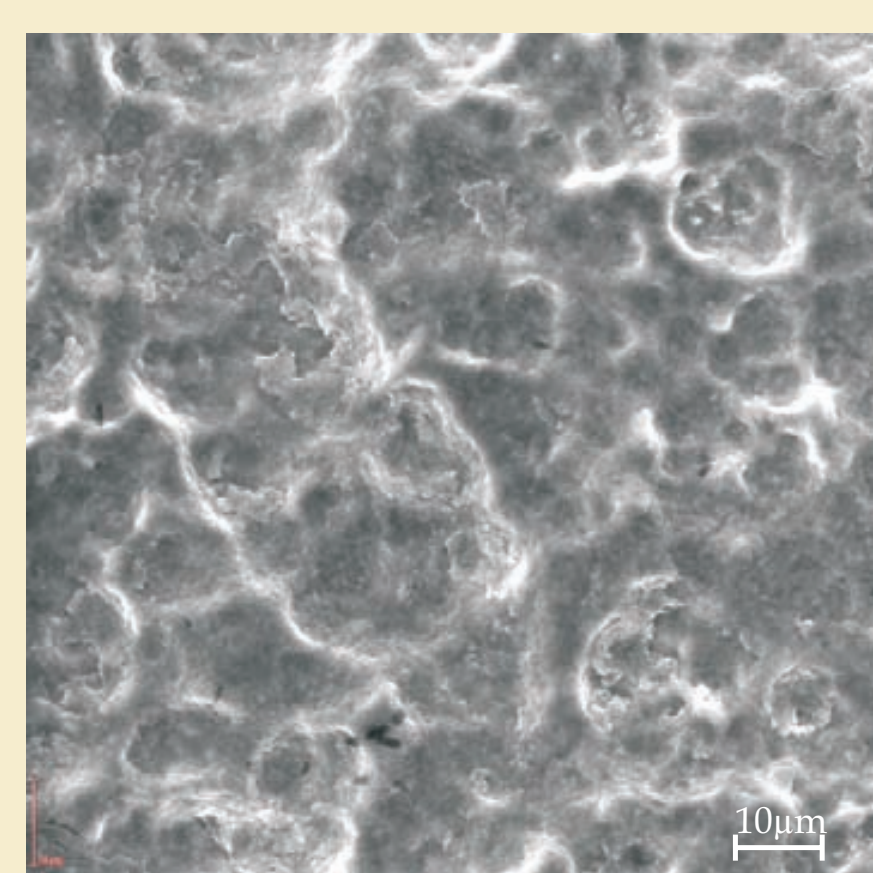
The surface porosity - observed after chemical etching - disappeared by micro-plasma treatment (MP1) and the surface was smoothed in fine-range (see SEM-pictures at the left hand side). This fact leads to a further decreasing of the electrochemically active surface area and is documented by the electrochemical parameters presented in the diagrams aside.

Impedance spectra

|Z| [Ohm]   phase [°]
- CB
- CE
- MP1

f [Hz]
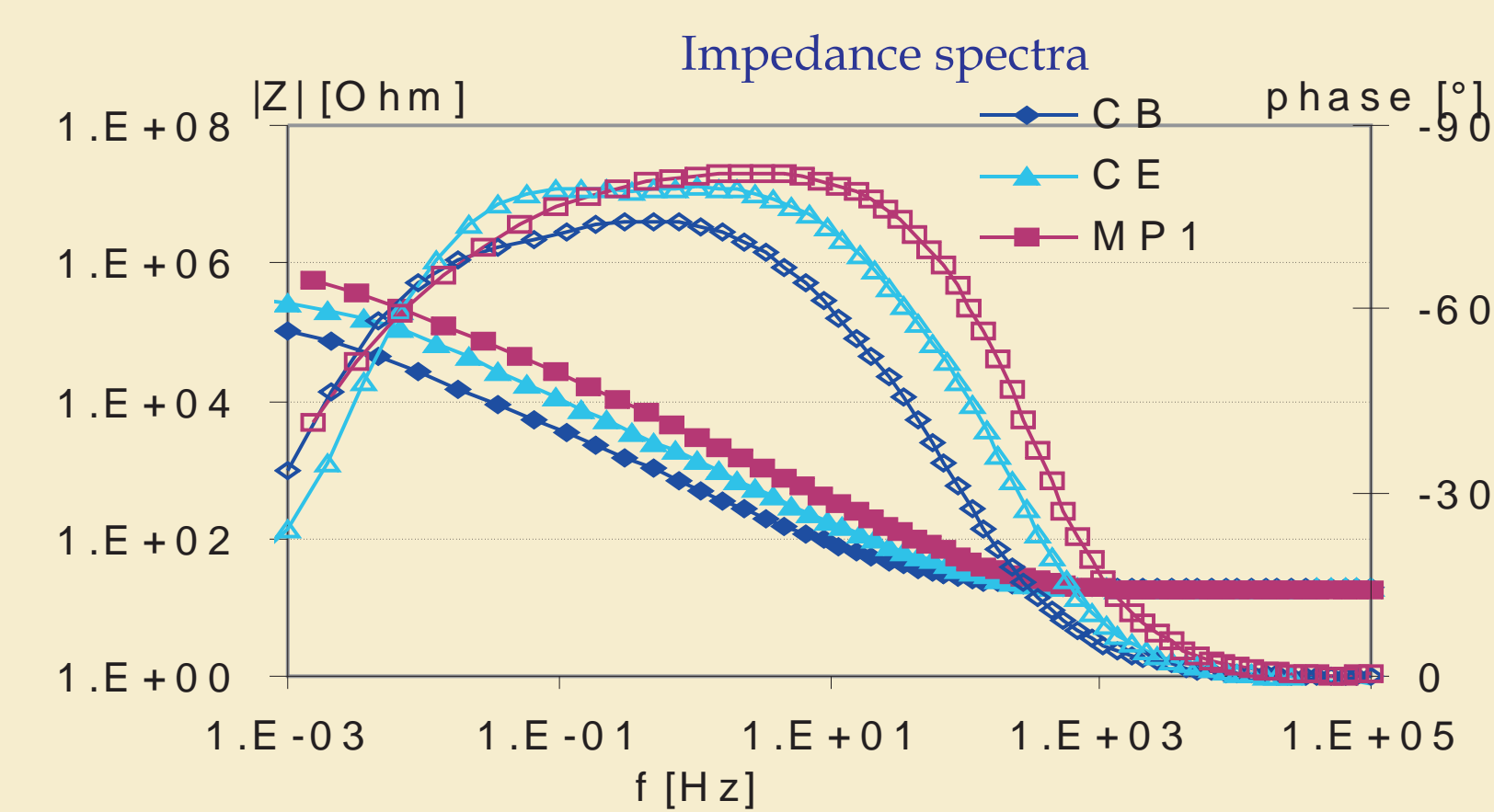
Micro-plasma treatment Version 2 (MP2)

electrolyte: 96% H_3PO_4; H_2O; $CuSO_4$ --> 12:20:1   **process parameters:** 20°C, 150V, 3 min

Characteristic electrochemical parameters

- I corr [nA]
- Q [µAs]
- C [µF]

CB | CE | MP2
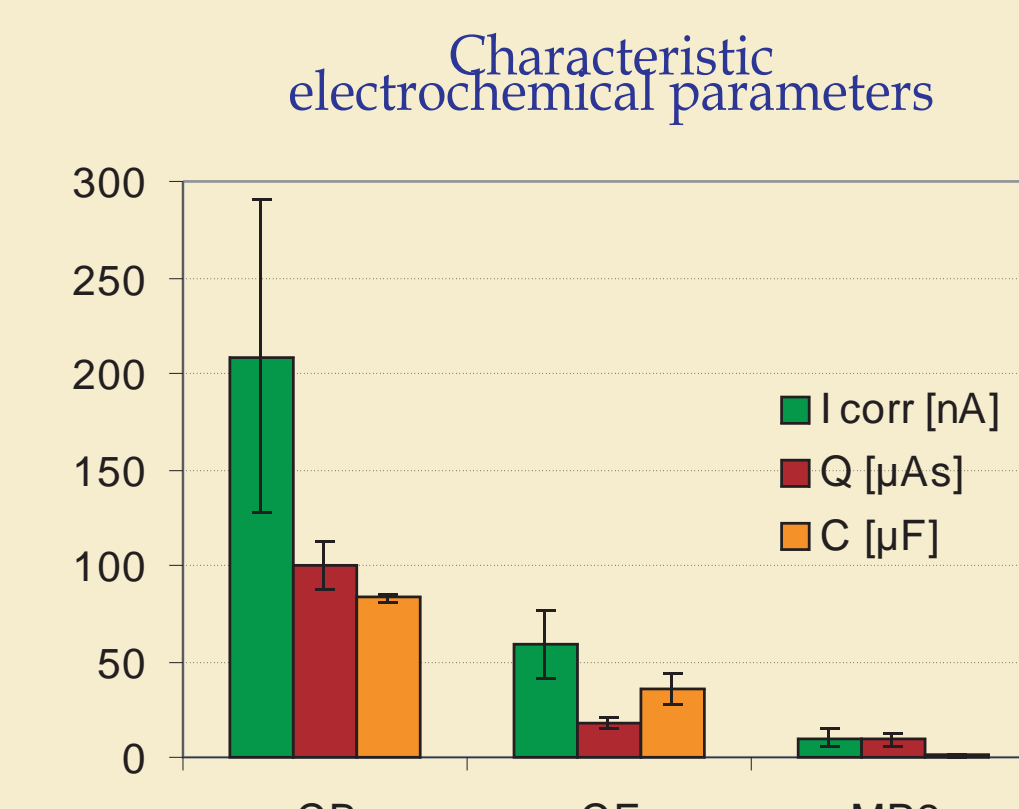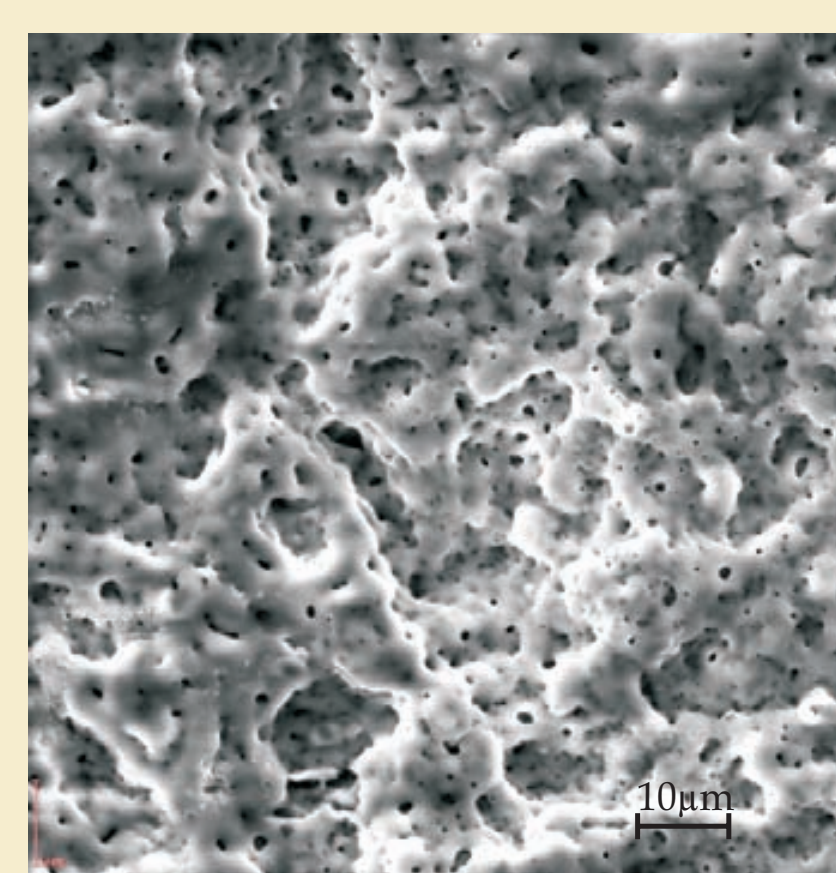
This treatment caused a ceramic-like coating on the sample surface (see at the left hand side). EDX analysis showed a considerable increasing of the O_2 content and also a notable content of Phosphorus. Due to this covering layer the corrosion current I_{corr} and Q extremely decreased, also the capacity obtained from EIS-measurements. The corrosion resistance R_{corr} and also R_p from the EIS received quite high values compared to the other preceding treatment steps (not shown). Moreover the impedance spectrum shows a modified behaviour compared with the others. This fact points to changed conditions at the material surface, i.e. the existence of a covering layer.

Impedance spectra

|Z| [Ohm]   phase [°]
- CB
- CE
- MP2

f [Hz]
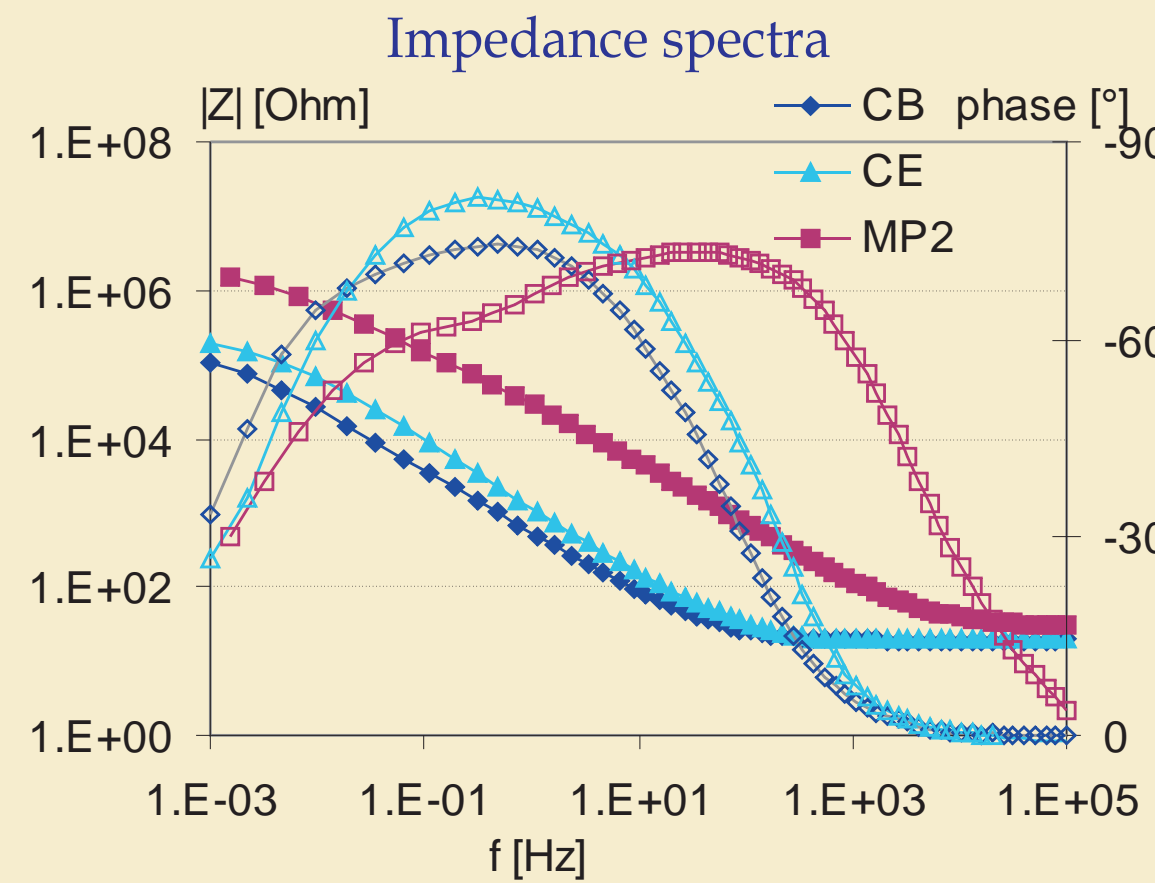
CONCLUSIONS AND SUMMARY

The Al_2O_3 particles remaining from CB-treatment were completely removed by chemical etching here. Chemical etching produced typically fine structured porous surfaces in micro- and nano-range. Through micro-plasma processing surfaces were levelled in the range of fine structures and the covering oxide layer was thickened (MP1).

Moreover a covering ceramic-like oxide layer with nano-pores and high phosphorus content was produced with a modified electrolyte (MP2).

Surface changes caused by the described processing methods were visualised and quantified by the combination of optical and electrochemical measurement methods quite well. In doing so the methods complemented one another as well as verified their results.

References

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[3] Li L.-H. et al.: *Improved biological performance of Ti implants due to surface modification by micro-arc oxidation*, Biomaterials 25 (2004), 14, p. 2867-2875
[4] Schuh, A. et al.: *Oberflächenuntersuchungen an Al_2O_3-rauegestrahlten Titanimplantaten in der Hüftendoprothetik*, Der Orthopäde 33 (2004), 8, p. 905-10
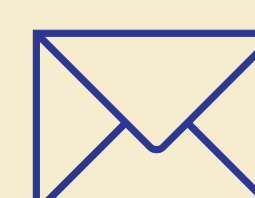
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