

## 1. INTRODUCTION

Titanium and titanium alloys are preferred materials for load bearing implants in dentistry, osteosynthesis and orthopaedics. The surface state of these implants modulates bone response and implant anchorage. This evidence brought implant manufacturers to turn away from the standard surface refinements and implement new surface treatments for more bone apposition and enhanced interfacial strength measured by removal torque or push-out tests.

Plasma-electrolytic effects are actually subject of studies and give a lot of applications like diverse metal coatings [1, 2, 3] or metal-cleaning processes [4, 5, 6]. Such anodic plasma treatments are cost-effective and comparatively non-polluting processes to modify surface topography and surface chemistry of several metals. This technique can be used for structuring of implant surfaces connected with a coating. Such coatings could be delaminated or fragmented and create un-wanted foreign body reactions at the interface between implant and bone.

The aim of our investigations here is to texture the implant surface at the low micro- and nanoscale without coating. For it the influence of the initial structure and electrical parameters of the plasma process on the final surface structure was analysed.

## 2. EXPERIMENTAL

Titanium (Ti) of technical purity (grade 2) was used for our investigations. We used samples in form of hexagon discs of 30 mm in diameter with several mechanical preparation (see "Influence of the pre-treatment").

### PLASMA PROCESS

The Ti-samples were immersed in an aqueous electrolyte prepared by dissolving sodium fluoride (1g/l...8g/l) and sodium carbonate (0.1g/l...1g/l) in deionised water. Pulsed DC voltage was applied to the electrochemical cell to execute the plasma process. The voltage ranged from 450V to 650V.

In the first test series the influence of the mechanical pre-treatment on the surface structure was investigated. In this series the current density while the plasma process was held constant at about 0.8 A/cm<sup>2</sup>.

In the second test series the influence of electrical plasma process parameters on the surface structure was investigated. In this series the current density while the plasma process was varied in three steps: S<sub>1</sub> = 0.6 A/cm<sup>2</sup>; S<sub>2</sub> = 0.8 A/cm<sup>2</sup>; S<sub>3</sub> = 1 A/cm<sup>2</sup>.

The procedures were stopped after 3min. Electrolyte temperature increased from 25°C to about 35°C during the process.

### MATERIAL CHARACTERISATION

**Surface profiling (SP):** sample length l<sub>m</sub> 15 mm, scan rate 0.5 mm/s roughness average R<sub>a</sub> (ISO 4287/1)

**Scanning electron microscopy (SEM):** SE-mode, BSE-mode

**Electrochemical methods:** 3-electrode-technique

**Electrolyte:** 80cm<sup>3</sup> of a phosphate buffered saline PBS (pH 7.2)

**Geometrical measuring area of samples:** 2.27 cm<sup>2</sup>

**Reference system:** saturated calomel electrode (SCE) KE-10

**Conditions:** room temperature (22 ± 1°C); not deaerated electrolyte solution

**Open circuit potential (OCP):** half an hour, E<sub>ocp</sub>  
**Linear Sweep Voltammetry (LSV):** potential scan from -0.5 V to 0 V vs. SCE in anodic direction, scan rate 0.5 mV/s current-voltage characteristic

Tafel analysis corrosion potential E<sub>corr</sub> corrosion current I<sub>corr</sub> corrosion resistance R<sub>ct</sub> cathodic Tafel-slope

**Electrochemical impedance spectroscopy (EIS):**

Frequency range: 1 mHz to 10 kHz,

single sine mode, AC-amplitude 10 mV

Working potential: open-circuit-potential E<sub>ocp</sub>

analysis of spectra by equivalent circuit method (EQC)

**Chronoamperometric experiment (CA):** 300 mV potential jump in anodic direction, recording of the resulting current transients for 30 s, resolution 10ms

integration of the current transients value for the moved surface charge Q

### EQUIPMENT

SP: T8000, Hommelwerke VS, Germany

SEM: S360, LEO, Germany; Quanta 400, FEI, USA

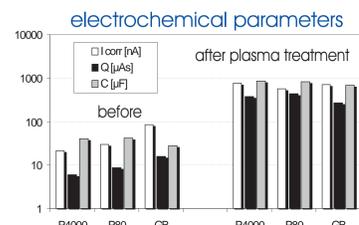
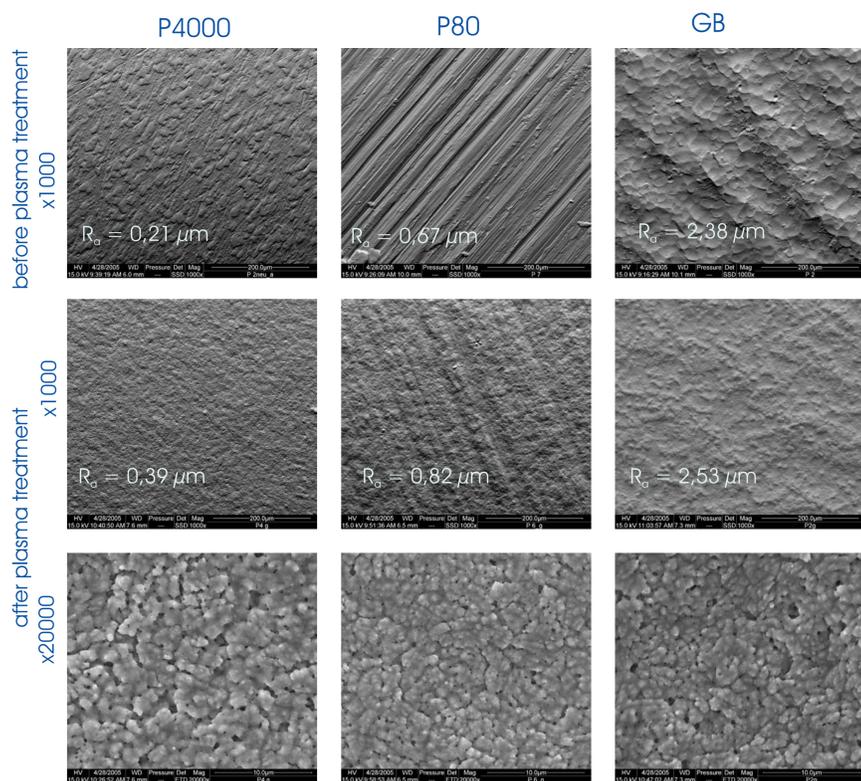
OCP, CA: AUTOLAB, Eco Chemie B.V., Netherlands

LSV, EIS, EQC: IM6e, ZAHNER-elektrik GmbH & Co. KG, Germany

## 3. INFLUENCE OF THE PRE-TREATMENT

The physical structure of the samples was modified by wet grinding with SiC paper (fine - P4000, rough - P80) and blasting with glass spheres (particle size 25-50 μm, 4.5 bar) (GB).

In the first row below the results of this pre-treatment are shown. The grinded surfaces (P4000, P80) clearly show grooves caused by grinding. The glass blasted surface (GB) is characterized by imprints of the glass balls. The underlying coarse structure could be caused by preceding machining. The average roughness R<sub>a</sub> increases from 0.21 μm for the fine structured sample (P4000) over 0.67 μm for the rough textured sample (P80) to 2.38 μm for the glass blasted surface (GB).



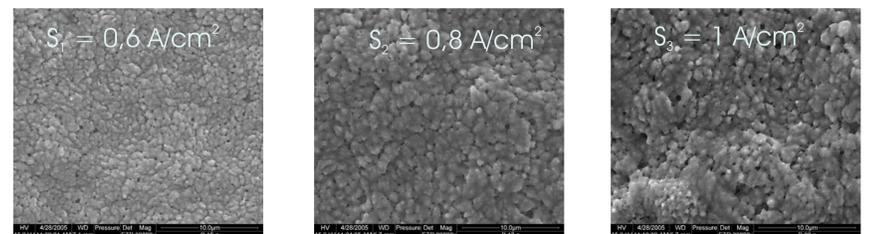
After plasma treatment (S=0.8 A/cm<sup>2</sup>) a new fine structure is visible that is overlaying the traces of the preparation procedure (middle row). The roughness average R<sub>a</sub> for all plasma treated samples is slightly increased compared to the pre-treatment. The new fine and porous surface structure is shown in the lower row at high magnification. There are no more differences visible caused by the initial structure. It is a very fine textured surface with structures at the nanoscale (< 1 μm).

With electrochemical methods the increasing of the surface area by the plasma treatment was evaluated. For this purpose the parameters I<sub>corr</sub>, Q and C were determined and compared (left hand).

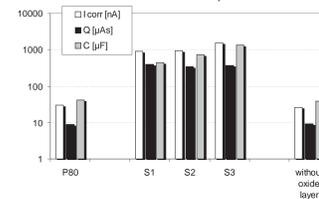
There is noticeable an increasing of the real surface area of at least one order of magnitude compared to the initial state. This high surface area is mainly caused by the porosity of the surface structure, also visible in the SEM-pictures. The differences between the samples after preparation disappear after the plasma treatment. There is no influence of the initial structure noticeable.

## 4. INFLUENCE OF PROCESS PARAMETERS

variation of the current density S



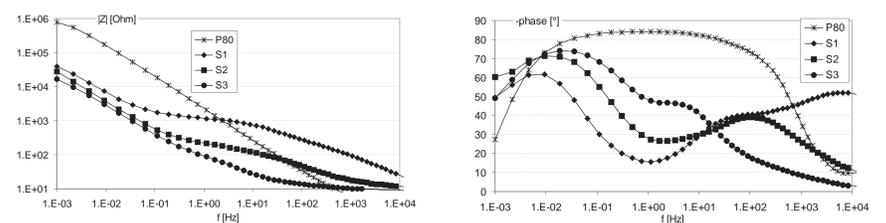
### electrochemical parameters



All samples got the same preparation (grinding P80). The process parameter current density was varied in three steps S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub> (see above). In the figures above the fine structure as result of this three process steps is shown. There are only small differences visible between the three steps.

This fact is also reflected in the electrochemical parameters I<sub>corr</sub>, Q and C. It seems that in the third step the porosity of the structure is the highest and there are more inhomogeneities than on the other surfaces.

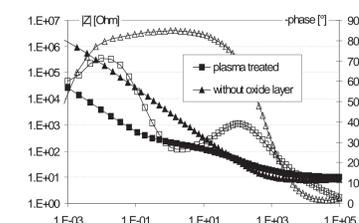
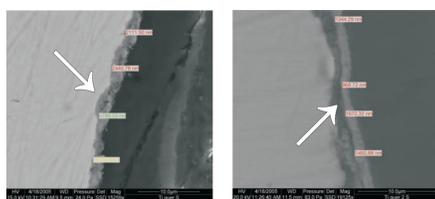
### Impedance spectra



The impedance spectra of the plasma treated samples show a modified behaviour compared to that of the initial state. Especially in the phase characteristic this difference becomes apparent. The clearly different second time constant in the phase characteristic points to a second capacity that is caused by a thick covering oxide layer on the surface. This second capacity shows differences depending on the process parameter current density. The increasing of this second capacity indicates an increasing porosity of the covering oxide layer.

## 5. OXIDE LAYER

To confirm the assumption of a covering layer on the plasma-treated samples cross sections of plasma treated samples were investigated. The left hand picture shows a porous covering layer of approximately 2.1 ± 0.4 μm thickness. In the picture aside this layer already begins to detach. The thick oxide layer was simply removed by ultrasonic procedures to examine the really interesting structure of the metal surface below the oxide layer.



The results of the electrochemical impedance spectroscopy (left hand) also confirmed the assumption of an oxide layer. After removing of the thick oxide layer the second time constant disappeared from the spectrum. This spectrum is similar to that measured before the plasma treatment.

Also the parameters I<sub>corr</sub>, Q and C are in the same order as before plasma treatment (see corresponding diagram at box 4 "Influence of process parameters").

Merely the SEM-picture (above) of the metal surface without the porous oxide layer (little picture) shows a modified surface structure compared to the initial state (large picture). There is a uniform fine structure in nanoscale (< 2 μm) similar to the plasma produced Ti-oxide surface but without their porosity.

## 6. SUMMARY

Electrolytic micro-discharge was used to produce evenly micro- and nano-textured metallic Ti-implant surfaces. Initially a thick porous Ti oxide layer was produced on the metal surface resulting from the plasma process. This layers produced a very high increasing of the real surface measured by EIS capacity, I<sub>corr</sub> and chronoamperometry. Thicker oxide layers (about 2 μm) could be removed simply. Surface fine-structures (in the low μm- and nm-range) textured by micro-plasma are independent of the mechanical pre-treatment of the Ti surface (P4000 grinding / P80 grinding / glass ball blasting). The plasma method described here can be used as a low-cost and non polluting technology for fine structuring of Ti implant surfaces.

### REFERENCES

1. E. I. Meletis, F. L. Wang, J. C. Jiang, Surf. Coat. Technol., 150, 2-3 (2002) 246
2. L. Yerokhin, X. Nie, A. Leyland, A. Matthews, S. J. Dowey, Surf. Coat. Technol., 122, 2-3 (1999) 73
3. J. Baszkiewicz, D. Krupa, J. Mizera, J. W. Sobczak, A. Bilinski, Vacuum, (article in Press)
4. R. R. Newyantseva, S. A. Gorbatkov, E. V. Parfenov, A. A. Bybin, Surf. Coat. Technol., 148, 01 (2001) 30
5. E. V. Parfenov, R. R. Newyantseva, S. A. Gorbatkov, Surf. Coat. Technol., (article in press)
6. E. V. Parfenov, R. R. Newyantseva, S. A. Gorbatkov, Surf. Coat. Technol., (article in press)

### Acknowledgement

This project was supported by the DFG. We thank Mr. Bahlo, IOW-Warnemünde, for his assistance with SEM.



Ulrich Beck  
University of Rostock, Department of Computer Science and Electrical Engineering  
Albert-Einstein-Str. 2, D-18051 Rostock  
+49 381 498 3590 Fax +49 381 498 3313  
E-Mail: ulrich.beck@uni-rostock.de