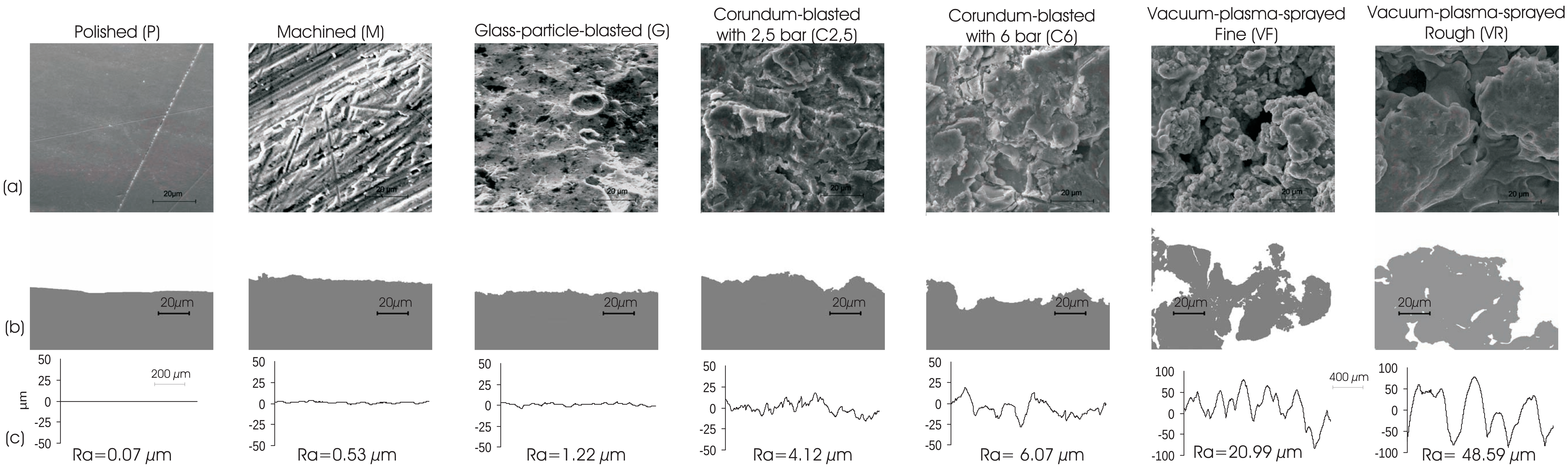
PHYSICAL AND CHEMICAL METHODS FOR THE SURFACE CHARACTERISATION OF TITANIUM IMPLANTS

R.Lange[1], A. Kirbs[1], B. Nebe[2], J. Rychly[2], H.-G. Neumann[3], U. Beck[1]

[1] University of Rostock, Dept. of Electrical Engineering and Information Technology, D-18051 Rostock, Germany
[2] University of Rostock, Dept. of Internal Medicine, D-18051 Rostock, Germany
[3] DOT Ltd., D-18059 Rostock, Germany

SEM-pictures (a) , cross sections (b) and surface profiles (c) of the analysed surface modifications



Surface profiling (SP): HOMMEL-TESTER; sample length 15 mm; scan rate 0.5 mm/s; calculation of average roughness R_a from the profile (ISO 4287/1)

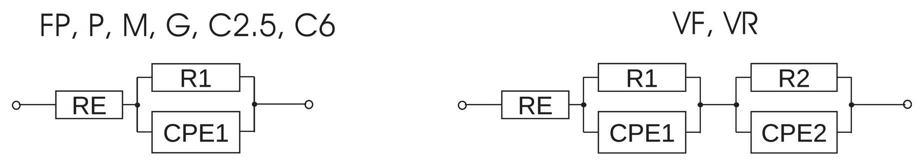
Determination of the "true" surface area

Determination of the parameter fractal dimension

Electrochemical Impedance Spectroscopy (EIS)

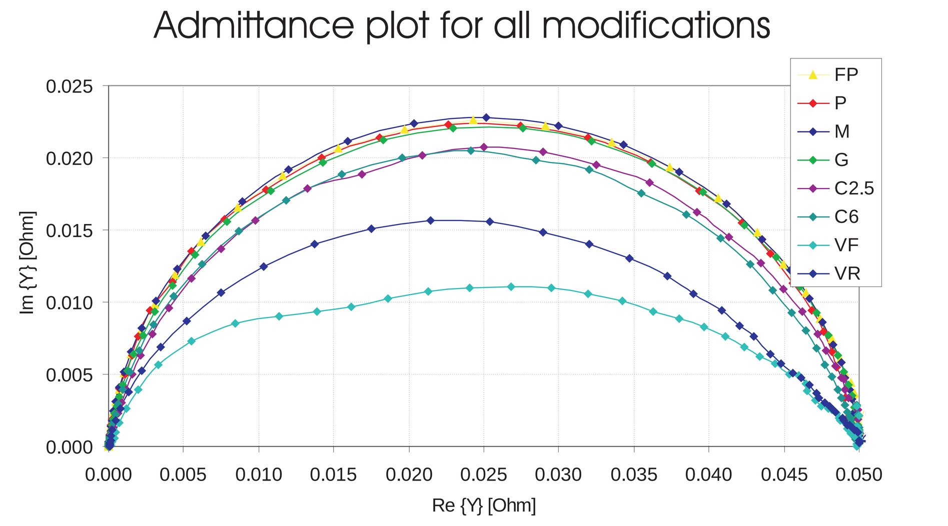
electrolyte: phospate buffered saline PBS pH 7.2 not deaerated at 22 °C
working electrode geometrical area: 2.27 cm^2
reference system: SCE
frequency range: 1mHz to 10 kHz
single sine mode: ac amplitude 10 mV with respect to open-circuit-potential (OCP)
measuring system: ZAHNER IM6e + THALES software

equivalent circuits:



The capacity C of the constant phase element (CPE) represents a measure for the "true" surface area

Admittance plot for all modifications



Semicircles representing the admittance are depressed with increasing roughness.
The parameter n of the CPE can characterise the roughness of the surface. For a blocking electrode the fractal dimension D_F can be calculated by

$$n \quad \frac{1}{D_F \quad 1} \quad 1$$

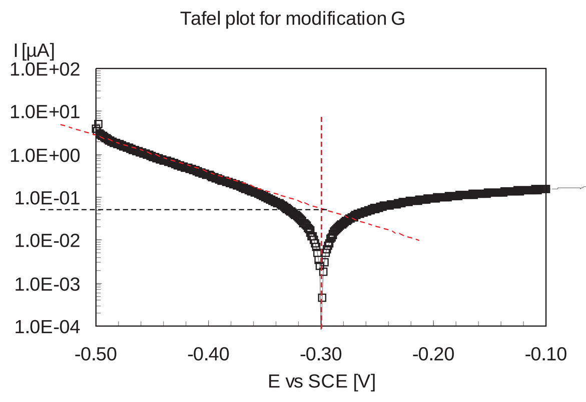
[1] T. PAJKOSSY, L. NYIKOS "Impedance of fractal blocking electrodes" J. Electrochem. Soc. 133 (10) (1986) 2061

FP - Fine polished sample (Mr. Velten, University of Saarland, Germany)

Linear Sweep Voltammetry (LSV)

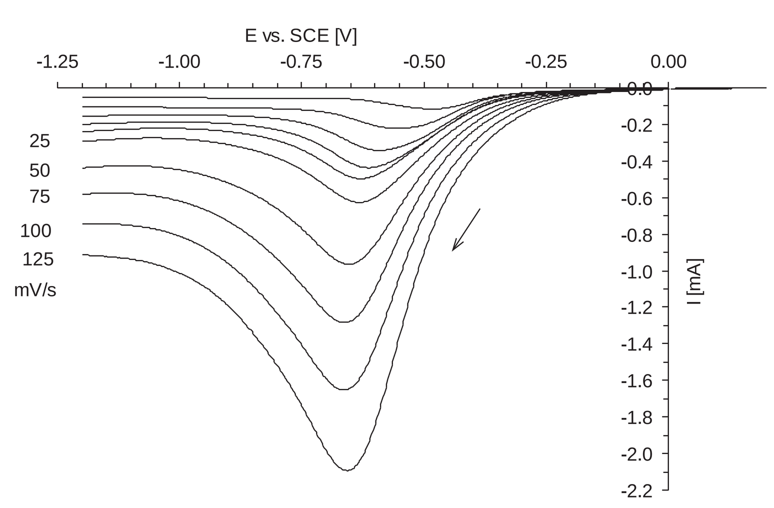
electrolyte: phospate buffered saline PBS pH 7.2 not deaerated at 22 °C
working electrode geometrical area: 2.27 cm^2 (titanium sample in blocking electrode mode)
reference system: SCE
Scan rate: 0.5 mV/s
potential range: -500 to 0 mV

Tafel plot for modification G



The corrosion current was determined by tafel analysis from the stationary current-voltage scan. Assuming equal exchange current density (comparable cathodic tafel slopes) for all surfaces the increasing of the surface area can be deduced from the increasing of the corrosion current.

Electrochemical reduction of ferricyanide
LSV scans with varied scan rates for C2,5



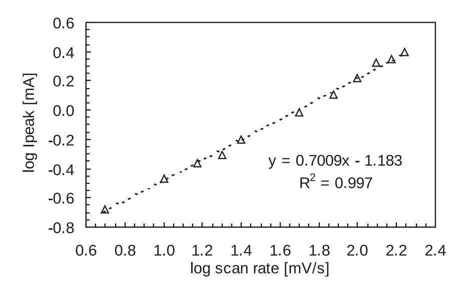
electrolyte: 10 mmol/l fericyanide $K_3[Fe(CN)_6]$ in 0.5 mol/l Na_2SO_4 as supporting electrolyte, not deaerated at 22 °C
potential scans from +0.2 V (SCE) to -1.2 V (SCE) in cathodic direction with varied scan rates from 1 to 200 mV/s
background correction
measuring system: AUTOLAB

estimation of D_F from slope a of the regression line in the plot log peak current i_{peak} vs. log scanrate:

$$a \quad \frac{D_F \quad 1}{2} \quad 2$$

[2] T. PAJKOSSY, L. NYIKOS "Diffusion to fractal surfaces III. Linear sweep and cyclic voltammograms" Electrochim. Acta 34 (2) (1989) 181-186

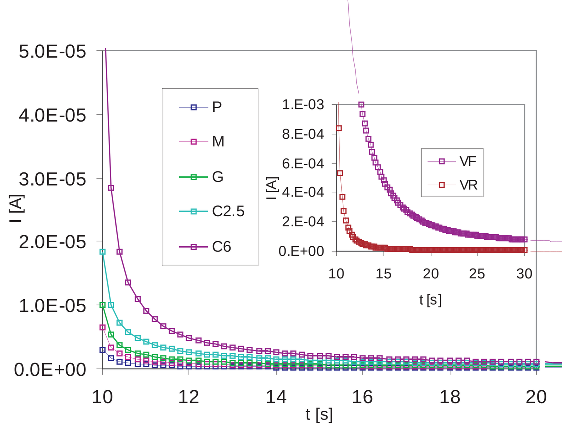
Results of the LSV procedure for C2,5



Chronoamperometry (CA)

electrolyte: PBS pH 7.2
working electrode geometrical area: 2.27 cm^2
reference system: SCE
conditioning: 60s at -300 mV
potential jump: 20 mV in cathodic direction
In a simple chronoamperometric experiment the amount of electric charge required for the reloading of the electrical double layer after a small potential jump was determined by integration of the I(t) curve.
This amount of electric charge is directly related to the electrode surface area.

Resulting current responses for all modifications



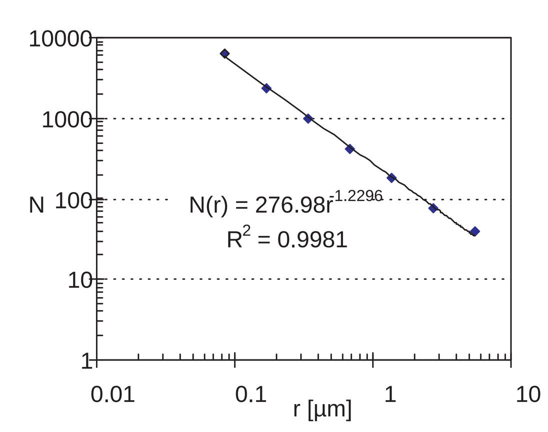
Digital Image Processing (DIP)

For the determination of the fractal dimension D_F cross sections of all surface modifications were made and investigated by SEM in several magnifications (50-,1000-, 500-, 1000-, 5000fold).
The border line of the cross sections was analysed using the box counting algorithm to get the fractal dimension $D_{F,B}$ (Corel Foto Paint, UTHSCSA Imagetool). The slope of the regression line in the log(N)=f(log(r))-plot represents the fractal dimension $D_{F,B}$ for the analysed one dimensional object (border line):

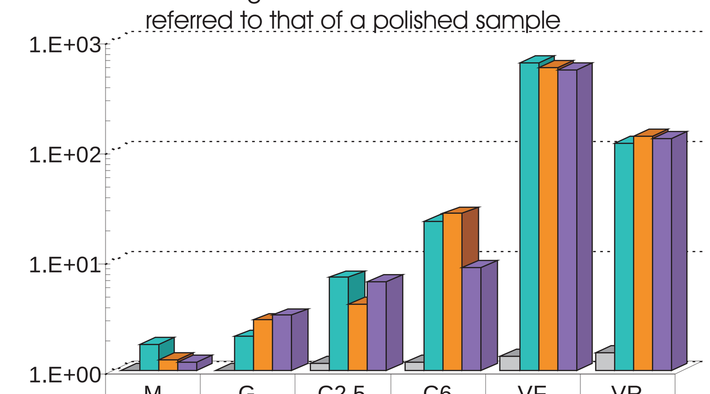
$$N \; r \quad const. \; r^{\; D_{F,B}}$$

For the transformation into a two dimensional context (surface) $D_{F,B}$ has to be increased by one assuming that the fractal dimension is the same in all directions.

Results of the box counting procedure for C2,5
1000fold magnification



Increasing of the "true" surface area referred to that of a polished sample



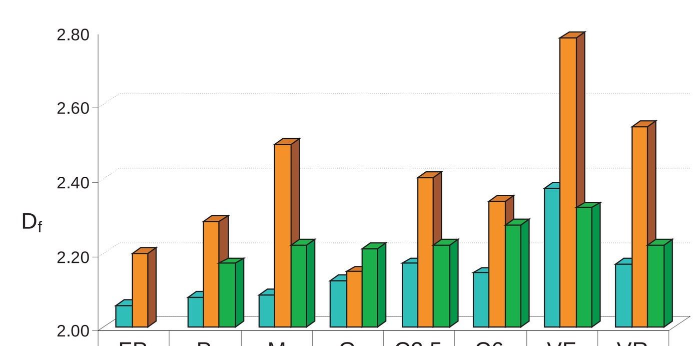
	M	G	C2.5	C6	VF	VR
SP	1.01	1.01	1.18	1.22	1.37	1.48
EIS	1.75	2.05	7.07	22.92	630.79	118.69
LSV	1.27	2.90	4.03	26.94	575.98	137.39
CA	1.20	3.20	6.50	8.80	551.00	130.00

Summary

The structure of the surface of implants is an important factor for biocompatibiliy. The aim of this work is a preferably complete and exact description of the surface of titanium modified by very different technologies common with implants. We can demonstrate that both the increasing of the "true" surface area and the fractal dimension can be determined by different electrochemical methods relatively easily. Data sets obtained by surface profiling are not suitable for this purpose.

We recommend the use of electrochemical measurements as non-destructive and fast methods to get information about the structure of metallic surfaces.

Comparison of the fractal dimension D_f obtained by 3 different methods



	FP	P	M	G	C2.5	C6	VF	VR
EIS	2.06	2.08	2.09	2.12	2.17	2.14	2.37	2.17
LSV	2.20	2.28	2.49	2.15	2.40	2.34	2.78	2.54
DIP		2.17	2.22	2.21	2.22	2.27	2.32	2.22

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U. Beck, Universität Rostock,
FB Elektrotechnik und Informationstechnik
Richard-Wagner-Str. 31, 18119 Warnemünde
+49-381-498 3590 Fax: +49-381-498-1126
e-mail: ulrich.beck@etechnik.uni-rostock.de