Development of biofunctional coatings on titanium implants to improve biocompatibility and osteoinductivity

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Introduction

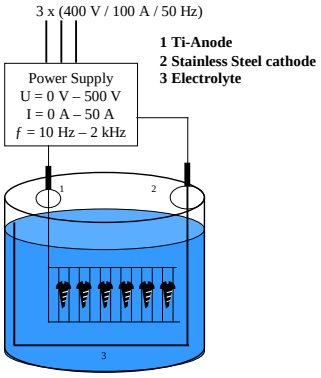
Titanium and its alloys were utilized as biomaterials in orthopedics since the end of the nineteen-seventies because of their very good corrosion resistance, advantageous mechanical properties and biocompatible interaction with the human body. Several disadvantages like body tissue irritations or escalated bone fracture risk in implant excision because of cytotoxic elements and increased removal torques can be eliminated very efficiently by a procedure called plasma chemical oxidation (PCO) in combination with appropriate finishing treatments.

The main technological advantage of these converted titanium surfaces is improved adhesion and bonding (> 20 MPa), which is particularly relevant in the aerospace industry. It can also be used to increase the oxide thickness for corrosion protection, for decreased ion release, coloration and for dielectric coatings on electrode materials e.g. DBD´s.

Experimental Setup

The experimental setup consists of a pulsed rectifier set *D400 G500/50 WRG-TFKX* from *Munk Ltd.* in Hamm, Germany and a specific electrolyte. The electric supply is realised by three feed cables (3 x 400 V / 50 Hz / 100 A) and delivers a positively pulsed directed current of 50 A and a negatively pulsed directed current of 30 A with voltages from 0 V to 500 V. The system control with a digital output provides constant voltages and currents with an accuracy of ±1% and ± 1,5% and a ripple content of w = 0,5 %. The adjustable pulse frequency ranges from 10 Hz to 1 kHz.

The experimental setup can be interpreted as an ordinary electrolysis cell in an aqueous electrolyte with a stainless steel cathode and a work piece anode made of titanium. Later process modes exhibit a multiphase reactor with an activating thermal arc discharge temporary developed in a pure oxygen atmosphere.



Ti / Ti oxide interface:

$$Ti^0 \Leftrightarrow Ti^{4+} + 4e^-$$

Ti oxide / electrolyte interface:

$$2H_2O \Leftrightarrow 2O^{2-} + 4H^+$$

(TiO_2 formation)

$$2H_2O \Leftrightarrow O_2 + 4H^+ + 4e^-$$

(O_2 formation)

Both interfaces:

$$Ti^{4+} + 2O^{2-} \Leftrightarrow TiO_2 + 2e^-$$

The titanium and oxygen ions formed in these electrochemical reactions have to be driven through the natural oxide film. This is carried out by the externally applied electric field and linearly increases the oxide film thickness with approximately 1.5 nm·V^{-1} to 3.0 nm·V^{-1}. The applied voltage drop mainly occurs across the oxide film because of its high resistivity compared to the electrolyte or metallic parts of the electric circuit. With a suitable electrolyte voltages above 150 V can be applied leading to further layer growth beyond the coloration regime. Above a certain voltage, mainly determined by the electrolyte, work piece and power supply settings, the oxide will be no longer resistive enough to prevent further current flow. The result is an increased oxygen formation together with local field strengths above 10^6 V·m^{-1} - 10^9 V·m^{-1} igniting a thermal arc discharge in oxygen surrounded by an aqueous electrolyte.

Summary

The objective target of the joint research project to develop surface modifications in order to improve the biological, chemical and mechanical properties of titanium implants in bio-inert and bio-active applications is achieved. The surface modification for hard tissue replacement prostheses possesses an adequate chemical composition to avoid adverse tissue reactions, corrosion resistance towards degradation in the human body and sufficient strength to sustain cyclic loading and chemical stress. Future project planning includes investigations in functional coatings providing antibacterial- / antibiotic properties. By the way, more effort will be applied to vary and understand the plasma discharge in an electrolyte. Basic measurements if the bio-active or bio-inert surfaces are suitable for subsequent layer-by-layer methods including further functional configurations are done and show good transferability for industrial surfaces.

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Investigation

The first central scope of the joint research project is to provide a bio-inert titanium coating for temporary implants. The second central scope deals with bio-active coatings for permanent implants as well as bio-inert coatings for temporary implants and its scientific investigation in terms of osteoblastic cell proliferation tests, cytotoxicity tests and tests to validate the applicability of the coatings for subsequent coatings e.g. multi-layer coatings deposited with dip-coating techniques, carried out at the Institut für Materialwissenschaft und Werkstofftechnologie. Figure 1 illustrates the surface topography of the obtained coatings on Ti-6Al-4V specimen providing optimized peak-to-valley height values compared to Ti-cp2 specimen. To ensure diffusion inhibiting properties of the coating, located above irritant elements containing bulk material, glow discharge optical emission spectra are presented in Fig. 2.

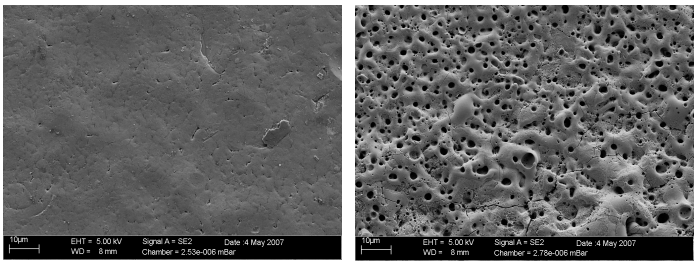

Fig.1: *Surface topography of a bio-inert TiOB-/TiOx- and bioactive TiOB/CaP-coating on Ti6Al4V specimen*

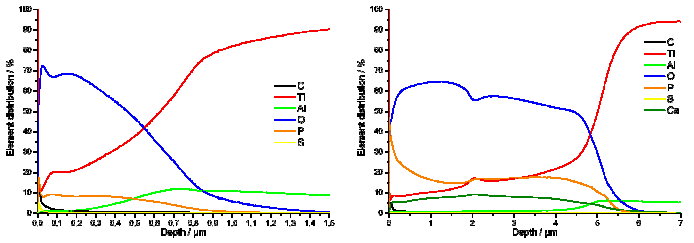

Fig.2: *GDOES-layer profiles of a bio-inert- and a bio-active TiOB coating*

Tab.1: *Composition of the bio-inert and bio-active TiOB-coating*

Coating	Ti / %	Al / %	O / %	P / %	C / %	Ca / %	Thickness
TiOB bio-inert	41,65	6,55	44,36	6,32	1,11	0	0,94 µm
TiOB bio-active	21,45	1,80	52,85	16,64	0,31	6,94	5,4 µm

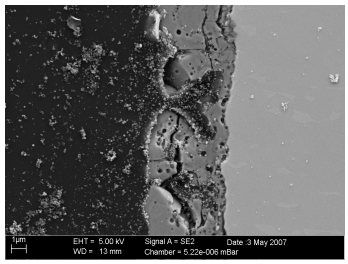

Fig.3: *Bio-active TiOB-coating (cross-section)*

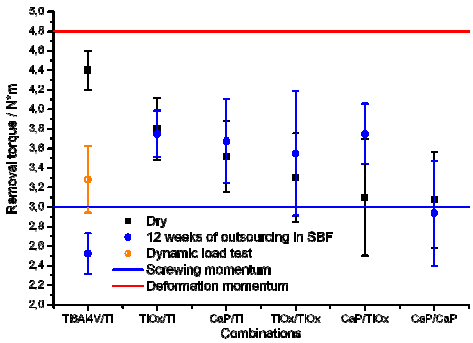

Fig.4: *Removal torques between osteosynthesis screw (Ti6Al4V) and –plate (Ti-cp2). A dynamic load test (30 N [15% ·F_{max}], 50 000 cycles, 6 mm distance from the screw-plate combination) was initiated to show mechanical effects*

Tab.2: *Steps of a steam autoclave cycle in detail*

Step	Procedure	Temperature / K	Time / s
1	Alkaline cleaning (KOH)	343,14	600
2	Acid neutralisation (H3PO4)	368,14	360
3	Flushing	393,14	800

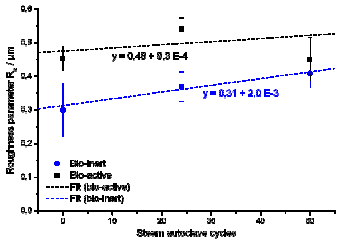

Fig.5: *Roughness parameter development in sterilisation degradation mechanisms*

The applicability for subsequent coating, e.g. multi-layer coating is examined. Therefore, deposition experiments based on alternating dip-coating in anionic (gelatine) – and cationic (chitosan) polymers are investigated. The titanium specimens were dip-coated in a typical aqueous solution of poly-(ethyleneimine) (PEI) for 20 minutes and afterwards rinsed with distilled water. Before the following dip-coating in gelatine- / chitosan- solution, the stability of the PEI-coating in the polymers´ solvents, 0,15 M NaCl, was tested for 20 minutes. The chemical composition was tested with XPS techniques (ESCA Microrprobe) and is illustrated in Fig. 6. On all surfaces PEI-layers tracing nitrogen is detectable. The normalisation of the nitrogen peak by subsurface titanium signals demonstrates good adhesion and stability of the PEI adhesive layer on technical titanium surfaces. Afterwards, the specimen were coated in each ionic polymer for ten minutes until 5 monolayers were created. XPS investigations identify the multi-layer components by characteristic carbon / nitrogen ratios corresponding to gelatine (3,2:1) and to chitosan (6:1) respectively.

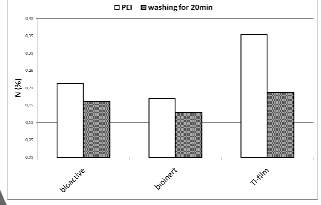

Fig.6: *XPS analysis of a PEI layer after the deposition and washing in 0.15M NaCl for 20 min*

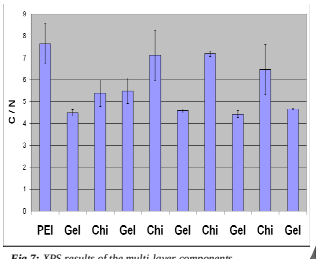

Fig.7: *XPS results of the multi-layer components*