Structure and Properties of Titanium-Based Coatings prepared by Metal Plasma Immersion Ion Implantation and Deposition

I. Tsyganov, M. F. Maitz[1], E. Wieser[1], E. Richter[1] and H. Reuther[1]
Lipetsk State Technical University, Moscowskaya 30, 398055 Lipetsk, Russia
[1]Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf e.V., P.O.Box 510119, 01314 Dresden, Germany
Forschungszentrum Rossendorf

Motivation

For medical materials in contact with blood it is important to minimize the tendency of their surface to adsorb blood proteins and to induce blood clotting, hence, to reduce the danger of thrombosis. Titanium-based coatings are a very promising approach in this direction.

Objectives

Synthesis of bioinert and blood compatible titanium-based coatings by Metal Plasma Immersion Ion Implantation and Deposition (MePIIID), modification of the surface layers by different partial pressures of O_2 and N_2 and subsequent ion implantation (P and Cr) into TiO_2

Investigation of the relation between physical properties of the titanium-based layers and blood compatibility (clotting time, thrombocyte adhesion, fibrinogen adsorption) for

- P- and Cr-implanted TiO_2 and
- TiN_xO_y

Summary

- MePIIID provides a useful technique to control composition and structure of titanium-based films. In dependence on the deposition parameters different titanium oxynitrides have been produced
- TiN and TiN_xO_y have lower blood clotting activation compared to TiO_2
- Thrombocyte adhesion and fibrinogen adsorption are lower for TiN_xO_y than for TiO_2
- This decrease is related to the decreasing contact angle and increasing surface energy
- The quantity of nitrogen incorporation and the surface roughness show no significant influence
- P and Cr implantation into TiO_2 clearly reduce the clot forming property of the surface

Experimental

Deposition parameters:

Specimen temperature (T_{max}):	25 – 500 °C
Gas flow rate (F):	60 – 180 sccm
Bias voltage (ion energy):	0 – 2.5 kV
Coating deposition rate (R_{dep}):	0.35 – 1.1 μm/min
Current of the cathodic arc discharge (I):	110, 140 A
Basic vacuum:	0.5 – 1 x 10^{-3} Pa
Working pressure:	0.5 – 1 x 10^{-1} Pa
Substrate:	SiO_2 on Si (100)
Implantation:	10^{15} P^+/cm² (30 keV); 5x10^{17} Cr^+/cm² (30 keV)
Post-implantation annealing:	900 °C for 1 h (vacuum)
Analysis AES:	depth distribution of the elements
XRD:	phase formation and identification
AFM:	roughness of the deposited films
Contact angle:	wettability, surface energy
Blood compatibility:	blood clotting time, thrombocyte adhesion, fibrinogen adsorption

MePIIID: metal deposition + plasma immersion ion implantation (PIII)
metal plasma by cathodic arc evaporation
implantation by pulsed negative substrate bias
supply of oxygen near the substrate

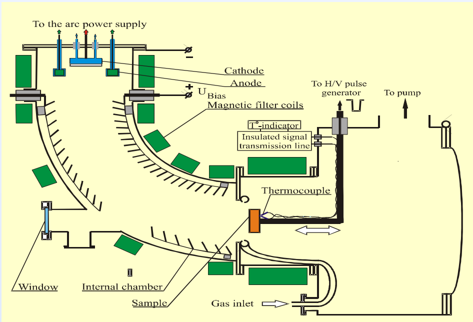

Fig.1. Schematic diagram of the MePIIID device

Layer properties

Oxide layers

Dependence of the TiO_2 structure on the deposition parameters

structure (XRD)	T, °C	F, sccm	U, kV
rutile + anatase	~ 450	180	- 2.5
anatase + brookite	~ 350	60	- 2.5
amorphous TiO_2- layer	~ 80	180	0
nanocrystalline anatase + brookite	~ 60	60	0

Oxynitride layers

Dependence on the relation of the O_2/N_2 partial pressures

crystalline phases (XRD)	average atomic composition (AES)	structure	$p(O_2)/p(N_2)$
rutile + anatase	TiO_2	TiO_2 (rutile + anatase)	only O_2
rutile + anatase + TiO	$TiN_{0.3}O_{1.7}$	$TiO_{2-x}N_x$ (rutile + anatase) + TiO	3/1
TiN + TiO	$TiN_{0.4}O_{1.6}$	TiN + TiO + TiO_2 (amorph)	1/1
$TiN_{1-x}O_x$	$TiN_{0.7}O_{1.3}$	$TiN_{1-x}O_x$ + TiO_2 (amorph)	1/3
TiN	TiN	TiN	only N_2

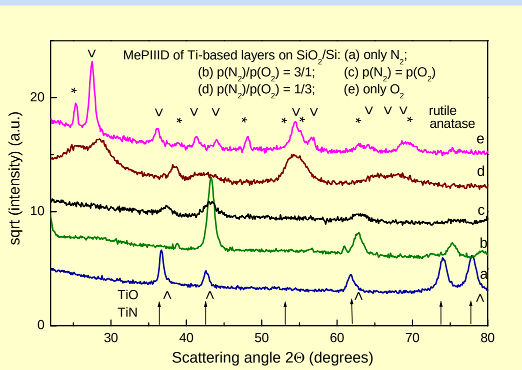

Fig.2. XRD pattern of Ti-based layers

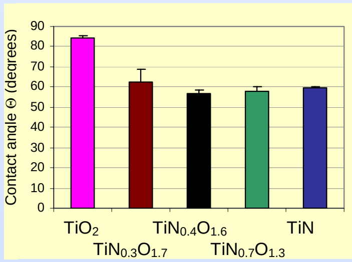

Fig.3. Contact angle with water for different layer compositions

- Decrease by incorporation of nitrogen

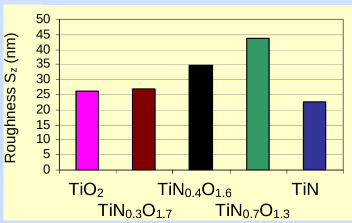

Fig.4. Roughness of different layer compositions

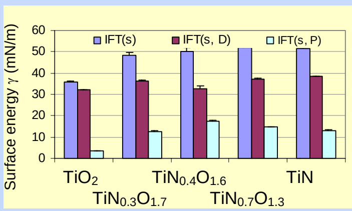

Fig.5. Dispersive IFT(s,D) and polar IFT(s,P) components of the coatings surface energy IFT(s)

Blood compatibility

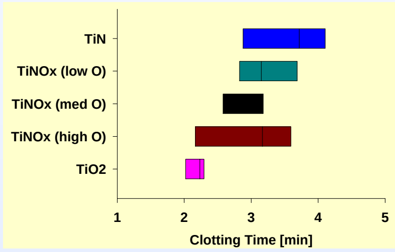

Fig.6. Clotting time on the titanium oxynitride layers (median and quartils of the blood clotting time on the test surfaces)

- It is longer than the also shown TiO_2 (rutile) value

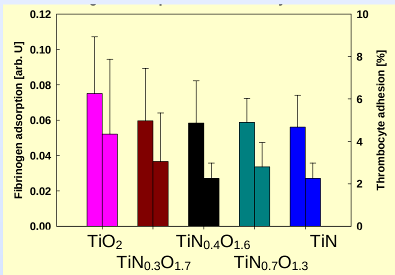

Fig.7. Thrombocyte adhesion and fibrinogen adsorption on the titanium oxynitride layers

- Both values are reduced by the nitrogen incorporation in comparison to TiO_2

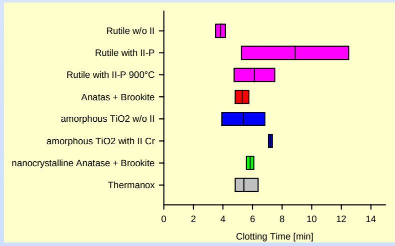

Fig.8. Clotting time on the TiO_2 layers (median and quartils of the blood clotting time on the test surfaces)

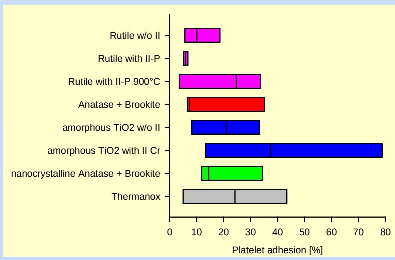

Fig.9. Platelet adhesion on the TiO_2 layers (bars indicate median and quartils of the percentage platelets from a sample platelet-rich plasma on the test surfaces)

- both P^+ and Cr^+ ion implantation (II-P and II-Cr) into TiO_2 increase the clotting time, i.e. reduce the activation of the clotting cascade by this surface, and decrease the thrombocyte adhesion

contact:
Dr. Igor Tsyganov
Tel.: +7 (0742) 722668
e-mail: zyganov@stu.lipetsk.su

Dr. Manfred Maitz
Tel.: +49 (351) 2602014
e-mail: m.maitz@fz-rossendorf.de