DEVELOPMENT OF NOVEL TITANIUM-BASED SURFACES USING PLASMA- AND ION BEAM TECHNOLOGIES

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Abstract

Ion implantation and plasma technologies have been proved to be useful techniques to control structure and surface properties of titanium-based materials. In this work the different properties such as microstructure, phase and element composition, microhardness and their influence on the biocompatibility of Ti-based coatings (pure Ti, nitride, oxide, oxynitride) produced by metal plasma immersion ion implantation and deposition (MePIIID) were investigated. The phase composition and correspondingly surface properties of the layers were strongly dependent on the partial pressure of the working gases (oxygen and/or nitrogen) in the vacuum chamber. Very homogenous deposition of the stoichiometric hydroxyapatite in simulated body fluid (SBF) on Ti-based layers, produced with MePIIID technology have been found for the Ti oxynitride coating with average atomic composition $TiN_{0.4}O_{1.6}$, consisting mainly of amorphous Ti oxide with nitrogen substitution.

Keywords: Titanium oxynitride, metal plasma immersion ion implantation, phase formation, simulated body fluid, hydroxyapatite

1. INTRODUCTION

The biocompatibility of metals is mainly determined by their surface properties. For medical materials in contact with human body it is important to maximize the tendency of their surface to adsorb anorganic (hydroxyapatite: HA - $Ca_{10}(PO_4)_6(OH)_2$, the main mineral component of bones), organic (proteins) and living (cells) parts of surrounding milieu to increase long-term stability of the artificial implants. To improve the biocompatibility of such implants, i.e. to ensure a stable connection between implant and mineralized bone, HA-coating is a promising treatment using methods like elektrochemical deposition, ion plating, plasma spraying, different modes of sputtering, biomimetic deposition in the simulated body fluid (SBF) etc (see, for example [1]). However, long time experiments reveal problems with the adhesion of the coating due to mostly large HA-layer thickness. Ion beam and plasma-based techniques as ion implantation (II), ion beam assisted deposition (IBAD) or plasma immersion ion implantation (PIII) have a large potential to improve the adhesion and the quality of surface layers. These technologies allow to modify the boundary layer of the base metal, to create gradient transition to the HA-layer and to optimize in this way the properties of biocompatible layers. Stimulation of HA-layer growth on titanium surface after calcium and phosphorus beam-line II and improvement of the properties of calcium phosphate layers after subsequent soaking in SBF has been already demonstrated in our experiments [2]. One promising method is the combination of deposition and ion implantation in the form of metal plasma immersion ion implantation and deposition (MePIIID) [3]. A major advantage of the MePIIID compared to the conventional II is the possibility of fast treatment of the complete products with complex, three-dimensional shape, which makes this technique very interesting for industrial application.

The aim of the present study was to investigate the relation between structure and biocompatibility in form of the biomineralization of the Ti-based layers (pure Ti, TiN, TiO_2, TiN_xO_y, Ca-implanted TiN_xO_y) deposited by MePIIID technique for a possible use as biocompatible coatings.

2. EXPERIMENTAL

2.1. Sample preparation

Ti-based layers were deposited by metal plasma immersion ion implantation and deposition (MePIIID) on the thermally oxidized monocrystalline Si (100) surfaces with RMS roughness below 0.6 nm. The schematic diagram of the MePIIID equipment and a detailed description of this method are presented elsewhere [3]. Briefly, MePIIID is a combination of metal deposition and plasma immersion ion implantation (PIII) using a metal plasma produced by cathodic arc evaporation. In our work Ti and Ca cathodes (diameter 72 mm) were used. The ions from the plasma are accelerated to the substrate by applying a negative bias voltage (-2.5 kV) to the substrate, allowing combined deposition and implantation. By supplying oxygen into the vacuum chamber near the substrate (working pressure ~10^{-1} Pa), Ti oxide and, by additionally supplying nitrogen, Ti oxynitride were formed at sample temperatures < 225 °C. Applying different partial pressures of O_2 and N_2 as presented in **Table 1**, four basic types of Ti-based coatings with various phase composition - pure Ti, titanium nitride TiN, titanium oxide TiO_2 and titanium oxynitride TiN_xO_y (sample description: TiNOX) were produced. After MePIIID of titanium, selected TiNOX samples were modified additionally by MePIIID of calcium (sample description: TiNOX-Ca).

2.2. Materials characterization

X-ray diffraction (XRD) measurements were carried out with a step scan diffractometer with a thin film attachment in grazing incidence geometry (ω = 1°) using Cu Kα radiation. The depth distribution of the elements in the deposited layer was studied by Auger electron spectroscopy (AES), using a Microlab 310F system (FISONS, UK) in combination with sputter etching by 3 keV Ar^+ ions directed at 48° with respect to the surface normal (current density about 1-2 μA/mm^2). The sample rotates around the surface normal during sputtering. The surface roughness of the deposited layers was measured by atomic force microscopy (AFM), using a Bioscope machine (Digital Instruments, USA) in tapping mode with a scan area of 5 × 5 μm^2. The roughness S_z reported below is the difference between the average of the highest five and deepest five points in the area.

The microhardness measurements of the deposited layers were carried out using an ultra-microhardness tester DUH-202 (Shimadzu, Japan) and a Vickers indenter with a tip angle of 136°. The maximum load was chosen as 10 mN. Ten indentations were performed on each surface layer tested.

2.3. Biomineralization tests

A part of the plasma treated samples was soaked in simulated body fluid (SBF-composition as described in [4]) over 28 days at a temperature of 37 °C (additional sample description: -HA). Prior to performing the mineralization experiments, all samples were ultrasonically cleaned successively in acetone, ethanol and water for 10 min each. The prepared SBF was filtered through a sterile vented filter unit (SterivexTM-GP, Millipore Co., Bedford, MA), consisting of a polyether sulfone membrane with a pore size of 0.22 mm located on a clean bench, to eliminate any dust particles and bacteria. Subsequently, the samples were taken out, gently washed with double distilled water and dried at room temperature. In all biomineralization tests the monocrystalline Si (100) was used as a reference. Morphology and element composition of the formed layers after soaking in SBF were studied using a high resolution scanning electron microscope (SEM) type DSM 982

GEMINI (Carl Zeiss, Germany) coupled with an energy dispersive spectrometer (EDS X-ray detector Pioneer (Noran)).

3. RESULTS AND DISCUSSION

3.1. Structure, phase composition and properties of the deposited layers

Microstructure and phase composition of the formed layers can be influenced in a controlled way by adjusting the deposition parameters. This offers the possibility for a systematic investigation of the correlation between biocompatibility and structure of the surface layers. The review of the selected parameters and the resulting characteristics of the obtained structures is presented in **Table 1**.

Table 1 Preparation conditions, structure and properties of Ti-based layers

Material	Relation of the partial pressures $p(O_2)/p(N_2)$	Subsequent treatment	Crystalline phases (XRD)	Average atomic composition (AES)	Structure	Rough-ness S_z (nm)	Microhard-ness *HV* (GPa)
Ti	- (without gas flow)	-	α-Ti (hcp)	Ti	Titanium	20.8	5.11
TiN	N_2 only	-	TiN (fcc)	TiN	TiN	22.6	18.12
TiO_2	O_2 only	-	Rutile (tetr.) + anatase (tetr.)	TiO_2	TiO_2 (rutile + anatase)	26.2	10.92
TiNOX	1/1	-	TiN (fcc) + TiO (fcc)	$TiN_{0.4}O_{1.6}$	TiN +TiO + TiO_2 (amorphous)	34.8	22.89
TiNOX+ Ca	1/1	Ca^+ (MePIIID)	TiN (fcc) + TiO (fcc)	$TiN_{0.4}O_{1.6}$ (Ca)	TiN + TiO + CaO + TiO_2 (amorphous)	39.3	23.37

The phases observed were strongly dependent on the relation of the gases' partial pressures forming the ambient. Without gas flow, crystalline film composed of the α-Ti phase with a hexagonal close packed (hcp) lattice was formed. For the nitrogen flow without oxygen, the XRD patterns (not shown) were typical for titanium nitride TiN with a face centred cubic (fcc) lattice. When using similar partial pressures for nitrogen and oxygen, broad diffraction peaks were observed, which can be interpreted as phase mixture of titanium nitride TiN and titanium oxide TiO, both with a fcc lattice. Enhanced oxygen flow leads to the beginning of the formation of rutile and anatase modifications of titanium oxide TiO_2 at the substrate surface, both with a tetragonal lattice.

The thickness of all produced layers measured by AES was about 1 μm. The average atomic composition in the coatings is presented in **Table 1**. The surface layer of the Ti-based sample obtained without gas flow was characterized by a very thin air-formed oxide film, about 7 nm in thickness. For pure N_2 flow the atomic concentration of N in the layer was close to stoichiometric TiN. For equal partial pressure of N_2 and O_2 the atomic concentration of O exceeded clearly the N and Ti concentration and was close to stoichiometric TiO_2. Because the XRD patterns do not show the additional peaks of Ti oxide phases at this partial pressure, the main component of this layer is an amorphous TiO_2 phase [5]. At pure O_2 as the working gas, according to the XRD results a crystalline mixture dominated by rutile with a contamination of anatase was formed. Anatase arose in the beginning of the deposition directly on the substrate surface as proved by XRD measurements with different incident angle.

The roughness of the prepared layers varied in a range of 20 nm to 40 nm with the highest roughness determined for the Ca-implanted $TiN_{0.4}O_{1.6}$ and the lowest roughness measured for the Ti surface (**Table 1**).

The AFM pictures (not shown) also indicate relatively large crystalline structures for the coating with the highest roughness. The other coatings appear denser with smaller single crystals. The roughness of all Ti-based layers is relatively low and their values are nearly equal, so that an effect of the surface roughness on biomineralization seems to be unimportant in this case.

The surface microhardness measured on Ti-based layers deposited with different partial pressures of N_2 and O_2 is presented in **Table 1**. As expected the lowest microhardness had Ti-coating The highest hardness showed the layer $TiN_{0.4}O_{1.6}$ with more complicate phase composition. The microhardness of other coatings was in between.

3.2. Biomineralization of the deposited thin films

After soaking in SBF, small, roundish HA precipitates were observed on separate surface areas of the unmodified monocrystalline Si reference samples (**Figure 1a**).

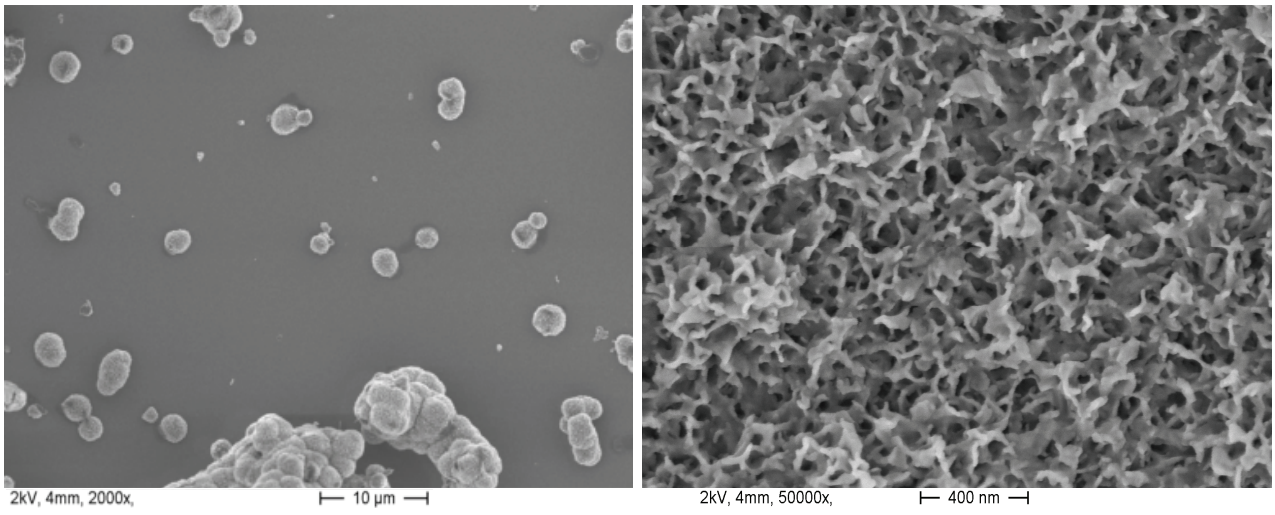

Figure 1 SEM investigation of the surfaces after soaking in SBF: a) small HA precipitates on the reference surface (monocrystalline Si); b) HA on the Ca-modified TiNOX -surface

But the MePIIID stimulated direct HA formation on the modified Ti-based surfaces in SBF. As the SEM investigations showed, all deposited layers were covered relatively uniformly and densely with HA. In the direction of improving the quality of the HA layer formed in SBF, the modified surfaces were in the following order: TiN → TiO_2 → Ti → TiNOX.

Among Ti-based layers the TiNOX structure proved to be particularly bioactive. Therefore, this structure was additionally treated by Ca plasma after the Ti-MePIIID in the same process in order to generate even more growth nuclei for HA. The typical morphology of HA on the Ca-modified TiNOX surface is shown in **Figure 1b**. HA has a branched structure which is well bound to the substrate, what could be very useful for artificial implants in the human body.

For all samples, the element composition and Ca/P ratio in the surface layer formed after soaking in SBF was determinated by EDX analysis. The EDX spectra were measured in two regions (particle, ground) as well as in the whole scanned area (survey) (**Figure 2a**).

As shown in the EDX spectra (**Figure 2b**), in the ground of all investigated layers were detected the chemical elements from the substrate (Ti, O, Si) and from the SBF solution (C, Mg). The main difference between as

the unmodified well as Ca plasma modified TiNOX samples (**Figure 2b**) compared with other titanium-based samples (pure Ti, TiO_2, TiN) is that Ca and P were also detected in the ground. This means that HA covered the whole surface and was connected to the substrate.

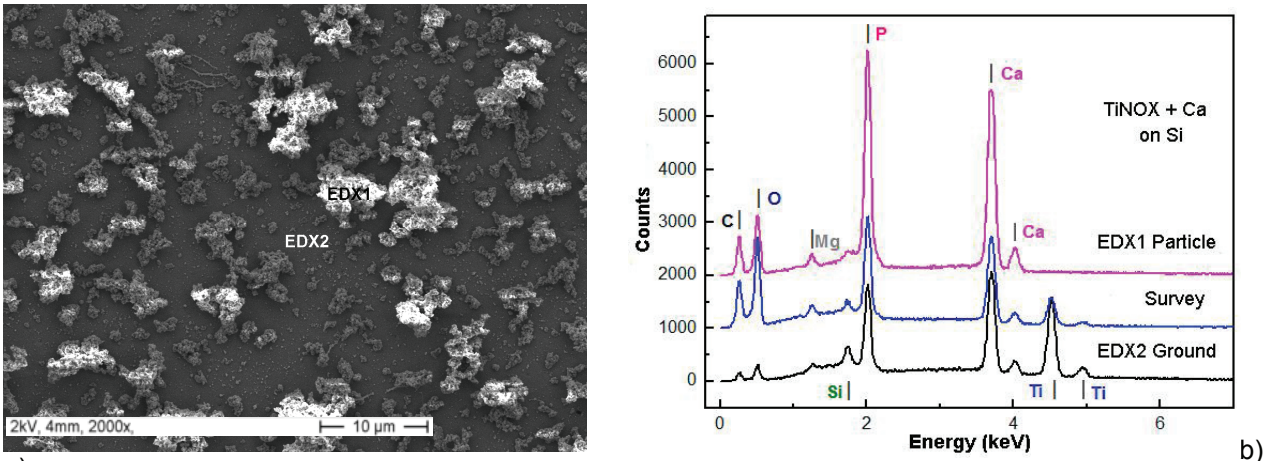

Figure 2 EDX investigation of the Ca-modified TiNOX surface after soaking in SBF: a) HA-particle (EDX 1) and the ground (EDX 2) of the scanned surface (survey); b) corresponding EDX-spektra

In **Table 2** are presented the results of the ratio Ca/P measured by EDX analysis for pure Ti, as well as for unmodified and Ca plasma modified TiNOX layers.

Table 2 Ca/P ratio on tested Ti-based layers after soaking in SBF

Sample	Ground	Survey	Particle
Ti	→ 0	1.51	1.65
TiN	→ 0	1.38	1.61
TiO_2	→ 0	1.43	1.63
TiNOX	1.52	1.72	1.64
TiNOX+Ca	2.39	1.82	1.90

As shown in **Table 2**, Ca/P ratio for pure Ti, TiN and TiO_2 (ground) is close to zero, which means that these Ti-based surfaces have not been homogeneously mineralized as a difference from the TiNOX layer. Ca/P ratio of the particles after soaking in SBF corresponds almost to the stoichiometric value for HA (1.67). A slight surplus of this value for the Ca-modified TiNOx layer is due to the excess of Ca in the surface because of the additional Ca-MePIIID.

Thus, the maximal intensity of Ca and P measured by the EDX method in the HA particles deposited from SBF as well as the presence of Ca and P in the ground of the layer confirm the improved biomineralization of the TiNOX structure in comparison with other Ti-based films.

4. CONCLUSION

Metal plasma immersion ion implantation and deposition (MePIIID) is an effective method for modifying the structure, composition and properties of titanium-based layers. The desired surface properties can be adjusted exactly by varying the deposition parameters during the MePIIID process. The biocompatibility of titanium

(titanium oxide) can be improved by incorporation of nitrogen into the surface layer. This is confirmed by very homogenous deposition of the stoichiometric hydroxyapatite in SBF on N-containing titanium oxide layers (TiNOX), produced with MePIIID technology, and improved formation of HA in SBF on $TiN_{0.4}O_{1.6}$ layer with additional Ca-MePIIID. In general, the good mechanical properties and biocompatibility of titanium oxynitride $TiN_{0.4}O_{1.6}$ without any toxic and expensive elements make this Ti-based layer interesting candidate for long-term studies *in vivo*. Next experiments with regard to the interaction of by MePIIID modified surfaces with human cells are currently being carried out.

ACKNOWLEDGEMENTS

Research is being carried out in the framework of the state order of the Ministry of Education and Science of the Russian Federation according to the project № 11.1446.2017/ПЧ.

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