DEPOSITION OF VARIOUS GRADIENT MULTILAYER COATINGS ON Ti-6AI-4V ALLOY USING MW CVD METHODS FOR ORTHOPAEDIC IMPLANTS

KAROL KYZIOŁ^{1*}, JULIA OCZKOWSKA¹, MAREK KLICH², ŁUKASZ KACZMAREK², AGNIESZKA KYZIOŁ³

¹ FACULTY OF MATERIALS SCIENCE AND CERAMICS, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, POLAND ² INSTITUTE OF MATERIALS SCIENCE AND ENGINEERING, ŁÓDŹ UNIVERSITY OF TECHNOLOGY, POLAND ³ FACULTY OF CHEMISTRY, JAGIELLONIAN UNIVERSITY,

*E-MAIL: KYZIOL@AGH.EDU.PL

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Introduction

Titanium and its alloys are considered to be the most applicable materials for bone implantations [1]. Even though innovative alloys such as e.g. Ti-6Al-7Nb have been recently replaced by Ti-6Al-4V alloy, it is still the most widespread alloy for orthopaedic applications. Thus, there is a necessity to modify surface of this material to improve its properties. The functionalized surfaces exhibit better mechanical and biological (e.g. osseointegration and biocompatibility) properties, that are crucial for successful implantation surgery [2,3]. Diamond-like Carbon (DLC) coatings are considered to meet these requirements, but their properties such as modulus of elasticity and residual stress cause unfavourable stress distribution at the substrate-coating interface. Therefore, deposition of gradient layers or doping them with silicon or nitrogen can solve this problem.

In this work, multi-layered nitrogen doped coatings of carbon-hydrogen and/or silicon-hydrogen structure obtained by deposition using Microwave Plasma Assisted Chemical Vapour Deposition method are presented.

Materials and Methods

Samples made from Ti-6Al-4V alloy (3 mm thickness) were mechanically polished, to achieve mirror-like surface, and coated in Plasma Assisted Chemical Vapour Deposition (PA CVD) system, equipped with microwave (2.54 GHz) antenna. Five various processes were performed - TABLE 1.

TABLE 1. Details of experimental series for Ti-6Al-4V modified with application of MW CVD system

Series	Type of coatings	Plasma nitriding
1C	SiCNH/SiCNH-CNH/CNH	No
2C	N ⁺ /SiNH-N ⁺ /N ⁺	Yes
3C	N ⁺ /SiCNH/SiCNH-CNH/CNH	Yes
4C	N ⁺ /SiNH/SiNH - SiCNH/SiCNH/ SiCNH-CNH/CNH	Yes
5C	SiNH/SiNH - SiCNH/SiCNH/ SiCNH-CNH/CNH	No

Series 2C, 3C and 4C were obtained with application of plasma nitriding process before particular multilayers deposition. While, series 2C was additionally subjected to plasma nitriding after deposition process.

Structure characterization of the resulting coatings in different atomic scale was carried out by SEM and IR spectroscopic method. Hardness and modulus of elasticity were determined by nanoINDENTER® G200 (Agilent technologies, USA) with continuous stiffness measurement. Additionally, preliminary biological study *in vitro* was performed: (*i*) cytotoxicity towards human

osteosarcoma MG-63 cell line was evaluated by MTT assay and (ii) release of Ti, V, and Al ions to cell culture media was detected by ICP-MS methods. Wettability and surface free energy (SFE) of tested samples were investigated using an automatic drop shape analysis system DSA 10 Mk2 (Kruss, Germany).

Results and Discussion

As a result of application of MW CVD method smooth modified surfaces of Ti-6Al-4V alloy with characteristic granular structure have been obtained - FIG. 1.

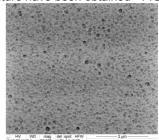


FIG. 1. SEM image for series 1C (mag. 50 000 x).

After plasmochemical functionalization the tested series (1C - 5C) showed surface roughness R_a in the range of $4.82 \div 3.35$ nm, with the highest value observed for modification 1C. IR spectra confirmed the presence of typical atomic groups for the resulting structures. It was showed that application of gradient coatings is a diffusion barrier for metal ions released from the modified alloy surface. All types of plasma modifications significantly changed of Young modulus of the functionalized substrates (up to ca. 1.2 μm from surface) in comparison with the untreated Ti-6Al-4V alloy. For instance, low hardness value of tested samples after modification is connected with the least dense, granular structure.

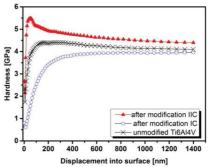


FIG. 2. Hardness profile of the unmodified and selected modified Ti6Al4V alloy in plasma conditions

Conclusions

In this investigation, it was demonstrated that for the majority of plasma-based surface modifications physicochemical properties such as roughness, wettability, and hardness were improved. The most significant improvement was observed in case of series 1C, consisted of deposition on the top CNH layer without pre- and post- plasma nitriding process. This, in turn, results in low values of hardness and Young modulus of the modified surfaces.

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