HYBRID, BIOACTIVE COATINGS FORMED ON TITANIUM ALLOYS SURFACE

ALICJA KAZEK-KĘSIK[1]*, AGNIESZKA NOSOL[1], JOANNA PŁONKA[1], MAŁGORZATA KROK-BORKOWICZ[2], ELŻBIETA PAMUŁA[2], WOJCIECH SIMKA[1]

[1] FACULTY OF CHEMISTRY,
SILESIAN UNIVERSITY OF TECHNOLOGY, POLAND
[2] FACULTY OF MATERIALS SCIENCE AND CERAMICS,
AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, POLAND
*E-MAIL: ALICJA.KAZEK-KESIK@POLSL.PL

[ENGINEERING OF BIOMATERIALS 143 (2017) 41]

Introduction

Plasma electrolytic oxidation (PEO) is one of widely used electrochemical methods for light metal surface functionalization [1-3]. Porous oxide layer might be composed by desirable, bioactive compounds incorporated from anodizing bath. However, the PEO method is limited to incorporation of compounds which are sensitive for solvents and spark discharges occur during the process. Especially drugs or vitamins cannot be incorporated into oxide layer using this technique. However, on the porous oxide layer these biologically active substances can be deposited with layer of degradable polymer.

One of the β-phase titanium alloy Ti-15Mo is considered as a promising material for bone implants. This titanium alloy is composed only of biocompatible elements, and exhibits low Young's modulus (~ 60 GPa) [4-6]. It is very easy to modify surface of the Ti-15Mo alloy by bioactive oxide layer. To provide antibacterial and therapeutic properties to the outer surface, drugs like doxycycline, cephalosporins (e.g. III or IV generation) or amoxicilline might be blended with polymer. These kinds of hybrid layers might be used especially for dental implants.

Materials and Methods

Surface of Ti-15Mo alloy was modified by plasma electrolytic oxidation process. The PEO process was carried out in solution composed of $Ca(H_2PO_2)_2$ and $Ca_3(PO_4)_2$. Applied voltage during the process was 300 V, when current density was 100 mA/cm^2. On the porous oxide layer the fast-degradable polymer (poly(D,L-lactide-co-glycolide - PLGA) was deposited using dip coating method. To obtain antibacterial properties of the surface, the polymer was blended with doxycycline (5% w/v polymer). Hybrid, oxide-polymer coatings were characterized using scanning electron microscope (SEM, Phenom ProX), Raman spectroscopy with CDD detector. Degradation of polymer layer and drug release was carried out in artificial saliva up to 4 weeks. Changes in polymer chain structure were monitored using ^{1}H NMR, when amount of released drug was determined using HPLC technique. Cytocompatibillity of the layers was evaluated using osteoblast-like MG-63 cells. Cell metabolic activity was evaluated using Alamar Blue reagent. The viability, attachment and distribution of the adhered cells were evaluated using live/dead staining.

Results and Discussion

FIG. 1. presents SEM image of the PLGA layer deposited on the porous oxide layer formed on Ti-15Mo alloy surface using PEO method. The polymer layer covered the oxide layer, however some characteristic structure of porous layer was still visible. Results from ^{1}H NMR confirmed that PLGA was degraded up to 4 weeks of immersion in artificial saliva at 37°C. Raman spectroscopy confirmed presence of polymer layer with and doxycycline. HPLC measurements confirmed that doxycycline was released within the first one hour during hybrid layer immersion in artificial saliva at 37°C.

Cytocompatibillity investigations showed that all of the layers were not cytotoxic. After 1 day of culture the number of cell increased on all of the investigated samples. The highest percentage of Alamar Blue reduction was for the sample with polymer layer without drugs. However, the experiment showed that the layer with doxycycline were slightly less cytocompatible. On all modified surfaces cells were well adhearing and small amount of dead cells was observed. After 3 and 7 days of culture, the samples with polymer layers exhibited better cytocompatibility than reference sample (unmodified Ti alloy) and only anodized sample.

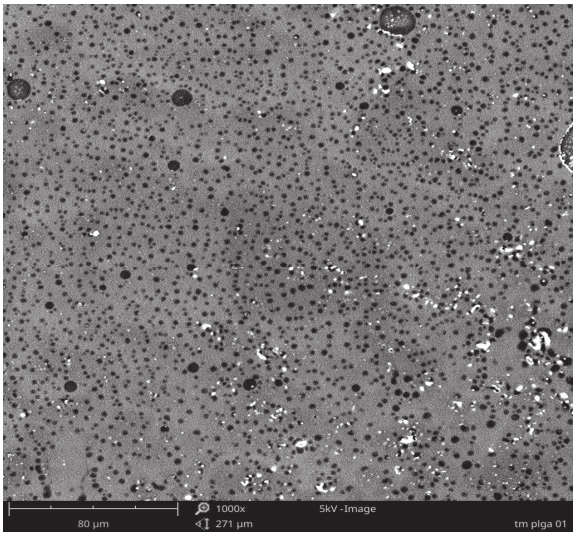

FIG. 1. SEM image of hybrid oxide-ceramic coatings formed on Ti-15Mo alloy surface. Magnification: x1000.

Conclusions

Surface of the Ti-15Mo alloy was functionalized in order to provide it bioactive and antibacterial properties. Doxycycline was released from the polymer layer in a very short time. Hybrid layers were found cytocompatible with the osteoblast-like MG-63 cell up to 7 days of culture. Next steps of the hybrid layer characterization will contain advanced biological experiments with mesenchymal steam cells and selected gram positive and gram negative bacteria.

Acknowledgments

This work was supported by the Polish National Science Center, number of project: UMO-2016/21/D/ST5/01652.
This work was supported by the Silesian University of Technology, Gliwice Poland, Rector's grant no. 04/010/RGJ17/0049.

References

[1] A. Gupta, M. Dhanraj, G. Sivagami, Indian J. Dent. Res. 21 (2010) 433-438.
[2] K. Rokosz, T. Hryniewicz, *et al.,* Mater. Sci. Forum Vol. 862 (2016) 86-95.
[3] A.R. Rafieerad, M.R. Ashra *et al., Mater*. Sci. Eng. C 57 (2015) 397–413.
[4] S. Radin, P. Ducheyne, J. Biomed. Mater. Res. 30 (1996) 273–279.
[5] W. Ji, F. Yang *et al.,* Biomaterials 33 (2012) 6604–6614.
[6] M. Sampath, R. Lakra et al., Colloids Surf. B: Biointerfaces 117 (2014) 128–134.