Oksana KALINKEVICH[1], Yevgen ZINCHENKO[1], Oleksandr OLESHKO[2], Anatoly SKLYAR[3], Vadim CHIVANOV[1], Wojciech SIMKA[4,5], Oleg MISHCHENKO[5], Aleksei KALINKEVICH[1], Maksym POGORIELOV[2], Sergei DANILCHENKO[1]

THE EFFECT OF CHITOSAN COATINGS ON THE CORROSION RESISTANCE OF Ti-Zr ALLOY WITH PEO-COATED SURFACE

[1]*Institute for Applied Physics, NAS of Ukraine*
58, Petropavlovska, Sumy, Ukraine.
[2]*Sumy State University*
2, Rimskogo-Korsakova Sumy, Ukraine
[3]*Sumy State Pedagogical University*
87, Romenska, Sumy, Ukraine.
[4]*Silesian University of Technology*
2A, Akademicka, Gliwice, Poland.
[5]*NanoPrime*
25, Metalowców, Dębica, Poland. E-mail:kalinkevich@gmail.com

ABSTRACT

Chitosan-based coatings were deposited on medical titanium-zirconium alloys with PEO-treated surface in different ways (dip-coating, spin-coating, electrodeposition) in order to increase both biocompatibility and corrosion resistance of the material surface. The method of electrodeposition was determined as the most optimal method for applying chitosan coatings, since in the model corrosion experiments the coating is stable, no cracks form on the PEO-treated surface, while the structure of the coating itself is preserved. The dip-coating method can be used to form asymmetric chitosan membranes with a structured lower surface and a smooth upper for use in dentistry, orthopedics.

KEY WORDS: *plasma electrolytic oxidation (PEO), coatings, TiZr alloys, chitosan.*

INTRODUCTION

Currently, the TiZr alloys are used to create dental and bone implants [1]. Such alloys are distinguished by mechanical strength and bioinertness, high corrosion resistance. At the same time, some studies indicate an adverse effect of chlorine ions on Zr, while titanium corrodes in the sodium chloride/lactic acid medium [2].

Chemical stability can be enhanced by PEO (plasma electrolytic oxidation) process. The complex nature of the process where plasma microdischarges take place results in complex and mutually dependant chemical and physical processes on the surface [3]. Depending on the PEO conditions, the properties of the oxide layer can be changed both in composition and in the three-dimensional surface structure. The presence of characteristic porous surfaces improves the osteointegration potential of implants, but at the same time it can contribute to degradation and corrosion in the biological environment (the emergence of cracks, etc.). Therefore, the need arises for additional protection, a coating that does not fundamentally destroy the structure obtained during PEO, but which additionally isolates the implant from biological media for some time. The creation of such coatings and their in vitro and in vivo behavior are actively studied [4].

To create such coatings, the biopolymer chitosan can be used [5-8]. Chitosan is a polysaccharide characterized by biocompatibility, some antimicrobial and otseointegrative properties, and the ability to degrade in the biological tissues over time. Also, it is environmental friendly. It is possible to include additional components in the chitosan films, for example, antibiotics or other drugs to combat microbial biofilms, preventing infection after implantation. A number of studies have noted the ability of chitosan to increase the corrosion resistance of metals and their alloys. Chitosan coatings obtained in various ways may differ in their characteristics. In our work, we used the three simplest, easiest to implement on an industrial scale, inexpensive methods of depositing chitosan on the PEO-treated surface of titanium-zirconium alloys and investigated their corrosion resistance in model media.

MATERIALS AND METHODS

In this work, samples of TiZr alloy with a PEO treated surface were obtained from *NanoPrime* (Dębica, Poland) [2, 3]. To obtain polymeric coatings, dip-coating, spin-coating (1000 rpm) and electric deposition methods were applied. For dip-coating and spin-coating 2% and 0.5% solutions of chitosan (300 kDa, 87% deacetylation) in 1% acetic acid were used. For electrodeposition, a 0.5% solution of chitosan in 1% acetic acid was used. Electrodeposition was carried out during 15 min. under constant voltage of 120 V. The resulting coatings were treated with 1% NaOH for crosslinking. To assess the biocompatibility, the SBF (simulated body fluid) test was employed, first introduced by T. Kokubo [9]. The original SBF [10] was used. The samples were incubated in the double concentration SBF (2SBF) for 5 days to accelerate the biomimetic calcium phosphate coating process [11]. To determine corrosion resistance, the samples were immersed in the solution containing 3% H_2SO_4 and 0.9% NaCl for 5 days.

Contact angle of water droplets on the PEO-treated surface was measured with OCA-15EC instrument (*DataPhysics Instruments*, Germany).

The phase composition of the surfaces was studied with the X-ray diffraction (XRD) using the diffractometer DRON4-07 (*Burevestnik*, Russia). The Ni-filtered CuKa radiation (wavelength 0.154 nm) was used with a conventional Bragg-Brentano geometry θ-2θ (where 2θ is the Bragg's angle). The current and the voltage of the X-ray tube were 20 mA and 30 kV, respectively. The samples were measured in the continuous registration mode (at the speed of 2°/min) within the 2θ-angle range from 25 to 100°. All experimental data processing procedures were performed with the program package DIFWIN-1, (*Etalon PTC* Ltd.). Pattern attribution was made using Qualx2 program package [12].

Scanning electron microscopy was used to control the changes in the state of the surface with the electron microscope REMMA102 (SELMI, Ukraine). This instrument allows visualization of sample surface with the resolution down to 10 nm. The accelerating voltage of the electron probe was 20 kV; the current of the probe was 2 nA. To avoid surface charge accumulation, samples were covered with the thin (30–50 nm) layer of silver in the vacuum set-up VUP-5M (SELMI, Ukraine).

RESULTS AND DISCUSSION

The TiZr alloy samples were PEO treated in the electrolyte containing calcium and phosphate ions. After the treatment the surface is covered with the thick oxide layer having uniform rough porous structure without visible cracks (fig. 1). Contact angle of the oxide layer on the surface was in the range from 50° to 60° indicating hydrophilic nature of the oxide layer. Contact angles of chitosan coating were in the range of 90°-100°; the slight swelling of chitosan was observed in the contact place of water droplet and chitosan film immediately after the measurement.

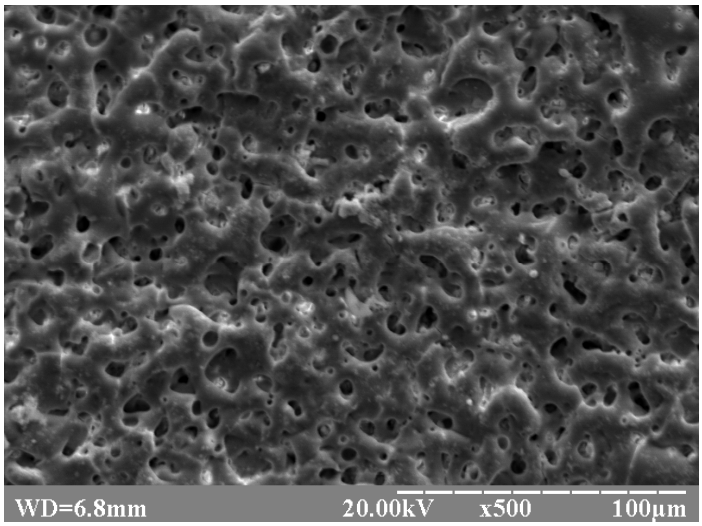

Fig. 1. The PEO treated surface of the TiZr sample, magnification 500x.

The X-ray diffraction pattern of metallic samples (TiZr alloy without PEO and organic coating) corresponds to the pattern of pure TiZr alloy (Qualx2 card #00-152-7316). After PEO treatment of the samples, in their XRD patterns emerge the peaks corresponding to TiZr oxide (fig. 2).

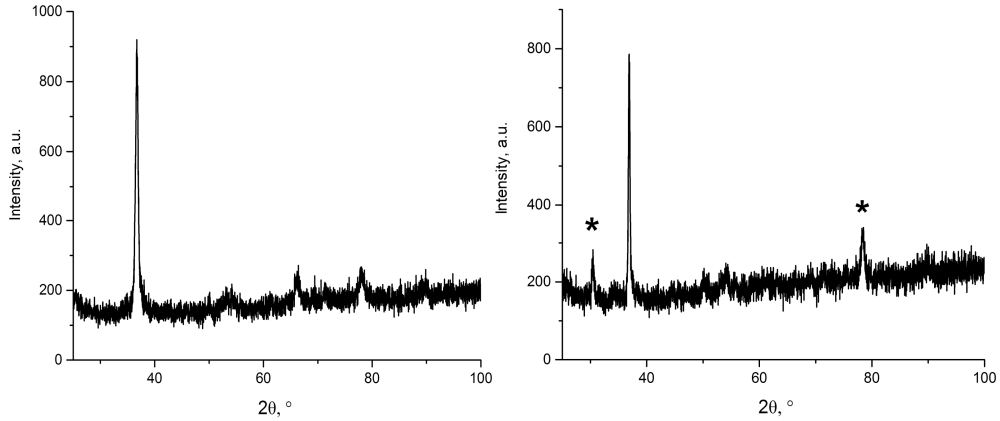

Fig. 2. XRD patterns of uncoated TiZr (left) and PEO-treated TiZr (right). Peaks marked with asterisks correspond to TiZr oxide.

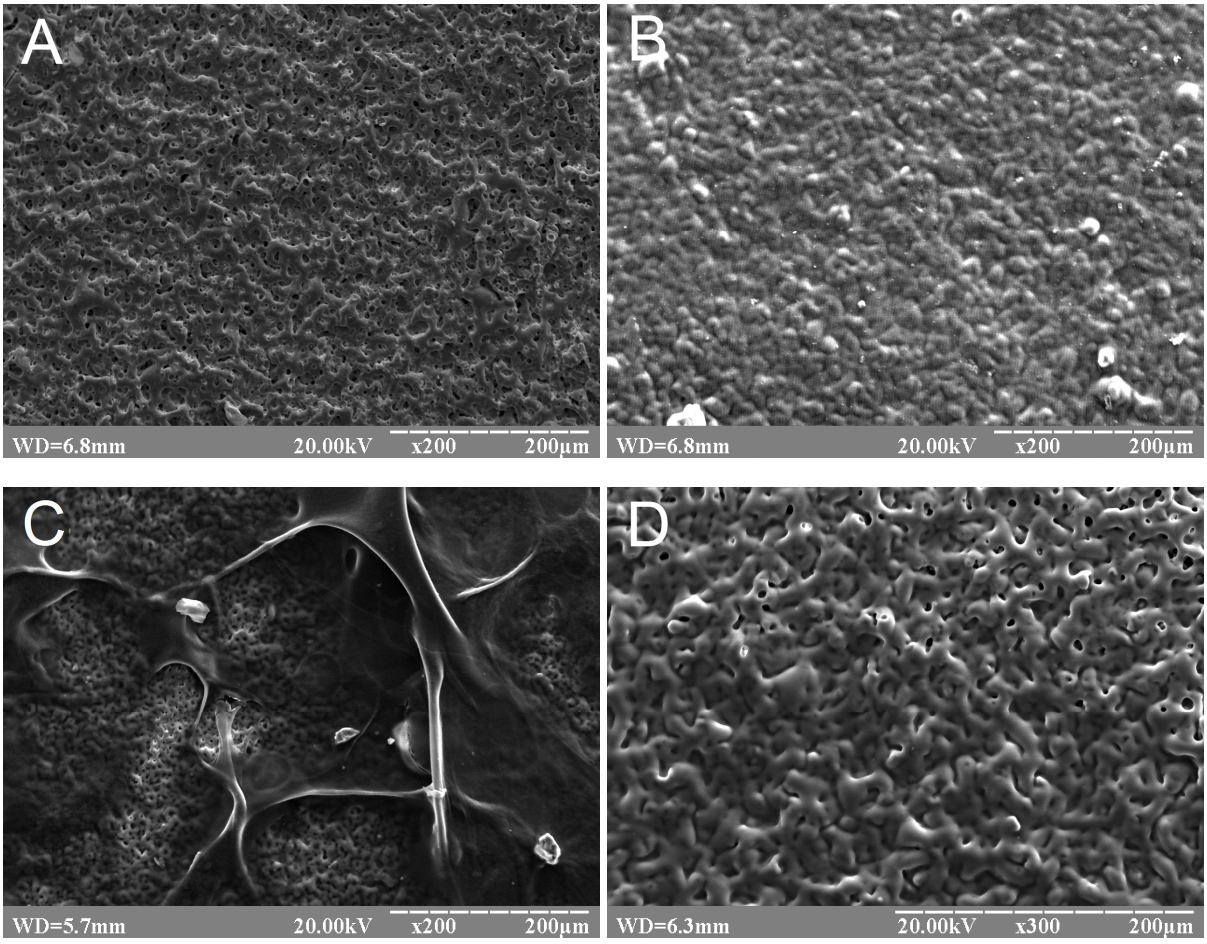

Fig. 3. The PEO treated surface of the TiZr sample without chitosan (A), dip-coated with chitosan (B), electrodeposited chitosan (C), spin-coated with chitosan (D).

The surface state and its changes were controlled at every stage of the experiments. There was significant difference in morphology of chitosan coating deposited on the oxide layer of TiZr depending on the method: dip-coating gives uniform film covering the pores in the oxide layer (fig. 3 B), electrodeposited chitosan film looks non-uniform, giving visible strands of denser material

between which one can see the surface of TiZr oxide (fig. 3 C), probably covered by thin chitosan layer (as it follows from corrosion tests described below), chitosan layer formed by spin-coating is uniform and covers the oxide layer remaining its roughness visible, except the pores (fig. 3 D).

To assess the biocompatibility of the alloys (as potential medical implants) with this complex multi-layered surface, the 2SBF tests have been used. The tests show that calcium phosphate salts readily deposited both on the "clean" PEO surface and the surface with a chitosan coating deposited by electrodeposition and spin-coating (fig. 4). In the case of dip-coating, the calcium salts do not form visible depositions on the surface, and moreover, some degradation of the chitosan film is observed.

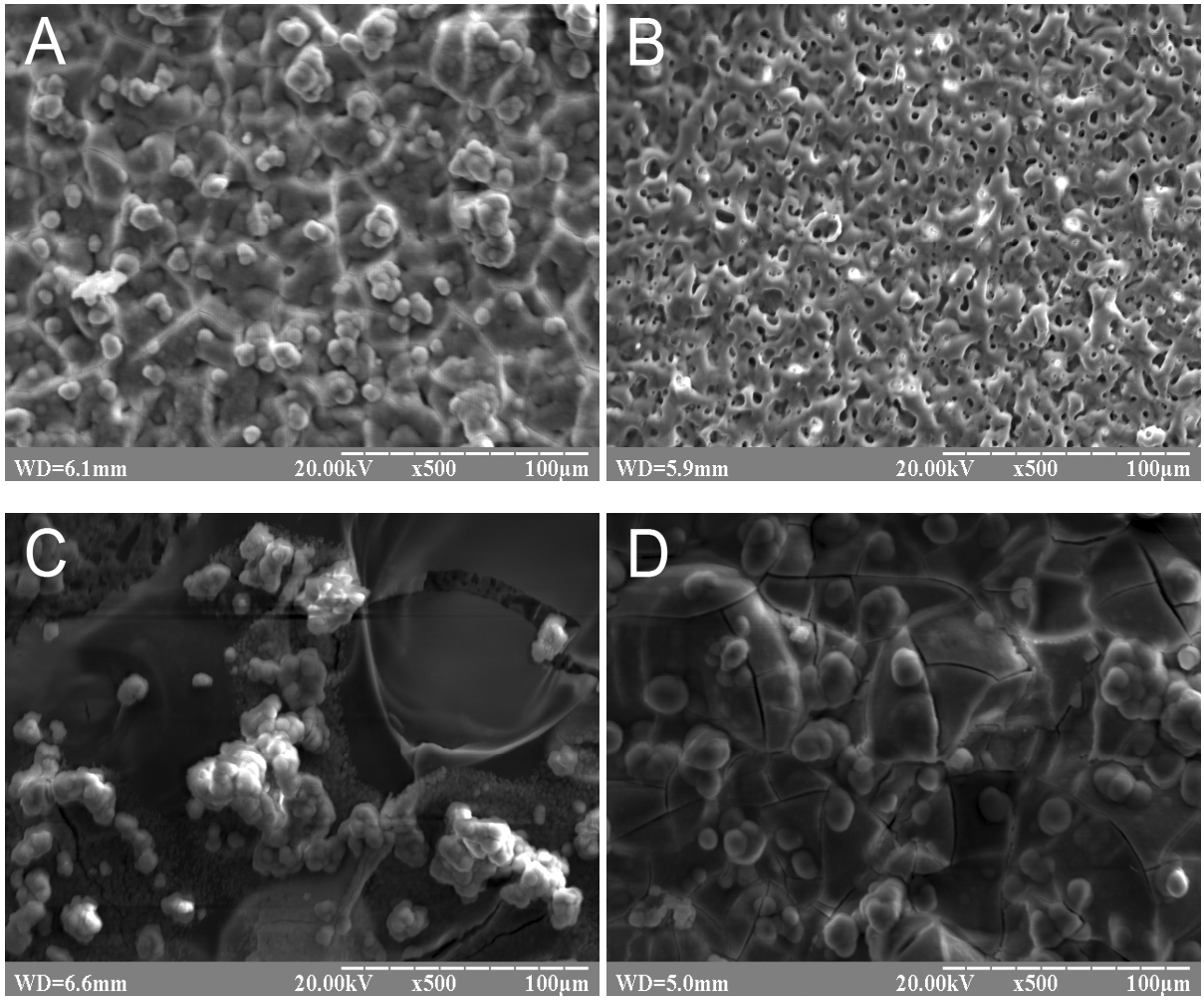

Fig. 4. The surface of the samples after 2SBF immersion without chitosan (A), dip-coated with chitosan (B), electrodeposited chitosan (C), spin-coated with chitosan (D).

To investigate the corrosion behaviour of the complex coatings, the samples were incubated in H_2SO_4/NaCl solution for 5 days. After the incubation, the surface of the samples was again studied by scanning electron microscopy (fig. 5). After the treatment, the deep cracks form on the PEO treated surface (TiZr oxide) without chitosan.

In the cases of dip-coated and spin-coated samples, a smooth film is formed on the surface (fig. 5 D and fig. 6, right). In the case of dip-coating variant, this film is easily peeled off from the sample surface. The Fig. 6 B shows the surface of the sample after corrosion test without the organic upper layer. In the Fig 6 the smooth upper surface of the chitosan film exfoliated from the TiZr sample surface is shown, as well as the rough structured side of this film which had been in the contact with the PEO-treated surface of the sample. So, the dip-coating method can be used to form asymmetric chitosan membranes with a structured surface. In the case of spin-coating, the organic layer after corrosion test it is firmly fixed on the sample, and therefore prevents the appearance of cracks on the

surface in aggressive acidic medium. Electrodeposited films subjected to corrosion tests both protect the PEO surface and preserve the structure of the polymeric coating itself (fig. 5 C).

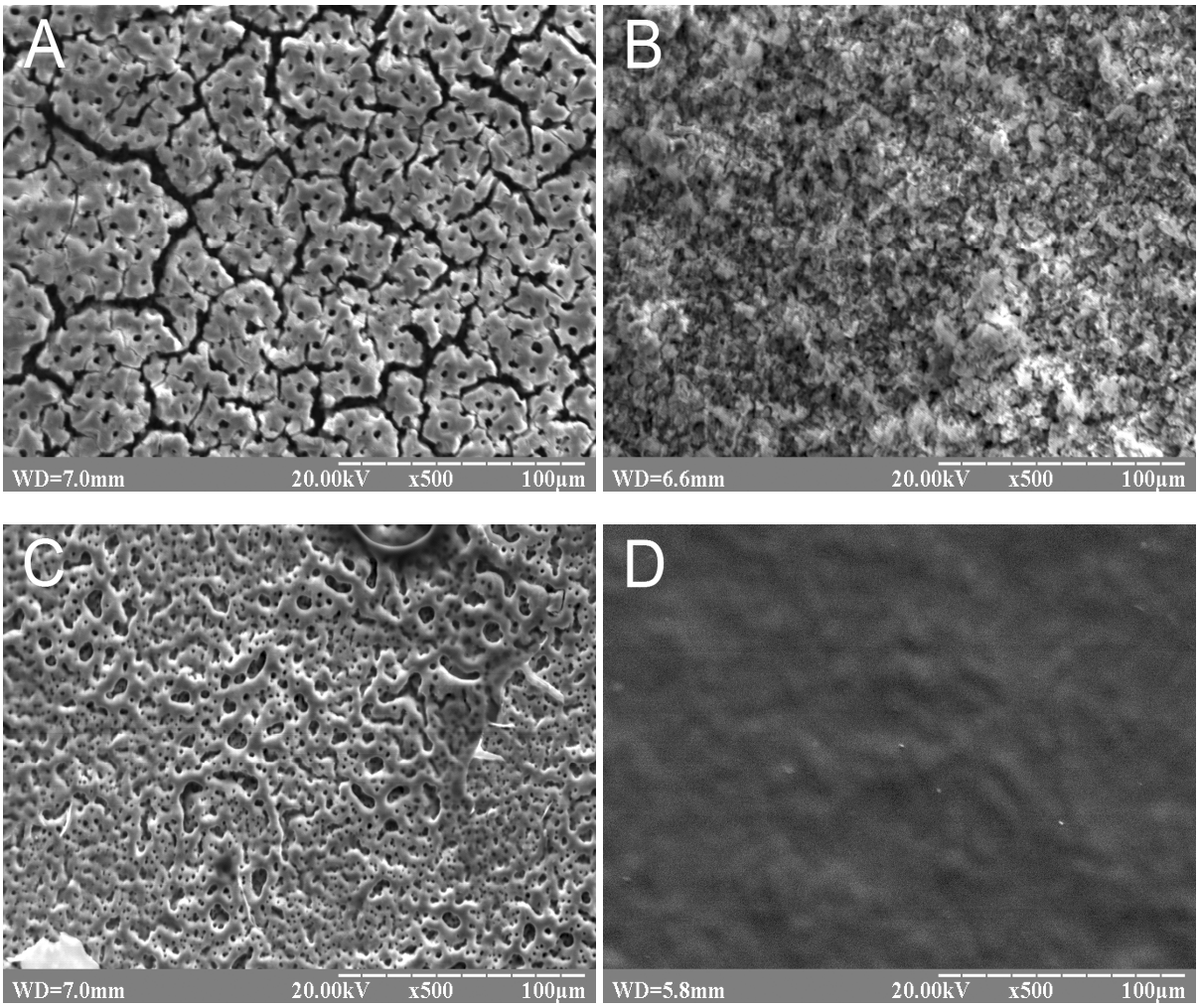

Fig. 5. The surface of the samples after incubation in H_2SO_4/NaCl solution without chitosan (A), dip-coated with chitosan (B), electrodeposited chitosan (C), spin-coated with chitosan (D).

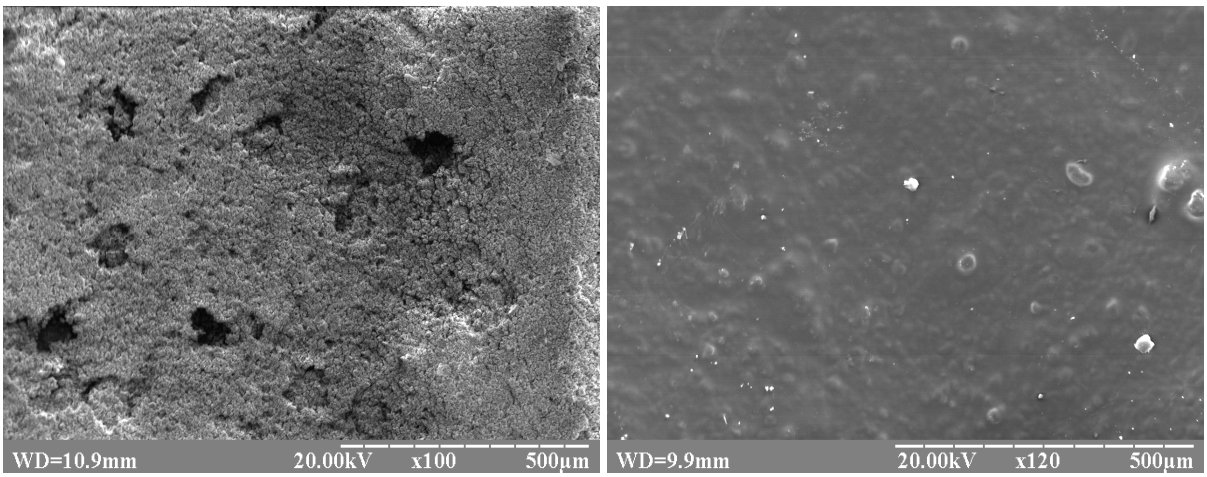

Fig. 6. Chitosan film from the dip-coated sample after corrosion test, bottom (left) and top (right).

CONCLUSIONS

The best method of chitosan coating deposition among the methods which were studied in this work is electrodeposition, since in this case no cracks form on the PEO-treated surface during corrosion tests, and the structure of the PEO-coating is preserved. The dip-coating method can be used to form asymmetric chitosan membranes with a structured lower surface and a smooth upper to be used biomedicine as separate materials.

Funding information: This work was partially supported by H2020 MSCA, grant NanoSurf 777926.

REFERENCES

1. Grandin H.M., Berner S., Dard M. A review of titanium zirconium (TiZr) alloys for use in endosseous dental implants // Materials. – 2012. – Vol. 5. – P. 1348-1360.
2. Evaluation of corrosion resistance of implant-use Ti-Zr binary alloys with a range of compositions / T. Akimoto, T. Ueno, Y. Tsutsumi, H. Doi, T. Hanawa, N. Wakabayashi // J. Biomed. Mater. Res. Part B: Appl. Biomater. – 2018. – 106B. – P. 73–79.
3. Formation of the coatings containing Ca and P on the surface of ZrNb and TiZr alloys in the presence of Cu nanoparticles by plasma electrolytic oxidation: surface structure and XRD studies / A. Kalinkevich, O. Kalinkevich, O. Oleshko, O. Mishchenko // Nanomaterials for biosensor and biomedical applications, Jurmala, Latvia 2-4 July. – 2019. – P. 58.
4. Ag nanoparticle-decorated oxide coatings formed via plasma electrolytic oxidation on ZrNb alloy / O. Oleshko, V. Deineka, Y. Husak, V. Korniienko, O. Mishchenko, V. Holubnycha, M. Pisarek, J. Michalska, A. Kazek-Kęsik, A. Jakóbik-Kolon, W. Simka, M. Pogorielov // Materials. – 2019. – Vol. 12(22). – P. 3742.
5. Self-healing protective coatings with “green” chitosan based pre-layer reservoir of corrosion inhibitor / M. L. Zheludkevich, J. Tedim, C. S. R. Freire, S. C. M. Fernandes, S. Kallip, A. Lisenkov, A. Gandini, M. G. S. Ferreira // Journal of Materials Chemistry. – 2011. – Vol. 21. – P. 4805-4812.
6. Supernak-Marczewska M., Zielinski A. Effects of the origin and deacetylation degree of chitosan on properties of its coatings on titanium // Coatings. –2020. – Vol. 10. – P. 99.
7. Fabrication and characterization of electrophoretically deposited chitosan-hydroxyapatite composite coatings on anodic titanium dioxide layers / A. Pawlik, M. Atiq Ur Rehman, Q. Nawaz, F.E. Bastan, G.D. Sulka, A.R. Boccaccini // Electrochimica Acta . – 2019. – Vol. 307. – P. 465-473.
8. Chitosan-based green and sustainable corrosion inhibitors for carbon steel / C. Verma, A.M. Kumar, M.A.J. Mazumder, M.A. Quraishi // Chitin-chitosan: myriad functionalities in science and technology. – 2018. – doi: 10.5772/intechopen.74989
9. Kokubo T., Takadama H. Simulated body fluid as a standard tool to test the bioactivity of implants. – Handbook of Biomineralization. Edited by M. Epple and E. Bauerlein. – Weinheim: Wiley-VCH Verlag GmbH. – 2007. – 440 p.
10. Kokubo T., Takadama H. How useful is SBF in predicting in vivo bone bioactivity? / Biomaterials. – 2006. – Vol. 27. – P. 2907–2915.
11. Formation of apatite on poly(α‐hydroxy acid) in an accelerated biomimetic process / Y. Chen, A.F.T. Mak, J. Li, M. Wang, A.W.T. Shum // J. Biomed. Mater. Res. Part B: Appl Biomater. – 2005. – 73B. – P. 68–76.
12. QUALX2.0: a qualitative phase analysis software using the freely available database POW_COD / A. Altomare, N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni, R. Rizzi // J. Appl. Cryst. – 2015. –Vol. 48. – P. 598-603.