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CORROSION BEHAVIOUR OF DIFFERENT METALLIC MATERIALS FOR BIOMEDICAL APPLICATIONS

KOROZIJSKO OBNAŠANJE KOVINSKIH MATERIALOV ZA BIOMEDICINSKE APLIKACIJE

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This paper presents a comprehensive review of strategies aimed at optimizing the corrosion resistance of permanent and biodegradable metallic biomaterials base don diverse surface treatments and coatings. It investigates the corrosion mechanisms of widely used biocompatible metallic materials, such as AISI 316L stainless steel, the Ti6Al4V alloy, NiTi, magnesium, and the FeMn alloy, highlighting key challenges that influence their degradation in a physiological environment. The study compiles findings on the corrosion behavior of these materials following the application of various surface-modification techniques, including surface oxidation, coating deposition, plasma treatments and laser texturing. These approaches are evaluated for their effectiveness in influencing material longevity and performance in short- and long-term biomedical applications.

Keywords: stainless steel, titanium alloys, NiTi, biodegradable alloys, corrosion

Ta članek predstavlja celovit pregled strategij za optimizacijo korozijskih lastnosti trajnih in biorazgradljivih kovinskih materialov z uporabo različnih površinskih obdelav in prevlek. Raziskava obravnava korozijske mehanizme uveljavljenih biokompatibilnih materialov, kot so nerjavno jeklo AISI 316L, zlitina Ti6Al4V, NiTi, magnezij in zlitina FeMn, ter izpostavlja ključne izzive, ki vplivajo na njihovo razgradnjo v fiziološkem okolju. Študija povzema ugotovitve o korozijskem obnašanju teh materialov po uporabi različnih tehnik površinske modifikacije, vključno s površinsko oksidacijo, nanosom prevlek, plazemskimi obdelavami in laserskim teksturiranjem. Ti pristopi so ovrednoteni glede na njihov vpliv na trajnost biomaterialov in njihovo delovanje v kratkotrajnih in trajnih biomedicinskih aplikacijah.

Ključne besede: nerjavno jeklo, titanove zlitine, NiTi, biorazgradljive zlitine, korozija

1 INTRODUCTION

Metallic biomaterials play a crucial role in modern medicine, particularly in orthopaedic, dental, and cardiovascular applications. Traditional metallic implants, such as stainless steel, titanium alloys and NiTi, are widely used due to their excellent mechanical properties, biocompatibility, and durability. However, one of the major challenges associated with these materials is their susceptibility to corrosion, which can lead to material degradation, ion release, and adverse biological reactions. Corrosion resistance is, therefore, a critical factor in determining the long-term performance and safety of metallic implants in the human body, which presents a highly corrosive environment due to bodily fluids, proteins, and fluctuating pH levels. Austenitic stainless steels are used for a variety of technological fields, including biomedical applications. The most used type is AISI 316L stainless steel, with a typical composition in mass fractions of 17 % Cr, 10 % Ni, 2–3 % Mo, balanced with Fe and minor elements, such as Mn, C, P, S and Si.[1,2] Austenitic stainless steels exhibit excellent mechanical properties, including a high ultimate tensile strength and superior corrosion resistance.[3,4] The corrosion mechanisms are strongly related to the formation of the passive film on the surface of AISI 316L.[5] Ti6Al4V is a dual-phase alpha-beta titanium alloy, which has been successfully employed in biomedical applications for decades.[6] Due to the rapid formation of a passive film, it displays low degradation rates, leading to outstanding biocompatibility. The microstructure, mechanical properties and corrosion resistance of the alloy are greatly affected by the thermomechanical history. The oxides of Al and V, which are incorporated into the passive film, are less stable than Ti-oxides, leading to their release in aggressive environments. Accumulation of these elements in nearby tissue may cause serious health issues.[6,7] NiTi alloys are also extensively used in biomedical applications owing to their unique combination of superelasticity, shape-memory effect, excellent corrosion resistance and biocompatibility.[8] However, nickel release remains a significant concern when using NiTi alloys in biomedical applications. Nickel has a diverse effect on the human body, including allergic reactions and toxicity.[9] Studies have shown that the Ni release rate increases with the exposure time and type of solution, indicating the need for a deeper understanding of the processes at the implant/human body.[8,10]

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In addition to conventional permanent implants, there is growing interest in biodegradable metals, such as magnesium, zinc, and iron-based alloys, which gradually degrade in the body and eliminate the need for surgical removal. These materials are particularly promising for temporary implants, such as bone-fixation devices and cardiovascular stents, where gradual degradation aligns with the healing process. However, their corrosion behaviour must be carefully controlled to ensure a balance between structural integrity and degradation rate, preventing premature failure or excessive ion release. Magnesium is regarded as non-toxic since it is essential to the human body.[11] However, it degrades rapidly in a physiological environment, resulting in local hydrogen release and alkalisation. An oxide layer is porous with poor barrier properties, leading to severe corrosion proliferation.[12] Increased biodegradability due to corrosion reduces mechanical stability before suitable bone recovery occurs.[13] Compared to Mg-based alloys, Fe-based alloys exhibit mechanical properties similar to stainless steel, making them more suitable for applications requiring high strength and ductility.[14] Alloying with manganese addresses issues related to the ferromagnetic properties of iron in certain imaging devices, such as magnetic resonance imaging. Mn is also a suitable alloying element due to microstructural, magnetic, corrosion, and toxicological considerations. However, the low corrosion rates remain a major issue for Fe–Mn-based alloys.[14]

This paper reviews different strategies for optimising the corrosion resistance of permanent and biodegradable metallic biomaterials, through various surface treatments and coatings. It explores the corrosion mechanisms of commonly used metallic materials, identifies factors affecting their degradation, and discusses approaches to improve their performance in short- and long-term biomedical applications.

2 EXPERIMENTAL

Materials. – Different biocompatible materials were investigated. The specimens were cut into discs of 15-mm diameter, ground with SiC emery paper down to 1200 grit and ultrasonically cleaned in ethanol prior to further treatments.

Austenitic stainless steel AISI 316L (17 % Cr, 10 % Ni, 2.1 % Mo, 1.4 % Mn, 0.38 % Si, 0.041 % P, 0.021 % C, <0.005 % S in mass fraction) was studied. Superhydrophilic and superhydrophobic epoxy coatings with as-received TiO_2 and surface-modified with fluoroalkylsilane (FAS) TiO_2 nanoparticles were applied on the specimens, respectively.[15]

Ti6Al4V alloy (6 % Al, 4 % V, 0.10 % Fe, 0.01 % Si, and 0.03 % C in mass fraction) was studied. The specimens were anodised in an electrolyte containing 20 g/L citric acid and 20 g/L $NaHCO_3$, by applying a potential of 30 V for 10 s.[6]

The NiTi alloy (55 % Ni, 45 % Ti in mass fraction) was studied. The electrodeposition of a hydroxyapatite (HAP) coating on the surface of the specimens was conducted to improve the corrosion resistance.[8]

A magnesium (99.9 % purity) sample was studied. Plasma surface modifications were performed using a low-pressure inductively coupled radio-frequency plasma system to alter the corrosion properties.[12] Two fundamentally different types of plasma were used, the first was H-mode plasma, where lower pressure and high power were applied, and the second was E-mode, where higher pressure and lower power were applied.[12]

FeMn alloy (18 % Mn in mass fraction) was studied. The specimens were additionally processed by laser texturing with a focal distance of 160 mm.[16]

Methods. – Potentiodynamic measurements were performed by using a BioLogic® SP-300 instrument and EC-Lab® V11.27 software in standard Hank's solution (8 g/L NaCl, 0.40 g/L KCl, 0.35 g/L $NaHCO_3$, 0.25 g/L $NaH_2PO_4 \times 2H_2O$, 0.06 g/L $Na_2HPO_4 \times 2H_2O$, 0.19 g/L $CaCl_2 \times 2H_2O$, 0.41 g/L $MgCl_2 \times 6H_2O$, 0.06 g/L $MgSO_4 \times 7H_2O$, 1 g/L glucose, pH = 7.8, Sigma-Aldrich chemicals). The electrochemical cell consisted of the investigated sample as a working electrode, a saturated calomel reference electrode (SCE, 0.242 V vs. SHE) and a platinum-mesh counter electrode, measurements were performed at a scan rate 1mV/s. Corrosion rates (v_{corr}) were calculated according to the ASTM G102-89 standard.[17]

Electrochemical impedance spectra (EIS) were measured in the frequency range from 65 kHz to 1 mHz with an AC amplitude of ±10 mV (peak-to-peak) during 3 days of immersion in a simulated physiological solution at 37 °C. EIS measurements were carried out at open-circuit potential (OCP). EIS data were fitted using the ZView program (Scribner, Southern Pines, North Carolina, USA). The chi square of fit values were between 0.001 and 0.005.

3 RESULTS AND DISCUSSION

The results of the corrosion behaviour in various biocompatible materials, i.e., AISI 316L stainless steel, Ti6Al4V alloy, NiTi, Mg and FeMn alloy, using different surface treatments aimed to enhance their corrosion resistance are presented. Different approaches for surface modification were employed, including surface oxidation, coating applications, plasma treatments and laser texturing.

The effect of surface modification on the corrosion behaviour of AISI 316L stainless steel in a simulated physiological Hank's solution at pH = 7.8 and 37 °C is illustrated in **Figure 1**. AISI 316L stainless steel was coated with superhydrophilic TiO_2-epoxy coating and superhydrophobic FAS/TiO_2-epoxy coating. The corrosion potential (E_{corr}) for the AISI 316L substrate was approximately –0.35 V vs. SCE. The alloy demonstrated a

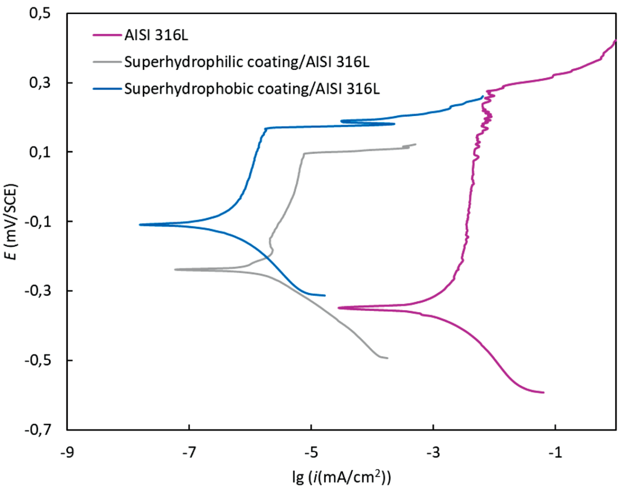

Figure 1: Potentiodynamic curves for AISI 316L substrate and coated with superhydophilic TiO_2/epoxy coating or superhydrophobic FAS-TiO_2/epoxy coating in a simulated physiological Hank's solution

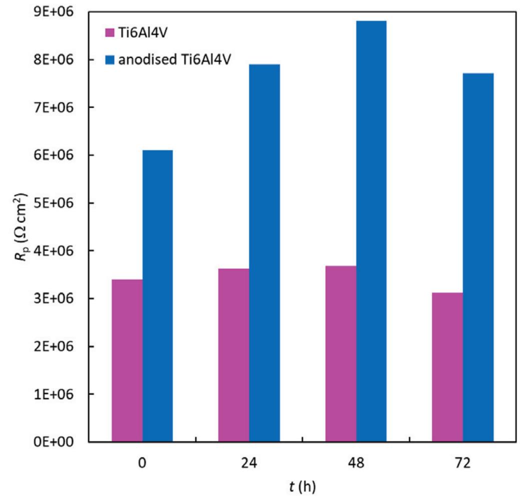

Figure 2: Polarization resistance calculated from EIS data, for Ti6Al4V alloy and after anodization in simulated physiological solution at 37 °C

broad passive region, with a breakdown potential (E_b) at 0.28 V vs. SCE. For AISI 316L coated with superhydrophilic as-received TiO_2/epoxy layer, the E_{corr} was approximately –0.24 V vs. SCE with reduced corrosion-current densities in the passive region compared to the substrate. The E_b was 0.09 V vs. SCE. For AISI 316L coated with superhydrophobic FAS-TiO_2/epoxy layer, the E_{corr} was approximately –0.11 V vs. SCE, the current densities in the passive region were the lowest, and an E_b was 0.16 V vs. SCE. Potentiodynamic data confirmed that all the coated specimens demonstrated improved corrosion resistance in amsimulated physiological solution, reflected in lower corrosion rates (v_{corr}) compared to the substrate (**Table 1**).[15]

Table 1: Corrosion rates for AISI 316L substrate and coated with superhydophilic TiO_2/epoxy coating or superhydrophobic FAS-TiO_2/epoxy coating calculated from potentiodynamic measurements in a simulated physiological Hank's solution.

Material	v_{corr} (μm/year)
AISI 316L	9.900
TiO_2-epoxy/AISI 316L	0.034
FAS-TiO_2-epoxy/AISI 316L	0.002

The Ti6Al4V alloy was electrochemically evaluated and compared to the anodised specimens by applying electrochemical impedance spectroscopy (EIS) for 3 days in a simulated physiological solution at 37 °C. The calculated polarisation resistances (R_p) are presented in Figure 2. The anodised specimen showed higher R_p values throughout the entire exposure period, reaching approximately 8 MΩ·cm^2 by the end. The untreated specimen had R_p around 3 MΩ·cm^2. The results indicate that during the anodization process a protective oxide layer was formed, which significantly reduced the interaction between the Ti6Al4V alloy and the surrounding environment, thus improving the protection against corrosion.[6]

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To improve the corrosion resistance of the NiTi alloy, a HAP coating was applied to the substrate. The results of the electrochemical study showed a significantly decreased corrosion rate of the sample coated with HAP compared to the untreated NiTi alloy (**Figure 3**). The corrosion study confirmed that the coating provided effective barrier properties, which are essential in biomedical applications for improving biocompatibility and minimizing nickel release.[8]

Plasma surface modifications were employed on the Mg to control its high degradation rate. An electrochemical study of untreated Mg, H-mode H_2/O_2 600-W and E-mode H_2/O_2 200-W samples was conducted in simulated physiological Hank's solution (**Figure 4**). A significant decrease of v_{corr} was observed in the plasma-modified specimens compared to the untreated Mg, which exhibited a v_{corr} of approximately 1.6 mm/year. The H-mode H_2/O_2 600-W plasma treatment with lower pressure and higher power reduced the v_{corr} to around 0.6 mm/year. The highest corrosion resistance was achieved with E-mode H_2/O_2 200-W Mg samples with

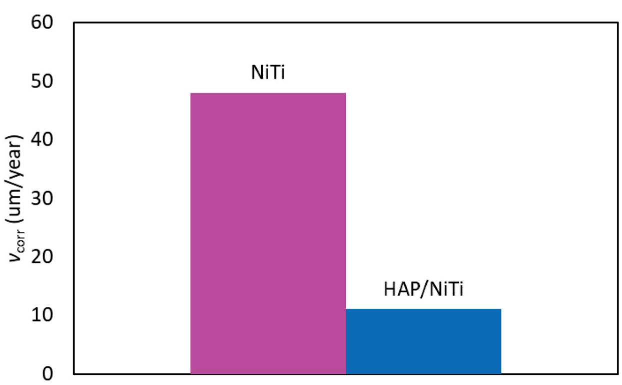

Figure 3: Corrosion rates calculated from potentiodynamic measurements for HAP-coated NiTi alloy and NiTi substrate in a simulated physiological solution at 37 °C

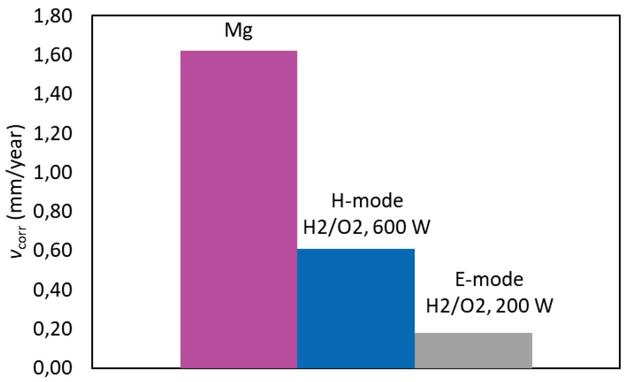

Figure 4: Corrosion rates calculated from potentiodynamic measurements for untreated Mg and plasma-modified H-mode H_2/O_2 600-W and E-mode H_2/O_2 200-W Mg in simulated physiological solution

higher pressure and lower power, resulting in a v_{corr} of 0.2 mm/year. This enhanced corrosion stability is attributed to the increased surface oxygen content, as confirmed by an XPS analysis.[12]

Laser texturing was used on the FeMn alloy to influence the corrosion behaviour through microstructural changes. The effectiveness of this surface modification was evaluated in a simulated physiological solution (**Figure 5**). Potentiodynamic measurements revealed that the untreated FeMn alloy exhibited the highest corrosion stability, while the laser-textured Fe–Mn sample showed the lowest. The enhanced degradability of the laser-textured alloy under biological conditions was evidenced by its higher v_{corr} and lower R_p compared to the untreated FeMn sample. The increased corrosion activity observed after laser texturing is attributed to the resulting superhydrophilic surface, which enhances fluid penetration and promotes surface degradation. Additionally, laser processing induces chemical changes on the surface, including the formation of high-temperature iron oxides. These oxides, along with changes in the surface morphology, contribute to the overall increase in corrosion.[16]

The results in this paper clearly demonstrate that the corrosion properties of biomedical materials can be effectively tailored through the application of different surface-modification techniques, including surface oxidation, the preparation of coatings, plasma treatments (lower pressure/high power mode and higher pressure/lower power mode) and laser texturing. These modifications specifically influenced the corrosion performance, highlighting the need for the selection of surface treatments based on the functional and clinical requirements of the implants. Improved corrosion resistance is essential for permanent implant materials, i.e., AISI 316L stainless steel and Ti6Al4V alloy, to ensure long-term structural integrity. On the other hand, a controlled degradation rate is crucial for biodegradable systems, such as Mg and the FeMn alloy, to enable controllable resorption during bone regeneration. Notably, the variations in corrosion behaviour across different surface-modification techniques and substrate materials reflect the complex relationship between the surface characteristics and the physiological environment.

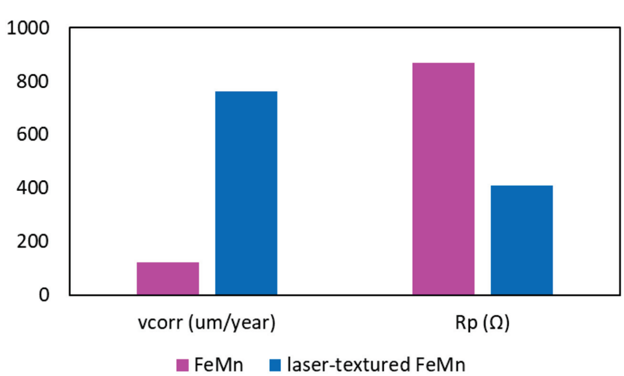

Figure 5: Corrosion rate and polarisation resistance calculated from potentiodynamic measurements for untreated FeMn alloy and laser-textured FeMn alloy in simulated physiological solutions

4 CONCLUSIONS

This study confirmed the efficiency of different surface-modification techniques, such as surface oxidation, coatings, plasma treatments and laser texturing, in altering the corrosion performance of biocompatible metallic materials including AISI 316L stainless steel, Ti6Al4V, NiTi, Mg, and FeMn alloys. Each treatment influenced the corrosion behaviour differently, depending on the material and the modification method, either enhancing the corrosion resistance for permanent implants or adjusting the degradation rate for biodegradable implants.

These findings highlight the crucial importance of surface-modification techniques in optimizing the corrosion behaviour, particularly under the demanding conditions associated with biomedical applications. A systematic understanding of the effects of various surface treatments is essential for the comprehensible selection and engineering of surface-modification strategies aimed at enhancing the performance, longevity and biocompatibility of metallic materials in physiological environments.

Data Availability

Data is available at Kocijan, Aleksandra (2025), Dataset for a publication: Corrosion behaviour of different metallic materials for biomedical applications, in the open repository DiRROS with PID: 20.500.12556/DiRROS-22179.

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5 REFERENCES

[1] A. Kocijan, M. Conradi, The corrosion behaviour of austenitic and duplex stainless steels in artificial body fluids, Mater. Tehnol. 44 (**2010**) 21–24

[2] A. Kocijan, D.K. Merl, M. Jenko, The corrosion behaviour of austenitic and duplex stainless steels in artificial saliva with the addition of fluoride, Corros Sci 53 (**2011**). doi:10.1016/j.corsci.2010.11.010

[3] M. Conradi, P. M. Schön, A. Kocijan, M. Jenko, G. J. Vancso, Surface analysis of localized corrosion of austenitic 316L and duplex 2205 stainless steels in simulated body solutions, Mater Chem Phys 130 (**2011**). doi:10.1016/j.matchemphys.2011.07.049

[4] L. Gil, S. Bruhl, L. Jimenez, O. Leon, R. Guevara, M. H. Staia, Corrosion performance of the plasma nitrided 316L stainless steel, Surf Coat Technol 201 (**2006**) 4424–4429. doi:10.1016/j.surfcoat.2006.08.081

[5] A. Kocijan, M. Conradi, P. M. Schon, Austenitic and duplex stainless steels in simulated physiological solution characterized by electrochemical and X-ray photoelectron spectroscopy studies, Journal of Biomedical Materials Research Part B-Applied Biomaterials 100B (**2012**) 799–807. doi:10.1002/jbm.b.32513

[6] M. B. Leban, T. Kosec, A. Kocijan, M. Conradi, I. Junkar, J. Kovac, Influence of the oxidizing technique on the biocompatible and corrosion properties of Ti6Al4V in a physiological environment, Appl Surf Sci 681 (**2025**). doi:10.1016/j.apsusc.2024.161486

[7] S. Shelly, S. L. Zaltsman, O. Ben-Gal, A. Dayan, I. Ganmore, C. Shemesh, D. Atrakchi, S. Garra, O. Ravid, D. Rand, H. Israelov, T. Alon, G. Lichtenstein, S. Sharabi, D. Last, F. Gosselet, V. Rosen, G. Burstein, A. Friedlander, R. Harel, G. Vogel, M. S. Beeri, Y. Mardor, Y. Lampl, G. Fleminger, I. Cooper, Potential neurotoxicity of titanium implants: Prospective, in-vivo and in-vitro study, Biomaterials 276 (**2021**). doi:10.1016/j.biomaterials.2021.121039

[8] A. Kocijan, Electrodeposition of a hydroxyapatite coating on a biocompatible niti alloy, Mater. Tehnol. 52 (2018). doi:10.17222/mit.2017.144

[9] M. Jenko, M. Godec, A. Kocijan, R. Rudolf, D. Dolinar, M. Ovsenik, M. Gorenšek, R. Zaplotnik, M. Mozetic, A new route to biocompatible Nitinol based on a rapid treatment with H_2/O_2 gaseous plasma, Appl Surf Sci 473 (**2019**). doi:10.1016/j.apsusc.2018.12.140

[10] M. A. Shafique, G. Murtaza, S. Saadat, Z. Zaheer, M. Shahnawaz, M. K. H. Uddin, R. Ahmad, Study of nickel ion release in simulated body fluid from C^+-implanted nickel titanium alloy, Surface Review and Letters 23 (**2016**). doi:10.1142/ S0218625X16500451

[11] Y. Guangyin, N. Jialin, Research Progress of Biodegradable Magnesium Alloys for Orthopedic Applications, Acta Metallurgica Sinica 53 (**2017**) 1168–1180. doi:10.11900/0412.1961.2017.00247

[12] A. Kocijan, J. Kovac, I. Junkar, V. Resnik Matic and Kononenko, M. Conradi, The Influence of Plasma Treatment on the Corrosion and Biocompatibility of Magnesium, MATERIALS 15 (**2022**). doi:10.3390/ma15207405

[13] M. Haghshenas, Mechanical characteristics of biodegradable magnesium matrix composites: A review, Journal of Magnesium and Alloys 5 (**2017**) 189–201. doi:10.1016/j.jma.2017.05.001

[14] A. Kocijan, I. Paulin, C. Donik, M. Hočevar, K. Zelič, M. Godec, Influence of different production processes on the biodegradability of an FeMn17 alloy, Mater. Tehnol. 50 (**2016**). doi:10.17222/mit.2016.055

[15] A. Kocijan, M. Conradi, C. Donik, Corrosion resistance of superhydrophilic and superhydrophobic TiO2/epoxy coatings on AISI 316L stainless steel, Mater. Tehnol., 52 (**2018**) 383–388. doi:10.17222/mit.2017.191

[16] Č. Donik, A. Kocijan, I. Paulin, M. Hočevar, P. Gregorčič, M. Godec, Improved biodegradability of Fe–Mn alloy after modification of surface chemistry and topography by a laser ablation, Appl Surf Sci 453 (**2018**) 383–393. doi:10.1016/j.apsusc.2018.05.066

[17] ASTM G102-89(2015)e1, Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements, (2015)