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CORROSION RESISTANCE OF Ti6Al4V ALLOY COATED WITH CAPROLACTONE-BASED BIODEGRADABLE POLYMERIC COATINGS

ODPORNOŚĆ KOROZYJNA STOPU Ti6Al4V POKRYTEGO BIODEGRADOWALNYMI POWŁOKAMI POLIMEROWYMI NA BAZIE KAPROLAKTONU*

The aim of this study was to determine the influence of long-term exposure of Ringer's solution on degradation of the anodically oxidated Ti6Al4V alloy coated with a biodegradable polymer coating. Polymeric coatings made of poly(glycolide-ε-caprolactone) – G-Cap and poly(glycolide-ε-caprolactone-lactide) – G-Cap-L were applied by a dip-coating method. Degradation was assessed on the basis of the results of pitting corrosion resistance and density of metal ions infiltrating to the solution. Studies were conducted for samples after 3, 6, 8, 10 and 12 weeks of exposure to the corrosive environment. In addition, topography of the surface of the polymer coating was assessed. As a result of potentiodynamic studies, the value of the polarization resistance and corrosion potential for the G-Cap and G-Cap-L coated samples were significantly decreased while simultaneous reduction of the density of metal ions infiltrating to the solution throughout the whole study period. There was also observed a faster degradation of the G-Cap coating compared to G-Cap-L, which showed local discontinuity after 12 weeks of exposure. The obtained results provide the basis for the development of polymeric coatings on surface of metal implants with predictable time / kinetics of degradation by selecting the composition of polymers while simultaneous limitation of metal ions infiltration into surrounding tissues.

Keywords: corrosion resistance, metal biomaterials, Ti6Al4V alloy, biodegradable polymeric coatings.

Celem pracy było określenie wpływu długotrwałego oddziaływania roztworu Ringera na proces degradacji utlenianego anodowo stopu Ti6Al4V pokrytego powłoką biodegradowalnego polimeru. Powłoki polimerowe wykonane z poli(glikolido-ε-kaprolaktonu) – G-Cap oraz poli(glikolido ε-kaprolaktono- laktidu) – G-Cap-L naniesiono metodą zanurzeniową (dip-coating). Proces degradacji w funkcji czasu oceniano na podstawie wyników badań odporności na korozję wżerową oraz gęstości masy jonów metalowych przenikających do roztworu. Badania przeprowadzono dla próbek po 3, 6, 8, 10 i 12 tygodniach ekspozycji na środowisko korozyjne. Ponadto oceniano topografię powierzchni powłoki polimerowej. W wyniku przeprowadzonych badań potencjodynamicznych stwierdzono wyraźne obniżenie wartości oporu polaryzacyjnego i potencjału korozyjnego dla próbek z naniesionymi powłokami G-Cap i G-Cap-L przy jednoczesnym wyraźnym ograniczeniu gęstości jonów metalowych przenikających do roztworu w całym okresie badawczym. Stwierdzono również szybszą degradację powłoki typu G-Cap w porównaniu do G-Cap-L, dla której po 12 tygodniu ekspozycji stwierdzono lokalnie występujące przerwania ciągłości. Uzyskane wyniki dają podstawę do opracowywania na powierzchni implantów metalowych powłok polimerowych o przewidywalnym czasie/określonej kinetyce degradacji, poprzez dobór składu polimerów z jednoczesnym ograniczeniem możliwości przenikania jonów metalowych do otaczających tkanek.

Słowa kluczowe: odporność korozyjna, biomateriały metalowe, stop Ti6Al4V, biodegradowalne powłoki polimerowe.

1. Introduction

The use of polymeric biomaterials, which are the subject of continuous, intensive research, is still widening. This is because of their good functionality and biocompatibility in the tissue environment. In particular, the large interest of researchers is focused on a group of synthetic bioresorbable polymers such as polylactide (PLA), poly

(ε-caprolactone) (PCL), polyglycolide (PGA), etc. [6, 9, 10, 17]. The wide range of applications of bioresorbable polymers in medicine is primarily concerned with the possibility of shaping their mechanical and physicochemical properties. Controlled degradation of polymers allows them to be used as carriers of drug substances to provide drug dosing with the desired kinetics until the desired therapeutic effect is

(*) Tekst artykułu w polskiej wersji językowej dostępny w elektronicznym wydaniu kwartalnika na stronie www.ein.org.pl

reached [14]. These polymers have a confirmed biocompatibility [17] and their final degradation products in the form of lactic, glycolic and hydroxyhexanoic acids are inert to the body and metabolized in the Krebs cycle [16].

The main limitation associated with the use of biodegradable polymers in medicine is related to the changing mechanical properties. This feature in some applications, for example, orthopedic implants for traumatic surgery may be unfavorable. In the absence of positive effects of treatment, the impaired implant ceases to function as a stabilizer. This may lead to a renewal of the injury. This will result in the need for a revision operation involving the removal of a fully degraded, mechanically impaired implant and replacing it with a new one. Revision check due to the progressive degradation of polymeric material may involve severe complications leading to much more traumatization of the surrounding tissue compared to the original implantation procedure. Therefore, despite continuous development of material engineering, resulting in the development of a variety of biomaterials, metal materials in many applications are still the dominant group.

Their universality is the result of many years of clinical experience and low cost of use. Because of its good and long-lasting mechanical properties, they allow long-term support and stabilization of implantation areas. However, metal biomaterials are characterized by limited biocompatibility in the human body. When subjected to synergistic influence of corrosive environments and mechanical factors they degrade [8, 13]. Among the wide range of metal biomaterials, titanium alloys are becoming increasingly popular. In particular Ti6Al4V ELI alloy is widely used for manufacturing of orthopedic prostheses. It exhibits good mechanical properties adapted to carry static and dynamic loads, high biocompatibility and corrosion resistance in the tissue environment. However, as a base material for endoprostheses and medical implants, it often causes allergic reactions due to the presence of vanadium, aluminum, and, less frequently, titanium [15, 20]. Therefore, in order to improve the biocompatibility of Ti alloys, a Ti6Al7Nb alloy was developed. By replacing the toxic vanadium with the inert niobium, the corrosion resistance and biocompatibility of the degradation products have been increased. However, the toxic / allergic effects of aluminium and titanium remain unresolved. Hence, the basic direction of research currently being developed is to modify the surface layer of Ti6Al4V alloy or apply coatings so that it is characterized by greater biocompatibility [20]. A common method of modifying the surface of titanium alloys is anodic oxidation. Interesting results were obtained by applying sol-gel and ALD coatings on titanium alloys [1, 2, 12, 15, 19]. However, despite numerous studies, the problem of harmful effects of metal biomaterial degradation products is still not fully resolved.

Therefore, the use of biodegradable polymeric coatings is an interesting way to modify the surface of metal implants to ensure the correct course of treatment. The metal substrate will ensure the mechanical stability of the treated tissue structures throughout the treatment period. The polymer coating, on the other hand, will be a barrier to the degradation of the metal biomaterial. In addition, it can support the process of treatment through local, controlled release of active substances. Local delivery of therapeutic substances will contribute to its effectiveness, while limiting the amount of while limiting the amount of used active substances compared to conventional pharmacotherapies [14, 19].

In the previous studies the influence of polymeric coatings on the corrosion resistance of metal substrates was mainly analyzed on coatings made of non-biodegradable polymers [3, 4, 5]. There are few reports on the influence of biodegradable coatings on the corrosion resistance of metal substrates [11, 18, 19].

Therefore, the principal aim of the work was to determine the influence of polymer coatings on the corrosion resistance of Ti6Al4V ELI alloy. Long-lasting exposure of titanium alloy with the polymer coatings made of poly(glycolide- ϵ -caprolactone) and poly (glycolide-

ϵ -caprolactone-lactide) in Ringer's solution was analyzed. In addition, the barrier properties of polymer coatings were evaluated based on the corrosion resistance of the metal substrate and the density of metal ions infiltrating to the solution. Based on microscopic observations, the polymer coating degradation process was evaluated as a function of time of exposure to the corrosive solution.

2. Material and methods

2.1. Material

Ti6Al4V ELI alloy samples were taken from a rod of 6 mm in diameter with chemical composition, structure and mechanical properties in accordance with ISO5832-3 [7]. The surface of the samples was subjected to modifications. They included grinding on 120 grit sandpaper and anodic oxidation. The anodic oxidation was performed in a bath containing phosphoric and sulfuric acid (Titan Color by Poligrat) at room temperature for 2 minutes at 97 V. The surfaces of the modified samples were characterized by a surface roughness $R_a = 0.65 \pm 0.05 \mu\text{m}$. Alloy samples were coated with biodegradable poly(glycolide- ϵ -caprolactone) (G-Cap) copolymer with comonomer ratio of 10:90 or poly (glycolide- ϵ -caprolactone-lactide) (G-Cap-L) 10:15:75. In both cases a bactericidal substance, ciprofloxacin, was placed in the polymer matrix. Biodegradable G-Cap and G-Cap-L polymers releasing ciprofloxacin were synthesized in the Center of Polymer and Carbon Materials of the Polish Academy of Sciences in Zabrze. Polymers were obtained by ring opening polymerization using non-toxic coordination initiator zirconium acetylacetonate $\text{Zr}(\text{acac})_4$ [6, 23]. Biodegradable polymeric coatings of G-Cap and G-Cap-L type were applied to metal implants by dip coating. In the first stage, the copolymers were dissolved in methylene chloride (1% by weight of polymer). Ciprofloxacin (10% by weight relative to the polymer) was added to the solution and thoroughly mixed. In such prepared solution, the sample was immersed using Dip Coater PTL-OV6P, MTI CORPORATION (immersion rate: 1500 mm / min, immersion time: 30 s, 1 dipping cycle). The implants with biodegradable coatings were dried in air for 48 h and then 72 h under vacuum.

2.2. Potentiodynamic studies

Pitting corrosion resistance studies were performed by potentiodynamic method in the Ringer's solution at $T = 37^\circ\text{C}$. The tests were performed using the VoltaLab PGP201 potentiometer, the reference electrode was a saturated calomel electrode (SCE), an auxiliary electrode was the platinum wire. Corrosion studies were started with the determination of the E_{OCP} open circuit potential in currentless conditions for 2h. Polarization curves were recorded from $E_{\text{start}} = E_{\text{OCP}} - 100 \text{ mV}$. The potential rate was equal to 3 mV/s. After reaching the anode current density of 1 mA/cm² or the potential of 4000 mV, the direction of polarization was changed. Based on the obtained curves using the Stern method, the values of the corrosion potential E_{corr} and the polarisation resistance R_p were determined.

2.3. Study of metal ions release

Concentrations of metal ions releasing into the solution were tested using a Yobin-Yvon JY 2000 spectrometer using the Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) method.

Corrosion resistance and metal ion release tests were carried out on the samples at the initial state, and with the polymer coatings, both non-exposed and exposed to the Ringer's solution ($\text{pH} = 7,0 \pm 0,2$) for 3, 6, 8, 10 and 12 weeks. During the exposure, the samples were kept in the heating chamber Binder FD 115 at $T = 37^\circ\text{C}$. The mass concentration of metal ions releasing into the solution was converted to mass density.

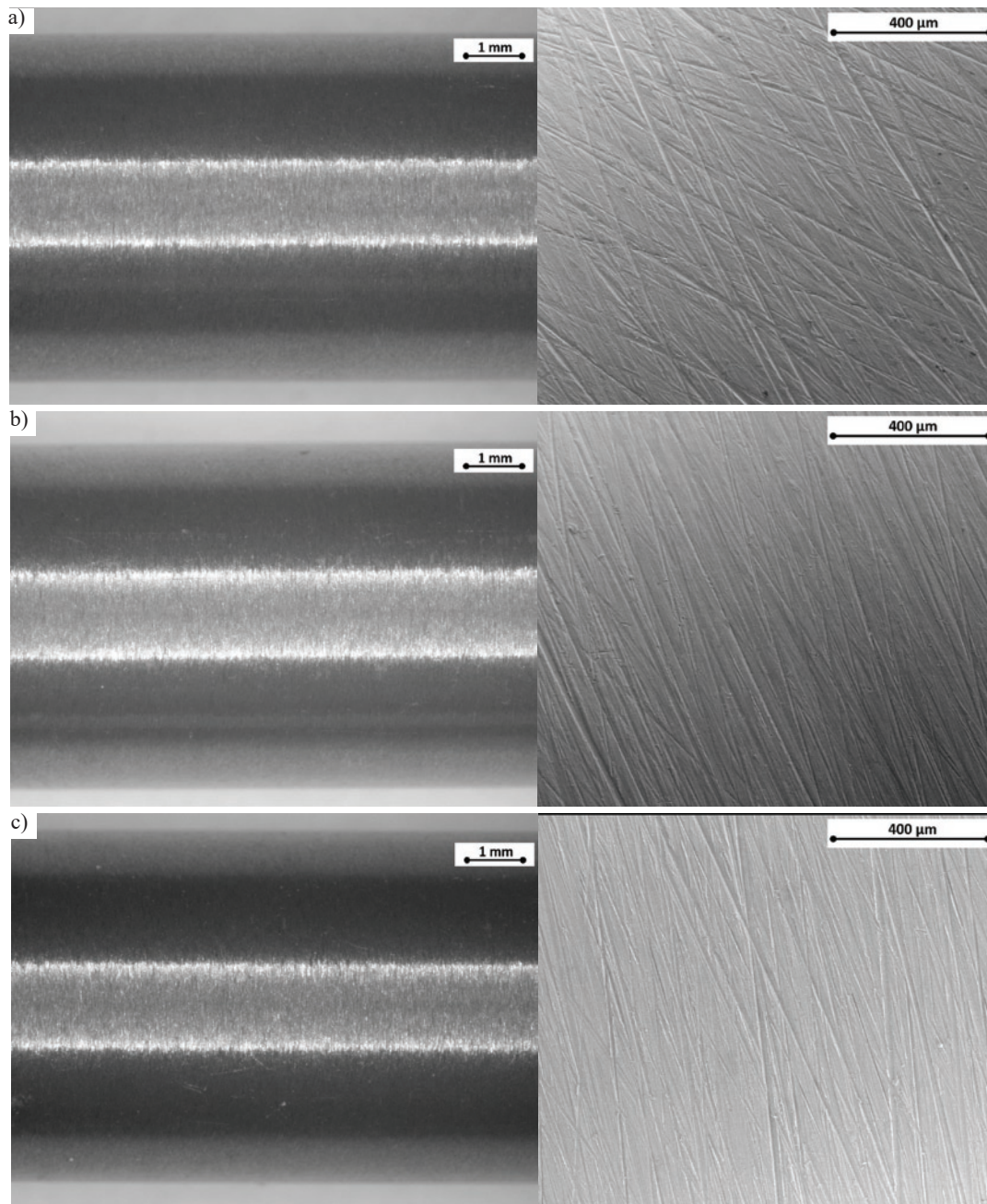


Fig. 1. Exemplary images of the samples' surface in the initial state (stereoscopic microscope – left; SEM – right): a) Ti6Al4V 97V, b) Ti6Al4V 97V + G-Cap, c) Ti6Al4V 97V + G-Cap-L

2.4. Surface observations

Observations of samples surface before and after corrosion tests and the exposure to the Ringer's solution were performed using the scanning electron microscope (SEM, Quanta 250 FEG, FEI Company, Oregon, USA) and the stereoscopic Zeiss Stereo Discovery V8 microscope with MC5s camera.

3. Results and discussion

3.1. Results of macro and microscopic observations of the samples in the initial state

After anodization, the prepared samples were characterized by uneven coloration – Fig. 1. Macro and microscopic observations of the samples in the initial state showed the occurrence of scratches

resulting from the mechanical treatment (grinding on sandpaper 120). Furthermore, it was found that the applied biodegradable coatings, G-Cap (Fig. 1b) and G-Cap-L (Fig. 1c), are homogeneous and continuous. The coatings are characterized by transparency, absence of air bubbles and dirt. Moreover, no detachment of the polymeric coating from the metal substrate was observed.

3.2. Results of pitting corrosion studies

Results of pitting corrosion tests of Ti6Al4V alloys and with the coatings made of the poly(glycolide- ϵ -caprolactone) – G-Cap) and poly(glycolide- ϵ -caprolactone-lactide) – G-Cap-L in the initial state and after the long-time exposure to Ringer's solution are summarized in Table 1 and Fig. 2.

For all the analyzed samples, polarization curves were recorded for which no breakdown potential was observed. This testifies the

resistance to pitting corrosion, which was confirmed during microscopic observation of the surface of the tested samples, in which no corrosion damage was observed. For all tested variants, the recorded potentiodynamic curves are characterized by a flat course showing the ideal passivity throughout the measuring range (+ 4000mV) – Fig. 2.

Detailed analysis of the obtained results of potentiodynamic studies showed diverse values of parameters describing corrosion resistance of the tested samples depending on time of exposure to the Ringer’s solution. The anodically oxidized samples and the samples with biodegradable polymers in the initial state (not exposed to the Ringer’s solution) were characterized by the highest values of corrosion potential E_{CORR} and polarization resistance R_p (Table 1). The exposure to the Ringer’s solution resulted in the decrease of both corrosion potentials as well as polarization resistances. In the case of corrosion potential, no clear tendency of the obtained potential values in the function of exposure time was observed. Regardless of the time of exposure (3, 6, 8, 10 and 12 weeks), the polarization resistance R_p was more than 5 times lower than recorded for the samples in the initial state. For all study periods, the recorded values of the polarization resistance R_p were close to each other – Table 1.

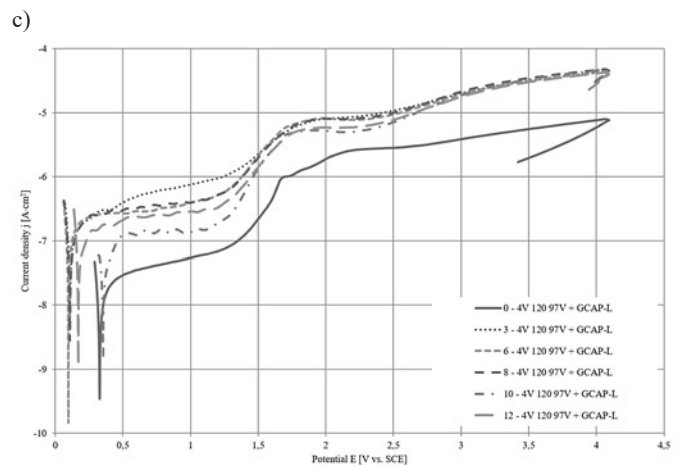
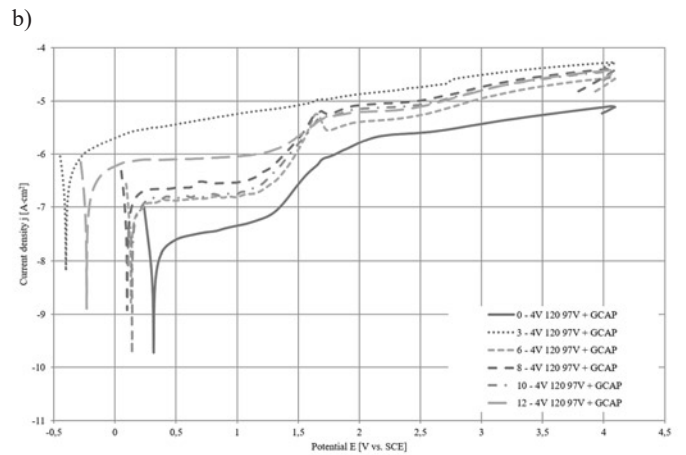
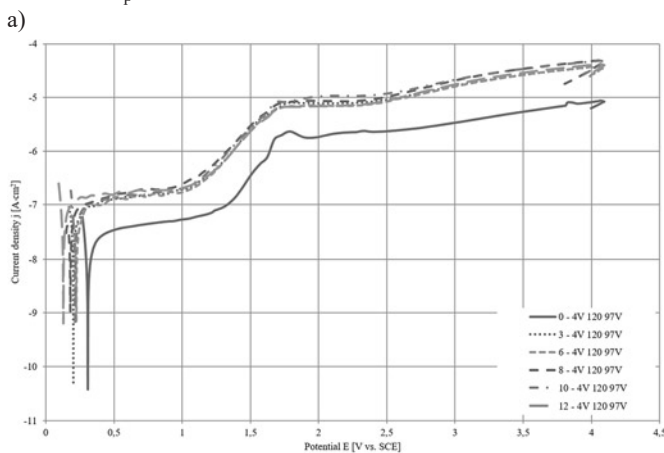


Fig. 2. Exemplary polarization curves for samples after different times of exposure to Ringer’s solution: a) Ti6Al4V 97V, b) Ti6Al4V 97V + G-Cap, c) Ti6Al4V 97V + G-Cap-L

Table 1. Results of pitting corrosion studies

No.	Sample	Time of exposure, weeks	Corrosion potential E_{CORR} mV	SD	Polarization resistance R_p , $M\Omega cm^2$	SD
1	4V 120 97V	0	311	51	2,11	0,25
2		3	156	68	0,400	0,030
3		6	177	99	0,42	0,14
4		8	147	51	0,308	0,070
5		10	204	17	0,360	0,080
6		12	191	83	0,360	0,080
7	4V 120 97V + GCAP	0	350	42	3,08	0,36
8		3	-328	86	0,169	0,060
9		6	85	145	0,35	0,20
10		8	13	129	0,210	0,090
11		10	200	83	0,52	0,15
12		12	-128	98	0,22	0,11
13	4V 120 97V + GCAP-L	0	323	35	2,03	0,29
14		3	105	66	0,250	0,040
15		6	207	97	0,210	0,020
16		8	163	73	0,303	0,080
17		10	289	93	0,42	0,10
18		12	173	33	0,210	0,080

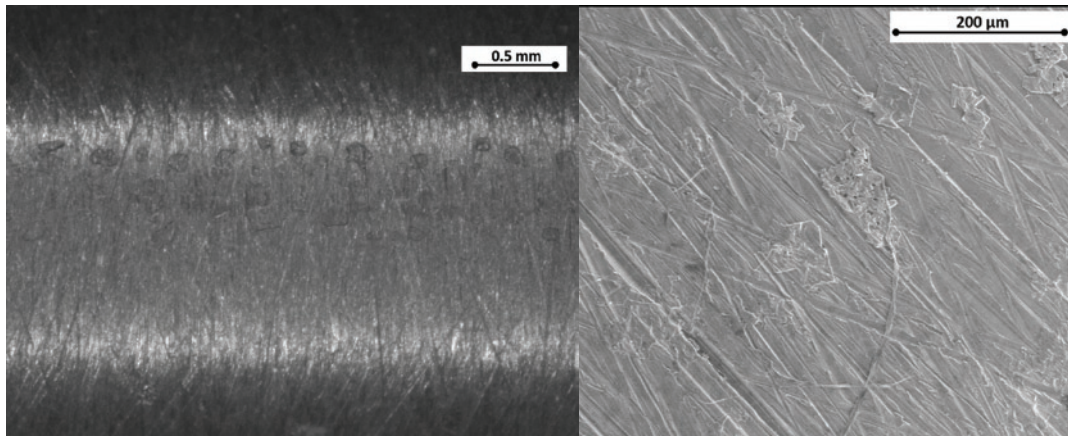


Fig. 3. Exemplary images (stereoscopic and SEM) of the surface of a Ti6Al4V-97V sample subjected to a 12-week exposure to Ringer's solution after pitting corrosion study

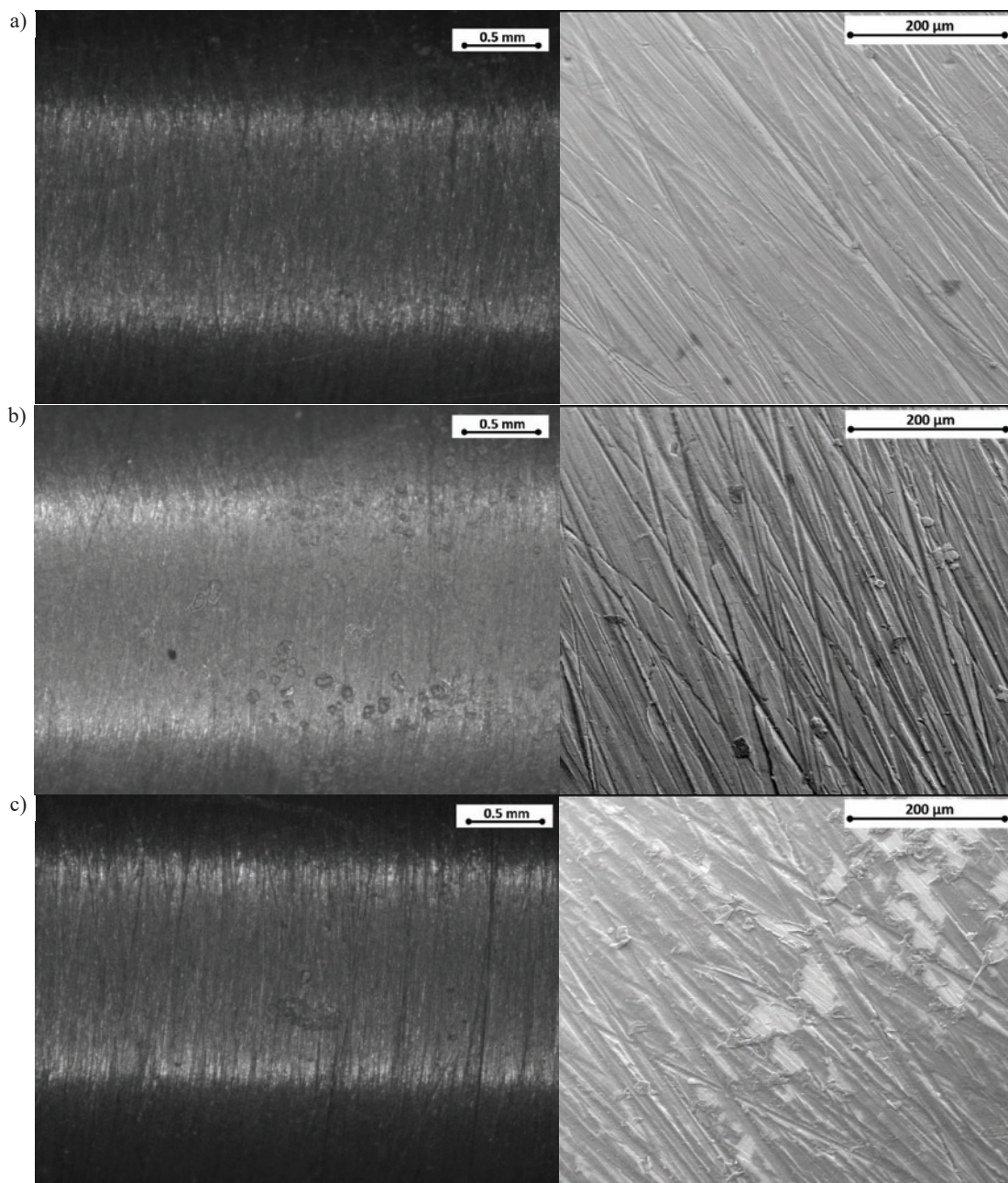


Fig. 4. Exemplary images (stereoscopic and SEM) of the sample surface of Ti6Al4V-97V + G-Cap after pitting corrosion study: a) after 3 weeks of exposure, b) after 8 weeks of exposure, c) after 12 weeks of exposure to the Ringer's solution

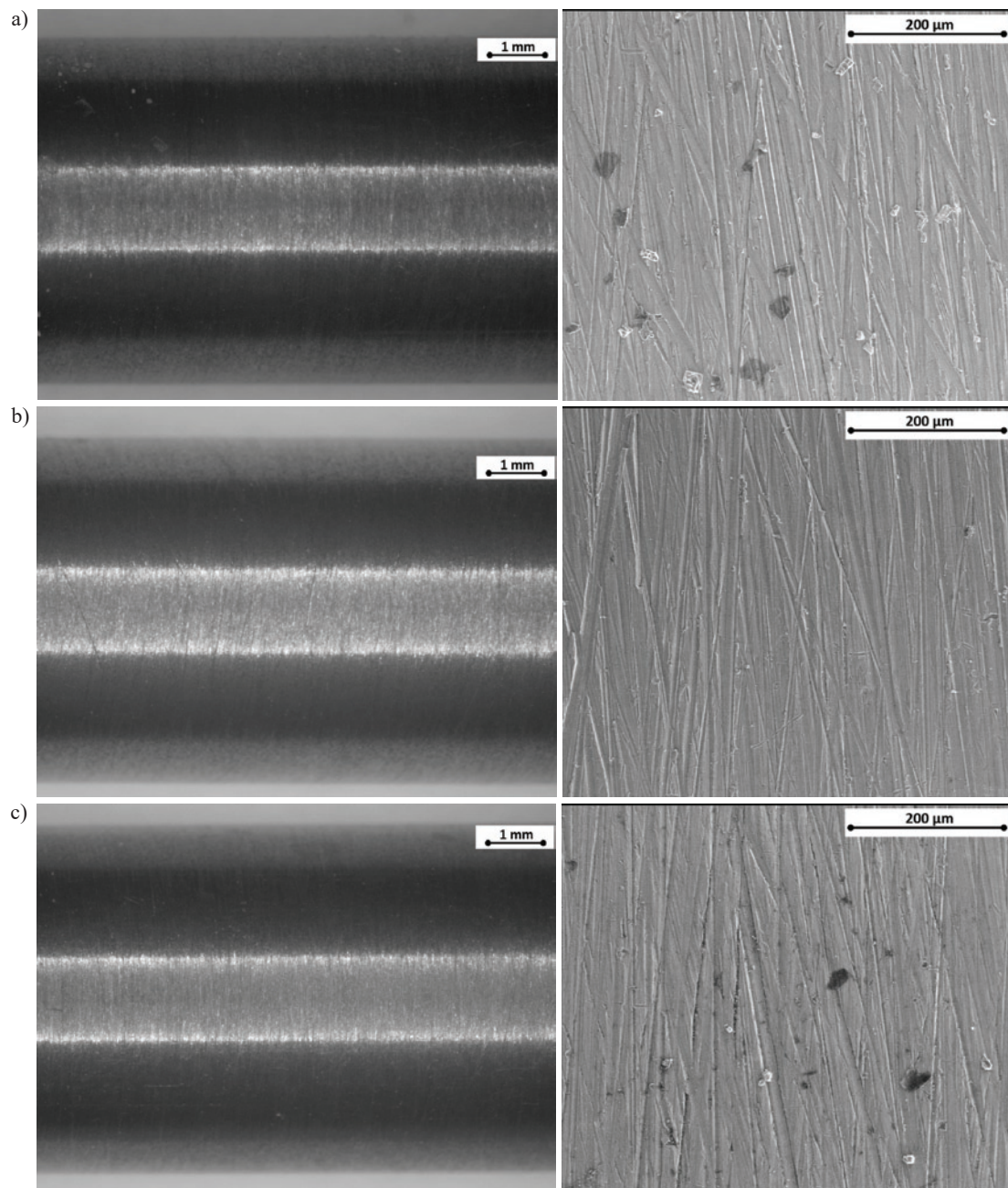


Fig. 5. Exemplary images (stereoscopic and SEM) of the sample surface of Ti6Al4V-97V + G-Cap-L after pitting corrosion study: a) after 6 weeks of exposure, b) after 10 weeks of exposure, c) after 12 weeks of exposure to the Ringer's solution

3.3. Macro and microscopic observations after long-term exposure to Ringer's solution and potentiodynamic studies

Both stereoscopic and scanning electron microscope observations have shown the presence of salt crystals on the surface derived from the Ringer's solution – Fig. 3. Moreover, observations did not show the presence of corrosion pits on the surface of the samples, thus confirming the results of the potentiodynamic tests. In the case of Ti6Al4V-97V + G-Cap samples, the polymer coating was discontinued at 12 weeks of exposure (Figure 4c). Macro and microscopic observations of the G-Cap-L coated samples showed no damage throughout the study period - up to 12 weeks – Fig. 5.

3.4. Results of metal ions release

The density of metal ions mass in the Ringer's solution after 3, 6, 8, 10 and 12 weeks of exposure is shown in Fig. 7. Analysis of the results showed that the highest density of metal ions (Ti, Al, V) permeating into the Ringer's was obtained for Ti6Al4V-97V alloy not coated with polymer coating - Fig. 4a, b, c. Deposition of the G-Cap or G-Cap-L coatings resulted in a decrease of the density of metal ions mass. This shows that application of the polymer coatings is a protective barrier to the penetration of metal degradation products into the Ringer's solution.

However, in the case of the G-Cap coating, the presence of metal substrate degradation products correlates with the observed discontinuity of the polymer coating. A similar relationship was observed in our earlier work on Ti6Al4V and Ti6Al7Nb alloys coated with Poly(Lactide-co-Glycolide) - PLGA, which contributed to a signifi-

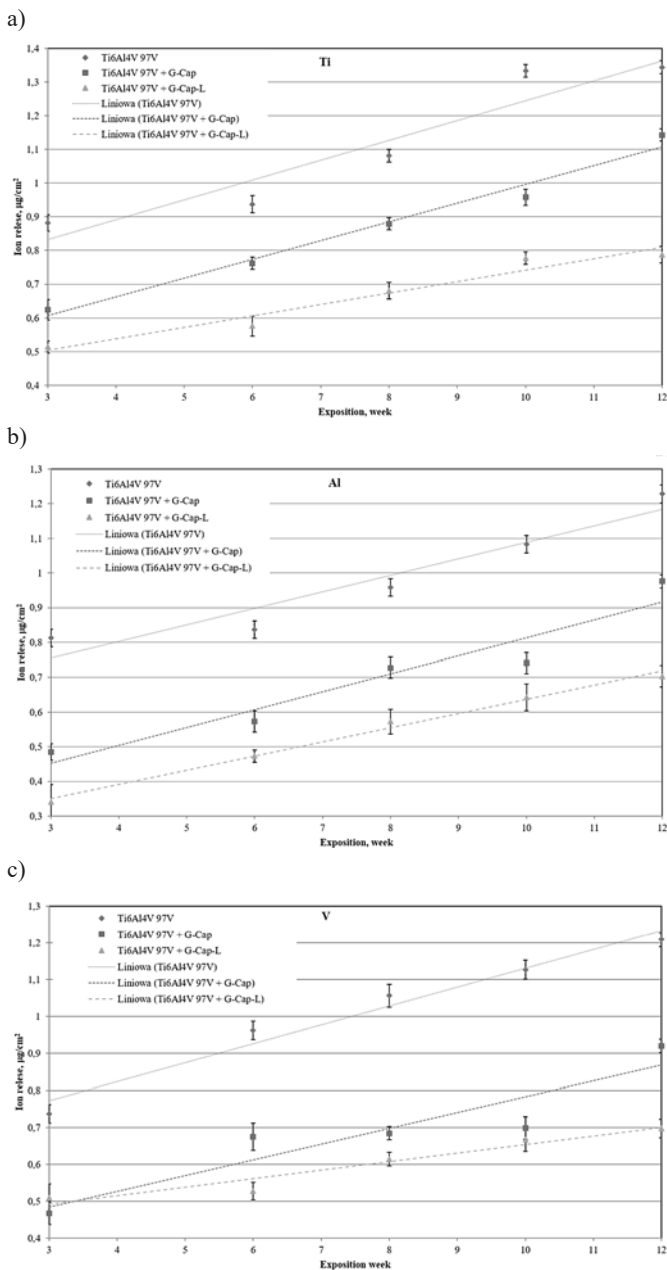


Fig. 6. Density of metal ion mass penetrating to the Ringer's solution: a) Ti ions, b) Al ions, c) V ions

cant decrease in the density of metal ions mass at a similar time, after 90-day exposure to the Ringer's solution [12].

From all the analyzed polymer coatings, the G-Cap-L was characterized by the best barrier properties. Furthermore, for both the G-Cap and G-Cap-L coatings a significant increase in the density of metal ions was observed in the last study periods (12 weeks) in comparison to the previous study periods (Fig. 6). This was caused by the local surface disintegration of the coating that exposed the metal substrate.

The obtained results were confirmed by the microscopic observations, where polymer coatings were locally discontinued after 12 weeks of exposure – Fig 3d.

4. Summary

The proposed surface treatment with the use of the biodegradable polymers poly(glycolide-ε-caprolactone) – G-Cap and poly(glycolide-ε-caprolactone-lactide) – G-Cap-L reduces the release of degradation products from the metal substrate, which *in vivo* conditions may result in the increase of biocompatibility. The polymer coatings on Ti6Al4V alloys are characterized by continuity, translucency, homogeneity, lack of air bubbles or contaminations. The potentiodynamic curves for all variants of surface modification in the initial state were characterized by a lack of hysteresis loops showing the resistance of the examined samples to pitting corrosion. Furthermore, it was found that deposition of the polymer coating did not contribute to a significant increase of the polarization resistance R_p (Table 1). As a result of exposure to the Ringer's solution, regardless of the applied surface modification method (anode oxidized samples and polymeric coatings), the course of the potentiodynamic curves has not changed. However, a significant decrease in the value of the polarisation resistance R_p was found. Over time, this value remained constant. Observations of the surface of the metal substrate after the potentiometric tests for both the samples in the initial state and the samples with the polymeric coatings showed no corrosion damage, which, together with the course of the potentiometric curves, clearly demonstrates the corrosion resistance of the anodized oxidized samples and the G-Cap and G-Cap-L coatings. Scratches visible on the surface are the effect of the performed surface modification.

The results of potentiodynamic studies do not show the unambiguously advantageous influence of the polymer coating on the corrosion resistance of the titanium alloy. The obtained results for both the G-Cap and G-Cap-L coatings are comparable to those of the anodized oxidized samples. This was observed regardless of the exposure time.

Observations of the polymer coating showed a diverse in the function of time course of coating disintegration. The course is also dependent on the type of polymer. It was found that the G-Cap [poly(glycolide-caprolactone)] coating was visibly disintegrating compared to the G-Cap-L [poly(glycolide-caprolactone-lactide)]. After 12 weeks of exposure to the Ringer's solution, discontinuity of the G-Cap coating (Fig. 4) was observed while the G-Cap-L coating was continuous.

The study of the release of metal substrate ions into the Ringer's solution carried out for different periods of exposure showed a diverse course of substrate degradation. The highest values of density of ions mass (Ti, Al, V) were recorded for the samples not coated with the polymer coatings. Deposition of the polymeric coatings has contributed to lowering the density of ions mass. The G-Cap-L coatings (Fig. 6) were characterized by better barrier properties (Fig. 6).

Analysis of the obtained results shows the beneficial influence of the polymer coatings deposited on Ti6Al4V alloy on biocompatibility of the substrate, characterized by the amount of metal ions released to the solution. As a result of the exposure of the G-Cap and G-Cap-L coatings, no deterioration of the corrosion resistance was observed compared to the corrosion resistance of the anodically oxidized samples. It has been found, however, that the polymer coatings reduce the kinetics of ion release. Good barrier properties of the G-Cap and G-Cap-L coatings with ciprofloxacin, and lack of negative influence on corrosion resistance of the metal substrate indicate their potential applications in medicine.

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