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Evaluation of surface free energy of bioactive coatings in titanium and magnesium alloy

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Abstract: Surface free energy (SFE) is a crucial parameter for predicting the cell adhesion and proliferation on implantation materials. In this work, the influence of bioactive calcium-phosphate coatings on the SFE of titanium and magnesium implants was studied. Results shows that the formation of bioactive coatings increase SFE by 139 % for magnesium alloy and 38 % for titanium, which in turn should have a positive effect on the adhesion and proliferation of osteoblasts.

Keywords: titanium, magnesium alloy, plasma electrolytic oxidation, biocompatibility, surface free energy

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Оценка свободной энергии поверхности биоактивных покрытий на титане и магниевом сплаве

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Аннотация. Свободная поверхностная энергия (СПЭ) играет важную роль для прогнозирования адгезии и пролиферации клеток на имплантационных материалах. В данной работе было изучено влияние биоактивных кальций-фосфатных покрытий на свободную поверхностную энергию титановых и магниевых имплантатов. Результаты показывают, что формирование биоактивных покрытий увеличивает СПЭ на 139 % для магниевого сплава и на 38 % для титана, что, в свою очередь, должно оказывать положительное влияние на адгезию и пролиферацию клеток костной ткани.

Ключевые слова: титан, магниевые сплавы, плазменное электролитическое оксидирование, биосовместимость, свободная энергия поверхности

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Introduction

Metal implants are the main material for bone surgery [1]. Titanium is widely used for production of dental and orthopedic implants, due to its high strength, corrosion resistance and bioinertness [2]. Magnesium is also of considerable interest as an implantation material, due to its biocompatibility, biodegradability and mechanical properties, which are closer to human bone tissue properties compared to other metals [3]. However, these metals have significant drawbacks, as a result of which the implant surface requires additional processing to improve osseointegration and increase the adhesion of bone tissue cells [3,4].

The coatings formation is one of the modification methods leading to the elimination of the disadvantages of metal surface. Plasma electrolytic oxidation (PEO) is one of the most promising methods of protecting metals from electrochemical dissolution and improving mechanical characteristics [5]; in addition, PEO is used to form bioactive coatings on implants [6,7].

The contact of the implant surface with the living tissue is important for osseointegration. The chemical composition of the implant determines directly the biocompatibility; roughness affects the contact area of the material with the biological environment and cell adhesion. In addition, the bone tissue cell adhesion is associated with wettability, which depends on the surface free energy (SFE) [8]. Many authors note that high-energy surfaces are more desirable for enhancing osteointegration and osteogenesis [9]. Thus, the study of the effect of the modification process on the SFE is important for the further practical application of PEO technology for the treatment of metal implants.

Materials and Methods

Rectangular sheets (35×25×1.5 mm^3) of VT1-0 commercially pure titanium (Ti) and MA8 magnesium alloy (Mg) (1.3–2.2 wt.% of Mn, 0.15–0.35 wt.% of Ce, Mg to balance) were used as the substrates.

PEO of the titanium was carried out in an electrolyte containing 30 g L^{-1} calcium glycerophosphate ($C_3H_7CaO_6P$) and 40 g L^{-1} calcium acetate ($Ca(CH_3COO)_2$) in a monopolar potentiodynamic mode [10], sample is designated as Ti-PEO. PEO of the magnesium alloy was carried out in an electrolyte containing 25 g L^{-1} calcium glycerophosphate ($C_3H_7CaO_6P$), 5 g L^{-1} sodium fluoride (NaF), and 7 g L^{-1} sodium metasilicate (Na_2SiO_3) in a bipolar mode [11], sample is designated as Mg-PEO. The use of different modes of PEO for magnesium alloy and titanium is due to differences in the mechanism of formation of the anode coating on various metals, described in more detail in previous studies [10,11].

The wettability of the investigated samples was studied by the sessile drop method using the drop shape analyzer DSA100 (KRЬSS, Germany). Contact angle (CA) technique is used to estimate wetting properties of the localized area of solid surface. According to this method, the angle between the baseline of the drop and the tangent at the three-phase point was measured. For calculations of CA, the Young-Laplace method was used. Before recording the CA results, the drop stabilized on the surface for 60 s. Deionized water (H_2O) and methylene iodide (CH_2I_2)

were used as test liquids. Before contact angle measurements, metal surfaces were mechanically treated with sanding papers from #150 to #2500 sequentially, washed with distilled water and degreased with alcohol in ultrasonic bath (Bandelin electronic, Germany). The surfaces of PEO coatings were washed with distilled water and dried at 25°C.

Surface free energy (γ_s) was calculated (Eq. 1) as the sum of the dispersed (γ_s^d) and polar (γ_s^p) interactions of a liquid droplet with the solid surface, calculated using a system of equations obtained on the basis of the Owens equation [12]:

$$\begin{cases} \gamma_s^d = \left[C_1\left(1+\cos\theta_w\right) - C_2\left(1+\cos\theta_{mi}\right)\right]^2 \\ \gamma_s^p = \left[C_3\left(1+\cos\theta_w\right) + C_4\left(1+\cos\theta_{mi}\right)\right]^2, \end{cases} \quad (1)$$

where θ_w, θ_{mi} are the CA for the surface in contact with water and methylene iodide, respectively. The constants C_1–C_4 are determined by the values of the liquid surface tension.

Results and Discussion

Based on the data of X-ray phase analysis and elemental composition [10,11], formed coatings include calcium-phosphate compounds, which can increase the formation rate of hydroxyapatite in body fluids. In addition to calcium phosphate compounds, the coatings consist of titanium dioxide (in the modification of rutile and anatase) for titanium, magnesium oxide and ortho-silicate for magnesium alloy.

Analysis of the wettability of bioactive surface layers on titanium and magnesium alloy indicates a significant decrease in CA in comparison with the metal surface (Table 1). In particular, coatings on Mg alloy exhibit properties close to superhydrophilicity in contact with water. However, the values are approximate, since the drop spreads at a high speed and is absorbed by the material, as a result of which it is difficult to register the real CA.

When wetting Mg-PEO with methylene iodide, the equilibrium CA = 15.7° and is not established immediately but for some time, approximately 30–60 s (Fig. 1). This behavior of liquids on the surface of bioactive coatings on magnesium alloy is a result of high roughness and large porosity, because of which, due to capillary effects, the drop gradually penetrates deep into the texture of the coatings, and spreads over the surface, and the CA, in turn, decreases (Fig. 1).

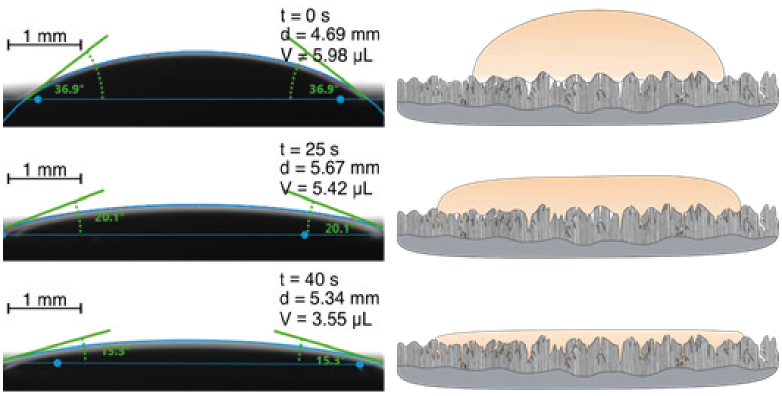

Fig. 1. Optical images (*a*, *c*, *e*) and wetting models (*b*, *d*, *f*) of methylene iodide CA for Mg-PEO surface after 0 s (*a*, *b*), 25 s (*c*, *d*) and 40 s (*e*, *f*) sitting the drop

At the initial stage of wetting (Fig. 1, *a*, *b*), the liquid/solid contact boundary contains both liquid/solid (f_{l-s}) and liquid/vapor (f_{l-v}) sections contained in the pores of the PEO layer. Thus, the wetting satisfies the Cassie-Baxter state (Eq. 2):

$$\cos\left(\theta_C\right) = f_{l-s}\cos\theta_Y - f_{l-v}, \quad (2)$$

where θ_C, θ_Y are Cassie and Young's CA, respectively.

Table 1

Wettability and components of surface free energy for different surfaces

Surface	Contact angle, °		Surface free energy, $mJ \cdot m^{-2}$		
	H_2O	CH_2I_2	γ_s^p	γ_s^d	γ_s
Mg	82.6 ± 0.6	54.9 ± 1.1	5.23 ± 0.12	28.3 ± 0.3	33.6 ± 0.4
Mg-PEO	5.4 ± 4.3	15.7 ± 0.9	31.35 ± 0.16	48.9 ± 0.2	80.3 ± 0.4
Ti	75.1 ± 0.3	43.7 ± 0.4	5.73 ± 0.14	37.7 ± 0.2	43.5 ± 0.4
Ti-PEO	41.4 ± 1.1	50.0 ± 1.2	26.0 ± 0.8	34.3 ± 0.7	60.2 ± 1.4

Notations: The results are presented as the mean ± standard deviation for 15 measurements.

Next, the contact area increases (Fig. 1, *c*, *d*), as can be seen from the increase in the contact line length (*d*). Accordingly, f_{l-s} increases and f_{l-v} decreases ($f_{l-s} = 1 - f_{l-v}$), which indicates partial filling of the coating pores. Further, there is no increase in the contact line length, and the CA and drop volume (*V*) decreases, therefore the drop goes deep into the texture of the coating ($f_{l-s} \to 1$) and wetting passes from the Cassie-Baxter state to the Wenzel state (Eq. (3)):

$$\cos(\theta_w) = r\cos\theta_Y, \tag{3}$$

where $f_{l-s} = r$ is the roughness parameter, θ_W is Wenzel's CA.

For Ti-PEO, a stable state is achieved immediately, and the wettability of such a surface improves compared to uncoated metal. Water CA decreases by almost half, and methylene iodide CA increases (Table 1), which is probably a consequence of the presence of titanium oxide on the surface in advantage. A significant difference in the wetting of Mg-PEO and Ti-PEO is due to differences in the morphology of the surface. The size and number of pores of Mg-PEO coatings significantly exceed Ti-PEO [10, 11].

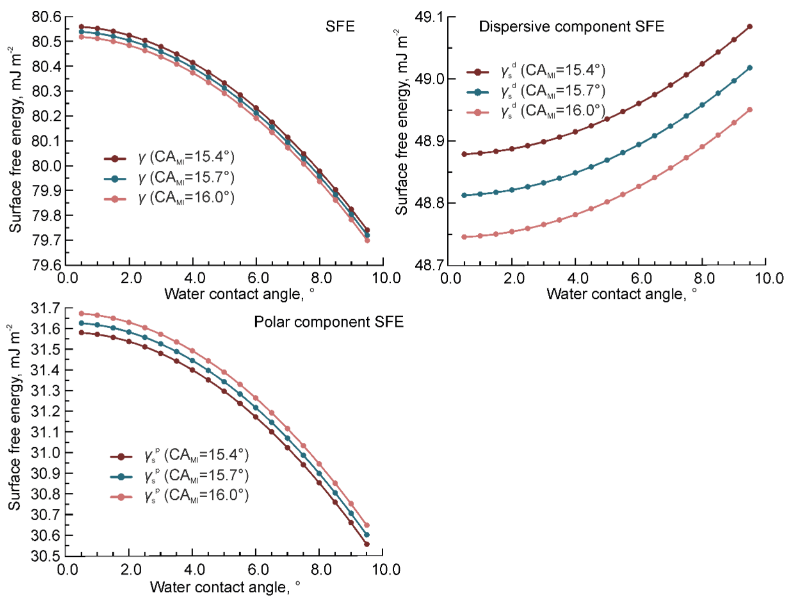

Fig. 2. Theoretical dependences of the SFE (γ, γ^d, γ^p) on the θ_w from 0 to 10° at different values of the θ_{mi}, by the Owens-Wendt equation.

As the CA changes due to formation of PEO coatings on the surface of titanium and magnesium, the value of SFE changes as well. To a large extent, the value of the polar component of the SFE changes for PEO coatings, which is due to a significant difference in the energy of interaction of the liquid with metal and metal oxides.

Since it is difficult to estimate the real water CA with the surface of Mg-PEO due to its high hydrophilicity, determining the value of SFE by the OWRK (Owens-Wendt-Rable-Kaelble) method is also non-trivial. Therefore, the Owens-Wendt equation was graphically presented in the area of the water CA 0–10°, with the value of the methylene iodide contact angle $(15.7 \pm 0.3)^{o}$ (Fig. 2).

The results show that at this site the value of the SFE is determined with an accuracy of 1 $mJ \cdot m^{-2}$, which is less than 1 % of the specified value. Also, decomposing the SFE by components, it is clearly seen that the polar component (0.9 $mJ \cdot m^{-2}$) makes the greatest contribution to this difference, and the dispersed component lies within the error (0.2 $mJ \cdot m^{-2}$). According to the data of the graphs, it can be assumed that the SFE of the Mg-PEO surface is 80.3 ± 0.4 $mJ \cdot m^{-2}$.

Conclusion

In general, it is possible to establish the positive effect from treating the metal surface by plasma electrolytic oxidation, since the value of the SFE increases by 139% for magnesium alloy and 38% for titanium. An increase in wettability and, as a consequence, the amount of surface energy is a favorable factor for the biocompatibility and cell adhesion on the surface of the implantation material [8].

REFERENCES

1. **Steinemann S. G.,** Metal implants and surface reactions, Injury. 27 (1996) S/C16-S/C22.
2. **Pałka K., Pokrowiecki R.,** Porous titanium implants: a review, Advanced Engineering Materials. 20 (5) (2018) 1700648.
3. **Roach P., et al.,** Modern biomaterials: a review—bulk properties and implications of surface modifications, Journal of Materials Science: Materials in Medicine. 18 (7) (2007) 1263–1277.
4. **Chouirfa H., et al.,** Review of titanium surface modification techniques and coatings for antibacterial applications, Acta biomaterialia. 83 (2019) 37–54.
5. **Mashtalyar D. V., et al.,** New approach to formation of coatings on Mg-Mn-Ce alloy using a combination of plasma treatment and spraying of fluoropolymers, Journal of Magnesium and Alloys. 10 (4) (2021) 1033–1050.
6. **Cheng Y., et al.,** Microstructure, corrosion and wear performance of plasma electrolytic oxidation coatings formed on Ti–6A*l*–4V alloy in silicate-hexametaphosphate electrolyte, Surface and Coatings Technology. 217 (2013) 129–139.
7. **Cerchier P., et al.,** Antibacterial effect of PEO coating with silver on AA7075, Materials Science and Engineering: 75 (2017) 554–564.
8. **Schwartz Z., Boyan B. D.,** Underlying mechanisms at the bone–biomaterial interface, Journal of cellular biochemistry. 56 (3) (1994) 340–347.
9. **Ferreirys C. M., et al.,** Surface free energy and interaction of Staphylococcus epidermidis with biomaterials, FEMS microbiology letters. 60 (1) (1989) 89–94.
10. **Mashtalyar D. V., et al.,** Bioactive coatings formed on titanium by plasma electrolytic oxidation: Composition and properties, Materials.13 (18) (2020) 4121.
11. **Mashtalyar D. V., et al.,** Antibacterial Ca/P-coatings formed on Mg alloy using plasma electrolytic oxidation and antibiotic impregnation, Materials Letters. 317 (2022) 132099.
12. **Owens D. K., Wendt R. C.,** Estimation of the surface free energy of polymers, Journal of applied polymer science. 13 (8) (1969) 1741–1747.

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