UKRAINIAN JOURNAL OF MECHANICAL ENGINEERING AND MATERIALS SCIENCE
Vol. 8, No. 4, 2022

Marianna Dyman[1], Andrii Moltasov[2], Sergii Kaliuzhnyi[3],
Oleksandr Kyslytsia[4], Tania Tsymbalista[5]

[1] Department of Strength of Welded Structures, E. O. Paton Electric Welding Institute of the National Academy of Sciences of Ukraine, 11, K. Malevych Str., Kiev, Ukraine, e-mail: mrs_d@ukr.net, ORCID 0000-0002-5886-124
[2] Department of Strength of Welded Structures, E. O. Paton Electric Welding Institute of the National Academy of Sciences of Ukraine, 11, K. Malevych Str., Kiev, Ukraine, e-mail: moltasov@gmail.com, ORCID 0000-0002-5025-4055
[3] Department of Protective Coatings, E. O. Paton Electric Welding Institute of the National Academy of Sciences of Ukraine, 11, K. Malevych Str., Kiev, Ukraine, e-mail: serg3319@ukr.net, ORCID 0000-0002-8132-3930
[4] Department of Protective Coatings, E. O. Paton Electric Welding Institute of the National Academy of Sciences of Ukraine, 11, K. Malevych Str., Kiev, Ukraine, e-mail: kisl@i.ua, ORCID 0000-0001-8894-4660
[5] Department of Protective Coatings, E. O. Paton Electric Welding Institute of the National Academy of Sciences of Ukraine, 11, K. Malevych Str., Kiev, Ukraine, e-mail: tstania@ukr.net, ORCID 0000-0001-9569-7776

RESEARCH OF THE STRUCTURE AND MECHANICAL PROPERTIES OF MICROPLASM POROUS COATINGS FOR BIOMEDICAL PURPOSES

Received: July 20, 2022 / Revised: August 30, 2022 / Accepted: September 30, 2022

https://doi.org/10.23939/ujmems2022.04.014

Abstract. The purpose of this work is to justify the feasibility of using the technology of microplasma sputtering from wire materials to obtain porous coatings for biomedical purposes, the modulus of elasticity of which is close to the corresponding characteristic of human cortical bone tissue. Analyzed the influence of the technological parameters of the microplasma sputtering regime on the degree of porosity of the coating. As a result, it was found that a decrease in current strength and consumption of plasma-forming gas, as well as a decrease in the speed of feeding the sprayed wire into the plasma jet lead to an increase in the porosity of the coatings. Even though these parameters are interrelated, for each individual material are limited by certain limit values, in case of non-observance of which the stable process of melting and dispersion of the sprayed wire in the plasma jet becomes impossible. Established the limit parameters of the microplasma sputtering process for titanium alloy VT1-00 and zirconium alloy KTC-110, which allows obtaining a coating with maximum porosity. Conducted studies of the adhesion strength of the obtained coatings, formed through a low-porous sublayer, with the maximum degree of porosity according to the ASTM C633-13 (2017) method which proven that the indicators of the adhesion strength of the coatings to the VT6 titanium alloy base at normal separation meet the requirements of the international quality standard ISO 13179- 1:2021.

Keywords: biocompatible coatings, microplasma spraying, wire materials, structure, porosity, static strength.

Introduction and Problem statement

One of the main problems with the use of metal endoprostheses in orthopedics and traumatology is the discrepancy between the modulus of elasticity of the bone and the implant, which slows down regeneration and osseointegration [1]. It is known that the modulus of elasticity of coatings depends on the porosity of the material [2]. Thus, reducing the difference between the modulus of elasticity of the bone and the implant is possible with the application of a porous coating on the surface of the implant by the method of microplasma spraying (MPS) [3], as the modulus of elasticity of such coatings can decrease by more than an order of magnitude, compared to the original sprayed material, depending from the mode parameters of sputtering [4].

In addition, increasing the porosity of the coating allows not only to reduce its modulus of elasticity, but also to increase the strength of the bond between the bone and the implant due to the growth of bone tissue into a rougher microrelief of the coating with the presence of open pores [5, 6].

The research was conducted within the framework of funding of the National Academy of Sciences of Ukraine under grant 0121U112006.

On the other hand, an increase in the degree of porosity leads to a decrease in other mechanical characteristics of the coating, including its strength, therefore, excessive porosity can cause premature destruction of the coating, and the difference in the modulus of elasticity of the coating and the base can cause its peeling due to uneven elongation and the occurrence of tangential stresses at bending at the interface of layers [7, 8]. In any of these cases, there will be a need for a prosthetics revision through repeated surgical intervention [9]. Thus, the approximation of the modulus of elasticity of the coating to that of bone, due to the increase in the porosity of the former, is possible only up to some of its limiting values. Therefore, the problem lies in the comprehensive analysis of the microstructure along with the determination of the adhesive strength of porous coatings.

Review of Modern Information Sources on the Subject of the Paper

Recently, a sufficient number of works have been devoted to the study of the microstructure of coatings in order to determine the most favorable pore size for the integration of bone tissue into the implant, which indicates a significant scientific interest in this issue. For example, work [10] provides some research data on the determination of the adhesion strength of a porous titanium powder coating to the adjacent bone tissues of laboratory animals, according to which, with pore sizes of 100–300 μm, the shear strength reaches its maximum after 2–3 months, while the increase pore size leads to a decrease in the adhesive strength of the bone with the implant. Experimental data on the osseointegration of titanium and hydroxyapatite-coated implants in dog bones are given in work [11], according to which it was concluded that the optimal size of open pores for effective integration of bone tissue is 300–500 μm. In work [12], it is recommended to ensure the presence of pores of different sizes (from less than 20 μm to more than 100 μm), while the pores must be interconnected. And in work [13] it is indicated that in titanium specimens, the pore size of 100–200 μm is better for stimulating cell adhesion and increasing antibacterial properties compared to pores of 355–500 μm or with completely dense specimens. As you can see, the given data significantly differs, therefore, by means of their comparative analysis, the pore size in the range of 50...300 microns can be considered acceptable. Studies [14] showed that the desired degree of porosity of the surface layers of the implant (coating) should be in the range of 15–35 %.

After analyzing the literary sources, it is easy to see that all of them refer to coatings made of titanium and its alloys. However recently, zirconium-based alloys are increasingly used in orthopedic practice, which are more biocompatible compared to titanium alloys, as they do not contain toxic elements [15]. Therefore, the purpose of the work is to study the microstructure and establish the strength indicators of coatings made of zirconium alloy KTC-110 with the maximum possible porosity, as well as their comparison with the parameters of similar coatings made of titanium alloy VT1-00.

In accordance with the set goal, the main tasks are quantitative analysis of the volumetric porosity of coatings made of KTC-110 and VT1-00 alloys and experimental verification of the compliance of their adhesion strength indicators with the requirements of current international standards.

Main Material Presentation

Basing off the currently known methods of forming coatings [16], the powder sintering method provides the highest porosity degree. Thus, in work [17], using this method, we were able to obtain powder coatings from the VT1-00 alloy with a porosity of 37 %. However, with an increase in the porosity of such coatings, the decrease in the modulus of elasticity is less intense, compared to the coatings applied by the

MPS method. Thus, according to the work [18], the coating made of the VT1-00 alloy, obtained by the powder sintering method, had a modulus of elasticity of 37.7 GPa with a porosity of 28.6 %, while according to the work [3], the coating made of the same alloy, applied by the method MPS, even with a porosity of 13.7 %, had a modulus of elasticity in the range of 35.4–38.5 GPa. Thus, it can be concluded that the MPS technology is more likely to be able to provide the elastic modulus of coatings in the range of changes in the corresponding characteristic of human cortical bone tissue (12–30 GPa [19]).

In case of using a powder spraying, to obtain a large number of volumetric pores with a size of up to 300 μm, the coating must be formed from partially solidified particles that are in a thermoplastic state and have a negligible velocity before contact with the substrate. If there is insufficient volume of the liquid phase in the partially melted particles, their interaction with each other does not ensure the formation of a strong connection, as a result there is a high probability of destruction of the coating due to low cohesive strength. Because of this, it is technologically difficult to ensure the desired structure of coatings when they are sprayed from powder materials. It is possible to avoid the disadvantages of powder spraying by forming highly porous coatings due to spraying using wire materials. In the process of sputtering of the wire the sputtered particles completely melt in the plasma jet [20], so their collision with the substrate occurs in the presence of a significant amount of liquid phase, as a result the formed coatings have sufficient cohesive strength due to a larger area of mutual contact between the particles during their deformation.

Per the experiments made in [21] as a result, a stable process of spraying titanium wire with a microplasma jet proceeds when using a wire with a diameter of 0.3 mm. Since the possibility of the droplet detaching from the wire by the plasma jet is determined by the surface tension of the metal σ, as for titanium (σ = 1.558 J/m^2) and zirconium (σ = 1.455 J/m^2) these values are very close, so for applying a coating of zirconium alloy KTC-110, was also used a wire with a diameter of 0.3 mm.

During microplasma sputtering, the degree of porosity of the coating depends on the volume fraction of the weak phase and the speed of the particles at the time of their contact with the substrate. Thus, the most dense structures with minimal porosity are formed from completely melted particles that have a sufficient speed to deform into a disk-like shape upon impact with the filing of the surface. Since the volume fraction of the insufficient phase in the particles increases with the temperature of the plasma current, it must be made as small as possible to increase the porosity.

The temperature of the plasma jet is determined by the strength of the current I, the voltage of the plasma arc U and the consumption of the plasma-forming gas G_{pl}, but the variation of these parameters is only possible within certain limits. So, with a current below 16 A, the amount of heat will be insufficient to ensure the process of melting and dispersing sprayed wires of a certain diameter, and the consumption of plasma-forming gas for the KTC-110 alloy must be at least 160 l/h, and for the VT1-00 alloy – at least 140 l/h At a spraying distance H of less than 40 mm, the dispersed particle will not have time to reach a speed sufficient enough to be fixed on the substrate by the time it collides with it, and overheating of the forming coating will also occur due to the influence of the plasma jet. The specified restrictions determine the limit parameters of the process, which allow obtaining a coating with maximum porosity (Table 1).

Table 1

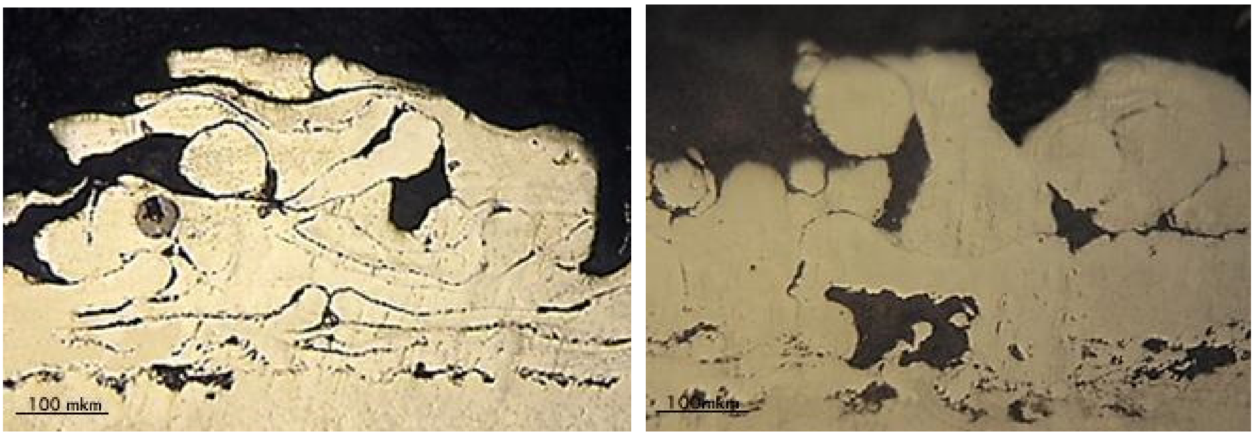
Parameters of the modes of microplasma spraying of wires

Wire material		VT1-00 (sub layer)	VT1-00 (coating)	KTC-110 (sub layer)	KTC-110 (coating)
Current strength (I), A		24	16	26	16
Plasma arc voltage (U), B		30	40	31	30
Gas consumption, l/h	Plasma-forming, (G_{pl})	220	140	160	160
	Protective, (G_p)	600	600	600	600
Spraying distance (H), mm		50	40	40	40
Wire feed speed (V_w), m/min		4.3	3.0	4.8	2.9

The voltage of the plasma arc is automatically regulated by the microplasmatron depending on the current strength and consumption of the plasma-forming gas, and therefore is a concomitant parameter of the process.

The speed of feeding the sprayed wire V_w into the interelectrode gap depends on the one hand on the power of the plasma jet, and on the other hand on the diameter of the wire and the thermophysical properties of the material. Since the melting temperature of zirconium (T_f = 1855 °C) is slightly higher than the corresponding melting temperature of titanium (T_f = 1672 °C), the feed rate of the KTC-110 alloy wire was assumed to be slightly lower for the minimum possible amount of heat released by the plasma jet, knife for VT1-00 alloy.

A structure analysis was made on the specimens of the obtained coatings, to determine the degree of porosity using an optical technique (image analysis method) according to ASTM E2109-01(2014) [22], which consists in determining the ratio of the area accounted for by the pores to the entire surface area. The digital image of the coating structures (Fig. 1) was processed using Image-Pro Plus software (Media Cybernetics, USA), which allows measuring the porosity content by highlighting inclusions that differ in color and brightness.



a *b*

Fig. 1. The structure of microplasma coatings with maximum porosity:
a – from KTC-110 alloy; b – from alloy VT1-00.

According to the results of data processing, the porosity of the KTC-110 alloy coating is 20.3 % with the size of the largest pores in the range of 80–230 μm, and the control specimens of the VT1-00 alloy coatings had a porosity of 25.0 % with the size of the largest pores in the range of 50–200 microns. Therefore, according to the investigated indicators, the obtained coatings are suitable for use on the surfaces of implants and endoprostheses.

However, in addition to the properties of the microstructure, biomedical coatings still have to meet certain requirements regarding their mechanical characteristics. In particular, sprayed coatings made of titanium and its alloys, which are applied to the surface of endoprostheses, in accordance with the requirements of the international quality standard ISO 13179-1:2021, must provide an indicator of adhesion strength to the base for separation σad, determined according to the ASTM C633 – 13 (2017) method, not less than 22 MPa. Therefore, to increase the adhesion strength of the coating to the base, it was applied through a pre-sprayed sublayer with a small fraction of porosity, which firmly connects to the base, and its rough surface provides adhesion to the next layer [23]. As a result, on the modes indicated in the table. 1, a sublayer of KTC-110 alloy was applied with a porosity of up to 3 % and of VT1-00 alloy with a porosity of up to 7 %.

According to the above-mentioned method of determining the adhesion strength of the grafting of gas-thermal coatings with the base at normal separation, a series of five cylindrical specimens with a diameter of 25 mm, coated on the end, with similar counter-specimens without coating, attached with glue, is subjected to axial stretching (Fig. 2) with fixation of the load, at which the destruction of the connection occurs.

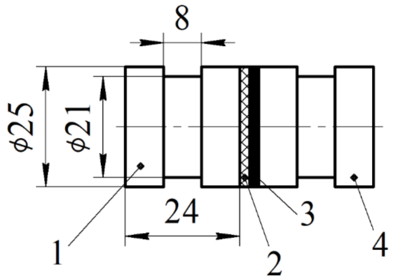


Fig. 2. Specimen placement scheme for determining the adhesion strength of the coating to the base during tear-off: 1 – specimen; 2 – coating; 3 – glue; 4 – counter-specimen

Coatings of KTC-110 and VT1-00 alloys were applied to cylindrical specimens of VT6 titanium alloy and connected to the counter-specimen using VK-9 glue (60 % epoxy resin and 40 % hardener), after which they were fixed motionless with force pressure of 5 MPa and held for at least 1 hour at a temperature of 60 °C for glue polymerization. As a result, 5 specimens with each of the coatings were obtained (Fig. 3).

a *b*

Fig. 3. Specimens for measuring the bond strength at normal separation with a coating: a – from alloy VT1-00; b – from KTC-110 alloy

A special tool was used to fix the specimens in the grips of the test setup. It has a hinged connection, which allows it to avoid bending stresses due to the eccentric application of the axial load (Fig. 4). This design of the device ensures a more uniform stress-strain state of materials in the area of contact between the coating and the base, since the axial force is applied normally to the interface between the coating and the base and simplifies the centering of the specimens during tests.

Fig. 4. Device for fixing specimens for tensile tests of coatings

Static tensile tests of pre-prepared specimens with a coating were performed on a universal mechanical machine 2054 P-5 at a speed of 2 mm/min with fixation of the maximum value of the axial force, which was observed before the destruction of the specimen (Fig. 5).

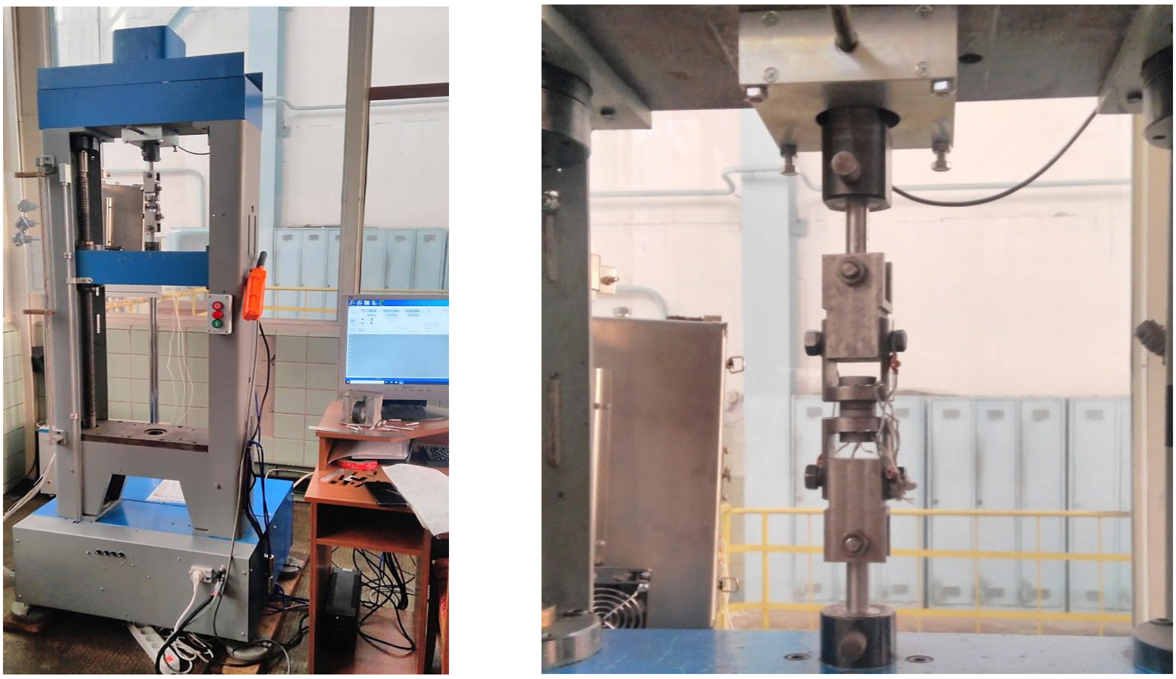


Fig. 5. Universal complex 2054 P-5 for mechanical tests with equipment for determining the adhesion strength of coatings to the base

After the connection was broken, the nature of the fracture zone was evaluated (coating-substrate, coating-glue, fracture inside the coating), as a result, it was established that the fracture of all 10 specimens occurred in the middle of the coating layer, which indicates its good adhesion to the base.

The adhesion strength of the coating at normal separation was calculated according to the formula

$$\sigma_{ad} = \frac{4P_{\max}}{\pi d^2}, \tag{1}$$

where Pmax is the maximum amount of effort achieved during the loading process; d is the diameter of the specimen.

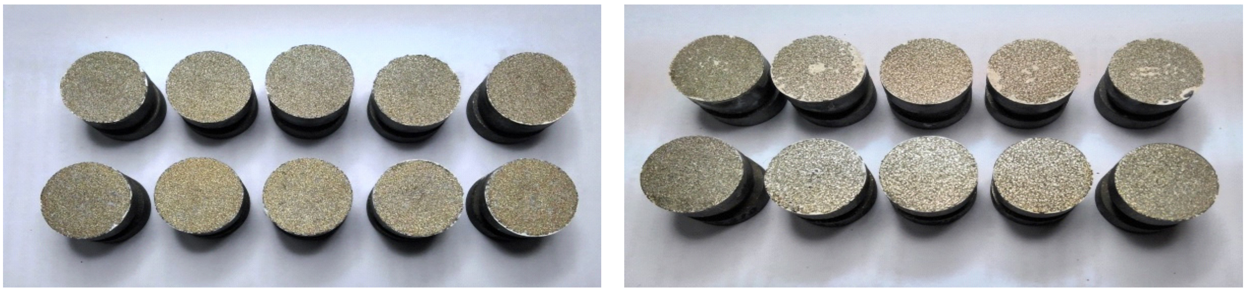
The results of the calculations (Table 2) showed that the tensile strength of the coating for the KTC-110 alloy is 23.8–32.2 MPa, and for the VT1-00 alloy – 25.8–31.2 MPa, which fully meets the requirements of the current standard ISO 13179-1:2021.

Table 2

Results of tests of specimens on the adhesion strength of coatings to the base

Specimen No.	Coating material	Force ($P_{\max}$), H	Cohesion strength (σ_{ad}), MPa
1	KTC-110	12940	26.8
2	KTC-110	15270	31.6
3	KTC-110	10440	21.6
4	KTC-110	15380	31.9
5	KTC-110	13540	28.0
6	VT1-00	14353	29.7
7	VT1-00	12894	26.7
8	VT1-00	14194	29.4
9	VT1-00	11955	24.8
10	VT1-00	15228	31.5

According to the results of the analysis of the nature of the destruction in the glue-coating-base system (Fig. 6), it was figured that the peeling of the coating from the base in all specimens is no more than 5 %, and the destruction occurred inside the coating. This indicates that the adhesion strength of the coating to the base exceeds the obtained values, and the formed porous coating on the specimens was not impregnated with an adhesive mixture to the base and interacted only with the surface, which confirms the correctness of the conducted experiment.



a *b*

Fig. 6. Coating destruction: a – from VT1-00 alloy; b – from KTC-110 alloy.

Conclusions

The limit parameters of the MPS process of wire materials, at which the coatings made of titanium and zirconium alloys will have the maximum degree of porosity were evaluated. Thus, at a current of 16 A, consumption of plasma-forming gas 140 l/h, a spraying distance of 40 mm, and a speed of feeding the sprayed wire of 3.0 m/min, it was possible to obtain a highly porous coating of titanium alloy VT1-00 with a porosity of 25.0 % and the size of the largest pores in the range of 50–200 μm, and at the consumption of plasma-forming gas 160 l/h, the speed of spraying wire 2.9 m/min and the same indicators of current strength and spraying distance – a coating made of zirconium alloy KTC- 110 with a porosity of 20.3 % and the size of the largest pores in the range of 80–230 microns.

Was confirmed that all investigated high-porous microplasma biocompatible coatings made of KTC-110 and VT1-00 alloy, which are applied through the sublayer, have the necessary adhesive strength of the bond with the base (more than 22 MPa) and meet the requirements of ISO 13179-1:2021.

References

[1] Shi H., Zhou P., Li J. et al. “Functional gradient metallic biomaterials: techniques, current scenery, and future prospects in the biomedical field” Frontiers Bioengineering and Biotechnologies, vol. 8, 2021, Article number 616845, https://doi.org/10.3389/fbioe.2020.616845

[2] Lopata L. A. “Zavisimost modulya uprugosti poroshkovyih pokryitiy ot ih poristosti pri elektrokontaktnom pripekanii” [“Dependence of the elastic modulus of powder coatings on their porosity during electrocontact sintering”], Tehnika v silskogospodarskomu virobnitstvi, galuzeve mashinobuduvannya, avtomatizatsiya [Engineering in agricultural production, industrial machine building, automation], no. 24 (p.II), pp. 91–96, 2011. [in Russian].

[3] Voinarovych S. G., Alontseva D. L., Kyslytsia O. N. et al. “Fabrication and characterization of Zr microplasma sprayed coatings for medical applications”, Advances in Materials Science, no. 2 (21), pp. 93–105, 2021, https://doi.org/10.2478/adms-2021-0013

[4] Moltasov A., Dyman M., Kaliuzhnyi S. et al. “Dependence of the elasticity modulus of microplasma coatings made of titanium grade VT1-00 and zirconium grade KTC-110 on their porosity”, Series on Biomechanics, no. 2 (36), pp. 142–153, 2022, https://doi.org/10.7546/SB.36.2022.02.14

[5] Savich V. V. “Razrabotka tehnologii izgotovleniya i konstruktsii bestsementnogo totalnogo endoproteza tazobedrennogo sustava sistemyi SLPS (Self Locking Porous System)” [“Development of manufacturing technology and design of a cementless total hip endoprosthesis system SLPS (Self Locking Porous System)”], I Sympozium Inzyneria Ortopedyczna I Protetyczna, IOP-97, Bialystok, 23–24 czerwca, 1997, pp. 515–525. [in Russian].

[6] Vilyams D. F., Rouf R., *Implantatyi v hirurgii* [Implants in surgery]. Moskow, Russia: Meditsina, 1978. [in Russian].

[7] Eliaz N. “Corrosion of Metallic Biomaterials: A Review”, Materials, no. 3 (12), Article number 407, 2019, https://doi.org/10.3390/ma12030407

[8] Kunčická L., Kocich R., Lowe T. C. “Advances in metals and alloys for joint replacement”, Progress in Materials Science, vol. 88, pp. 232–280, 2017, https://doi.org/10.1016/j.pmatsci.2017.04.002

[9] Mehboob H., Chang S.-H. “Evaluation of the development of tissue phenotypes: Bone fracture healing using functionally graded material composite bone plates”, Composite Structures, no. 1 (117), pp. 105–113, 2014, https://doi.org/10.1016/j.compstruct.2014.06.019

[10] Tumilovich M. V., Savich V. V., Shelukhina A. I. “Influence of shape and size of particles on the osseointegration of porous implants made of titanium powder”, Doklady BGUIR 2016, no. 7 (101), pp. 115–119.

[11] Kalita V. I., Mamaev A. I., Mamaeva V. A. et al. “Structure and shear strength of implants with plasma coatings”, Inorganic Materials: Applied Research, no. 3 (7), pp. 376–387, 2016, https://doi.org/10.1134/S2075113316030102

[12] Liu W., Liu S., Wang L. “Surface modification of biomedical titanium alloy: Micromorphology, microstructure evolution and biomedical applications”, Coatings, vol. 9, Article number 249, 2019, https://doi.org/10.3390/coatings9040249

[13] Matassi F., Botti A., Sirleo L. et al. “Porous metal for orthopedics implants”, Clinical Cases in Mineral and Bone Metabolism, no. 2 (10), pp. 111–115, 2013.

[14] Civantos A., Dominguez C., Pino R. J. et al. “Designing bioactive porous titanium interfaces to balance mechanical properties and in vitro cells behavior towards increased osseointegration”, Surface and Coatings Technology, vol. 368, pp. 162–174, 2019, https://doi.org/10.1016/j.surfcoat.2019.03.001

[15] Matuła I., Dercz G., Barczyk J. “Titanium/Zirconium functionally graded materials with porosity gradients for potential biomedical applications”, Materials Science and Technology, no. 9 (36), pp. 972–977, 2020, https://doi.org/10.1080/02670836.2019.1593603

[16] Shi H., Zhou P., Li J. et al. “Functional gradient metallic biomaterials: techniques, current scenery, and future prospects in the biomedical field”, Frontiers Bioengineering and Biotechnologies, vol. 8, Article number 616845, 2021, https://doi.org/10.3389/fbioe.2020.616845

[17] Oh I.-H., Nomura N., Masahashi N., Hanada S. “Mechanical properties of porous titanium compacts prepared by powder sintering”, Scripta Materialia, no. 12 (49), pp. 1197–1202, 2003. https://doi.org/10.1016/j.scriptamat.2003.08.018

[18] Nomura N., Oh I.-H., Hanada S. et al. “Effect of nitrogen on mechanical properties of porous titanium compacts prepared by powder sintering”, Materials Science Forum, vols. 475–479, pp. 2313–2316, 2005. https://doi.org/10.4028/www.scientific.net/MSF.475-479.2313

[19] Long M., Rack H. J. “Titanium alloys in total joint replacement – A materials science perspective”, Biomaterials, no. 18 (19), pp. 1621–1639, 1998, https://doi.org/10.1016/S0142-9612(97)00146-4

[20] Borisov Yu. S., Kyslytsia O. M., Voinarovych S. G. et al. “Investigation of plasmatron electric and energy characteristics in microplasma spraying with wire materials”, The Paton Welding Journal, no. 9, pp. 18–22, https://doi.org/10.15407/tpwj2018.09.04

[21] Borisov Yu. S., Kyslytsia A. N., Voinarovych S. G. “Peculiarities of the process of microplasma wire spraying”, The Paton Welding Journal, no. 4, pp. 21–25, 2006.

[22] Wejrzanowski T., Spychalski W., Różniatowski K., Kurzydłowski K. “Image based analysis of complex microstructures of engineering materials”, International Journal of Applied Mathematics and Computer Science, no. 1 (18), pp. 33–39, 2008. https://doi.org/10.2478/v10006-008-0003-1

[23] Borisov Yu. S., Harlamov Yu. A., Sidorenko S. L., Ardatovskaya E. N. *Gazotermicheskie pokryitiya iz poroshkovyih materialov* [Gas-thermal coatings from powder materials]. Kiev, Ukraine: Naukova dumka, 1987. [in Russian].