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MICROPLASMA SPRAYING OF COATINGS USING ZIRCONIUM WIRE

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ABSTRACT

The work is devoted to studying the process of microplasma spraying of coatings from zirconium wire. Technological possibility of formation of porous biocompatible Zr-coatings with bulk porosity in the range from 2 to 20 % and up to 300 μm size is demonstrated. It is shown that controlling the content of bulk porosity in Zr-coating allows changing elasticity modulus, reducing it by 14 times compared to the source cast material that allows getting closer to a bone modulus and reducing the stress shielding effect. The values of the adhesion strength of Zr-coating to the base from an alloy of VT6 grade were determined, its average value being higher than 26.9 ± 4.7 MPa and meeting the international requirements of ISO 13179-1:2021. Based on the obtained investigation results, the values of technological parameters were established for spraying of biocompatible Zr-coatings by the method of microplasma spraying of the wire from KTTs-110 grade alloy that allows forming functional coatings on the surface of different types of endoprostheses, which will provide a stronger and more reliable bonding of the endoprosthesis with the osseous tissue.

KEYWORDS: microplasma spraying, zirconium coating, endoprostheses, porosity, adhesion

INTRODUCTION

The development and application of biocompatible materials intended for using as substitutes for biological tissues and organs are one of the primary tasks of the modern materials science and medicine. Nowadays, in the world medical practice, metallic endoprostheses with a porous Ti-coating are most widely used [1]. Hip joint endoprostheses with Ti-coating on their surface are manufactured by well-known world manufacturers, including Procter & Gamble, DePuy, Stryker and are used as systems of cementless fixation in trauma medical practice [1, 2]. Nowadays, such cementless systems are implanted to patients of all ages and are getting ever more widespread due to the presence of a network of pores of a complex shape and a developed surface morphology, which promotes germination of osseous tissue, providing a reliable secondary fixation of an endoprostheses with a bone. An ingrowth of osseous tissues in the implant pores is a continuous process, which leads to the formation of three-dimensional lattices and a partial or complete filling of a porous space in Ti-coating [3, 4].

Analysis of literature sources shows different opinions regarding the optimal size of the coating pores for the implant surfaces. One of the researchers who dealt with the issue of establishing the regularities of the process of bone formation during implantation of hydroxyapatite ceramics with different sizes of pores to rats, were the staff scientists of the I.M. Frantsevich Institute of Materials Science of the NASU. In their research works, they used samples with pores in the ranges of 20–45, 80–150, 150–350 and 600–800 μm. According to the authors, more intense bone formation was observed at the sizes of pores of 80–150 μm [5]. The authors of [6] also showed that for a successful ingrowth of blood vessels it is necessary to provide the size of a pore of at least 150 μm.

However, from the results of the literature analysis, it is impossible to make a clear conclusion about the optimal size of pores, since this value is probably significantly dependent on the research conditions. Thus, in the range of 25–500 μm pores, the most positive effect on fixation and growth of pore cells was manifested by the pores of 25 and 200 μm, in the range of 85–325 μm — 325 μm, in the range of 75–900 μm — 400 μm, and in the case of studying a range of 300–1000 μm, the best fixation and growth of cells occurred at 600 μm [7].

In [8], the authors conducted studies on laboratory animals to determine the adhesion strength of cylindrical implants, made of a porous coating produced from titanium powder of different fraction, with adjacent osseous tissues. They showed that within 2–3 months, the shear strength reaches a maximum of 17–18 MPa in the range of pores sizes of 100–300 μm. At the same time, the pore larger than 300 μm reduced the adhesion strength of a bone with the implant. In addition, it was shown that the adhesion strength of

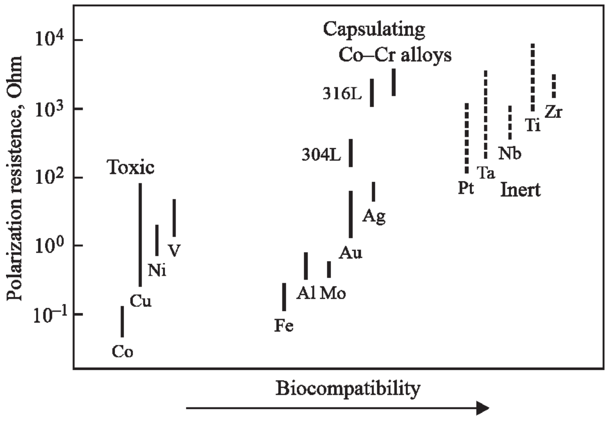

Figure 1. Relationship between polarization resistance and biocompatibility of pure metals, Co–Cr alloys and stainless steel [9]

the implants with an osseous tissue, on the surfaces of which, coatings from spongy particles were produced, having a microporous surface, is by 8–11 % higher than that in the implants produced from spherical powders. This is explained by the fact that in the case of a contact of the coating formed from spongy particles with an osseous tissue, a more closer bonding is formed due to a complex and developed configuration of a porous space.

In recent decades, there is a growing interest to more advanced materials that can be used in the manufacture of endoprostheses. One of such materials is zirconium that has high corrosion resistance, electrolytic neutrality and a necessary mechanical strength. Currently, taking into account the high biocompatibility of zirconium (Figure 1), the prospect of this material for using in the manufacture of endoprosthesis is considered [10].

According to the available literature data on the practical use of zirconium and alloys on its base, they are bioinertic materials that do not suppress the growth of osseous and soft tissues, and also do not cause visible morphological changes in inner organs [11].

At the same time, despite the progress in the use of zirconium and its alloys in the medical practice, insufficient attention is paid to the study of zirconium coatings and technologies of their spraying on the surfaces of different endoprostheses. One of such technologies that can be used to form biocompatible coatings on the surfaces of endoprostheses is microplasma spraying (MPS), developed by scientists of the PWI of the NASU [12, 13].

The aim of the work is to investigate the process of microplasma spraying of coatings from Zr-wire with the evaluation of the impact of MPS parameters on the structure, as well as mechanical characteristics of produced coatings, such as elasticity modulus and adhesion strength of a coating with a base.

EQUIPMENT, MATERIALS AND RESEARCH PROCEDURES

To conduct studies, the coatings were sprayed from Zr-wire of a solid cross-section of grade KTTs-110 with a diameter of 0.3 mm, on the surfaces of the samples from VT6 alloy. The chemical composition of the wire is shown in Table 1. Previousy, the surface of the samples was subjected to gas-abrasive treatment using a normal electrocorundum of grade 25AF-30 according to GOST 28818–90 at compressed air pressure of 0.6 MPa.

The Zr-wire spraying was carried out in the MPN-004 installation for microplasma spraying. This installation is designed for spraying wear-resistant, corrosion-resistant, thermal protective, biocompatible, decorative and other types of coatings used in various fields of engineering.

The MPN-004 installation consists of a power source and a panel for current, gas consumption and wire feed rate control. The plasma jet is formed by the microplasmatron of the original design using argon gas of the highest or the first grade. The feed of spraying wire materials is provided by the MP-04 feed mechanism, which is placed on the casing of the microplasmatron. The temperature mode of operation of the casing parts of the microplasmatron is provided by an autonomous cooling unit.

To carry out the experiments, in order to evaluate the influence of MPS parameters on the structure formation of zirconium coatings, the method of multifactorial planning of the experiment with a half-replica 2^{4-1} was chosen. As independent variable factors, current strength, plasma gas consumption, spraying distance and wire feed rate were chosen.

The microstructure and surface morphology of the produced Zr-coatings were studied in a scanning electron microscope SEM 515 (Philips, the Netherlands).

For the qualitative and quantitative analysis of a bulk porosity, an optical procedure (image analysis method) was used, which consists in determination of the area proportion, that contains detected pores, to the entire cross-sectional area of the coating. Digital images were processed with the use of Image-Pro Plus software (Media Cybernetics, USA), which allows measuring porosity (identifying inclusions that

Table 1. Chemical composition of Zr-wire of KTTs-110 grade, wt.%

Zr	Nb	Hf	Fe	Ca	O	Si	Ni	C	Cr
99.5	0.9–1.1	0.01	0.05	0.03	0.11–0.14	0.02	0.02	0.02	0.02

Table 2. Matrix of planning the experiment of MPS from Zr-wire

Mode number	*I*, A	Q_{pl}, l/h	*H*, mm	V_w, m/min
1	26	240	120	4.8
2	26	240	40	2.9
3	26	160	120	2.9
4	26	160	40	4.8
5	16	240	120	2.9
6	16	240	40	4.8
7	16	160	120	4.8
8	16	160	40	2.9

differ in color and brightness) and determining the percentage of pores in the cross-sectional area of the coating.

Mechanical measurements of the adhesion strength of the coatings to the base were carried out by the method of a normal separation according to the adhesive procedure using VK-9 glue (Khimprom, Ukraine) in accordance with the ASTM C633-13(2021) standard in a mechanical rupture machine MTS318.25 (MTS Systems Corporation, USA) (Figure 2).

The procedure of studying the dependence of elasticity modulus on bulk porosity of the coating consisted in the three-point bending of coated samples when the coating is in the compression and in the tension zones and by recording the load diagram. The functional relationship between porosity and elasticity modulus of the coating was established by constructing linear regression curves by the method of least squares, a more detailed description of the procedure is presented in [14].

Figure 2. MTS318.25 testing complex with fixed Zr-coated samples

RESEARCH RESULTS AND DISCUSSION

To study the structure and bulk porosity of microplasma coatings from Zr-wire, coated samples were produced according to the matrix of the mathematical planning of the experiment (Table 2).

Analysis of the microstructure of the surfaces of the microplasma zirconium coatings showed that de-

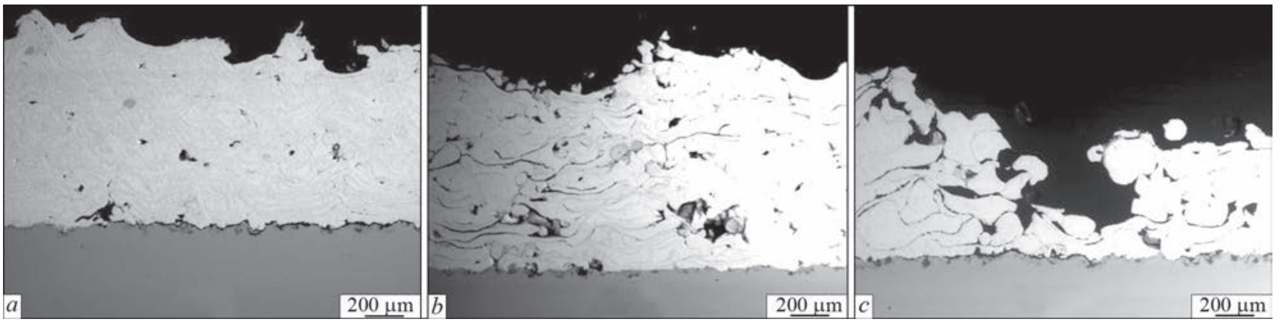

Figure 3. Microstructure of zirconium coating: *a* — mode 4; *b* —7; *c* — 8

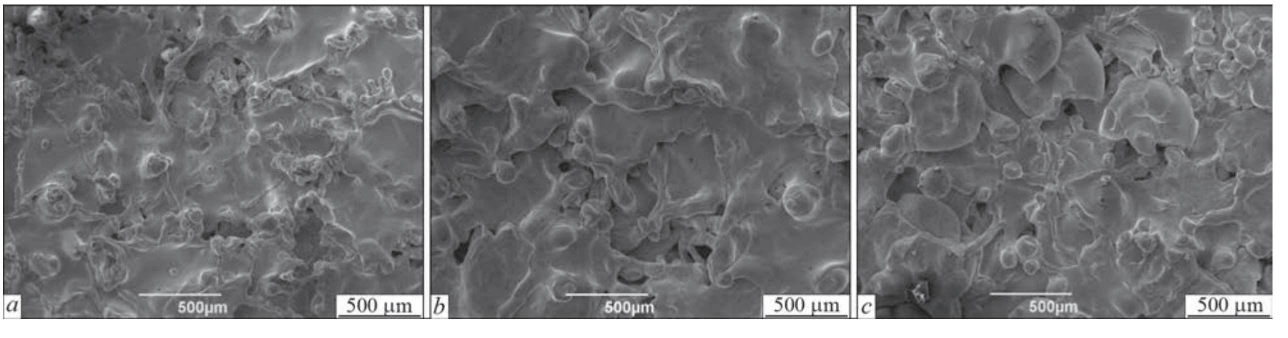

Figure 4. Morphology of zirconium coating surface: *a* — mode 4; *b* — 7; *c* — 8

Table 3. Average value of porosity of microplasma Zr-coatings depending on mode MPS parameters

Mode number	1	2	3	4	5	6	7	8
Porosity, %	3.5±0.14	4.0±0.02	6.0±0.4	2.8±0.1	8.7±0.78	3.6±0.14	8.3±0.72	20.3±2.0

pending on the technological mode of spraying, the coatings can be divided into 3 groups (Figures 3, 4):

1. If, when approaching the base, the particles are completely molten, then depending on their velocity, temperature before the impact, degree of their deformation and crushing during layering, the structures, shown in Figure 3, *a* can be formed. Such dense structures are formed from completely molten particles and have a typical, in most cases, lamellar structure (modes Nos 1, 2, 4, 6).

2. If, when approaching the base, together with the molten particles, the particles that began to solidify are present, then the structures are formed, which are characterized by lamellas of a greater thickness than in the structures of the 1st group, with a larger number of pores and partially deformed particles that were fixed (Figure 3, *b*). When the particles that began to solidify hit the surface of the base, the thermal and kinetic energy is not sufficient for a complete deformation of the particles, which, in the case of their significant number, leads to the formation of granular-disc-like and granular structures with the presence of pores. Such structures are typical for the coatings produced on the modes with a longer spraying distance (modes Nos 3, 5, 7).

3. If the coatings formation occurs from (partially) solidified (but those that are in a plastic state) particles and have an insignificant velocity, then the coatings are formed with a structure, that is characterized by a large number of bulk pores with a size of up to 300 μm (Figure 3, *c*). The coatings with such a structure cannot be produced in the case of forming coatings from powder materials, since a high probability of its destruction due to a low cohesive strength arises. This is explained by the presence of a significant number of unmolten particles with an insufficient volume of a liquid phase, the interaction of which does not provide strong bonds in the process of the coating formation. In the case of the wire spraying, when due to a short spraying distance and the process features, that guarantee a complete melting of sprayed particles in the plasma jet, which subsequently provides a collision of the particles with the base, that are completely or partially in the liquid phase, resulting in the formation of the coatings with a sufficient cohesive strength due to a larger area of mutual contact between the particles during their deformation.

The performed analysis of the surfaces of the produced Zr-coatings showed that the surfaces of the coatings have a developed morphology, which was formed from the molten and partially solidified particles that were fixed on the surface due to the existing liquid phase (modes Nos 4, 7, 8). Such particles provide the formation of a coating with a larger specific surface area, which contributes to the further reliable fixation of the implant in a bone.

The results of the studies of the average bulk porosity of Zr-coatings produced by the method of microplasma spraying on the modes, according to the matrix of the experiment, are presented in Table 3.

The analysis of the data on bulk porosity (Table 3) shows that the maximum values of bulk porosity of Zr-coatings produced on the mode No. 8, are 20.3 ± 2.0 %, and the pores size is in the range of 100–300 μm (Figure 4). The presence of such percentage of bulk porosity and the size of pores in the coatings on the surfaces of endoprostheses, according to literature data [1, 3], will contribute to germination of vessels to the pores of the coating, which will positively affect the formation and nutrition of an osseous tissue that will provide a reliable fixation and osseointegration of an endoprosthesis in the human body.

However, a considerable amount of bulk porosity in the coating can change the mechanical properties

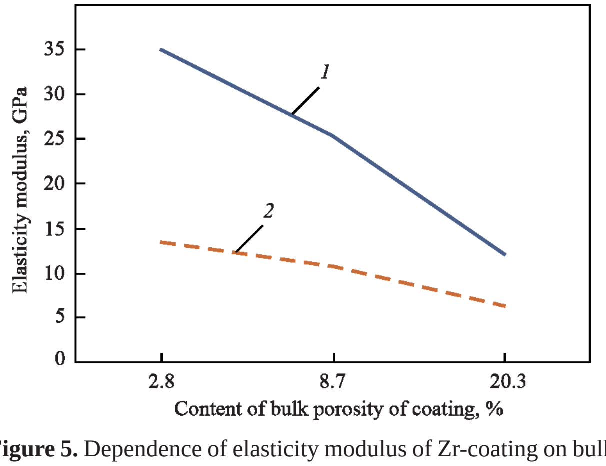

Figure 5. Dependence of elasticity modulus of Zr-coating on bulk porosity: *1* — butt; *2* — tension

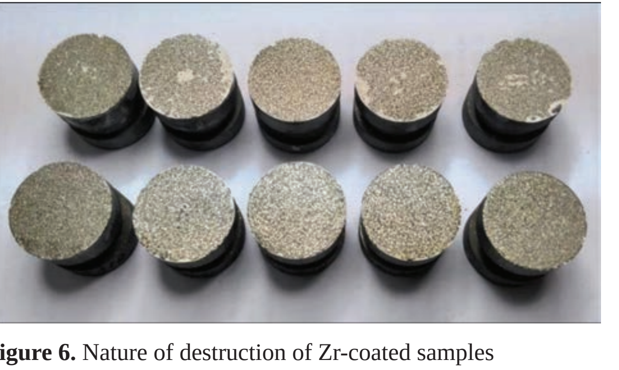

Figure 6. Nature of destruction of Zr-coated samples

of both the most formed coating as well as the entire structure as a whole [3]. From literature sources it is known that for some ceramic, metal and metal-ceramic materials, the value of bulk porosity significantly affects the value of elasticity modulus [15]. Previous studies on finding a functional relationship of bulk porosity with elasticity modulus showed that elasticity modulus of microplasma Zr-coatings depends on bulk porosity (Figure 5) [14]. An increase in bulk porosity of the coating allows changing elasticity modulus of Zr-coating, reducing it in the range: 13.5–6.5 GPa (tension) and 35–12 GPa (compression).

From the abovementioned it can be concluded that by changing the value of bulk porosity, it is possible to influence elasticity modulus of the coating and approach it to a bone modulus, which is 0.2–18 GPa [15]. This will provide a reduction in the stress shielding effect, that affects a bone resorption and ultimately will provide a more reliable fixation of a metal implant [16].

With an increase in coating bulk porosity, its mechanical properties are accordingly reduced, but they should meet certain requirements. In particular, for titanium coatings on the surfaces of endoprostheses, in accordance with the requirements of the international standard of quality ISO 13179-1:2021, the average static adhesion peel strength of the coating with the base should be greater than 22 MPa.

The obtained result of the study and calculation of the average adhesion strength of the microplasma zirconium coatings, sprayed (mode No. 8) to the base of VT6 alloy, is 26.9 ± 4.7 MPa. After mechanical tests, the zones of destruction of the coating–counter sample were evaluated (Figure 6), that showed the destruction occurs in the middle of the coating layer. The amount of the coating left on the surface of the base is more than 95 %. Therefore, the obtained value characterizes the cohesive strength of the coating. This indicates that the value of the average adhesion strength of the microplasma zirconium coating, sprayed to the titanium base, exceeds 26.9 ± 4.7 MPa and meets the requirements of ISO 13179-1:2021.

CONCLUSIONS

1. As a result of the analysis of literature data, the prospect of using Zr-coatings on the surfaces of parts of endoprostheses contacting with a bone, and the requirements for the coatings microstructure were determined.

2. The technological feasibility of forming porous coatings from Zr-wire with the adhesion strength of more than 26.9 ± 4.7 MPa with the base from VT6 alloy with the porosity from 2.8 to 20.3 % and the size of pores of up to 300 μm was shown.

3. It was found that controlling the content of bulk porosity of Zr-coating, it is possible to change elasticity modulus, reducing it by 14 times from the source material, which allows approaching the modulus of a bone and reducing the stress shielding effect, which will make possible to use these coatings on the surfaces to provide a more reliable and stronger adhesion between the implant and a bone.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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