

Microplasma spraying of hydroxyapatite coatings on additive manufacturing titanium implants with trabecular structures

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This paper presents new results of microplasma spraying (MPS) of laboratory-synthesized hydroxyapatite (HA) powder coatings onto trabecular substrates obtained by selective laser melting (SLM) of a certified titanium medical alloy powder. The aim of the study was to establish the possibility of combining the technologies of MPS and additive manufacturing (AM) for the possible production of custom-designed implants with increased surface biocompatibility, as well as to establish the MPS parameters that ensure chemical purity of the HA coating and satisfactory adhesion of the coatings to the substrate. The structural-phase compositions of the initial HA powder and the plasma-sprayed HA coating were studied by X-ray diffraction analysis and transmission electron microscopy, and the adhesion strength of the coating was tested according to the F1147 standard of the American Society for Testing and Materials (ASTM). The main results of the study are the following: the application of the MPS technology for HA coating with an average thickness of $150 \pm 50 \mu\text{m}$ on trabecular substrates obtained by the SLM method has been shown. The parameters of MPS of HA coatings onto titanium implants with a trabecular surface have been established. It is also proved that using the appropriate MPS parameters, it is possible to obtain a HA coating with a 95% level of HA phases, 93% level of crystallinity, and the adhesion strength to the trabecular substrate of $24.7 \pm 5.7 \text{ MPa}$, which complies with the requirements of the international medical standard (International Organization for Standardization [ISO] 13779-2:2018). These results are of significance for a wide range of researchers developing plasma spray technologies for the manufacture of biocompatible coatings.

Keywords: *additive manufacturing (AM), implants, trabecular surface, microplasma spraying (MPS), selective laser melting (SLM), hydroxyapatite (HA)*

1. Introduction

Nowadays, small-scale production of customized medical implants and prototyping have become more accessible owing to additive manufacturing (AM). AM is a type of manufacturing technology in which materials such as powder, plastic, or metal are applied layer by layer to produce a 3D model from a computer-aided design (CAD) model [1]. This method differs from traditional manufacturing techniques in that instead of

removing material – as in computerized numerical control (CNC) machining of an implant, for example – it adds materials layer by layer. It can be said that AM is the process of selectively combining materials to manufacture objects in a layer-by-layer manner using digital information about the parts, i.e., 3D CAD models [2]. AM is often referred to as 3D printing (3DP), rapid prototyping (RP), or stereolithography.

AM allows the design and manufacture of personalized prostheses and implants; it is also used to produce microporous structures with controlled

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pore size. Biocompatibility is an important consideration when choosing materials for medical implants. The tissues of the human body interact with most foreign materials upon contact. In some cases, this leads to rapid destruction of the foreign material; in others, it can lead to tissue damage. Preference is given to choosing materials that are biocompatible, meaning that they do not damage tissues and their rate of degradation is either extremely slow or controlled.

An essential aspect related to the choice of materials for medical orthopedic and dental implants, which must grow into the patient's bone, is the requirement to provide a certain porosity of the endoprosthesis. Firstly, the presence of pores of a certain size and configuration provides a structure similar to bone and increases the surface area of the implant, which makes it easier for bone tissue to penetrate into the pores of the implant, enhancing the osseointegration of the implant after implantation; secondly, by changing the number of pores, it is possible to control the modulus of elasticity and the stiffness of the implant; thirdly, the weight of the implant can be reduced. The porous structures of the implant are effectively produced by AM, while the layered character inherent in AM processes allows the design and manufacture of an implant with gradient porosity [3]. It should also be noted that new methods for measuring the porosity of 3D-printed medical products using micro-computed tomography are currently being developed, as in the study by Asghari Adib et al. [4], to characterize gelatin methacryloyl (GelMA)-based biomaterials for intracorporeal AM of tissue engineering scaffolds. Such precise control of porosity is very important for the development of implant-manufacturing technologies, since the mechanical properties of the specimens depend on the direction of force application in relation to the direction of 3D printing, and the porosity of the internal structure affects the tensile strength of the product.

The main biocompatible metal materials for AM porous orthopedic and dental implants are titanium alloys, including powder alloys for selective laser melting (SLM) [5]. The SLM method also makes it possible to obtain implants directly from hydroxyapatite (HA) and various biocompat-

ible ceramics. HA is the main inorganic component of mammalian bones, which provides it with properties such as biocompatibility and osseointegration with bone tissue. A systematic characterization of 3D-printed bone scaffolds from composite powders of HA and polyvinyl alcohol (PVOH) is presented by Cox et al. [6]. This method is considered promising because it facilitates osteoconduction and osseointegration in vivo.

One of the challenges for the widespread introduction of additively manufactured metal or ceramic implants is the fact that all of the above materials have high melting points and are quite expensive, as are the equipment for their SLM – which is currently the main AM technology for the manufacture of trabecular structures – for patient-specific metal implants.

The challenge for medical implantologists in general is the problem of engraftment of the implant in the patient's body [7]. One of the reasons for the rejection of the endoprosthesis by the patient's body is bone tissue necrosis (which occurs when the implant surface is destroyed and deformed and metal particles penetrate into the surrounding body tissues, or due to the development of periprosthetic bacterial infections), which limits the use of modern implants [8]. The implant surface is the first to come into contact with living tissue when the implant is placed in the human body; therefore, the initial reaction of living tissue to the implant material depends on the properties of its surface. The surface treatment of the implant should ensure its nontoxic and antibacterial properties, and at the same time, the implant should provide osteoconductivity and osseointegration in order to reduce patient recovery time and extend the life of the implant [9].

One of the important modifiable properties of the surface of orthopedic implants is the porosity of the surface layers of the implant. A number of studies of the influence of the average pore size, bulk porosity, thickness, and other parameters of biocompatible coatings made of various materials on the osseointegration of orthopedic implants have shown that the use of thick (from 50 μm to 700 μm) porous coatings makes it possible to ensure reliable fixation of the implant in tissues by increasing

the contact area with bone tissues [10]. Such coatings have a structure similar to bone, which allows the penetration of bone tissue into the pores of the implant. The surface roughness of the implant also affects the response of cells and tissues; increased roughness increases the surface area of the implant adjacent to the bone and, accordingly, the number of osteoblasts on it, thereby improving the fixation of the implant in the bone [11].

In recent years, studies have been carried out on the possibility of using thermal plasma spraying of powders or wires of refractory materials for AM coatings of implants. For example, Kalita *et al.* [12] reported the production and successful clinical trials of titanium implants with 3D bioactive plasma titanium coating in dogs. Kussaiyn-Murat *et al.* [13] used an industrial robotic arm for microplasma layer-by-layer spraying of tantalum coatings on a titanium implant, ensuring the movement of the robot along a 3D model obtained by scanning the implant surface. There is still a steady interest in increasing the biocompatible properties of the surface of metal implants using coatings from materials based on calcium phosphate [14]. HA-coated implants show a promising combination of the mechanical properties of metals and the various biofunctions inherent in calcium phosphate-based bioceramics [15].

The formation of a thermal plasma coating is characterized by the ingress on the implant surface of a large number of particles more or less melted in the plasma jet, forming so-called splats, between which pores are formed. In this case, the porosity and roughness of the coating surface depend on the size, rate, and degree of melting of the particles constituting it [16]. The pore size is affected by both the actual size of the coating particles and their shape [17]. Understanding the mechanisms of coating formation makes it possible to select specific parameters of thermal plasma spraying to obtain the required coating microstructure. Currently, thermal plasma spraying techniques are widely used in applications related to the metal-working industry [18], but for the biomedical field, this is an innovative issue with potential that is currently being explored [19]. Thus, thermal plasma spraying is a suitable method for obtaining coat-

ings of refractory metals or ceramics, providing the melting of material particles in a plasma jet, but at the same time, treatment of the surface of an implant with a plasma jet can lead to its volumetric heating, causing deformation of the implant during cooling. Therefore, the choice of parameters for thermal plasma spraying of coatings from biocompatible materials on medical implants requires scientific justification in order to impart the required properties to the implant surface (increased biocompatibility), avoid overheating, and, at the same time, effectively use rather expensive coating materials. Heating and deformation can be especially noticeable for a small-sized porous implant, such as a 3D-printed titanium intervertebral disk with a trabecular structure, since titanium has a relatively low thermal conductivity and thin septa of the trabecular structure can noticeably deform during thermal plasma spraying of the coating, distorting the original 3D model. The problem of bulk overheating of the implant can be avoided by using conventional thermal plasma spraying of a suspension of HA powders, as described previously [19–21], or by microplasma spraying (MPS) of HA powders [22, 23]. It is noted that the mechanical and antibacterial properties of HA coatings and their ability for bone repair depend both on the parameters of plasma spraying [19, 23] and on the composition of the coating [20–22].

Currently, one of the promising methods of thermal plasma spraying of biocompatible coatings on implants of small endoprostheses, such as, for example, details of elbow joints, dental implants, or intervertebral disks is MPS. MPS makes it possible to apply coatings of both powder and wire materials on substrates of various materials. Due to the small diameter of the spray spot, which is from 3 mm to 5 mm, the loss of the sprayed material during MPS is significantly less than with conventional thermal plasma spraying. Due to the low power of the microplasmatron, the thermal effect of the MPS process on the substrate is minimal, which makes it possible to obtain coatings on thin-walled and small-sized parts without their deformation and overheating. At the same time, MPS makes it possible to obtain porous coatings on metal endoprostheses from refractory and biocompatible met-

als (such as Ti, Ta, etc.) and alloys based on them [24], as well as ceramics (HA) [22], which also improves biocompatibility and secondary fixation of the implant due to the ingrowth of bone tissue into the coating pores. The authors of this paper have experience of successful MPS of biocompatible titanium and HA coatings on CNC-machined titanium alloy orthopedic implants [24–26] and are now studying the possibilities of MPS of HA coatings on the trabecular surfaces of titanium implants manufactured by the AM method (specifically SLM) in order to combine the advantages of these two modern and promising technologies for the manufacture of patient-specific implants with increased surface biocompatibility for medical application in the future.

The goal of the study was to establish the possibility of combining the technologies of MPS and AM for the possible production of custom-designed implants with increased surface biocompatibility, as well as to establish the MPS parameters that would ensure the chemical purity of the HA coating and satisfactory adhesion of the coatings to the substrate.

2. Materials and methods

Trabecular implant parts (Figure 1A) and trabecular honeycomb substrates (Figure 1B) were fabricated according to their 3D computer models by SLM of certified Ti6Al4V titanium alloy (powder) (Table 1) using an AM system for metal products, namely, Mlab cusing R (Concept Laser, Lichtenfels, Germany). Ti6Al4V alloy is a Grade 5 titanium alloy (according to International Organization for Standardization [ISO] 5832-3) and is classified as Type 4 (according to ISO 22674).

The parameters of the SLM process for all specimens, including the adhesion test specimens, were as follows: the laser power was equal to 95 W, the wavelength was 1,070 nm, the printing speed and the scanning speed were equal to 5 cm³·hr^{−1} and 800 mm·s^{−1}, respectively. Moreover, the average titanium powder particle size varied from 5 μm to 63 μm, and the layer thickness was 25 μm. The SLM parameters were chosen in accordance with the recommendations of the manufacturer of

Table 1. Chemical composition of Ti6Al4V titanium alloy (powder) according to ISO 5832-3

Element	Wt.% of element
Fe	<0.3
N	<0.05
O	<0.2
Al	5.5–6.75
C	<0.08
V	3.5–4.5
H	<0.015
Ti	Balance

ISO, International Organization for Standardization

titanium alloy powder and equipment for SLM Mlab cusing R (Concept Laser). The manufacturing method and design of a titanium implant (intervertebral disk), including a trabecular structure with a cell size of 2 mm, are currently the subjects of patenting.

Visualization of specimens with a trabecular structure and measurement of their porosity were performed using industrial computed tomography (Phoenix Vtomex M300; Waygate Technologies, Hürth, Germany) by scanning and processing data from all specimens using the VGStudioMAX software (Volume Graphics GmbH, Heidelberg, Germany), with the reconstruction of volumes by reverse engineering.

HA powder synthesized for MPS in the laboratories of D. Serikbayev East Kazakhstan Technical University was used as a spray-coating material. The process of synthesis of HA powder with chemical composition Ca₁₀(PO₄)₆(OH)₂ and with a Ca/P ratio of 1.65 by a chemical precipitation method was described in the authors' previous paper [25].

The choice of the parameters for MPS of the HA powder was based on the analysis of the results of the experiment on MPS of HA coatings on titanium substrates accomplished in a two-level fractional factorial design (2⁴-1), described in detail in the authors' previous paper [26]. The interpretation of the experimental results was carried out by regression analysis. The following parameters were selected as the variables: electric current (*I* in amperes [A]), plasma gas flow rate (*Q*, standard litre per minute [slpm]), spraying distance (*H*, millimeters [mm]) and powder feed rate (*V_{pow}*, grams per

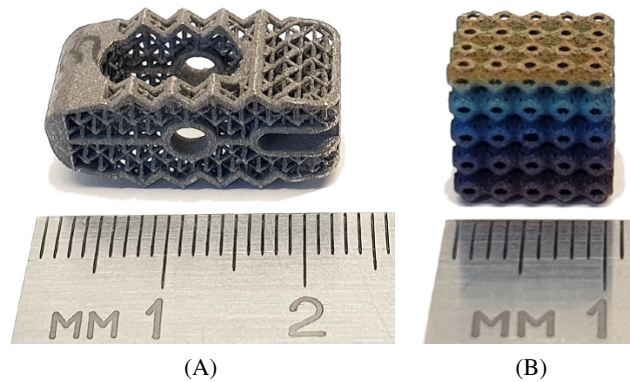


Fig. 1. Specimens of titanium trabecular substrates: detail of the endoprosthesis of the intervertebral disk (A); honeycomb structure (B)

minute [g/min]). The key criteria were the coating phase composition, the degree of crystallinity (A_{ph} – the proportion of the amorphous phase, HA_{cryst} – the proportion of the crystalline phase), and the coating transfer efficiency (CTE). In powder coating, transfer efficiency is the ratio of the mass of the sprayed coating to the mass of the sprayed material fed into the plasma jet. Thus, the CTE characterizes the efficiency of the spraying process. Material losses during thermal plasma spraying occur due to spattering, evaporation, and rebound from the substrate of the sprayed material. Transfer efficiency is provided as a percentage, with 100% being the most desirable. The results of X-ray diffraction (XRD) analysis presented in a previous paper [26] showed that the phase compositions of all microplasma-sprayed HA coatings complied with ISO 13779-2 [27]. However, the parameters indicated below provided the highest CTE (89%) for MPS of HA coating on titanium substrates after gas-abrasive treatment. Thus, for the process to be most cost-effective, allowing the desired thickness of HA coating (no less than 100 μm) in one pass of a plasma jet along the 3D-printed titanium substrate, the following values of the parameters were considered appropriate: $I=45$ A, $Q=1.0$ slpm, $H=160$ mm, $V_{pow}=0.4$ g·min⁻¹.

MPS of the HA powders was carried out using an MPS-004 microplasmatron (produced by E.O. Paton Institute of Electric Welding, Kyiv, Ukraine) [28]. The microplasmatron was mounted

on an industrial robotic arm (Kawasaki RS-010LA; Kawasaki Robotics, Akashi, Japan). It is able to move horizontally along a computed trajectory at a set speed. The speed of linear movement of the plasmatron along the substrate was chosen to be 50 mm·s⁻¹. This speed was chosen experimentally to ensure plasma spraying of a coating with uniform thickness. Experiments have shown that this speed of linear movement of the microplasmatron does not lead to disturbances in the plasma jet flow due to air resistance and, therefore, ensures the stability of the spraying process. Moreover, Ar served as a plasma-forming and transporting gas for MPS; additional heating of the substrate was not carried out. Using a robotic arm allows precise spraying of coatings with a uniform speed of movement of the plasmatron along a given trajectory and accurately maintains the spraying distance and the perpendicular alignment of the plasma jet to the substrate surface. Before MPS, the surfaces of the specimens were degreased with acetone and subjected to ultrasonic cleaning.

The study of the microstructure and assessment of coating thickness were performed using scanning electron microscopy (SEM) (JSM-6390LV; JEOL, Tokyo, Japan).

The structural-phase compositions of the HA powder and HA coating were determined using an X'Pert PRO diffractometer (PANalytical, Almelo, the Netherlands). The interpretation of the XRD patterns was carried out using the Rietveld method

and licensed data of the American Society for Testing and Materials (ASTM) card file. X'Pert HighScore Plus software (Malvern Panalytical, UK) was used to calculate the coating's impurity. Three purity measurements were carried out for each of the XRD patterns. Diffraction scans of the HA powder and coatings were carried out in accordance with ASTM F2024-10 [29].

Electron diffraction patterns of specimens of HA powder were obtained by transmission electron microscopy (TEM) on JEM-2100 (JEOL). TEM specimen preparation techniques are described in detail in a previous paper [30]. Ten TEM images were analyzed, and an average of five diffraction patterns were used to calculate the crystal lattice parameters.

The data of the structural-phase composition obtained using TEM were compared with the data obtained using XRD.

The adhesion strength of coatings to substrates was measured in a static tensile experiment according to the ASTM F1147 [31] standard using a 2054 R-5 (TechMash, Neftekamsk, Russia) universal mechanical testing complex with equipment for testing the adhesion strength of coatings to a substrate. In accordance with ASTM F1147 [31], a complete, assembled test assembly consists of two solid parts, one with a coated surface and one with an uncoated surface. The dimensions of the cylindrical test specimens (in mm) are shown in Fig-

ure 2.

The substrate area upon which the coating was applied was calculated to be $4.91 \pm 0.006 \text{ cm}^2$. The thickness of the plasma-sprayed HA coating was $150 \pm 30 \text{ }\mu\text{m}$. Coated specimens were glued with counterspecimens using a two-component viscous-flow adhesive of the VK-9 brand (Khimprom, Pervomaik, Ukraine) with immovable fixation of the specimens with a compression force of 0.01 MPa, keeping in this state at a temperature of 60°C for at least 1 hr until the glue polymerized completely. Further, the test was carried out at room temperature; five glued samples were tested, and the results were subjected to standard statistical processing. The failing stress (in megapascals) of the adhesive bond area was calculated using Eq. (1):

$$S = \frac{F}{A}, \quad (1)$$

where S – adhesion strength, F – maximum load to failure, and A – cross-sectional area.

The surface roughness of the 3D-printed cylindrical specimens was measured in accordance with ISO 21920-2 [32] using a MarSurf PS 10 profilometer (Mahr, Göttingen, Germany). Five measurements were taken for each tested specimen, and then their average was calculated.

3. Results and discussion

The results of visualization and analysis using computed tomography of titanium substrates with trabecular structure are shown in Figures 3–5 for the honeycomb structure and in Figures 6 and 7 for details of the endoprosthesis of the intervertebral disk.

According to the results of computed tomography analysis, the largest defect volume for the honeycomb structure was 0.003 mm^3 , the defect length was 0.45 mm (Figure 4), and the ratio of the volume of defects to the volume of material was 0.41% (Figure 5). The largest defect found in the endoprosthesis part (Figure 6A) had a volume of 0.04 mm^3 , with a defect length of 1.099 mm (Figure 6B), and the ratio of the volume of defects to the volume of material was 2.28% (Figure 7).

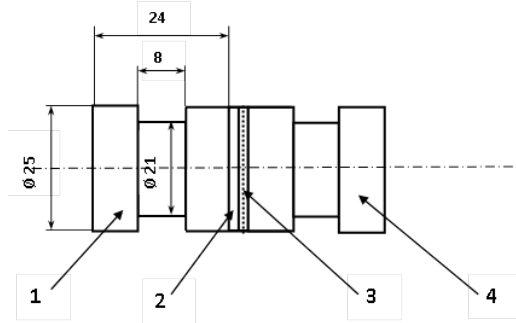


Fig. 2. Schematic representation (with dimensions in centimeters) of the assembled test assembly for testing the adhesion strength of coatings to a substrate: 1 — specimen No. 1; 2 - sprayed coating; 3 - a layer of adhesive bonding agent (a layer of glue); 4 – specimen No. 2

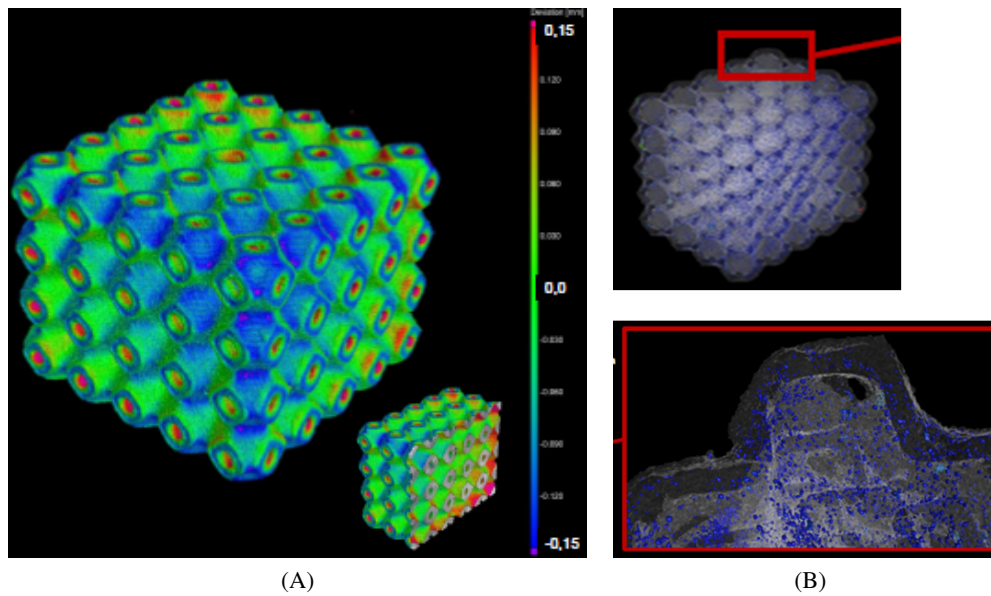


Fig. 3. Results of automated analysis with a color map of the deviations of a real specimen with a honeycomb structure from its stereolithographic (stl) model (A); visualization of the distribution of pores on a translucent three-dimensional model (B)

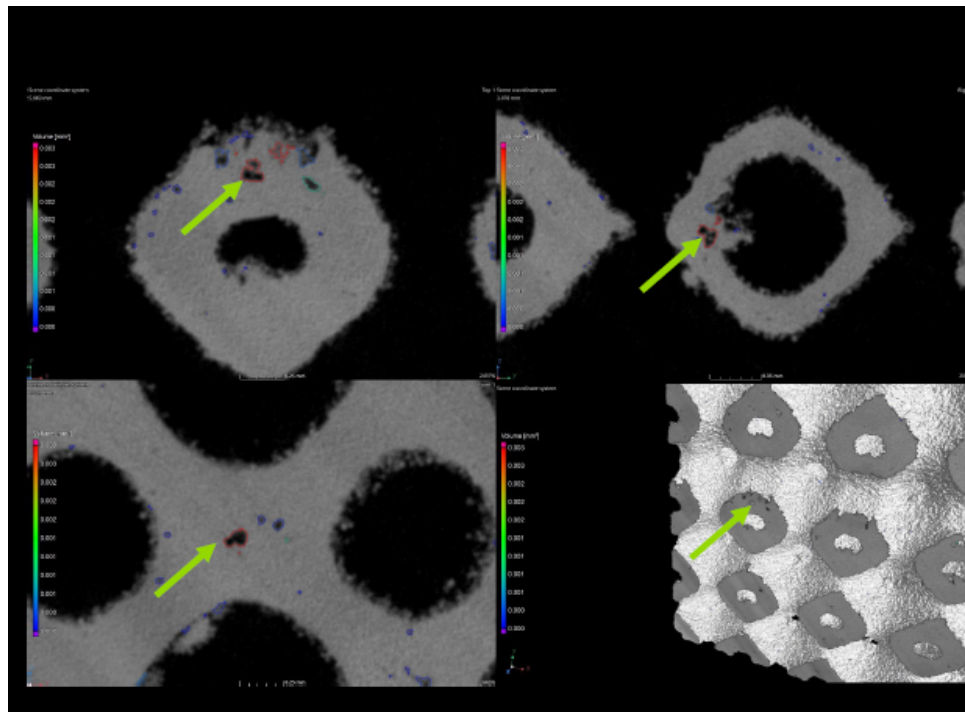


Fig. 4. Results of automated analysis of the porosity of a specimen with a honeycomb structure; the arrows indicate the largest defect found at the indicated point



Fig. 5. Results of statistics on the analysis of the porosity (number of pores by volume) of a specimen with a honeycomb structure; statistics circled in red frame

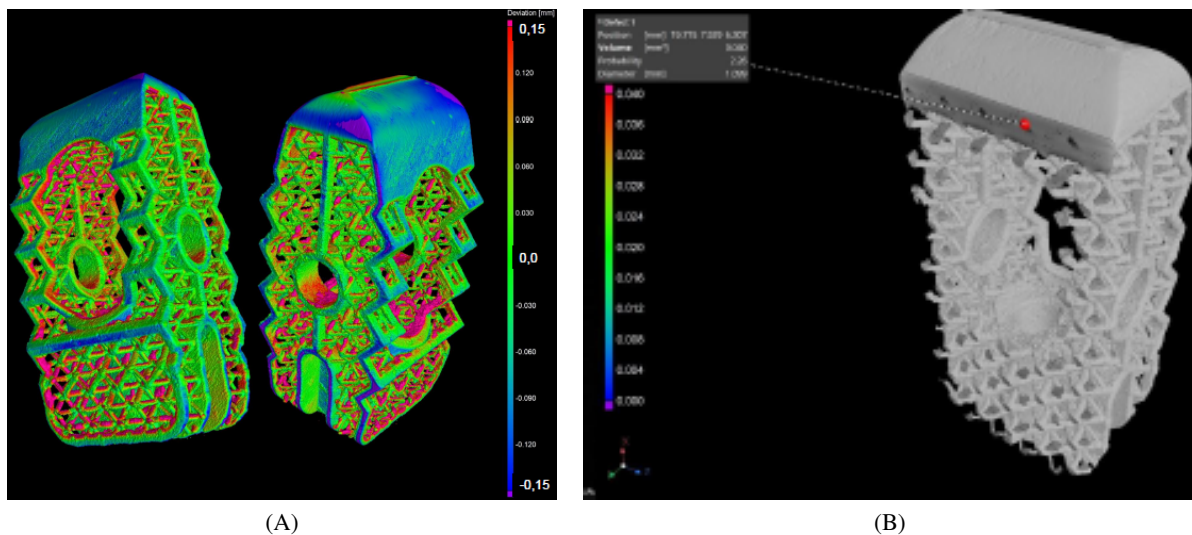


Fig. 6. Results of automated analysis with a color map of deviations of a real part of the endoprosthesis from the stereolithographic (stl) model (A); the largest defect found (B)

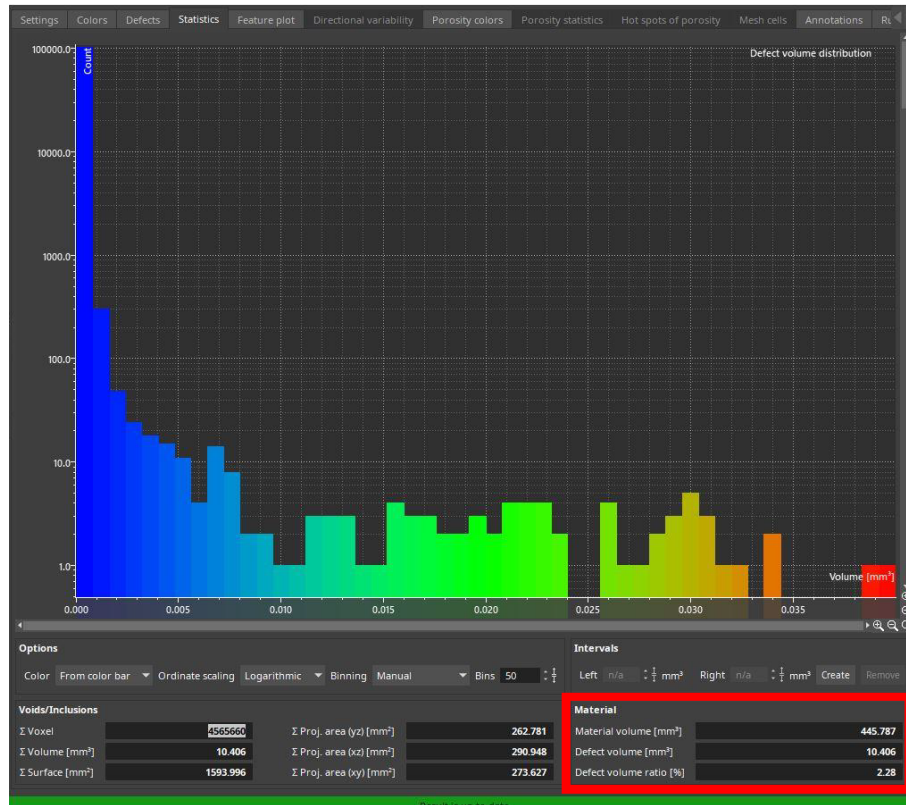


Fig. 7. Results of statistics on porosity analysis (number of pores by volume) for the part of the endoprosthesis; statistics circled in red frame

Thus, there is a good correspondence between the external and internal geometries of the cages of the 3D-printed titanium trabecular structures and their initial stereolithographic (stl) models (Figures 3 and 6A), which can further ensure the correctness of implantation and fixation of the endoprosthesis. External arbitrary porosity of the surface is important to ensure uniform growth of bone tissue. Internal porosity is critical to prevent failure of the stressed areas of the endoprosthesis. As follows from the analysis of defects, their sizes and the ratio of the volume of defects to the volume of material are insignificant; therefore, the defects are not critical for the strength of the specimens obtained by SLM of the titanium alloy powder.

The SEM and TEM images of the HA powder particles and the XRD pattern of the HA powder are presented in Figure 8.

According to results of SEM analysis (Figure 8A), the HA powder particles have irregular

shape with smooth edges; the particle size is in the range of 40–90 μm . According to results of TEM analysis (Figure 8B), the microelectron diffraction pattern corresponds to the hexagonal phase of HA with unit cell parameters respectively equal to $a = 0.94 \text{ nm}$, $b = 0.94 \text{ nm}$, and $c = 0.69 \text{ nm}$. According to the results of XRD analysis (Figure 8C), the phase composition of the initial HA powder was fully crystalline $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The percentage of crystallinity of the HA powder was calculated using the area of crystalline peaks in the region of $2\theta = 15^\circ\text{--}45^\circ$ and the area of the amorphous diffuse background in this region. The purity of HA powder and HA coatings was evaluated by calculating the areas of all non-HA peaks that were found in the diffraction pattern. The impurity area was measured by calculating the area in the region where the highest peaks of the impurity phases were present. The impurity peaks that would be expected to be present in HA powders and

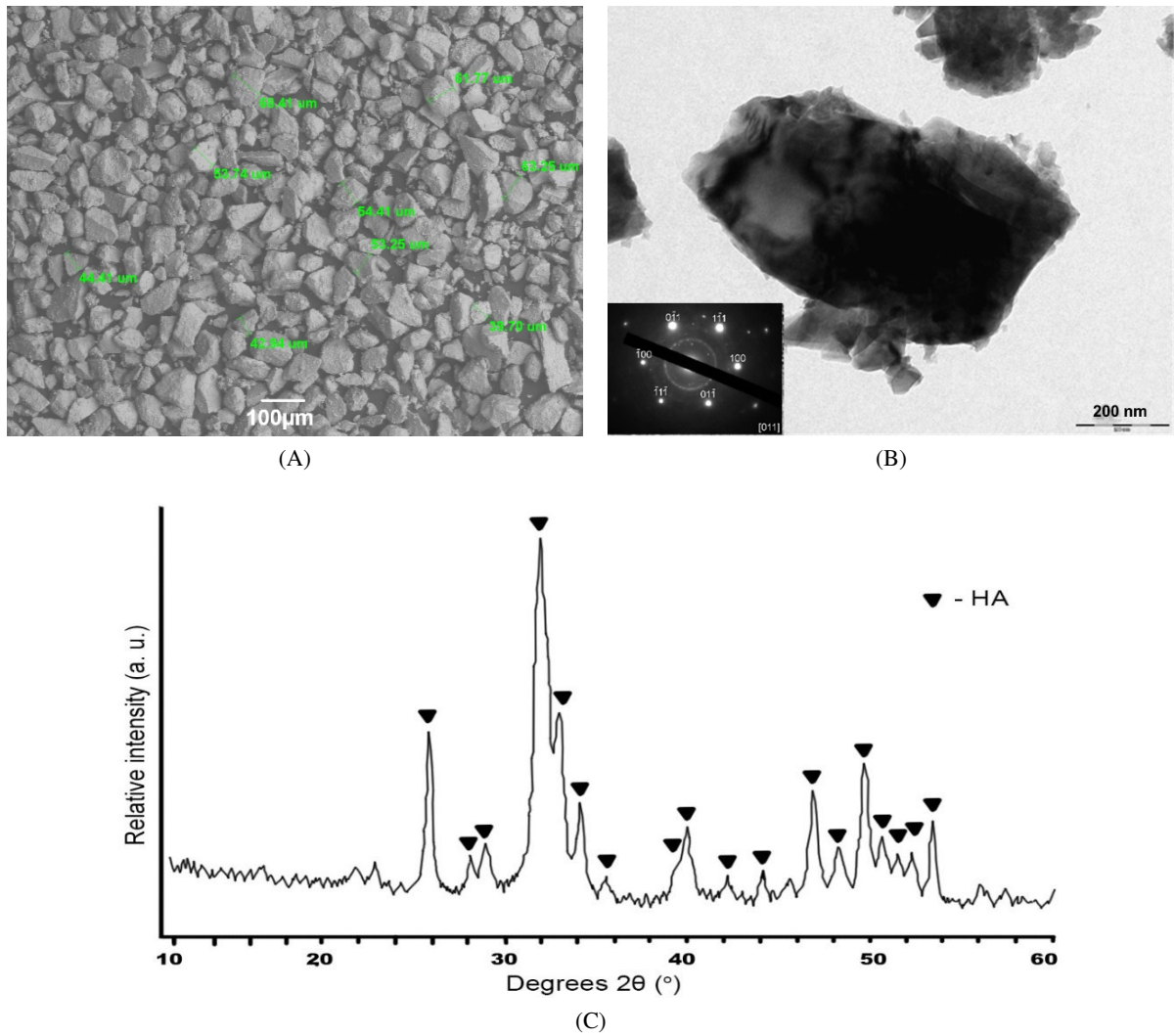


Fig. 8. HA powder feedstock: SEM image of HA particles indicating particle size (A); TEM image of the HA powder particle with the corresponding indexed microelectron diffraction pattern with zone axis [011] (B); XRD pattern of HA powder (C). SEM, scanning electron microscopy; TEM, transmission electron microscopy; XRD, X-ray diffraction

HA coatings were those of tetracalcium phosphate (TTCP), α -tricalcium phosphate (α -TCP), and β -TCP. It was found that the main phase (99.5%) was HA, with a hexagonal crystal system P63/m and the lattice parameters of $a = 0.9423$ nm, $b = 0.9423$ nm, and $c = 0.6883$ nm. Thereby, the purity of HA powder was found to be 99.5%, which met the purity requirement (not less than 95%) set out in the ASTM standard F1185-03 [33]. The results of XRD analysis are in good agreement with the results of TEM analysis.

MPS of HA powders on titanium alloy AM substrates was carried out with parameters specified in the Materials and Methods section. The average coating thickness was 150 ± 50 μ m. The SEM images of HA coating on a titanium trabecular 3D-printed substrate and the XRD pattern for microplasma-sprayed HA coating are shown in Figure 9.

As can be seen from Figure 9A, the coating is uniformly distributed over the surface of the substrate, penetrating into its pores with an aver-

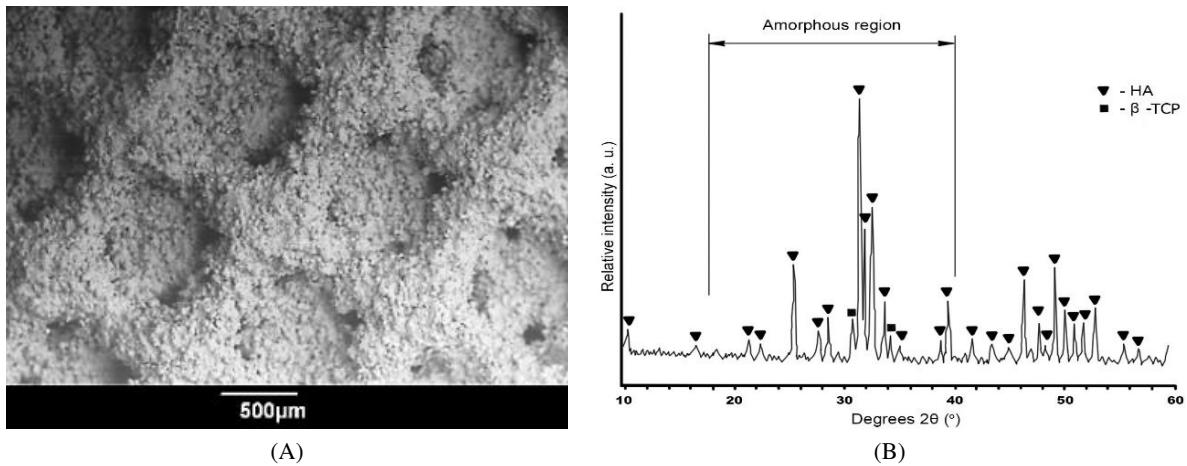


Fig. 9. HA-coating: SEM image of HA coating on a titanium trabecular 3D-printed substrate (A) and XRD pattern of microplasma-sprayed HA coating (B).

HA, hydroxyapatite; SEM, scanning electron microscopy; TCP, tricalcium phosphate; XRD, X-ray diffraction



Fig. 10. Specimens of 3D-printed titanium substrates with HA microplasma coating before (A) and after (B) tensile adhesion tests. HA, hydroxyapatite

age diameter of 800 μm to a depth of up to one layer of the trabecular structure of the substrate. It was established by XRD (Figure 9B) that the parameters specified for MPS of HA powder in the Materials and Methods section provide the required structure-phase composition in the HA coating: 93 wt.% of the crystalline phase, 5 wt.% of β -tricalcium phosphate (β -TCP) phase, and 2 wt.% of the amorphous phase. The highest peaks of HA and β phases for HA coatings were located at $2\theta = 32^\circ$ and 31° , respectively; the areas of the amorphous phase were found on the XRD patterns between 18° and 38° 2θ (Figure 9B). All the diffraction patterns in the range from 37.0° to 37.3° 2θ were thoroughly investigated, but even weak peaks

of harmful calcium oxide (CaO) were not found. The purity of the coatings was found to be 95.0%. The measurement error was 0.05. This shows that the purity of the microplasma-sprayed HA coating meets the 95% purity requirements of ISO 13779-2 [27].

High values of crystallinity (93%) of the HA coating also meet the crystallinity requirement (not less than 50%) set out in the ISO 13779-2 [27] for HA coatings used for implants for surgery. According to a number of studies reviewed by Dorozhkin [23], crystalline HA coatings for implants demonstrate a low dissolution rate in vitro, with less resorption and more direct bone contact in vivo, while amorphous HA undergoes rapid dissolution

in a physiological environment. Therefore, it can be assumed that it is desirable to have a high degree of crystallinity in HA coatings. It can be emphasized here that Ohki et al. [34] also noted the absence of harmful CaO compound in HA coatings obtained by thermal spraying. Moreover, Rakhadilov and Baizhan [35] note the presence of characteristic sharp HA peaks on the HA coating diffraction patterns, along with the absence of CaO, which demonstrates good crystallinity of the HA phase of the coating obtained by gas detonation spraying of HA powder on the surface of Ti–6Al–4V alloy. Results of the authors' previous scientific study [26] showed the same results as in this study for the values of purity and crystallinity of the microplasma-sprayed HA coating on a pure titanium sublayer. Thus, it can be assumed that thermal plasma spraying, firstly, is suitable for the manufacture of HA coatings for implants, and secondly, the properties of HA coatings depend to a greater extent on the spraying parameters than on the substrate structure.

The average roughness of 3D-printed tensile specimens was $R_a = 26.6 \pm 3.4 \mu\text{m}$, which is >3 times the average surface roughness of titanium tensile specimens after gas abrasion [26].

The adhesion strength of the HA coating calculated using Eq. (1) was $24.7 \pm 5.7 \text{ MPa}$, which met the requirements of ISO 13779-2 [27], according to which the adhesion strength of thermally sprayed coatings of HA should be no less than 15 MPa. Specimens of 3D-printed titanium substrates with HA microplasma coating before and after the tensile adhesion test are shown in Figure 10.

It should be noted that in 80% of cases, the destruction had an adhesive character. As can be seen from a comparison of Figure 10A and Figure 10B, the coating basically did not break down during the tensile adhesion test; the detachment occurred along the glue itself, which indicates good adhesion of the coating to the substrate and strong adhesion of the coating particles to each other. Such a rather high adhesion strength of the coating was most likely due to the correct choice of the MPS parameters. It was shown in a previous paper by the authors [26] that by varying the MPS parameters, it was possible to obtain three groups of microstructures of HA coatings depending on the degree of

heating of the powder particles when they collide with the titanium substrate made on a CNC machine and are subjected to gas-abrasive treatment.

Group 1. If the particles are completely melted when approaching the substrate, then depending on their speed, temperature before impact, the degree of their deformation, and crushing when laid in the layer, dense structures can be formed.

Group 2. When approaching the substrate, if, together with the molten particles, there are particles that have begun to solidify, then the structures are characterized by the presence of pores and granular inclusions of fixed solidified particles.

Group 3. If coatings are formed from particles that have begun to solidify at a low speed, then such particles form a coating with a structure characterized by a large number of pores ranging in size from $20 \mu\text{m}$ to $200 \mu\text{m}$.

In this study, the MPS parameters leading to the formation of the coating microstructure described in Group 2 were used. Under such parameters, most of the HA powder particles are sufficiently heated in the plasma jet to melt completely or partially, or at least soften, which is important for adhesion. At the same time, these MPS parameters could facilitate the presence of pores in the coating, which is desirable for accelerating the ingrowth of bone tissues into the implant. Further studies are required to establish the effect of MPS parameters on the porosity of HA coatings on 3D-printed substrates, as well as to evaluate and compare the effect of the roughness of titanium substrates manufactured using different technologies on the adhesive strength of HA coatings.

Thus, this study proves that it is possible to obtain a HA coating with satisfactory purity, crystallinity, and adhesion to a 3D-printed titanium substrate using MPS of HA powder. A robotic MPS for applying coatings from HA powder on AM titanium implants has been implemented. Moreover, it can be concluded that HA coatings can be applied to 3D-printed products without preliminary gas-

abrasive surface treatment of the products. Thus, the combination of AM and MPS technologies in the future might reduce the labor intensity of the thermal plasma spraying technology, eliminating not only the gas-abrasive treatment itself but also related operations such as preparing corundum, applying protective masks to untreated surface areas, and washing the product from traces of corundum after gas abrasion. The next stage of research includes the above-mentioned study of the effect of MPS parameters on the porosity of HA coatings on 3D-printed substrates and the assessment of the effect of the substrate itself on the adhesion of the coating, as well as the study of the biocompatibility of microplasma-sprayed HA coatings (in vitro tests) and MPS of various materials such as tantalum and zirconium on titanium AM implants.

4. Conclusions

1. Using AM technology, namely, the method of SLM of Ti6Al4V titanium alloy powder, implant parts and substrates with a trabecular structure were manufactured; these 3D-printed products corresponded to their stereolithographic models with high accuracy, which was confirmed by computed tomography analysis.
2. The application of the technology of MPS of HA coating with an average thickness of $150 \pm 50 \mu\text{m}$ on trabecular substrates obtained by the SLM method has been shown. The parameters of MPS of HA coatings onto titanium implants with a trabecular surface have been established.
3. It has been proven that using appropriate MPS parameters, it is possible to obtain a HA coating with 95% content of HA phases, 93% crystallinity, and adhesion strength of $24.7 \pm 5.7 \text{ MPa}$ to the trabecular substrate, which meets the requirements of the ISO 13779-2 standard (Implants for surgery). The MPS parameters for this result are as follows: electric current is equal to 45 A, plasma gas flow rate is 1.0 slpm, spraying distance is 160 mm, powder feed rate is $0.4 \text{ g} \cdot \text{min}^{-1}$, and the speed of linear movement of the plasmatron along the substrate is $50 \text{ mm} \cdot \text{s}^{-1}$.
4. It has been demonstrated that by combining AM and MPS, it is possible to eliminate the operation of preliminary gas-abrasive surface treatment by obtaining 3D-printed products with high average surface roughness of $R_a = 26.6 \pm 3.4 \mu\text{m}$.

Thus, this study shows promising results in the application of MPS of HA coatings on titanium trabecular substrates in order to improve the biocompatibility of AM implants. The results of the research are of significance for a wide range of researchers developing technologies for thermal plasma spraying of biocompatible coatings and technologies for AM of patient-specific porous implants.

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