Darya ALONTSEVA[1], Bagdat AZAMATOV[1], Sergii VOINAROVYCH[2], Oleksandr KYSLYTSIA[2], Tomasz N. KOLTUNOWICZ[3], Aigerim TOXANBAYEVA[4]

D. Serikbayev East Kazakhstan State Technical University (1), E. O. Paton Electric Welding Institute, Ukraine (2), Lublin University of Technology (3), K. Satpayev Kazakh National Research Technical University, Kazakhstan (4)

doi:10.15199/48.2020.04.32

Development of Technologies for Manufacturing Medical Implants Using CNC Machines and Microplasma Spraying of Biocompatible Coatings

***Abstract**. The paper describes the main technological approaches for manufacturing medical implants from titanium alloy using Computer Numerical Control (CNC) machines and microplasma spraying of hydroxyapatite (HA) coatings. New approaches to the formation of coatings with the desired structure and properties and the challenges of developing the technologies for producing modified implants are discussed.*

Streszczenie.** W artykule opisano główne podejścia technologiczne do wytwarzania implantów medycznych ze stopu tytanu przy użyciu maszyn CNC do sterowania numerycznego i mikroplazmowego natryskiwania powłok hydroksyapatytowych (HA). Omówiono nowe podejścia do tworzenia powłok o pożądanej strukturze i właściwościach oraz wyzwania związane z opracowaniem technologii wytwarzania zmodyfikowanych implantów.* ***(Rozwój technologii wytwarzania implantów medycznych z wykorzystaniem maszyn CNC i rozpylania mikroplazmowego powłok biokompatybilnych)

Keywords: CNC machines, microplasma spraying, hydroxyapatite coatings, medical implants.
Słowa kluczowe: maszyny CNC, natryskiwanie mikroplazmowe, powłoki hydroksyapatytowe, implanty medyczne.

Introduction

Nowadays, the production technologies of medical implants are constantly being improved in order to accelerate a patient's recovery and increase the service life of the implant, with special attention being paid to applying biocompatible coatings on the implant surface [1]. The most advanced technologies for manufacturing patient-oriented medical implants include the integration of additive manufacturing (AM) technology or rapid prototyping (RP) with Computer Numerical Control (CNC) machining [2, 3], as well as with 3D scanning and computed tomography technologies [4]. At present, there are numbers of materials and manufacturing technologies available to produce orthopedics implants [2-5]. These technologies such as AM or RP, CNC, hybrid CNC and high precision machining technology can make significant impact in the field of biomedical engineering and surgery [3].

However, despite the variety of existing approaches to the production of orthopedic implants with coatings from biocompatible materials, it is rather difficult to select a satisfactory combination of equipment and techniques for the development of flexible production of inexpensive medical implants. Since the market for medical implants is very competitive, the successful development of implants manufacturing technologies may be provided with the novelty of technological approaches, coupled with patient-oriented production. In order to create a technology for the production of patient-oriented implants from local materials in the Republic of Kazakhstan, the authors of this paper are developing a technology for manufacturing cheaper and patient specific medical implants.

The manufacturing process involves two main approaches:

1) implant lathing by numerically controlled machines, followed by surface purification and quality control;
2) Microplasma Spraying (MPS) of biocompatible Ti wires and hydroxyapatite (HA) powders onto implants using an industrial robot to obtain the two-layer Ti/HA coating with a dense Ti sublayer that provides good adhesion to the substrate and a porous HA top layer, which can accelerate implant growth with bone.

Hydroxyapatite (HA) is the calcium phosphate mineral $Ca_{10}(PO_4)_6(OH)_2$ of the apatite group, which is chemically similar to the apatite of the host bone, and is a source of calcium and phosphate for the bone-HA interface [6-8]. HA coatings improve osseointegration and can significantly reduce the duration of implantation of the endoprosthesis, provide a reliable connection with the bone and increase the reliability of implants [1, 7-10]. In case of thermal spraying of HA powder, the chemical composition of the final HA coating is dependent on the thermal decomposition occurring during spraying. The high temperatures experienced by HA powder particles in the plasma spraying process lead to the dehydroxylation and decomposition of the particles. At temperatures of above 1050°C HA decomposes to tricalcium phosphate β-TCP -$Ca_3(PO_4)_2$ and tetracalcium phosphate TTCP-$Ca_4(PO_4)_2O$, and above 1120°C β-TCP is converted to α-tricalcium phosphate -$Ca_3(PO_4)_2$. [9]. Thus the resulted coating phase composition depends on the thermal history of the powder particles. The higher the plasma jet temperature and the longer the exposure of the particles to plasma, the greater the degree of phase transformation is. According to the ISO standard specification ISO 13779-2:2000 [11], the maximum allowable content of non-HA phases in a HA coating is 5%, and the percentage of crystallinity is no less than 50% [11]. The degree of crystallinity of the HA coating largely affects the process of osseointegration [9]. The amorphous phase of HA has a higher rate of dissolution, which reduces the recovery time of the patient, but at the same time some reduction of the reliability of fixation of the endoprosthesis in the bone is also possible. Thus, increased crystallinity appears to slow resorption of HA, which leads to a slight decrease of bone ingrowth [9], yet provides reliable fixation of the implant in the bone [6, 10]. The sublayer from unalloyed titanium is used to improve the adhesion of the upper HA layer and because of its highly corrosion resistance, bio inertness and biocompatibility.

The technology of Microplasma Spraying has been chosen based on the analysis of existing technologies for the production of biocompatible coatings, of which the most widely applicable are the technologies of plasma spraying [1, 6, 10]. Among the different existing plasma spraying processes, the Microplasma Spraying (MPS) is particularly characterized by low plasma power (up to 4 kW), small spray spot (up to 15 mm), and a possibility of forming a laminar jet with the length of up to 150 mm, which heats the refractory material in a stream of Ar plasma and provides low heat input into the substrate [10]. The process provides Ti wire or HA powder deposition on small-sized parts and components, including those with fine sections, this being unachievable with any other methods. The MPS generally provides a micro-rough surface and a higher degree of porosity (~20%) that in case of biocompatible coatings facilitates bony tissues in-growth; in most cases the bond strength of MPS coatings with substrates is good enough [10, 12]. However, there are still a number of challenges, and the most important among them is the problem of the formation of coatings with specified structure and properties.

The aim of this work was to develop the technologies for manufacturing medical implants using CNC machines and microplasma spraying of biocompatible coatings, including the selection of modes for microplasma spraying of HA powder to obtain a porous HA coating with the desired structural phase composition.

Experimental procedure

To manufacture the medical implants the Computer Numerical Control (CNC) machines have been used: CTX 510 ecoline CNC turning and milling machine (DMG MORI, Germany) and DMU 50 CNC milling machine (DMG MORI, Germany). The universal mobile 3D scanner “scan3D Universe” (SMARTTECH3D, Poland) has been used to obtain a 3D model of a physical object for further digital and real processing.

The following sequence of technological processes has been developed:

1) Receiving prototypes of implants modified by the Research Institute of Traumatology and Orthopedics of the Republic of Kazakhstan. 3-D scanning of implants’ prototypes and 3-D designing using the SolidWorks software. Preparation of design documentation according to USDD (Unstructured Supplementary Service Data).
2) MasterCam for SolidWorks programming. Transfer of the controlling program in G codes to the machine column and Siemens programming on CNC machines. Implant lathing by CNC machines. Implant quality visual and dimensional inspection.
3) Implants' surface preparation for coating. Microplasma spraying of biocompatible coatings followed by testing the laboratory prototypes of medical implants for compliance with the requirements of International Standards Organization [11, 13].

Prototypes of some medical implants made of titanium alloy, such as the hip joint endoprosthesis (Fig.1), have been obtained and tested. At this stage of the research, no clinical tests on humans or animals have been carried out.

Before microplasma spraying, the surfaces of the samples were degreased with acetone and subjected to ultrasonic cleaning. To ensure proper adhesion of the coatings, it is important to pre-treat the surfaces of the substrates to increase their roughness. For surface activation, gas abrasive treatment is used. Since the activity of the base rapidly reduces due to the adsorption of chemical gases from the atmosphere and oxidation, the time between the gas abrasive preparation and the coating of the surface should not exceed 2 hours. Samples before coating are stored in a tightly closed container. Gas abrasive surface treatment was carried out on the CONTRACOR machine (Russia) using normal grade A14 electrocorundum.

Fig.1. Prototypes of hip joint endoprosthesis modified by the Research Institute of Traumatology and Orthopedics of the Republic of Kazakhstan

Microplasma spraying of the powders and wires has been carried out by microplasmatron MP-004 (produced by E.O. Paton Institute of Electric Welding, Kiev, Ukraine) [14]. The microplasmatron has been mounted on an industrial robot arm (Kawasaki RS-010LA, Kawasaki Robotics, Japan). It is able to move horizontally along a computed trajectory at designed speed.

The thickness of the coatings has been varied from 100 μm to 300 μm by changing the modes of microplasma spraying. The speed of linear movement of plasmatron along the substrate was chosen to be 50 mm/min. Argon served as a plasma-forming and transporting gas; additional heating of the substrate was not carried out.

Implants made of medical titanium alloy of Grade 5 ELI (ISO 5832-3) were used as substrates for microplasma spraying. HA powder with the particle size in the range of 40 to 90 μm and with the ratio Ca/P of 1.67 was used as a sprayed coating material. The process of synthesis of hydroxyapatite powder was described in our paper [10]. For the deposition of titanium coatings, wires of VT1-00 (GOST 19807-91) unalloyed (commercially pure) titanium with a diameter of 0.3 mm were used.

Experimental methods of analysis of materials structure and chemical compositions included Scanning Election Microscopy (SEM) by JSM-6390LV (“JEOL”, Japan) with Energy Dispersive X-ray (EDX) microanalysis system INCA ENERGY (Oxford Instruments, UK), X-ray diffraction (XRD) by X’Pert PRO (“PANalytical”, the Netherlands), infra-red (IR) spectroscopy by FT801 FT-IR spectrometer (SIMEX, Russia).

To evaluate the porosity of biocompatible coatings, the images being obtained by the scanning electron microscope JSM-6390LV (JEOL, Japan) were processed using ZAF/PB, Micro Capture, and Atlas computer-aided programs. The measurements were carried out on the polished cross section of the coatings as per ASTM E2109-01 standard [15].

The crystallinity and the structure-phase compositions of HA powders and plasma sprayed HA coatings were measured by X’Pert PRO diffractometer (PANalytical, the Netherlands). The interpretation of the X-ray diffraction patterns was carried out using Rietveld method and licensed data of the PCF DFWIN (140,000 connections), the ASTM card file and Diffracts Plus software. The percentage of crystallinity of the HA powder was calculated using the area of crystalline peaks in the region 20 to 40° 2θ and the area of the amorphous diffuse background in this region.

Discussion

The experimental studies of the influence of such parameters of microplasma spraying as amperage (I, A), plasma gas flow rate (V_{pg}, slpm), spraying distance (H, mm) and powder consumption (P_{powder}, g/min) on the surface morphology, porosity and structural-phase transformations in the HA coatings in the process of micro-plasma spraying have been performed. The coating experiments for MPS were accomplished in a two level fractional factorial design (2^{4-1}).

XRD and IR-spectrometry analysis confirmed that the phase composition of the initial HA powder was fully crystalline $Ca_{10}(PO_4)_6(OH)_2$ with the ratio Ca/P of 1.67.

The plasma spraying of HA powders was carried out using nine different modes (Table 1), the key criteria were the phase composition and the degree of crystallinity (A_{ph} – the proportion of the amorphous phase, $HAc_{ryst.}$ – the proportion of the crystalline phase), and the powder consumption ratio (PCR). Using the method of mathematical planning, an experiment was conducted to determine the degree of influence on the PCR of such factors of the MPS process as amperage, plasma gas flow rate and spraying distance. The regression equation (1) for the PCR is as follows:

$$PCR\% = 2.575I - 0.246V_{pg} - 0.203H + 4.06P_{powder} - 0.825 \quad (1)$$

The analysis of the equation (1) shows that in the case of increasing the amperage, the PCR grows due to the rise of the plasma jet temperature and more intense heating of the powder particles. With these values of the micro-plasma spraying parameters the amperage magnitude has the strongest impact on the value of the PCR. The increase in gas flow rate leads to a decrease in the PCR. This is because the increase in gas flow rate leads not only to a decrease in the temperature of the jet and, therefore, the temperature of the particles reduces, but also to the increase in the speed of the jet. The growth in the speed of the jet increases the speed of powder particles, which in turn, reduces their time in high temperature zone of the plasma jet and also leads to insufficient heating. As the distance of spraying rises, the fall of the PCR is due to partial cooling of the sprayed particles during the approach to the substrate. The consumption of powder under conditions of MPS also has some influence on the degree of the particles heating, and, therefore, on the PCR. Thus, the increase in the powder consumption leads to the decrease in the speed of the jet, thereby increasing the time of heating the particles in a plasma jet, and thus the degree of fusion penetration. With the increase of the amount of powder introduced into the jet, the PCR will grow till the stored energy of the plasma jet can heat the incoming powder to the melting temperature of the powder material. Then plasma supercooling takes place, and there will come a point when the quantity of molten powder particles will start to decrease. The comparison of calculated and experimental results shows their good convergence (Table 1).

The analysis of the received results of X-ray diffraction analysis presented in Table 1 shows that the phase compositions of all coatings comply with ISO 13779-2: 2000 [11]. The areas of existence of amorphous HA have been found on the X-ray diffraction patterns between 28.9 and 34.2 2θ (°). The peaks in the X-ray diffraction patterns match the standard diffraction pattern for HA (JCPDS 9-432), which provides evidence that the analyzed coatings are in the HA zone. All the diffraction patterns in the range of 37.3 2θ (°) were thoroughly investigated, but even weak peaks of Calcium oxide (CaO) were not found. This confirms that the purity meets the requirements of ISO 13779-2:2000 [11]; no harmful CaO compound is formed through the MPS coating of HA powder. However, the mode No.3 provides the highest powder consumption ratio (Table 1) and the smallest diameter of the spraying spot – 8 mm (with a maximum of 12 mm corresponding to Mode No.1). Thus, we consider the mode No.3 to be optimal, the most cost-effective. This mode allows obtaining a desired HA coating thickness (about 100 μm) in one pass of a plasma jet.

The images of microstructure of microplasma sprayed under specified above mode HA coating are presented in Fig.2 and Fig.3. Pore sizes in the coating are in the range of 20-60 μm, and the porosity is about 30% (Fig.2). Regarding the results of measuring the level of porosity in the HA coating it should be noted that for biocompatible coatings open porosity is essential – the egress of the pore on the surface of the coating, where the bone grows. Therefore, in this case, it would be more correct to talk about the relief or morphology of the surface, perhaps by measuring the diameters of the pore craters on the surface of the coating. In our experiment, the maximum pore diameter on the surface of the HA coating was about 100 μm (Fig. 3).

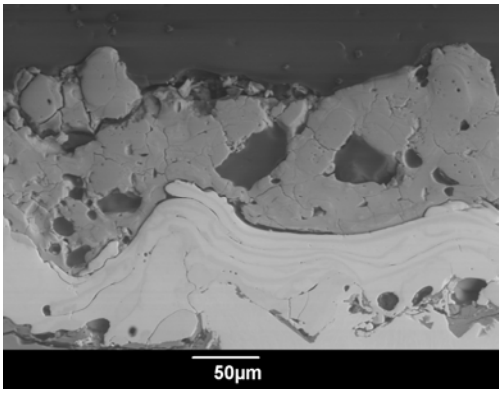

Fig.2. The SEM image of cross-section of HA coating sprayed by Mode No.3 (Table 1) onto titanium sublayer

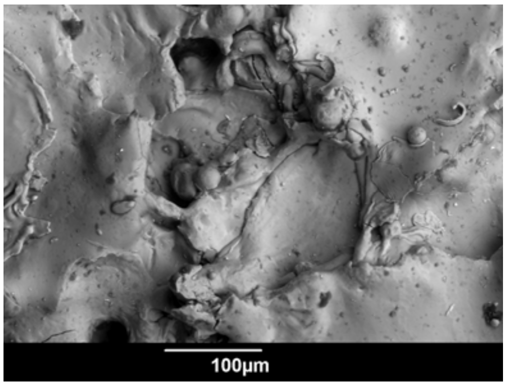

Fig.3. The SEM image of HA coating sprayed by Mode No.3 (Table 1) onto titanium sublayer

It is assumed that to increase the biocompatibility of the implants rapid accretion with the bone, the implant surface should be covered with a biocompatible coating with an extensive surface morphology, with pore sizes in the coating from 20 to 100 μm, and closed porosity of at least 30% [5-10]. Thus, the HA coating is designed to meet these requirements. The use of robotic movement of plasmatron allowed to deposit coatings onto implants with complex surface geometry with high accuracy. Thus, the chosen equipment and techniques allow machining such a challenging material as titanium, efficiently manufacture small-batch or custom one-off complex parts and handle the complex geometries, which is in good agreement with the data presented in the papers [2, 3].

Table 1. The dependence of the powder consumption ratio (PCR), phase composition and crystallinity of HA coating on the spraying parameters

Mode No.	Set spraying parameters				Powder Consumption Ratio		Phase composition and crystallinity of HA coating			
	I, A	V_{pg}, slpm	H, mm	P_{powder}, g/min	PCR,%	PCR, % estimated	HA $Ca_{10}(PO_4)_6(OH)_2$	β- TCP $Ca_3(PO_4)_2$	A_{ph}	$HA_{cryst.}$
1	45	2.0	160	1.2	54	58	97	3	5	92
2	45	2.0	80	0.4	64	71	98	2	0	98
3	45	1.0	160	0.4	89	89	95	5	2	93
4	45	1.0	80	1.2	69	69	96	4	0	96
5	35	2.0	160	0.4	29	29	97	3	4	93
6	35	2.0	80	1.2	48	48	97	3	3	94
7	35	1.0	160	1.2	40	47	95	5	7	88
8	35	1.0	80	0.4	56	60	98	2	0	98
9	40	1.5	120	0.8	60	59	94	6	4	90

Conclusions

The technologies for manufacturing medical implants using CNC machines and microplasma spraying of biocompatible coatings have been developed and prototypes of orthopedic implants have been obtained.

The modes for microplasma spraying of HA powder have been selected; they allow to obtain the porous HA coating with the thickness up to 100 μm with a 95% level of HA phases and 93% level of crystallinity controlled by changing the spraying modes. The small size of the spraying spot (up to 8 mm) provides a significant reduction in powder consumption when depositing on implants of small size compared to conventional plasma spraying.

The results of the research are of significance for a wide range of researchers developing the technologies of manufacturing of orthopedic implants with biocompatible coatings.

The authors gratefully acknowledge funding from the Ministry of Education and Science of the Republic of Kazakhstan under the target financing program for the 2017-2019 years by the program 0006/PTF "Production of titanium products for further use in medicine" and support from the Polish Ministry of Science and Higher Education from science fund of the Lublin University of Technology, at the Faculty of Electrical Engineering and Computer Science FN-28/E/EE/2019, entitled 'Researches of electrical, magnetic, thermal and mechanical properties of modern electrotechnical and electronic materials, including nanomaterials and diagnostic of electrical devices and their components'

***Authors**: Prof. Darya Alontseva Ph.D., D.Sc., Bagdat Azamatov Ph.D. (Eng.), D. Serikbayev East Kazakhstan State Technical University, 69, Protozanov Street, 070004 Ust-Kamenogorsk, Kazakhstan, E-mail: dalontseva@mail.ru, azamatovy@mail.ru;*
Sergii Voinarovych Ph.D. (Eng.), Oleksandr Kyslytsia Ph.D. (Eng.), E.O. Paton Electric Welding Institute, 11 Bozhenko Street, 03680, Kiev, Ukraine, E-mail: serge.voy@gmail.com, kisl@i.ua;
Associate Professor Tomasz N. Koltunowicz Ph.D., D.Sc. (Eng.), Lublin University of Technology, 38D Nadbystrzycka Street, 20-618, Lublin, Poland, E-mail: t.koltunowicz@pollub.pl;
Ph.D. student Aigerim Toxanbayeva, Department of Engineering Physics, K. Satpayev Kazakh National Research Technical University, 22 Satpayev Street, Almaty, 050013, Kazakhstan, Email: aigerim.toxanbayeva@mail.ru.

REFERENCES

[1] Tobin E.J., Recent coating developments for combination devices in orthopedic and dental applications. A literature review. Advanced Drug Delivery Reviews 112 (2017), 88-100
[2] Abdul Rani A.M., Fua-Nizan R., Yazid Din M., Abdu Aliyu A.A., Manufacturing Methods for Medical Prostheses – A Review. International Medical Device and Technology Conference (2017), 138-142
[3] Shuib S., Nur A., Sulaiman S., Sahari B.B., Manufacturing methods of implant for use in orthopedic applications: Hip prosthesis. A Regional Conference on Engineering Mathematics, Mechanics, Manufacturing & Architecture (EM^{3}ARC) 2007
[4] Moayedfar M., Abdul Rani A.M., Emamiana S., Haghighizadeh A., Jafari N., Manufacture of medical orthopaedic implants using computed tomography imaging and rapid prototyping, ARPN Journal of Engineering and Applied Sciences 11 n.1, (2016), 177-180
[5] Matassi F., Botti A., Sirleo L., Carulli C., Innocenti M., Porous metal for orthopedics implants, Clin Cases Miner Bone Metab, 10 n.2, (2013), 111-115.
[6] Karachalios T., (Ed.), Bone-Implant Interface in Orthopedic Surgery. Basic Science to Clinical Applications, Springer, London (2014)
[7] Jing W., Zhang M., Jin L., Zhao J., Gao Q., Ren M., Fan Q., Assessment of osteoinduction using a porous hydroxyapatite coating prepared by micro-arc oxidation on a new titanium alloy, International Journal of Surgery 24 Part A, (2015), 51-56
[8] Goodman S.B., Yao Z., Keeney M., Yang F., The future of biologic coatings for orthopaedic implants, Biomaterials 34 n.13, (2013), 3159-3534
[9] Vahabzadeh S., Roy M., Bandyopadhyay A., Bose S., Phase stability and biological property evaluation of plasma sprayed hydroxyapatite coatings for orthopedic and dental applications. Acta Biomaterialia 17 (2015), 47-55
[10] Dorozhkin S.V., Calcium orthophosphate deposits: Preparation, properties and biomedical applications, Materials Science and Engineering: C 55 (2015), 272-326
[11] Implants for Surgery- Hydroxyapatite. Part 2: Coatings of Hydroxyapatite. International Organisation for Standards. BS ISO 13779-2:2000, 2000
[12] Alontseva D.L., Borisov Yu.S., Voinarovych S.G., Kyslytsia O.N., Kolesnikova T.A., Prokhorenkova N.V., Kadyroldina A.T., Development of technology of microplasma spraying for the application of biocompatible coatings in the manufacture of medical implants. Przeglad Elektrotechniczny 94 n.7, (2018), 94-97
[13] ISO 13179-1:2014 Implants for surgery. Plasma-sprayed unalloyed titanium coatings on metallic surgical implants. Part 1: General requirements. ICS: 11.040.40 Implants for surgery, prosthetics and orthotics
[14] Borisov Iu.S., Voinarovich S.G., Fomakin O.O., Iushchenko K.A., Decl. Pat. UA V23K10/00 Plazmotron dlia napilennia pokrittiv, (Ukraina (UA); no 2002076032; Zaiavl.19.07.2002r. Opubl. 16.06.2003, Bul. no 6
[15] ASTM E2109-01 (2014) Standard Test Methods for Determining Area Percentage Porosity in Thermal Sprayed Coatings, ASTM International, West Conshohocken, PA, 2014
[16] ISO 4287:1997 (2015) Geometrical Product Specifications (GPS). Surface texture: Profile method. Terms, definitions and surface texture parameters