

DEVELOPMENT OF MICROPLASMA SPRAYING TECHNOLOGY FOR APPLYING BIOCOMPATIBLE COATINGS

D.L. Alontseva^{1*}, Yu.S. Borisov², S.G. Voinarovych², O.N. Kyslytsia²,
N.V. Prokhorenkova¹, A.V. Russakova¹, A.L. Krasavin¹, G.S. Bektasova³

¹Serikbayev East Kazakhstan State Technical University, Protazanov Street 69
070004, Ust-Kamenogorsk, Kazakhstan

²Paton Electric Welding Institute, Bozhenko Street 11, 03680, Kiev, Ukraine

³East-Kazakhstan State University, 30th Gvardeyskya Street 34, 070004, Ust-Kamenogorsk, Kazakhstan

*e-mail: dalontseva@mail.ru

Abstract. This paper describes the equipment and technology of microplasma spraying from powder and wire materials for applying biocompatible coatings for medical implants and instruments. The authors observe the challenges and prospects of the implementation of the technology for manufacturing medical products and point out the successful application of microplasma spraying technology for applying biocompatible coatings for hip implants.

Keywords: biocompatible coating, hydroxyapatite, medical implant, microplasma spraying

1. Introduction

Currently, the thermal spraying methods of coatings for various purposes are being developed all over the world [1, 2]. As noted in Ref. [2], the properly applied thermal spray coatings have many field of using and many advantages over the coatings obtained by competing methods. The thermal spraying is based on heating or melting a coating material and spraying it onto a surface to obtain coatings with desired properties and adhesion strength to a substrate. The ways of thermal spraying are distinguished by technological simplicity, compactness and transportability of equipment. They allow adjusting in a wide range mechanical and other property of the resulting coatings (adhesion, hardness, porosity, wear resistance, etc.) depending on a sprayed material, surface treatment products, spraying, etc.

For optimum coatings by thermal spraying it is required to conduct several consecutive technological processes [2 - 5]. For example, to ensure proper coating adhesion it is important to have the substrate previously prepared, e.g. increase its roughness by sandblasting or other way. Some coatings require additional heat treatment or sealing after application. The treatment of complex configuration surfaces presents a challenge for implementing the thermal spraying technology and requires automated manipulations with a plasma source along with robotic control for appropriate treatment of a surface [1, 2].

One of the main methods of thermal deposition of coatings is plasma spraying. Paton Electric Welding Institute (EWI) has developed a new method of thermal coating-microplasma spraying (MPS) [6, 7]. We believe that this technology should ensure a consistent quality of coatings due to the high requirements of medical products. One of the claimed types of medical products is the prosthesis of a hip joint. They are usually produced by casting, forging or cutting on turn-milling machine; their surface being additionally processed to give them a roughness and increase biocompatibility.

The human body and implant create together a new biotechnical system, where the body, enzymes of the immune and endocrine systems, influences the implant with its tissues, and the implant in turn, influences the body with its design, chemical composition, surface macrostructure and many other properties [8]. The general requirements for medical implants are reduced to withstanding repetitious cyclic loads, to having corrosion resistance in physiological environments and to be biocompatible. Titanium implants are most favorable for using [8-10] because titanium is biocompatible and a non-corrosive material. In addition, titanium is characterized by a low specific gravity that allows make rather light and stabile implants. To obtain reliable fixation of orthopedic implants in a bone, it is necessary to make them porous that ensures germination of bone tissue into the pores. Increasing the number and size of pores could increase the biocompatibility of the endoprosthesis surface with a human flesh [8-10]. However, there are some limitations on the pore size, depending on an operation type. In addition the strength and elasticity of the material are important. Modern coarse-pored materials have an elasticity of 20-35% at a load of 16 N/cm. Fine-porous materials, usually being heavier have an elasticity of only 4-16% at the same load [10]. Another important requirement for a number of implants is that they should be rough. Roughness ensures the connection of bone tissue with the implant and thereby prevents rejection. Implants with a rough surface stay in the bone better and remain less susceptible to harmful effects of forces acting on them [11, 12].

The cementless roots of hip joint prostheses are made from titanium-based alloys: Ti-Al-V or Ti-Al-Nb. They have a rough surface, allowing the bone to grow into a root. They are installed in the bone by the method of "press-fit", i.e. they are driven into the canal of femoral bone after its shape having been adapted to the shape of the root by special rasping files. The surface of the cementless root of the hip joint endoprosthesis can be covered with special substances that facilitate the bone ingrown, or rough with micropores, which is provided by a special treatment, for example, by plasma spraying. Sometimes there is a combination of a surface with a porous coating and plasma spraying of special substances. In this case it is very important that the surface pores are not clogged with a new coating, the surface must remain extensive [13].

Among the substances that cover the root to facilitate bone ingrowth, in the most cases hydroxyapatite (HAp) is used. Hydroxyapatite (HAp) is the calcium phosphate mineral $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ belonging to the apatite group. It is the main mineral constituent of bones (about 50% of the total bone mass) and teeth. In medical implanting, synthetic hydroxyapatite is used to coat implants that promote the growth of a new bone. At present, hydroxyapatite (HAp), which is obtained by roasting bones of cattle with subsequent grinding, is used as the bioactive material for endoprosthetic coatings [12-15]. Powders are produced with a wide dispersion spectrum and include particles of up to 50-100 μm in size. Synthesis of artificial HAp is carried out, mainly, by precipitation from aqueous solutions of calcium salts with ammonium hydrogen phosphate [14]. According to this method, amorphous, difficult-to-filter precipitates of hydroxyapatite of variable composition are formed, which during the drying process are agglomerated, sintered and, as a consequence, require additional grinding.

There is a variety of methods for applying HAp coatings to metallic, including titanium, implants: thermal spraying [15-17], magnetron sputtering, ion-stimulated precipitation [18], laser ablation [17, 19], chemical vapor deposition, electrophoretic deposition, sol-gel, biomimetic methods, etc. The main commercial application has plasma coating [12, 14, 15], in spite of such disadvantages as low adhesion strength to a substrate, heterogeneity of morphology, crystallinity and phase composition. The adhesion of the plasma coating to the substrate depends on many technological parameters such as the substrate surface roughness, the temperature of the plasma jet and the substrate, the powder dispersion and the spacing distance.

As shown in Ref. [17], the most important factor is the powder dispersion. It is known that bioactive powder coatings deposited directly on a titanium base can lose contact with the substrate, while the bond of the coating to the bone tissue remains sufficiently stable [14]. One of the ways to improve the adhesion strength of a coating to a titanium base is to use transition layers to ensure a smooth transition of properties from the coating material to the substrate material [10, 14].

At present, various methods of applying biocompatible coatings are used in the development and manufacture of promising types of implants. The most effective of all these, in our opinion, and also in the opinion of other authors, is plasma coating [2, 10, 12, 14]. The aim of this work is to develop a robotic microplasma spraying technology for applying biocompatible coatings on medical implants and tools.

2. Equipment

Within the activities of modern technologies development by Serikbayev East Kazakhstan State Technical University, the experimental laboratory industrial complex for plasma treatment of materials based on an industrial robot has been established. Kawasaki RS-010LA (Kawasaki Robotics, Japan) industrial robot is a device consisting of moving parts with six degrees of freedom to move according to a predetermined track. The robot manipulator characteristics are as follows: positioning accuracy – 0.06 mm; maximal linear speed – 13100 mm/s; engagement zone - 1925 mm; working load capacity - 10 kg.

MP-004 microplasmotron for applying the powder or wire coating produced by Paton Electric Welding Institute (EWI), Ukraine is mounted on the robot arm. EWI has developed a number of microplasma deposition plants; MPS-004 being the latest generation plasma spraying plant, which includes a power supply unit with a water cooling unit, a control box, a microplasmotron with an offset rotating cooled anode, an interchangeable mechanism for feeding wire, and a microplasmotron MP-004; the design of which is patented [20]. The microplasma spraying is distinctive of the low power consumption (MP-004 power is up to 2.5 kW) and the possibility of coating deposition in a laminar jet flow mode using pure argon as a plasma gas. The sprayed materials utilization rate at MPS is established as 0.6...0.9. Both powder and wire can be used as a source material for spraying. The system assembly has been carried out by Innotech LLP, Kazakhstan.

Experimental techniques used include: transmission electron microscopy (TEM) by JEM-2100 (JEOL, Japan), energy dispersive X-ray spectrometry (EDX) by INCA Energy TEM 350 (Oxford Instruments, Great Britain), scanning electron microscopy (SEM) by JSM-6390LV (JEOL, Japan), X-ray diffraction (XRD) by X'Pert PRO (PANalytical, the Netherlands).

3. Materials

Samples from titanium superpose biocompatible alloy of Grade 5 ELI quality class of a standard composition in the delivery condition (rods of various diameters) have been used as substrates. Its chemical composition includes the following limiting values:

Ti –base, Fe max 0.25%, N max 0.05%. O max 0.13%, Al max 5.5–6.5%, C max 0.08%, V max 3.5-4.5%, H max 0.012%.

We also used rods with a diameter of 20 mm of Ti-6Al-4V alloy of the similar composition in accordance with Russian State Standard ISO 5832-3-2014 ("Implants for surgery. Metallic materials. A deformable alloy titanium-based, 6-aluminum and 4-vanadium"). The discs were cut from the rods for further research. The 0.3 mm diameter titanium wires for microplasma spraying have been used as well as solutions of calcium nitrate $\text{Ca}(\text{NO}_3)_2$ and ammonium hydrogenphosphate $(\text{NH}_4)_2\text{HPO}_4$,

triethylphosphine ($(\text{C}_2\text{H}_5\text{O})_3\text{P}$) and calcium nitrate tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ for hydroxyapatites (HAp) synthesis.

4. Experimental

Processing of SEM images to determine the volume fraction and pore size in the coatings have been carried out using ZAF / PB, MicroCapture and Atlas software. M-691 precision ion polishing system (Gatan, USA) has been used to prepare TEM foils by the Ar^+ ion sputter etching method. The morphology and structure of different phases in titanium alloys and their volumetric fraction in the material has been determined by TEM. The method of arbitrary secant line to define the volume fraction of phases according to the TEM-images and CrystalMaker software to define the crystal-lattice parameter according to the TEM-diffraction pattern has been used. The transmission electron microscope data were compared with the data of the structure-phase composition, obtained by X-ray diffraction analysis. Interpretation of the X-ray diffraction patterns has been carried out using the licensed data of the PCF DFWIN (140,000 connections) and Diffracts Plus, the ASTM card file.

Microhardness tests have been performed with Durascan 10/20 digital microhardness meter (EMCO-TEST, Austria). The tests have been carried out according to GOST 9450-60 for the cross-section of a coated specimen. An indentation load of 1N has been applied with an average pitch of 25 μm in the coating and 40 μm in the substrate. Five measurements have been performed and the statistical average has been determined.

5. Results and discussion

There is a possibility of microplasma spraying for a wide range of coatings from metals, alloys; oxides, carbides and bioceramics (hydroxyapatite, tricalcium phosphate) [5, 6, 21]. Some properties of microplasma coatings from the wire with diameter 0.3 mm are shown in Table 1.

Table 1. Properties of microplasma sprayed coatings

Sprayed material	Microhardness, MPa	Oxygen content, %
Inconel 82	303...370	2.9...5.8
W	1880...2060	3.3...13.8
NiCr ($\text{Ni}_{80}\text{Cr}_{20}$)	309... 361	3.1... 15.1
Ti	320...550	0.88...2.8

The successful application of microplasma spraying technology for applying biocompatible coatings for hip implants at Paton EWI is demonstrated in Fig. 1a. The prototypes of coatings from hydroxyapatite) Ni-based (Fig. 1b and Co-based (Fig. 1c) powders have been obtained at Serikbayev EKSTU, using a robotic complex of microplasma processing.

The study of Ni or Co-based coatings [22-24] has shown that nanosized reinforcing particles of intermetallic phases of lamellar morphology are formed in the coatings leading to twofold or even fourfold increase of the coating microhardness compared to the substrate.

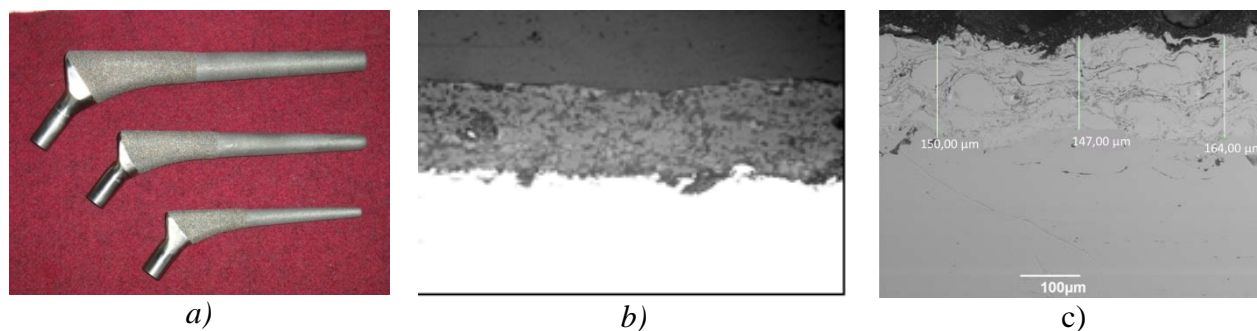


Fig. 1. Coatings obtained by microplasma spraying:
a) components of hip implants, b) hydroxyapatite coating, c) Co-based powder coating

Combining the experience of Kazakhstan and Ukraine scientists, we have developed the scientific foundations for the technology of robotic microplasma coating from biocompatible materials onto substrates made of titanium alloys. The research has been performed in four main directions:

- Materials selection and manufacturing (synthesis of hydroxyapatite) for microplasma deposition of coatings from biocompatible materials onto substrates from titanium alloys.
- Control algorithm development for industrial robot manipulators and development of relevant software to ensure precise coatings on the surface of complex shapes and controllability of the entire spraying process.
- Selection of abrasive processing and microplasma spraying modes to make the coating have satisfactory adhesion and desired surface morphology and porosity.
- Investigation of the structure and properties of the coating-substrate system.

An optimized method for the synthesis of powders of a biocompatible material, hydroxyapatite, has been designed. We have developed a technical data specification and selected abrasive flow machining equipment to treat the surface before coating. To solve the problem of providing the desired trajectory of the plasma source, we have developed software, which converts the drawings made in AutoCAD and Compass to the robot controller by selecting the graphics primitives (line, arc, etc.) from the drawings and transferring them into the commands for the robot arm movement. The certificate of intellectual property of the Republic of Kazakhstan has been received for this program [25].

Determining the structural-phase composition of the substrate from the Grade 5 Eli alloy was studied by X-ray diffractometry, the results are summarized in Table 2. We have identified that the peaks of Ti- β phase on X-ray diffractograms are very weak that allows considering the volume content of this phase in the material studied being negligible.

Table 2. Structural-phase composition of titanium alloy Grade 5 Eli

Phase	Crystal system	Space group	Space group number	Lattice parameter a, [Å]	Lattice parameter b, [Å]	Lattice parameter c, [Å]
Ti- α	Hexagonal	P63/mmc	194	2.95	2.95	4.68
Ti- β	Cubic	Im-3m	229	3.30	3.30	3.30

The results of electron-diffraction pattern decoding are in excellent agreement with the results of X-ray diffraction analysis, presented in Table 2. In addition, the results of TEM indicate the residual stresses in the alloy structure, which, apparently, were not completely removed by reducing thermal treatments in the process of rod making. Figure 2a demonstrates dislocation clusters at the subgrain boundaries and in individual foil paper grains. On the

subgrain dark-field image of the α -phase reflex, bending extinction contours are visible (Fig. 2b). The volume fraction of the sections characterized by dislocation clusters has been established by the method of arbitrary secants. It appears to be very small, no more than 3% in the field of the foil paper. Thus, it is found that the alloy is stress-free. Locally persisted stresses localized in the subgrains of an alloy up to 500 nm in size (Fig. 2b) and with a volume fraction of less than 3% in the bulk do not pose a threat to the macrostress formation able to destruct during subsequent machining.

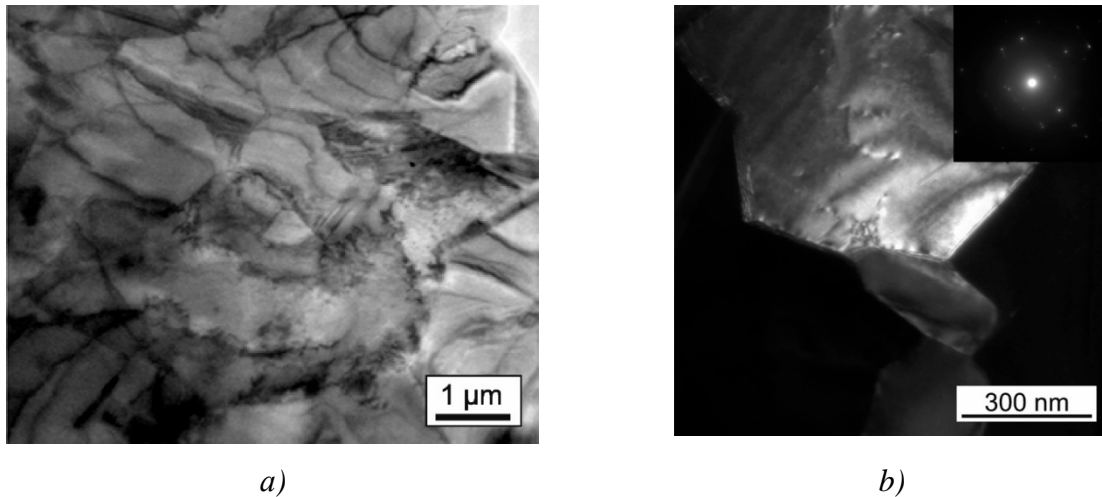


Fig. 2. TEM image of substructure of titanium alloy Grade 5 Eli with the corresponding microdiffraction pattern

- a)* Dislocation clusters at subgrain boundaries,
b) Dark-field image of grain with deformations, taken in the reflex of α -phase

The substrate surface was treated with an abrasive-jet method before coating. Gas abrasive treatment must be applied to activate the surface. Since the activity of the substrate surface is rapidly reduced due to chemical adsorption of gases from the atmosphere and oxidation, the time between gas-abrasive surface preparation and coating spraying should not exceed 2 hours. The product must be stored in a sealed container (in a desiccator) in the interval between two processing operations. The mode specified in Table 2 is recommended for gas-abrasive surface treatment of the titanium-alloy endoprostheses. Considering the working conditions of the products (their presence in a body), normal electrocorundum grade 12A, 13A, 14A or 15A according to GOST 2MT 793-80 is used as an abrasive for surface preparation.

Table 3. Mode of gas-abrasive processing of substrates from titanium alloys

Average diameter of abrasive particles, mm	0.6...0.8
Pressure of compressed air, MPa	0.4...0.6
Distance from a nozzle cut to a machined surface, mm	100...120
Incidence angle of a abrasive jet on the surface to be treated, degrees	60...90
The linear speed of a gun, mm / min	250...600

Spraying modes have been selected experimentally, based both on the results published by other researchers and on our own previous experience [5, 6, 21-26]. We have varied the spraying distance, the power and speed of the source, the powder feeding by the powder dispenser, etc. During spraying it is necessary not to change the set values of microplasma spraying parameters. The microplasma jet should be stable, without pulsations. The powder

feeding into the plasma jet should be even, without the formation of an anodized powder on an anode, or blockage of the powder supply hole. Besides, it is necessary to exclude formation of drop-shaped particles on the surface.

One of the main requirements for hydroxyapatite coatings on implants is compliance with their specified phase composition and ensuring the necessary adhesion strength to the implant surface. To achieve the required adhesion strength, it is recommended to use a titanium sublayer with a developed surface relief, the sublayer being applied by the microplasma spraying of titanium wire with its thickness of 150 ... 200 μm . Then a coating of hydroxyapatite powder with an average particle diameter of 40 ... 63 μm is applied to this sublayer by microplasma spraying. Table 3 lists the two main spraying modes selected experimentally for these processes.

Table 4. Modes of micriolasma spraying onto substrate from titanium alloy

Spraying parameters, [unit measure]	Coating material	
	Ti-wire	HAp-powder
Current intensity [A]	16	45
Plasma forming gas (Ar) flow rate, [liter/min]	3	2
Protective gas (Ar) flow rate, [liter/min]	7	4
Spraying distance, [mm]	40	160
Wire/powder utilization rate, [m/min]/ [g/min]/	3	0.4

We have obtained prototypes of coatings from hydroxyapatite powders (Fig. 1b) and Co-based alloy powders (Fig. 1b) as well as from titanium wires (Fig. 3) using the robotic complex. The morphology of titanium coating surface has been studied by scanning electron microscopy. It can be seen that the surface is porous and rough (Fig. 3). The observed porosity is 10.0 vol. % on the average with a pore size of 20 ... 100 μm . The coating of HAp over the titanium sublayer does not reduce the porosity and should increase the biocompatibility of the coating-substrate system as a whole.

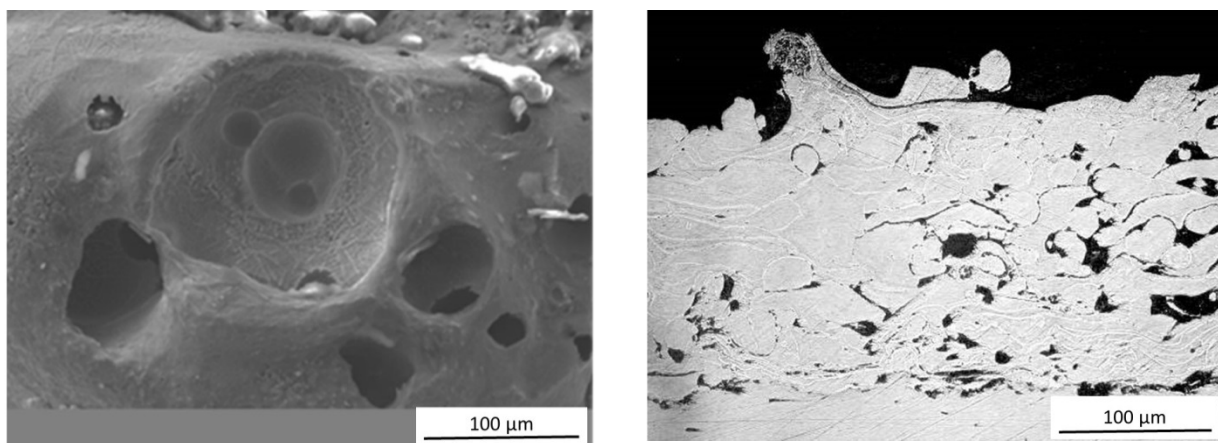


Fig. 3. SEM structure image of a titanium powder coating applied by microplasma method on a titanium alloy substrate:
a) surface image, *b)* cross section of a coated sample

6. Conclusions

Summarizing the results presented by other researchers [1-4, 7, 10, 14, 17] and our own experience, we can say that the technologies of thermal spraying include the selection and use of equipment (guns, power supplies, manipulators, etc.), materials (powders, wires or rods),

as well as technical and technological know-how (experience). Only when all these key technology components are used correctly, one can get a desirable coating with controlled structure and satisfactory adhesion. As noted in Refs. [1-4, 7], the main disadvantage of the coatings obtained by gas-thermal methods is their high porosity and occasional poor adhesion to a substrate. At times, the porosity can be useful ensuring reliable fixation of orthopedic implants into bones because of the intergrowth into the bone tissue pores; however it needs to be controlled. In this case, the microplasma spraying method can provide desired and controlled porosity of the coatings.

Successful deposition of biocompatible coatings with sustained characteristics on parts of complex shape, which are endoprostheses, requires steady travelling the plasma source along the product sprayed surface. For this purpose, it becomes necessary to equip the deposition plant with a robot manipulator, as it was done at Serikbayev EKSTU. The main challenges are the use of new materials and ensuring the required quality of coatings (adhesion, porosity, and biocompatibility).

Paton Electric Welding Institute (Ukraine) has developed equipment and technology for microplasma spraying of coatings from the wide range of materials, including biocompatible materials. Serikbayev East Kazakhstan State Technical University (Kazakhstan) and Paton EWI have worked out a robotic micro-plasma spraying complex for applying biocompatible coatings on different implants made of titanium and its alloys. The experience with the use of this complex has turned out to be successful. We have obtained the prototypes of two-layer coatings of titanium- hydroxyapatite on substrates made of titanium alloys for medical purposes.

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