- [4] A.D. Pye, D.E.A. Lockhart, M.P. Dawson, C.A. Murray, A.J. Smith, A review of dental implants and interaction, Journal of Hospital Infection, v. 72, pp. 104-110, 2009.
- [5] Roger Narayan, Biomedical Materials, Springer Science+Business Media, LLC, p. 573, 2009.
- [6] Lilja M. 2013 Bioactive Surgical Implant Coatings with Optional Antibacterial Function Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology 1091 (Room: Acta Universitatis Upsaliensis)
- [7] Farooq I, Irman Z, Farooq U, Leghari A, Ali U. 2012Bioactive Glass: A Materials for the Future World Journal of dentistry 3 199–201.
- [8] Berkovitch N, Ginzburg P, Orenstein M: Concave plasmonic particles: broad-band geometrical tunability in the near-infrared. Nano Lett 2010, 10: 1405–1408. 10.1021/nl100222k.
- [9] Lucas D, Kim JS, Chin C, Guo LJ: Nanoimprint lithography based approach for the fabrication of large-area, uniformly-oriented plasmonic arrays. Adv Mater 2008, 20: 1129–1134. 10.1002/adma.200700225.
- [10] Zhang XY, Hu A, Zhang T, Lei W, Xue XJ, Zhou Y, Duley WW: Self-assembly of large-scale and ultrathin silver nanoplate films with tunable plasmon resonance properties. ACS Nano 2011, 5: 9082–9092. 10.1021/nn203336m.
- [11] Liang C, Zhong K, Liu M, Jiang L, Liu S, Xing D, Li H, Na Y, Zhao W, Tong Y, Liu P: Synthesis of morphology-controlled silver nanostructures by electrodeposition. Nano-Micro Lett 2010, 2: 6–10.
- [12] Hongshui Wanga, Xueliang Qiao, Jianguo Chen, Shiyuan Ding, Preparation of silver nanoparticles by chemical reduction method // Colloids and Surfaces A: Physicochem. 2005.-V.256.-P.111–115.
- [13] K. Loza, J. Diendorf, C. Sengstock, L. Ruiz-Gonzalez, J. M. Gonzalez-Calbet, M. Vallet-Regi, M. Köller, M. Epple, The dissolution and biological effect of silver nanoparticles in biological media // Journal of Materials Chemistry.-2014.-V.2.-P.1634-1643.
- [14] A. Sharonova, K. Loza, M. Surmeneva, R. Surmenev, O. Prymak, M. Epple, IOP Conference Series: Materials Science and Engineering 116 (2016) 012009.
- [15] S. Banerjee, K. Loza, W. Meyer-Zaika, O. Prymak, and M. Epple, Structural Evolution of Silver Nanoparticles during Wet-Chemical Synthesis, Chem. Mater., 2014, 26 (2), pp 951–957 DOI: 10.1021/cm4025342.
- [16] A. Ivanova, R.A. Surmenev, M.A. Surmeneva, T. Mukhametkaliyev, A.A. Sharonova, I.Yu. Grubova, K. Loza, S. Chernousova, O. Prymak, M. Epple, Antibacterial AgNPs/CaP biocomposites, IEEE, 2014. —P. 472-474.

# DEVELOPMENT OF THE MICROPLASMA SPRAYING TECHNOLOGY FOR APPLYING BIOCOMPATIBLE COATINGS

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## I. INTRODUCTION

Currently, the methods of thermal spraying of coatings for various purposes are being developed all over the world [1, 2]. As noted in the work [2], properly applied thermal spray coatings have many uses and many advantages over the coatings obtained by competing methods. The process of thermal spraying is based on the heating or melting of coating material and spraying it onto the surface with the aim of obtaining coatings with desired properties and adhesion strength to the substrate. The processes of thermal spraying are distinguished by technological simplicity, compactness and transportability of the equipment. The use of the methods of thermal spraying of coatings allows to adjust in a wide range of mechanical and other properties of the resulting coatings (adhesion, hardness, porosity, wear resistance, etc.) depending on the kind of sprayed material, surface treatment products, spraying, etc. These features of processes of thermal spraying determine the universality of their application, the diversity of areas and types of possible use.

For optimum coatings by thermal spraying are required to conduct several consecutive technological processes [2-5]. For example, to ensure proper adhesion of the coating it is important that the substrate was previously prepared, for example, increased its roughness by means of sandblasting or in any other way. Some coatings require additional heat treatment or sealing after application. The treatment of surfaces of complex configuration presents a challenge for the implementation of the thermal spraying technology and requires automated manipulations of the 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. The E. O. Paton Electric Welding Institute (EWI) has developed of a new method of thermal coating- microplasma spraying

(MPS) [6, 7]. We believe that these technologies should ensure a consistent quality of coatings due to the high requirements of medical products.

The aim of this work was to develop a robotic microplasma spraying technology for applying biocompatible coatings on medical implants and tools.

#### **II. EXPERIMENT**

E. O. Paton EWI has carried out a series of design and technological works resulted in developing a number of microplasma deposition plants (MPS-001, MPS-002, MPS-003). MPS-004, a latest generation plasma spraying plant, includes a power supply unit with a water cooling unit, a control box, a microplasmotron with an offset rotating cooled anode (the design of the microplasmotron is patented [8]), an interchangeable mechanism for feeding wire, and a microplasmotron MP-004 (Figure 1 a). The process of microplasma spraying is distinctive of the low power consumption (microplasmotron 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.

Within the activities of modern technologies development by D. Serikbayev EKSTU an 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. MP-004 microplasmotron for applying the powder or wire coating produced by E. O. Paton IEW, Ukraine is mounted on the robot arm. The assembly of the system has been carried out by Innotech LLP, Kazakhstan. Kawasaki RS-010LA robot manipulator characteristics are as follows: number of degrees of freedom – 6; positioning accuracy – 0.06 mm; maximal linear speed – 13100 mm/s; engagement zone – 1925 mm; working load capacity – 10 kg.

The study has dealt with the starting materials for coating deposition: powders, wires and resulting coatings obtained by means of microplasma spraying, as well as substrates (in most cases 3 steel substrates treated by sandblasting were used). The range of materials in the study was broad enough to ensure the mastering of technological processes for different materials.

Experimental methods of analysis included Transmission Electron Microscopy (TEM) by JEM-2100 ("JEOL", Japan) with Energy Dispersive X-ray Spectrometry (EDX) INCA Energy TEM 350 ("Oxford Instruments", Great Britain), Scanning Election Microscopy (SEM) by JSM-6390LV ("JEOL", Japan), X-ray diffraction (XRD) by X'Pert PRO ("PANalytical", the Netherlands), Microhardness test of the samples was performed with Durascan 10/20 digital microhardness meter (EMCO-TEST, Austria).

### **III. RESULTS**

The result of the research of E. O. Paton EWI in microplasma spraying [5-9] testifies to the possibility of applying this method to spraying a wide range of coatings from metals, alloys; oxides, carbides and bioceramics (hydroxyapatite, tricalcium phosphate). Some properties of microplasma coatings from the wire with diameter 0.3 mm are shown in Table 1.

Sprayed material	Microhardness	Content of oxygen, %
Inconel 82	303370	2.95.8
W	18802060	3.313.8
NiCr (Ni <sub>80</sub> Cr <sub>20</sub> )	309 361	3.1 15.1
Ti	320550	0.882.8

Table 1. Microhardness and content of oxygen of microplasma sprayed coatings

It is noted the successful application of microplasma spraying technology for applying biocompatible coatings for hip implants (Figure 1a) and the introduction of technology in the production of such implants on JSC "MOTOR SICH" (Ukraine).

At D. Serikbayev EKSTU were obtained prototypes of coatings from hydroxyapatite (Figure 2b) and Co-based powders (Figure2c) using a robotic complex of microplasma installation. To solve the problem of providing the desired trajectory of the plasma source, software was developed that converts the drawings made in AutoCAD and Compass into commands for the robot controller. [10].

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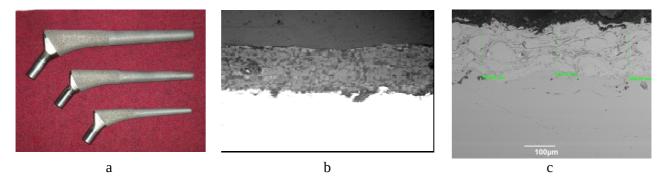


Figure 2. The coatings obtained by microplasma spraying: a – components of hip implants (the examples of products with biocompatible coating deposited by microplasma spraying at the E. O. Paton EWI); b – hydroxyapatite coating; c – Co-based powder coating

The results of the study of the structure and properties of Co-based coatings, published in the papers [11, 12], showed that in the coatings nanosized reinforcing particles of intermetallic phases of lamellar morphology are formed, which leads to 2-or even 4-fold increase of microhardness of the coatings compared to the substrate.

### **IV. DISCUSSION**

Summarizing the results presented in [1-5] and from 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 desirable coating with controlled structure and satisfactory adhesion. As noted by several researchers [1-5], the main disadvantages of the coatings received by the gas-thermal methods are their high porosity and occasional poor adhesion to the substrate. Porosity can at times be useful, as in the case of ensuring reliable fixation of orthopedic implants into bones on account of the intergrowth into the pores of the bone tissue, etc., yet in this case it needs to be controlled. The MPS method is of the greatest interest for applying biocompatible coatings on medical implants. The use of the microplasma spraying method in this case can provide desired and controlled porosity of these coatings.

Successful deposition of biocompatible coatings with sustained characteristics on parts of complex shape, which are endoprostheses, requires steady travelling of the plasma source along the sprayed surface of the product. For this purpose, it becomes necessary to equip the deposition plant with a robot manipulator, as it was done at D. Serikbayev EKSTU.

Thus, there is reason to believe that the use of this complex will allow to develop a technology for depositing biocompatible coatings on a wide range of implants. Yet, effective implementation of this task requires extensive retrofitting of the existing complex with devices for surface cleaning and treatment, as well as testing technology on samples of titanium and its alloys produced at UK TMP JSC, Kazakhstan enterprise, the world leader in production of titanium. The main challenges are the use of new materials and ensuring the required quality of coatings (adhesion, porosity, and biocompatibility).

## **V. CONCLUSIONS**

The E. O. Paton EWI (Ukraine) developed equipment and technology for microplasma spraying of coatings from the wide range of materials, including biocompatible materials. D. Serikbayev EKSTU (Kazakhstan) and E. O. Paton EWI set a robotic micro-plasma spraying complex for applying biocompatible coatings on different implants with the aim of development of technology for medical implants made of titanium and its alloys produced by UK TMP JSC. The experience of getting coating from biocompatible materials with the use of this complex was successful.

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#### REFERENCES

- R.C. Tucker, Jr. Introduction to Coating Design and Processing ASM Handbook// Thermal Spray Technology.-2013.-Vol 5A.- P.76-88
- [2] Vardelle A., Moreau Ch., Nickolas J., Themelis A. Perspective on Plasma Spray Technology Plasma Process.-35.- 2015.- P. 491–509
- [3] S.Kuroda, J. Kawakita, M.Watanabe, H. Katanoda, Warm spraying—a novel coating process based on high-velocity impact of solid particles// Sci. Technol. Adv.- 2008.-Mater. 9 (3): 033002. DOI:10.1088/1468-6996/9/3/033002
- [4] L.Wang, H.Wang, S.Hua, X. Cao, Plasma Science and Technology.- 2007.- Vol 9.- p.52 DOI: http://dx.doi.org/10.1088/1009-0630/9/1/11.
- [5] Borisov Y., Sviridova I., Lugscheider E., Fisher A. Investigation of the Microplasma Spraying Processes //Proceedings of the International Thermal Spray Conference.- Essen, Germany.- 2002.- P.335-338
- [6] Borisov Iu.S., Voinarovich S.G., Kislitca A.N. Mikroplazmennoe napylenie s ispolzovaniem provolochnykh materialov// Avtomaticheskaia svarka. 2002 № 3. P.54-55
- [7] E. Lugscheider, K. Bobzin, L. Zhao and J. Zwick Assessment of the Microplasma Spraying Process for Coating Application //Advanced Engineering Materials Special Issue: Thick Coatings for Thermal, Environmental and Wear Protection.- 2006.-Vol 8.- Issue 7.- P. 635–639. DOI: 10.1002/adem.200600054
- [8] Decl. Pat. UA V23K10/00 Plazmotron dlia napilennia pokrittiv / Borisov Iu.S., Voinarovich S.G., Fomakin O.O., Iushchenko K.A. (Ukraïna (UA)); № 2002076032; Zaiavl.19.07.2002r. Opubl. 16.06.2003, Bul. № 6.
- [9] K.A. Iushchenko, Iu. S.Borisov, S.G.Voinarovich, A.N. Kislitca, E.K.Kuzmich-Ianchuk Dvukhsloinoe biokermetnoe pokrytie titan-gidroksiapatit // Avtomaticheskaia svarka. 2011.– No 12. P. 46 49
- [10] D. Alontseva, A. Krasavin, O. Ospanov Software Development for a New Technology of Precision Application of Powder Coating Multifunctional Systems AIS Proceedings //11th International Symposium on Applied Informatics and Related Areas.- Székesfehérvár, Hungary.- 2016.-P.140-143
- [11] D. Alontseva, N.Prokhorenkova Forming Strengthening Nanoparticles in the Metal Matrix of Plasma deposited Powder Alloys Coatings//IOP Conference Series: Materials Science and Engineering, Volume 87, 2015. – P.1-9. doi:10.1088/1757-899X/87/1/012026
- [12] D. Alontseva, A. Krasavin, A.Russakova, T.Kolesnikova, G.Bektasova Effect of Irradiation with DC Plasma Jet on the Structure Phase Compositions and Properties of Powder Ni and Co based Coatings//Materials Science (Medžiagotyra), Vol. 22 (2). 2016. P. 238-242. DOI:10.5755/j01.ms.22.2.7699

# THE EFFECT OF COOLING RATE ON THE CRYSTALLIZATION OF ALUMINUM ALLOYS UNDER PRESSURE

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### I. INTRODUCTION

One of the most important problems directly influencing the efficiency of the use of metal products is the management of structure and properties formation of the applicable metals and alloys at their transition stage from melt (liquid) to solid [1]. In modern technological processes of material working temperature as a physical parameter defines the state in the treated material. This state also depends on pressure. In our case a material state is considered as the function of thermodynamic parameters. It is therefore essential from now on to regard temperature as not so much a 'degree of hotness' but as one of the most important thermodynamic parameters that change the structure and properties of treated materials. From this perspective, studying the mechanisms of temperature change and formation of temperature patterns acquire significant practical importance.

Unlike the conventional approach, which tends to use cooling rate as a defining thermodynamic parameter of the crystallization's mechanism and kinetic, the paper dwells on the influence of the additional factor, i.e. pressure, which when combined with the cooling rate can be used for the targeted change of physical, chemical and mechanical properties of alloys.

The purpose of this study is therefore to expand the concept of possible pattern changes of interatomic interactions and bonds under such conditions, when the pressure of up to 100 MPa/s is being exerted with a fixed speed rate onto the molten metal with the temperature 150..200 K higher than crystallization temperature.