

Development of technology of microplasma spraying for the application of biocompatible coatings in the manufacture of medical implants

Abstract. This paper describes the equipment design of E. O. Paton Electric Welding Institute and technology of microplasma spraying of coatings from powder and wire materials for applying biocompatible coatings for medical implants. The given equipment was introduced at an experimental robotics complex for microplasma spraying at D. Serikbayev East-Kazakhstan State Technical University. By this example the authors discuss the challenges and prospects of the development and implementation of microplasma spraying technology.

Streszczenie. W artykule opisano konstrukcję sprzętu w E. O. Paton Electric Welding Institute oraz technologię natryskiwania mikroplazmy powłok z proszków i materiałów drucianych w celu nanoszenia biokompatybilnych powłok na implanty medyczne. Dany sprzęt został wprowadzony do eksperymentalnego kompleksu robotyki do natryskiwania mikroplazmy na Uniwersytecie Technicznym D. Serikbayev East-Kazakhstan. Na tym przykładzie autorzy omawiają wyzwania i perspektywy rozwoju i wdrażania technologii mikroplazmatycznej. **Technologia natryskiwania mikroplazmy powłok z proszków i materiałów drucianych w celu nanoszenia biokompatybilnych powłok na implanty medyczne**

Keywords: microplasma spraying, biocompatible coatings, medical implants.

Słowa kluczowe: rozpylanie mikroskopowe, biokompatybilne powłoki, implanty medyczne,

Introduction

The multi-purpose methods of Thermal Coating Spraying, such as: Plasma Spraying, Combustion Flame Spraying, Arc – Spraying have become popular all over the world [1, 2]. Thermal spray coatings effectively increase the wear resistance and the corrosion resistance of the surface and its resistance to oxidation and corrosion at high temperatures. It is significant that thermal spraying is a relatively “cold” process, and the substrate is usually not heated above 65°C, which ensures its minimal thermal degradation [2].

The treatment of surfaces of complex configurations presents a challenge for the implementation of the thermal spraying technology and requires automated manipulations of the jet and/or the substrate along with robotic control for appropriate treatment of a surface [1, 2].

Summarizing the results presented in [1-4], we can note 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.

One of the major methods of gas-thermal deposition of coatings is plasma spraying. Plasma guns that generate a turbulent plasma jet with the electric power up to 200 kW and a spot diameter of the sprayed material of 15...30 mm are most commonly used for this purpose. The use of such plasma guns for spraying small-sized parts or thin-wall parts can lead to their overheating and distortion due to high heat power of a plasma jet. In addition, in the case of spraying small parts or local areas of surfaces (5...10 mm or less) there is a considerable loss of the sprayed material. Besides, masking the areas that are not to be treated requires additional operations.

These circumstances have led to the development of a new method of thermal coating, microplasma spraying (MPS), by the E. O. Paton Electric Welding Institute (EWI) [5, 6]. The microplasma spraying method is characterized by a small diameter of a spraying spot (1 ... 8 mm) and low (up to 2 kW) power of plasma, which results in low flow of heat into the substrate [5-7]. These characteristics are very attractive for the deposition of coatings on small parts or in

case high accuracy is required, in particular for applying biocompatible coatings in the manufacture of medical implants.

The aim of this work was to develop such technology for automated micro plasma deposition of metal coatings using an industrial robot that is suitable for producing biocompatible coatings for medical implants.

Experimental procedure

A series of design and technological works which resulted in developing a number of microplasma deposition plants (MPS-001, MPS-002, MPS-003) has been carried out by E. O. Paton EWI. 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 MP-004 microplasmotron (Fig.1 a).

The process of microplasma spraying is distinctive of 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. In this regard, and according to the design of the microplasmotron, the MPS process has the following distinctive characteristics:

- since the expansion angle of a laminar plasma jet makes only 2...6° (instead of 10...18° for turbulent plasma jets), and the nozzle diameter is small (1...2 mm and less), it is possible to reduce the size of the deposition spot to 1...8 mm;
- low thermal power of a microplasma jet allows reducing the heating of a substrate, which provides the possibility of applying coatings on small-sized and thin-walled products without excessive local overheating and warpage;
- the use of a microplasmatron with an offset anode allows for the flow of the sprayed material directly into the arc discharge, the highest temperature area of the plasma jet, which is advantageous for coating deposition on such high-melting-point material as Al₂O₃, ZrO₂, W;
- the use of a jet of protective gas, argon, helps reduce the degree of oxidation of the sprayed material;
- a laminar plasma jet has a low sound level (30...50 dB),

which allows using the equipment for microplasma spraying without a special sound-proof chamber;
 - the equipment has high mobility due to the presence of its own cooling system. The plant requires 1 cylinder of compressed argon and AC of 220 V (380 V), 50 Hz. Both powder and wire can be used as a source material for spraying.

An experimental laboratory industrial complex for plasma treatment of materials based on an industrial robot was established at D. Serikbayev East Kazakhstan State Technical University (EKSTU) within the activities of development of modern technologies. KawasakiRS-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. It is controlled by an E40F-A001 programmable controller. MP-004 microplasmotron for applying the powder or wire coating

produced by E. O. Paton EWI, Ukraine, is mounted on the robot arm (Fig.1b). The assembly of the system was carried out by "Innotech", LLP, Kazakhstan.

KawasakiRS-010LA robot manipulator characteristics:

- Positioning accuracy – 0.06 mm;
- Maximal linear speed - 13100 mm/s;
- Engagement zone - 1925 mm;
- Working load capacity - 10 kg.

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

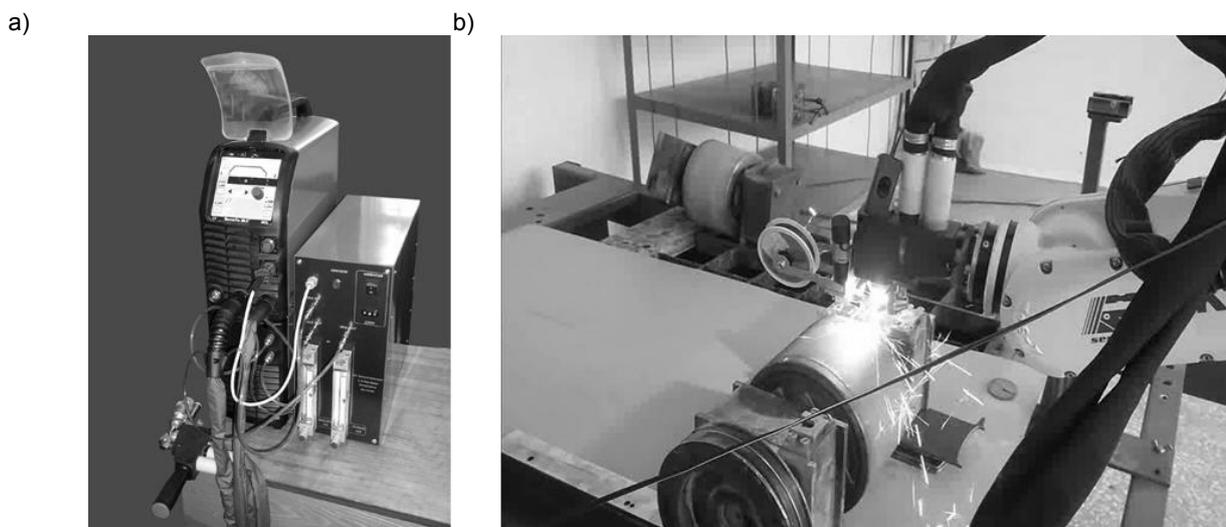


Fig.1. External view of MP-004 manufactured by E. O. Paton EWI, Ukraine (a) and the process of micro-plasma deposition of wire coating on the surface of a cylindrical shaft (b) at the experimental site for micro-plasma surface treatment at D. Serikbayev EKSTU.

To analyze the structure and composition of coatings formed by micro-plasma spraying the methods of transmission and scanning electronic microscopy with elemental analysis, XRD analysis and optical microscopy were used. Microhardness of coatings and substrates was also investigated.

The experience of E. O. Paton EWI in microplasma spraying [5,6,8,9] testifies to the possibility of applying this method to spraying a wide range of coatings from metals (Al, Cu, Ni, Ti, W, Mo, etc.); Al-, Cu-, Fe-, Co-, Ni-alloys; oxides (Al₂O₃, TiO₂, ZrO₂), carbides (WC, Cr₃C₂); and bioceramics (hydroxyapatite, tricalcium phosphate). Some properties of microplasma coatings are shown in Table 1.

Table 1. Microhardness and content of oxygen of microplasma sprayed coatings from 0.3 mm diameter wire

Sprayed material	Microhardness, MPa	Content of oxygen, %
Inconel 82	HV0.05, MPa 303...370	2.9...5.8
W	HV0.05, MPa 1880...2060	3.3...13.8
NiCr (Ni80Cr20)	HV0.05, MPa 309... 361	3.1... 15.1
Ti	HV0.025, MPa 320...550	0.88...2.8

New technology for applying biocompatible coatings on hip implants has been developed by the E. O. Paton EWI (Fig. 2 a, b). It was implemented at "MOTOR SICH," JSC (Ukraine) producing such implants. Other developed technologies include the technology for applying biocompatible coatings on implants for interbody spondylosyndesis (Fig.2 c) and dental implants (Fig.2 d) [9].

The prototypes of Ni-based protective coatings from wires and powders (Fig. 3) were produced at D. Serikbayev EKSTU using the robotic complex for microplasma deposition.

To solve the problem of providing the desired trajectory of the plasma source, we have developed the software which converts the drawings made in AutoCAD and Compass for 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 parameters for additional processing of coatings by a plasma jet were selected on the basis of mathematical modelling of the temperature fields arising in the "coating-substrate" system when heated by a travelling plasma source [10]. The results of the study of the structure and properties of these coatings, published in the works [11,12], showed that nanosized reinforcing particles of intermetallic phases of lamellar morphology are formed in the coatings, which leads to 2- or even 4-fold increase of microhardness of the coatings compared to the substrate.

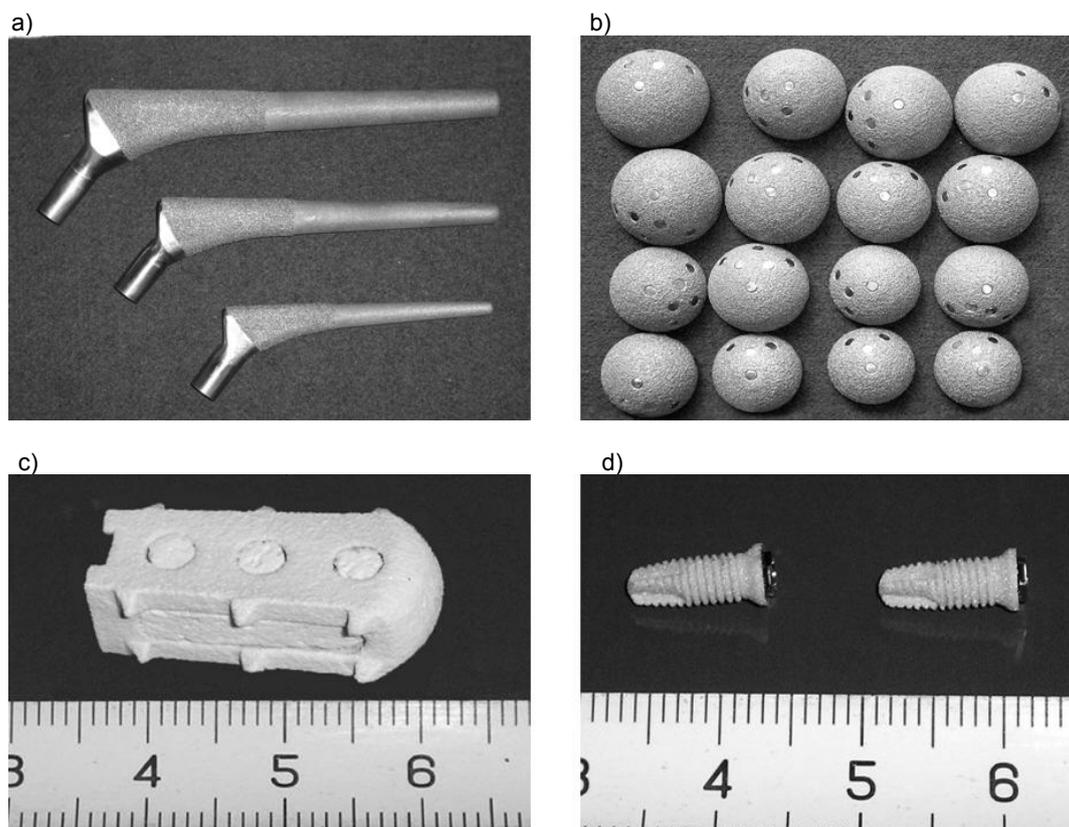


Fig.2. Examples of products with biocompatible coating deposited by microplasma spraying at the E. O. Paton EWI: components of hip implants (a), (b); implant for interbody spondylosyndesis (c); dental implants (d).

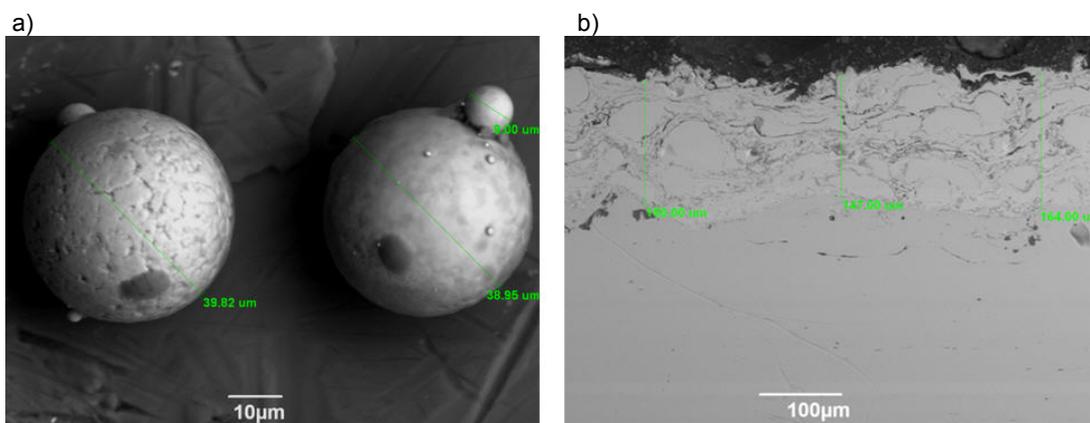


Fig.3. SEM images of NiCrBSi alloy powder particles (a) and the cross-section of the powder coating deposited by MPS on a steel substrate (b) External view of MP-004 manufactured by E. O. Paton EWI, Ukraine (a) and the process of micro-plasma deposition of wire coating on the surface of a cylindrical shaft (b) at the experimental site for micro-plasma surface treatment at D. Serikbayev EKSTU.

Discussion

The MPS method is of the greatest interest for applying biocompatible coatings on medical implants. Titanium wire, titanium or bioceramics powders based on calcium phosphates can be used as materials for coating. 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 plasmotron 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. The experience of getting coatings from powders and wire of a range of alloys with the use of this complex was successful, the results were published in [11,12]. At this stage, no clinical tests on humans or animals have been carried out, but there are successful cases of microplasma spraying technology practices of applying biocompatible coatings to hip joint endoprostheses and technology implementation when producing such endoprostheses at MOTOR SICH JSC (Ukraine) [9].

Thus, there is reason to believe that the use of this complex will allow developing a technology for depositing

biocompatible coatings on a wide range of implants, including dental 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), 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).

Conclusions

The equipment and technology for microplasma deposition of coatings have been developed by E. O. Paton EWI. The specificity of the microplasma spraying process coating deposition lies in the possibility of employing a laminar jet flow mode using pure argon as orifice gas and low power of the microplasmatron (up to 2.5 kW). This allows reducing the size of the spray spot to 1...8 mm, which provides coating deposition on small-sized and thin-walled products with minimal sprayed material losses. It also makes possible microplasma spraying of coatings on parts of small size and thin walls without their excessive local overheating and warpage. Deployment of a jet of protective gas, argon, provides depositing coatings of metals with oxygen content of 0.9-3.3 %. The MPS method allows applying a wide range of materials: metals, alloys, bioceramics (hydroxyapatite, tricalcium phosphate), etc.

A robotic micro-plasma spraying complex for applying biocompatible coatings on different implants has been set by D. Serikbayev EKSTU and E. O. Paton EWI with the aim of development of technology for medical implants made of titanium and its alloys produced by UK TMP, JSC.

Acknowledgements

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".

Authors: Prof., dr hab. phys. Darya Alontseva, associated professor, dr. inż. Nadezhda Prokhorenkova, senior lecturer Tatyana Kolesnikova, Ph.D. student Albina Kadyroidina D. Serikbayev East Kazakhstan state technical university, 69, Protozanov Street, 070004 Ust-Kamenogorsk, Kazakhstan, E-mail: Darya Alontseva <daontseva@mail.ru>; Nadezhda Prokhorenkova <nadin_kaz@mail.ru>, Tatyana Kolesnikova <takol@list.ru>, Albina Kadyroidina <heartwarmer@bk.ru>;

Head of the department of electrothermal processes of material processing, prof., dr hab. inż. Yuri Borisov, senior researcher, dr. inż. Sergii Voinarovych, senior researcher, dr. inż. Oleksandr Kyslytsia, E. O. Paton Electric Welding Institute, 11 Bozhenko Street, 03680, Kiev, Ukraine, E-mail: Yuri Borisov <borisov@paton.kiev.ua>, Sergii Voinarovych, <serge.voy@gmail.com>, Oleksandr Kyslytsia <kisl@i.ua>

REFERENCES

- [1] R.C. Tucker, Ed Introduction to Coating Design and Processing, *ASM Handbook, Thermal Spray Technology* Volume 5A, 2013, pp.76-88.
- [2] Vardelle A., Moreau Ch., Nickolas J., Themelis A.: Perspective on Plasma Spray Technology, *Plasma Process*, 35, 2015, pp. 491–509.
- [3] Kuroda S., Kawakita J., Watanabe M., Katanoda H., Warm spraying - a novel coating process based on high-velocity impact of solid particles, *Sci. Technol. Adv. Mater.* 9 (3): 033002. (2008). DOI:10.1088/1468-6996/9/3/033002.
- [4] Wang L., Wang H., Hua S., Cao X., Plasma Science and Technology. 9, 52 (2007). 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, *The International Thermal Spray Conference, Essen, Germany, 2002*, p.335-338.
- [6] Borisov Iu.S., Voinarovich S.G., Kislitca A.N. Microplasma spraying using wire materials, *Avtomaticheskaja svarka* [Automatic welding], 2002, no3, pp.54-55.
- [7] Lugscheider E., Bobzin K., Zhao L. and Zwick J., Special Issue: Thick Coatings for Thermal, Environmental and Wear Protection, *Advanced Engineering Materials*, Volume 8, Issue 7, 2006, pp. 635–639, DOI: 10.1002/adem.200600054.
- [8] Decl. Pat. UA V23K10/00 Plazmotron dlia napilennia pokryttiv / Borisov Iu.S., Voinarovich S.G., Fomakin O.O., Iushchenko K.A. (Ukraine (UA)); no 2002076032; Zaiavl.19.07.2002r. Opubl. 16.06.2003, Bul. no 6.
- [9] Iushchenko K.A., Borisov Iu. S., Voinarovich S.G., Kislitca A.N., Kuzmich-lanchuk E.K., Two-layer biochemical coating of titanium-hydroxyapatite, *Avtomaticheskaja svarka* [Automatic welding], 2011, No 12, pp. 46 – 49.
- [10] Krasavin A.L., Alontseva D.L., Denisova N.F. *Raschetnyy temperaturnykh profilej v dvuh-slojnykh poglotiteljah s postojannymi teplofizicheskimi ko'effitsientami pri nagreve dvizhushchimsja istochnikom* [Calculation of temperature profiles in the two-layer absorbers with constant physical characteristics heated by a moving source] Certificate of authorship, KZ, No 0010558, 2013.
- [11] Alontseva D., Krasavin A., Ospanov O. Software Development for a New Technology of Precision Application of Powder Coating Multifunctional Systems, *11th International Symposium on Applied Informatics and Related Areas*. Szekesfehervar, 2016, pp.140-143.
- [12] Alontseva D., Krasavin A., Prokhorenkova N., Kolesnikova T., Plasma – Assisted Automated Precision Deposition of Powder Coating Multifunctional Systems, *Acta Physica Polonica A*, Volume 132, No 2, 2017, pp.233-235. DOI: 10.12693/APhysPolA.132.233