TWO-LAYER BIO-CERMET TITANIUM–HYDROXYAPATITE COATING

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It is suggested using two-layer bio-cermet (titanium–hydroxyapatite) coatings for titanium alloy endoprostheses. A combination of porous titanium with an external hydroxyapatite (HA) layer provides high strength of adhesion of such coatings to the surfaces of endoprostheses (24–25 MPa) and subsequent active growth of bone tissue into them. The microplasma spraying technology allows formation of the HA layer with the 88–98 % content of the crystalline phase, thus providing a high degree of utilisation of the powder (up to 90 %) in spraying and increasing the cost effectiveness of the process.

Keywords: *microplasma spraying, medical-application coatings, bio-compatible coatings, porous titanium, hydroxyapatite, endoprosthetics, hip joint*

Metal implants with bio-active ceramic coatings are widely applied now in medical practice. These implants are characterised by a triple positive effect: increased rate of formation of the bone tissue, possibility of formation of bond with the bone (osteointegration), and decrease in formation of metal corrosion products. This allows substantial reduction of the time of implantation of an endoprosthesis, provides the reliable bond with the bone and improves reliability of the implants. The most extensively used bio-active ceramics are ceramics based on calcium phosphate, i.e. hydroxyapatite (HA), or other calcium phosphates close to it in composition [1, 2].

Bio-ceramic coatings of HA are deposited by using different methods (magnetron sputtering, electrophoretic deposition, sol gel method, etc.), including plasma spraying, which has received a real practical application in production of coated endoprostheses [2–5].

The following main requirements to quality of the bio-ceramic coatings were worked out on the basis of clinical application of endoprostheses with such coatings: sufficiently high strength of adhesion to the endoprosthesis surface (15 MPa or more, according to standard ISO 13779–2), high content of the crystalline phase (not less than 70 %), and presence of developed porosity providing ingrowth of the bone tissue.

Phase composition of a coating (degree of crystallinity) has a considerable effect on the osteointegration process. During this process the amorphous HA phase has a higher rate of dissolution, thus reducing the time of recovery of a patient but, at the same time, decreasing reliability of fixation of an endoprosthesis in the bone.

A drawback of the conventional plasma spraying method is formation of coatings with a high content of the amorphous phase, which is caused by conditions of both heating of the HA particles (because of the need to use working gases with increased thermal conductivity, i.e. Ar + H_2 and Ar + He mixtures) and their solidification on the substrate surface [6].

In the last years the E.O. Paton Electric Welding Institute has developed the microplasma spraying method and equipment, allowing spraying of ceramic coatings by using the laminar jet of argon plasma [7]. A low thermal conductivity of argon decreases the intensity of heating of the particles, thus decreasing the temperature gradient across their sections. In spraying of the HA coatings this allows avoidance of overheating of the melt of HA and formation of toxic products of its decomposition (CaO). Low velocities of the HA particles under conditions of the laminar jet lead to formation of coatings from the particles with a lower deformation degree and, hence, lower rate of hardening on the substrate, which provides the high content of the crystalline phase (up to 95–98 %).

In this connection, the E.O. Paton Electric Welding Institute completed a package of work on development of the compositions and technology for deposition of bio-ceramic coatings on endoprostheses by using microplasma spraying [8–10].

The technology for microplasma spraying of two-layer bio-cermet (Ti + HA) coatings on implant surfaces was developed to increase strength of adhesion of the coatings to the bone implant surfaces. This technology allows deposition of a titanium coating with regulated porosity by microplasma spraying using a variant of wire spraying.

The two-layer bio-cermet coatings are deposited by using microplasma spraying system MPN-004 (Figure 1), which comprises a power source with a cooling unit, control unit, plasmatron, as well as the interchangeable wire feed mechanism and powder feeder MPD-004 (Figure 2).

The spraying materials for the two-layer bio-cermet coatings are the 0.3 mm diameter titanium wire of the VT1-00 grade used for deposition of the titanium coating with developed porosity, as well as the HA powder used for deposition of the bio-active upper

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layer, the phase composition of the HA powder produced by Scientific-and-Technical Service Centre «RAPID» being fully crystalline $Ca_{10}(PO_4)_6(OH)_2$ with the Ca/P-1.67 ratio.

Appearance of the surface and structure of the bio-cermet coating are shown in Figure 3.

The costs of the HA coating deposition process depend on the consumption of the HA spraying powder, the price of the latter being very high. Experimental studies of the material utilisation factor (MUF) for HA in deposition of the two-layer bio-cermet coating show that in the case of microplasma spraying it is 1.5–2 times higher than in traditional plasma spraying. For instance, according to literature data, the maximal values of MUF in plasma spraying of HA on a plate are 50–62 %, whereas in microplasma spraying the maximal value of MUF amounts to 90 % [10]. Under conditions of microplasma spraying the spraying spot has a form of ellipse with an axes ratio of 1.1–1.3 and size of 8–15 mm (instead of 30–40 mm in conventional plasma spraying), depending on the spraying process parameters. The calculations of losses of the HA powder show that the total losses of the material (for recoil and spattering, and losses caused by geometric factor) in microplasma spraying on implants 8–10 mm in size (dental, intervertebral cages) are 20–40 %, whereas in traditional plasma spraying they amount to 85–90 %.

Figure 1. Appearance of microplasma spraying system MPN-004

The investigations conducted resulted in establishing the quantitative dependence of phase composition of the HA coating on such microplasma spraying parameters as current, plasma gas flow rate, spraying distance and powder consumption. Thus, the content of the crystalline phase of HA in a coating, as well as the content of the amorphous phase in it are most strongly affected by the spraying distance. The amount of tricalcium phosphate (β-TCP) in the coating greatly depends on the plasma gas flow rate and spraying distance. Therefore, by varying the microplasma

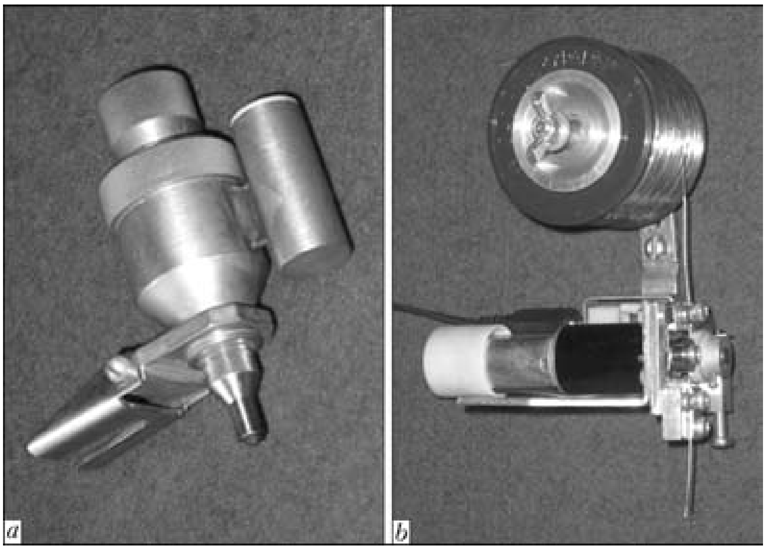

Figure 2. Appearance of powder feeder MPD-004 (*a*) and wire feed device MPP-04 (*b*)

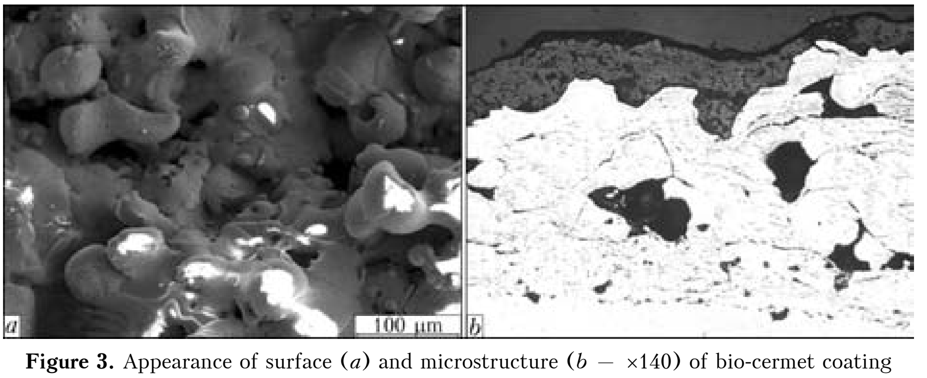

Figure 3. Appearance of surface (*a*) and microstructure (*b* — ×140) of bio-cermet coating

Figure 4. Examples of items with bio-cermet coatings produced by microplasma spraying: *a* — hip joint endoprostheses; *b* — cermet implant for interbody vertebral spondylosyndesis; *c* — dental implant

spraying parameters (current, plasma gas flow rate, spraying distance and powder consumption) it is possible to control phase composition of the HA coatings at a content of the HA crystalline phase ranging from 88 to 98 %, degree of amorphism in a range of 0 to 7 % and TCP content (degree of decomposition of HA) in a range of 0 to 6 %. Hence, it is possible to control formation of the HA coatings with the specified phase composition.

Strength properties of the two-layer bio-cermet coatings should provide their integrity and long-time reliable functioning in an organism. According to standard ISO 13779–2, sufficient strength of adhesion of the coatings to the substrate should be not less than 15 MPa. Spraying of the two-layer bio-cermet coatings by using a titanium coating with developed porosity (pores with a size of 100–150 μm) provides the adhesion strength equal to 25.2 ± 0.85 MPa.

Toxic-hygienic estimation of the bio-cermet coatings was carried out by the Institute of Macromolecular Chemistry of the NAS of Ukraine*. According to standard ISO 10993–2, samples of the coatings were implanted to white rats. Histological investigations of such tissues around the implanted coatings showed that the bio-cermet coatings of HA and titanium (Ti + HA) are non-toxic, bio-compatible with live tissues, and exert no irritating and sensitising effect.

The bio-medical investigations allowed a conclusion on the safety and bio-compatibility of endoprostheses with the microplasma bio-cermet coatings (Ti + HA). Recommendations on deposition of the bio-cermet coatings by the microplasma spraying method were worked out on the basis the investigation results.

The developed microplasma spraying technology was applied for deposition of coatings on hip joint endoprostheses, implants for interbody vertebral spondylosyndesis [11] and dental implants (Figure 4).

CONCLUSIONS

1. Microplasma spraying of bio-ceramic HA coating is characterised by the possibility of producing layers with a high degree of crystallinity (88–98 %), which can be controlled by varying the spraying process parameters. Small size of the spraying spot (3–8 mm) provides substantial decrease (2–3 times) in powder consumption during spraying on small-size implants, compared to conventional plasma spraying.

2. The two-layer bio-cermet coating (porous titanium + HA) provides the strength of adhesion to endoprosthesis equal to 24–25 MPa and intensification of growth of the bone into the coating surface.

3. Toxic-hygienic examinations of the microplasma bio-cermet coatings proved their being non-toxic and bio-compatible with live tissues.

4. The bio-cermet coatings (Ti + HA) and technology for their microplasma spraying were used for coating of hip joint endoprostheses, dental implants, intervertebral cages etc.

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