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AN INNOVATIVE APPROACH TO THE ESTABLISHMENT OF LONG-TERM IMPLANTS FOR SPINAL FUSION BONE SPINE

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Abstract. The result of the research on implementation of the AMAO method for manufacturing high quality implants for locomotor apparatus are presented; the peculiarities of functional coatings formed on titanium implants surface to enhance biocompatibility with bone tissues are adduced. According to the sanitary and hygienic examination data it is concluded that titanium implants with oxide-ceramic coatings, formed under AMAO method, are safe for application in clinical medicine.
Keywords: osteosynthesis, implants, functional coatings, oxide-ceramic, elastic deformation.

1. Introduction

Injuries of the locomotor apparatus are people’s most widespread damages. It is caused by increasing of domestic, traffic, and occupational traumatism. The number of complex fractures, especially of spinal column, pelvis, and intra-articular damages, is increasing correspondingly and it is a subject to surgical treatment using different hardware. The problem of the surgical treatment of spinal column diseases (neoplastic processes, degenerative damages, scoliosis), hip joint is urgent nowadays, and the implantable device, the fixator, and the endoprosthesis are left in the body of the patient for life. In tote in Belarus there are up to 9000 patients a year who need operations of this kind. It is proved worldwide that the most effective method to treat complex intra-articular fractures in different locations is osteosynthesis [1, 2]. But up to the present time the CIS countries have not paid sufficient attention to the technique of implementation of the external bone osteosynthesis. Nearly every big Scientific Research Institute developed its unique fixator, the unified systems approach was absent, and the modern bio inert materials were not used. Not only the performance of mechanical or physiological functions is of great importance for an implant but also the surrounding tissues and fluids adaptability to it and their mutual impact.

Titanium, cobalt-chromium-molybdenum alloys, and also corrosion-resistant steel-molybdenum alloys with 20–24% chromium content by mass are regarded as biocompatible materials. These metals have the maximum wide set of mechanical properties and have been used to produce the most stressed orthopedic implants until recently. They usually used nothing but the steel of 12X18H9T grade to produce steel implants, but this grade is inferior to the western analogue of 316L in bio inertness and corrosion-resistance [3]. In addition the operational experience with steel constructions has revealed a number of grave shortcomings during the operation. The low corrosion-resistance of the steel leads to the metallosis onset (up to 5–7% of cases) that can provoke productive inflammation in combination with a consecutive infection and, as a result, causes destabilization of the construction, nonunion, and fatigue fractures (up to 12% of complications) and increases dramatically the treatment costs for patients.

The developed countries, thanks to the mutual work of traumatologists- orthopedists, biophysicists, technologists, have achieved great success in the field of osteosynthesis as a surgical method for bone fragments stabilizing, prosthetic joints implanting. The most remarkable recent success is related to the wide usage of bio inert, biocompatible constructions for implanting especially if long-term performance in tissues is necessary. In consideration of the negative experience with steel and ferroalloys constructions the western companies have launched the production of ceramic solids, graphite composites constructions, titanium alloy implants [4].

2. Experimental part

Young modulus, it is equal to 18-20 GPa in living bone tissue [5, 6], is an important parameter of implant materials for replacement of bone structures and dental implants defining which defines their bio-mechanical concordance to bone and other biological tissues. When elastic deformations occur in the "bone-implant" system the tissue load depends on the implant material Young modulus and bone tissue ratio – the less the ratio, is the less the probability of necrosis and the bone destruction by the implant pressure is. Figure 1 shows that titanium, of all implant materials, has the closest Young modulus to bone tissue and it is 110 GPa and two times lower that steel has, i.e. any elastic deformations in the "bone-implant" system cause two times less pressure to the tissue and, as a result, decrease dramatically the probability of necrosis and the bone destruction and allow making a conclusion about the most optimal bio-mechanical parameters of this metal for manufacturing of the cyclical load implants.

At present time carbon-filled plastic is widely used in implant constructions thanks to its high inertness in acidic and alkaline mediums in the wide scale of temperatures and pressures and also to the pronounced thromboresistance. The carbonic tissues combine the features of synthetic graphite and textile plasticity. They are obtained when viscose textile is thermal processed. The modulus of elasticity of the carbon-filled plastic (21–24 GPa) is rather close to such of bone tissues (Figure 1) that makes this material promising for orthopedics [1, 2].

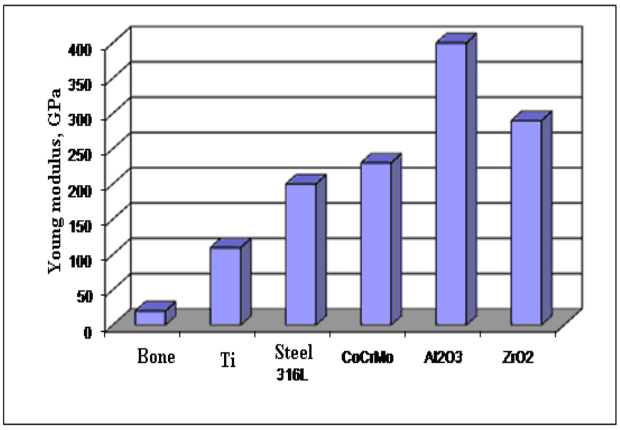


Fig. 1. Young modulus for various materials

But the complete absence of osteo-integration of such dense and non-porous carbon materials is more reasonable to use not for the direct implanting but as a load element in apparatuses for external fixation. In addition the high cost of this material limits the possibility of its implementation too.

Pure titanium is the most applicable from the point of view of functionality and low cost as well as bio inertness and biocompatibility. But this material has rather low strength characteristics and weakly stable in alternating loads. That is why titanium alloys (VIAM titanium 1-0, VIAM titanium – 6, VIAM titanium – 15 and others) are used more widely as their biocompatibility and bio inertness are conditioned by oxide film TiO_2 with the structure of anatase and rutile as pure titanium has. The more the width of the oxide film and the percentage of anatase in it is, the higher the bio inertness and biocompatibility is [7]. The content of anatase and rutile in the oxide film of titanium alloys is up to 60–70 % and the rest is various elements of the alloy (Al, Fe, V, N, C and others). It is believed that the influence of these elements upon the surrounding tissues in contact causes host reaction, non-engraftment and loosening (e.g. for replacement arthroplasty). So the western orthopedic companies use, when manufacturing implants, various methods of artificial oxidation that means technologies for increasing of the width and percentage of TiO_2 with the structure of anatase and rutile in the film.

The problem of biocompatibility effects crucially the on-going osteo- integration and stability of the endoprosthesis components in the bone tissue. The oxide film TiO_2 shows its worth in the body as hydroxylon chemisorbent OH^- and imparts amphoteric character to the implant surface that leads to high adhesion of the biological tissue and the implant, stimulates its quick integration into the tissue preserving its normal nourishing. Meanwhile the surface roughness degree is an important factor which can stimulate additionally the implant osteo- integration.

The nowadays common oxidation of a titanium construction in chemical acids solution does not allow obtaining the homogeneous structure of the film and to prognosticate its composition. ALTIMED Company manufactured SLPS endoprostheses in accordance with the well-known and already used method of vacuum magnetron deposition of titanium oxide film did not prove its value as it required high production standards and thorough surface cleaning. The research data of the distant endoprostheses has revealed the cases of insecure junction of the sputtered film with the implant because of the violation of the above-mentioned requirements. As a result a part of the coating was removed spontaneously because of the body's macrophage reaction.

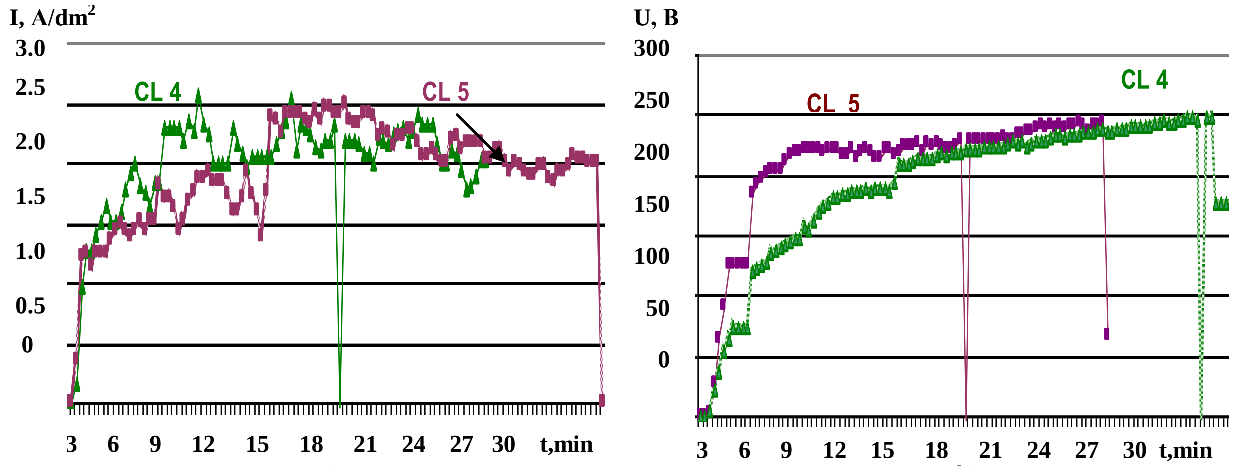
The method of anodic micro-arc oxidation (AMAO) is the most promising and corresponding to the up-to-date demands to form oxide coatings. AMAO method assures a reliable and high-strength jointing of the coating with the implant body. Additionally the micro-arc oxidation allows performing surface of micro texturing to increase the contact area of the implant and the surrounding bone tissues that substitutes preliminary mechanical texturing and reduces labour-intensiveness for an implant manufacturing, its cost, and eliminates detrimental impurities from its composition when they get there during mechanical operation.

Nevertheless anodic micro-arc oxidation (AMAO) method has not been implemented for a long time for orthopedic implants manufacturing because of the difficulty to obtain oxide coatings with controlled compositions and structures. Thanks to the results, the author has got during study of the developing of methods to intensify electrolytes process and activation, a practical possibility to make a coating on the surface of titanium alloys; the coating is based on TiO_2 with varicose spinal conjunctions additives which, depending on their phase composition, can work as a corrosion protection and impart enhanced mechanical parameters to the ceramics. The oxide ceramics with controlled surface structure allow making graft layers in it to optimize the coating biocompatibility via stable calcium-phosphate fullerene-containing graft structures with added superdispersed diamonds which provide enhanced compatibility on the molecular level to body's bone tissues.

All above-mentioned have determined the practicability and effectiveness of the technique of making functionally adapted coatings on the implants surfaces for the bone fractures and locomotor apparatus deformations osteosynthesis. A manufacturing process of forming of oxide-ceramic coatings on titanium implants surfaces has been developed for this purpose and Specifications of implant manufacturing for interbody spinal fusion with oxide-ceramic coatings were finalized. It is an actual and vitally important problem to create modern design of orthopedic implants which is not inferior to the western analogues and 2 – 2.5 times cheaper than them, and obtains enhanced biocompatibility and mechanical parameters.

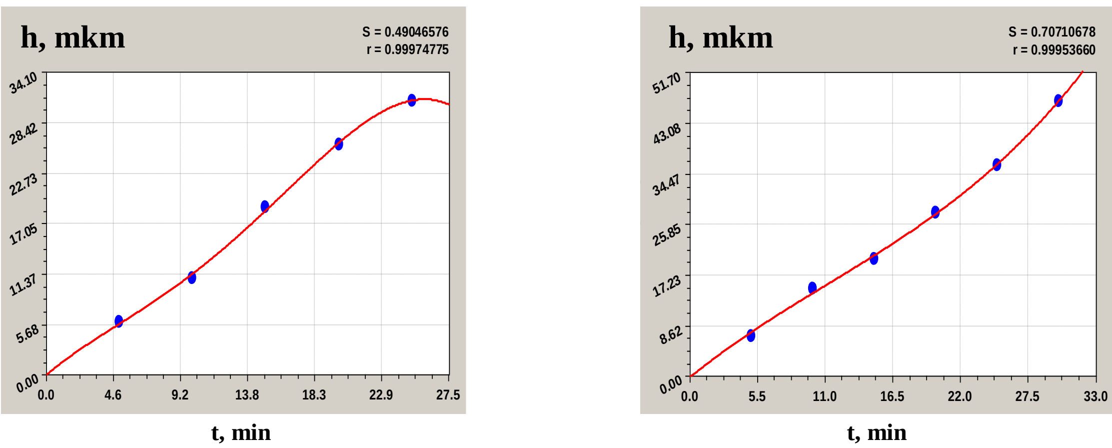
To achieve error-free and long-term performance in a body the oxide coating on the titanium alloys implant surfaces must have predominating quality of titanium dioxide with structure of anatase and rutile in their composition [8, 9]. Several base composition electrolytes have been developed [8] to make the coatings on sample surfaces made of technical and high-strength titanium alloys designed for medical implants manufacturing: Caustic Liquor 4 (CL 4) with minimal quantity of additive ingredients, which can negatively influence on the performance characteristics of an implant coated in this solution, and Caustic Liquor 6 with hydroxyapatite additives $Ca_{10}(PO_4)_6(OH)_2$ with certain concentration of glycerin or gelatin which is a mixture with high biocompatibility with body's tissues [10]. Caustic Liquor 5 (CL 5) and Caustic Liquor 7 (CL 7) have been used for electrical activation of both mixtures by adding charged poliradicals (superdispersed diamonds – SDD) highly compatible with blood to intensify the AMAO process of titanium alloys. One more approach to optimize the parameters of the made oxide coatings which helps to increase their biocompatibility was to graft fullerene-containing structures on their surface as they have shown high affinity with blood. "Grafting" was made just on the surface of the oxides by the method of molecular stratifying. First of all porous oxide layer was obtained in AMAO process, then it was saturated with fullerenes and had been being thermally processed under temperature 723–753 K for several hours [8].

The methods for electrolytes activation were used to obtain coatings with necessary compositions and efficient thicknesses on the titanium alloys surfaces, and the formed coatings parameters under alteration of operating AMAO methods in real-time were studied to check their effectiveness (Figures 2 and 3).



a) b)

Fig. 2. Real-time alteration of pulse current values (a) and voltage (b) during AMAO of VIAM titanium alloy in studied electrolytes



a) in Caustic Liquor 4 (CL 4)

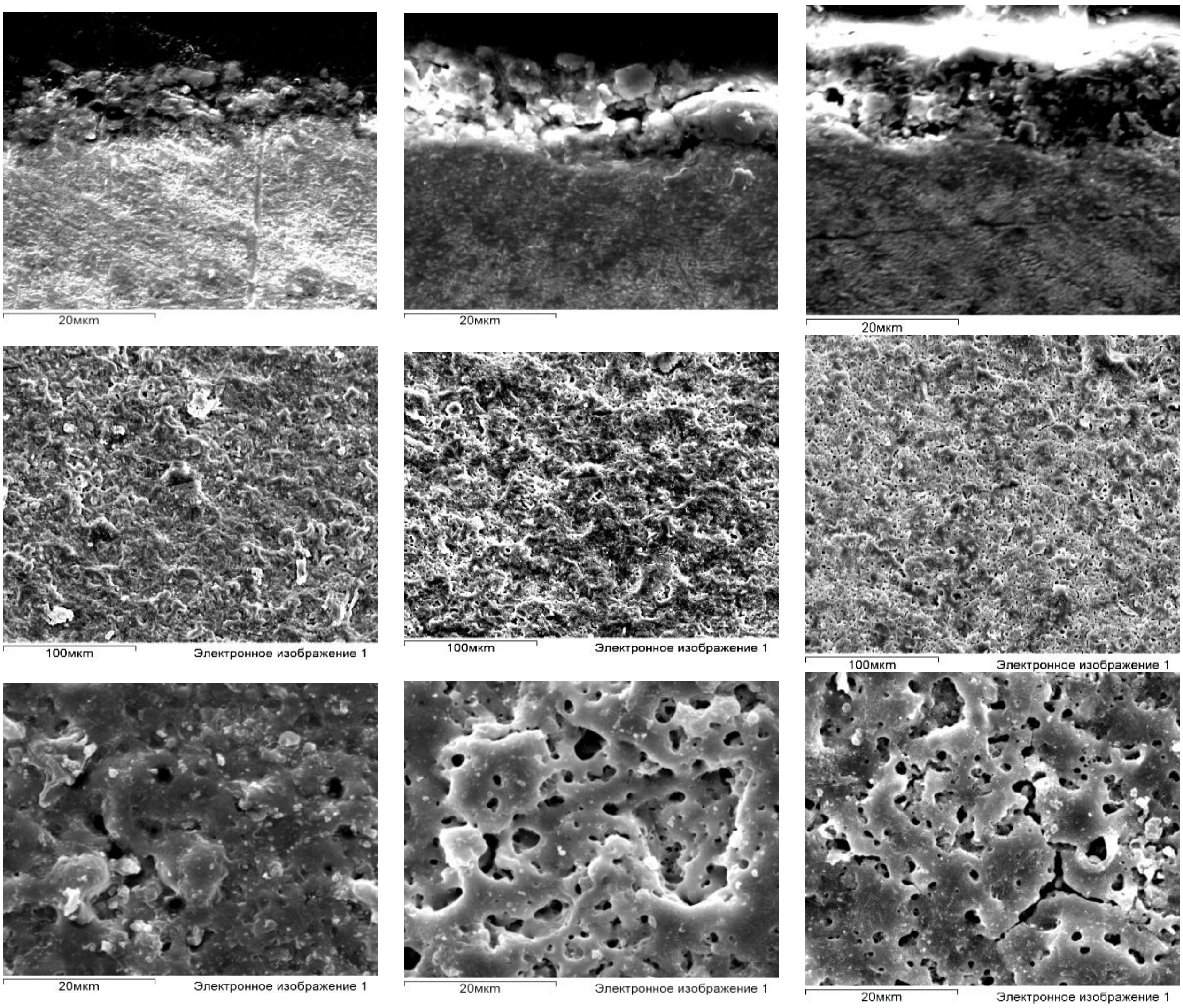
b) in Caustic Liquor 5 (CL 5)

Fig. 3. The coating thickness obtained in different electrolytes on the surface of the sample of VIAM titanium alloy

The diagrams in Figure 3 show that in the activated with additives SDD electrolyte there are more preferable conditions for monotonous building up of the surface with increasing AMAO process period.

The dominating role of the electrolyte composition and energy state was ascertained when the peculiarities of oxidized VIAM titanium 1–0 titanium alloy structure formation were studied. The comparison of the photo of the microstructure and the topography of the coatings surface, obtained in the activated electrolytes, showed that the thinnest (10–15 μm) layer with a great number of structural defects on the surface and a low number (not more than 10-15%) of small spherical with diameter 1–3 μm was obtained in the activated SDD solution Caustic Liquor 5 (CL 5) (Figure 4, a). The thicker (more than 20 μm) layer with pronounced relief on the surface and a bug number of branched large pores, connected with canals was obtained in Caustic Liquor 6 (CL 6) with additives of hydroxyapatite (Figure 4, b).

The presence of hydroxyapatite with glycerin and gelatin mixture in the solution leads to the decreasing of the charge density and lower values of surface tension and determines conjunction forming in colloidal and highly dispersed state. It helps to shift the arcing voltage to higher values and it is an important condition for obtaining thicker layers. The thickest (more than 30-35 μm) coating with small pores relatively uniformly distributed along the surface, with pronounced relief on the surface, and the absence of visual mechanical or structural defects was obtained in Caustic Liquor 7 (CL 7) (Figure 4, c). This coating is the most preferable for reliable performance in the body. The pores are connected with short canals and it gives the possibility to fill this coating, while using it in orthopedic medicine, with pharmaceutical compositions for enhancing implanting in the body's tissues and eliminating the possibility of graft rejection.



a) Caustic Liquor 5 (CL 5) with CDD

b) Caustic Liquor 6 (CL 6) with hydroxyapatite

c) Caustic Liquor (CL 7) with CDD and hydroxyapatite

Fig. 4. Microstructure and topography of the coatings surface on the surface of the sample of VIAM titanium 1-0 alloy obtained in the electrolytes under study by AMAO method

In the Figure 5 there is the structure and the surface of the highly dispersed AMAO coating with heterogeneous grafted layer, obtained by immobilizing method on the base of fullerene-containing conjunctions. The fullerene density on this coating is observed perfectly along the whole area which means high uniformity and graft density (Figure 5, b) [8, 11, 12].

a)

b)

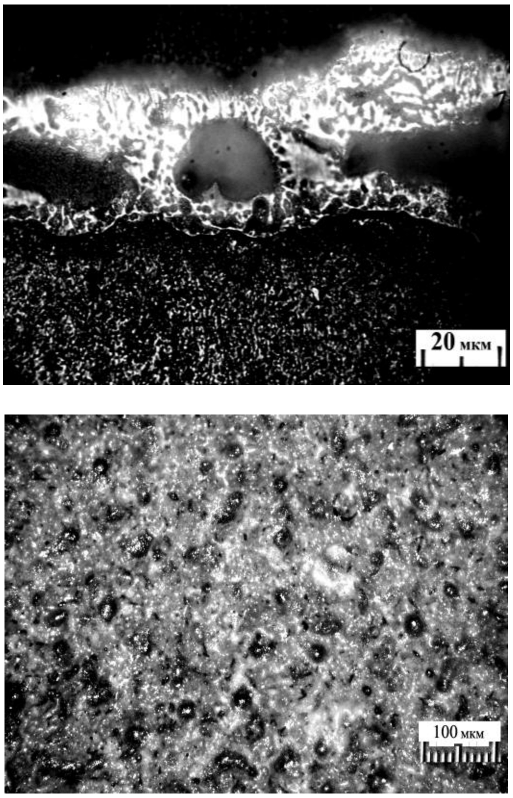
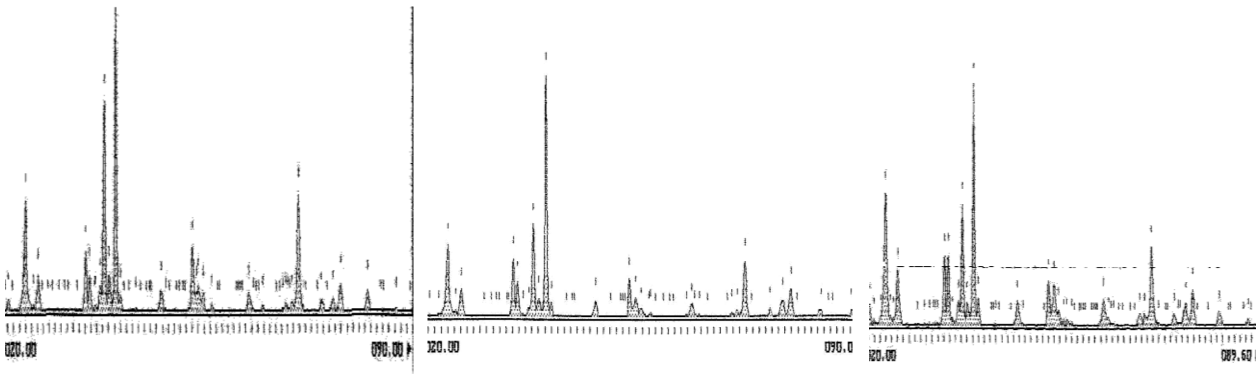


Fig. 5. Microstructure and topography of the coating with grafted structures on the base of fullerene-containing conjunctions on the surface of VIAM titanium 6 titanium alloy sample

The grafted fullerene layer is an aggregation of functional groups of grafted molecules and substances covalently bound on the surface of the formed oxide coating. The composition oxide – fullerene grafted layer – titanium base is notable for the presence of so-called anchor group (by arrows), which provides the grafted layer rigid fixation on the surface of the carrier and is a promising coating in orthopedic medicine.

The diffraction pattern of the coating, obtained in the electrically activated electrolyte on the surface of VIAM titanium 6 alloy (Figure 6, a), shows its homogenous phase composition on basis of titanium dioxide with rutile, anatase, and pure titanium in hexagonal modification structure. Titanium dioxide total content is 65%, and the mean values of microhardness on the surface are 15-17 MPa, that is high-degree strengthening. Other ingredients, with higher level of Gibbs energy than titanium dioxide has, are absent, and it guaranties the coating retains the necessary set of features in the body for a long period of time. The diffraction pattern of the coating from Caustic Liquor 6 (CL 6) with hydroxyapatite (Figure 6, b) meets the microstructure study results either; according to the study it has been mad a conclusion about the process chaotic behavior in the given electrolyte. The coating phase composition is less homogenous with pure titanium domination – up to 38.3% and lower oxide content – less than 62%. The amount of titanium dioxide with anatase structure, which is the most preferable for the conjunction of vitalized tissue, is lower than in the layer from Caustic Liquor 5 (CL 5) with CDD.



TiO_2(21.1276Rut 29.5–29.5 %
TiO_2(21.1272Ant 35–35 %
α.Ti[44.1294]He35.5–35.5 %

a) in Caustic Liquor 5 (CL 5) with CDD

TiO_2 [21.1276 Rut 31.7–31.7% TiO_2 [21.1272 Ant 30.0–30.0 %
αTi [44.1294]He 38.3–38.3 %

b) in Caustic Liquor 6 (CL 6) with $Ca_{10}(PO_4)_6(OH)_2$

TiO_2(21.1276Rut 37.2–37.2 %
TiO_2(21.1272Ant 40.8–40.8 %
α.Ti [44.1294]He 22.0–22.0 %

c) in Caustic Liquor 7 (CL 7) with CDD and $Ca_{10}(PO_4)_6(OH)_2$

Fig. 6. Diffraction patterns from the coatings surfaces formed in the electrolytes under study on the surface of VIAM titanium 6 titanium alloy samples

The notable instability of coating phase composition is proved also by the results of microhardness measurement, the mean values of which are altering from 10.7 MPa to 14,7 MPa along the surface. The X-ray diffraction study of the coating from Caustic Liquor 7 (CL 7) with hydroxyapatite and poliradicals has proved the practicability of the usage of this combination. The coating phase composition contains 78% of titanium dioxide where anatase is ~ 40%. The average maximum of microhardness is 16–18.2 MPa.

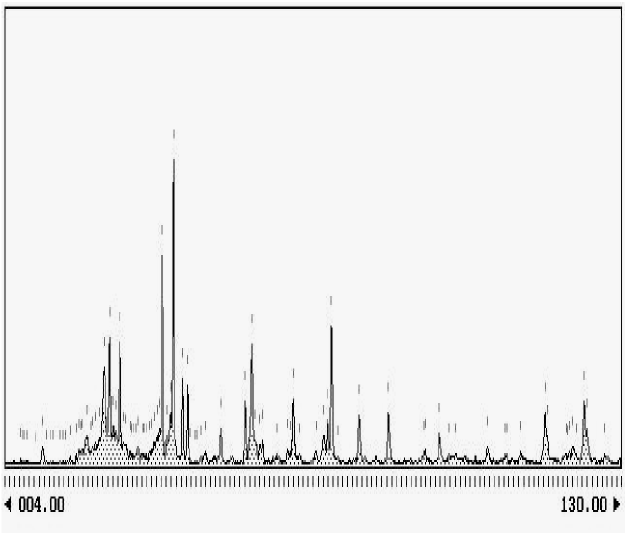
The content of the main elements in the upper layers of the surface is given in Table 1.

Table 1
Distribution of the elements in the coatings on titanium obtained in the electrolytes under study

Quantitative characteristic	Content of elements, %												
	Al			**Si**			**Ti**			**O**			**Ca**
	CL 4	CL 5	CL 6	CL 4	CL 5	CL 6	CL 4	CL 5	CL 6	CL 4	CL 5	CL 6	CL 5
Average	4,75	4,39	4,34	0,48	2,38	2,24	53,95	50,23	52,0	40,81	40,98	40,98	2,01
Standard deviation	0,72	0,9	0,79	0,67	0,76	0,70	1,68	1,74	1,69	0,29	0,19	0,19	0,52
Max.	5,26	5,40	5,12	0,95	3,19	3,0	55,14	51,51	52,0	41,02	41,27	41,07	2,46
Min.	4,24	3,32	3,12	0,0	1,5	1,3	52,76	47,68	48,0	40,61	40,86	40,51	1,33

These data shows that the coatings, made in the created electrolytes, do not contain harmful impurities of Fe, V, N, C and meet one of the above-mentioned performance criterion for coatings.

The phase composition of the coating with grafted structure is illustrated in the diffraction pattern in Figure 7.



NaAlSiO[19.1184] 8,8 – 8,8 (7,5 – 7,5)%

NaO3 [18.1235] 3,8 – 3,8 (3,2 – 3,2)%

P_2O_5 (5.318)Ort 13,3 – 13,3 (13.0 – 13,0)%

P_4O_7 (38.932)Mon 2,0 – 2,0 (1,7 – 1,)%

SiO_2 (4.0359)Cub 11,0 – 11,0 (9,3 – 9,)%

Ti_3O_5 [40.806]Mon 1,5 – 1,5 (1,3 – 1,)%

Ti_9O_{17} [18.1405T 21,3 – 21,3 (18,0 – 18,)%

TiO_2 [21.1272]Tet 29,5-29,5(28,2-28,2)% Anatase

TiO_2 [21.1276]Tet 7,4 – 7,4 (6,3 – 6,)% Rutile

C_{60} [a=10.02 c=16.38]GP 1,4-1,4(1,2-1,2)% Fullerene

Fig. 7. Results of the identification of oxide-ceramic coating with Fullerenes graft on VIAM titanium 6 alloy substrate

One of the most important parameters of the coatings on titanium implants is **adsorptive capacity**. The alternating current volt-amperometric method has been used to define this parameter and the dependence of charge density and surface tension alternation on electrode potential upon the titanium surface and upon the samples of obtained coatings in the range of potentials -3-0V in physiological saline of chloride sodium 0.9% solution has been studied. The research shows that all samples with coatings have considerably less adsorption activity than the titanium without coating (Figure 8, a, b) [11]. It is a positive factor because high biocompatibility is determined by weak ion exchange on the implant – vitalized tissue separation surface. Adding hydroxyapatite in the mixture with glycerin and gelatin into the electrolyte increases a little the charge density and the liquid surface tension alternation on the surface of the obtained coating. Nevertheless the surface adsorptive activity is of general importance only for saturating the implant with antibiotics in the case when this implant has been working in the body for a short period of time. On the contrary intensifying oxidation of adding poliradicals allows obtaining more passive coatings.

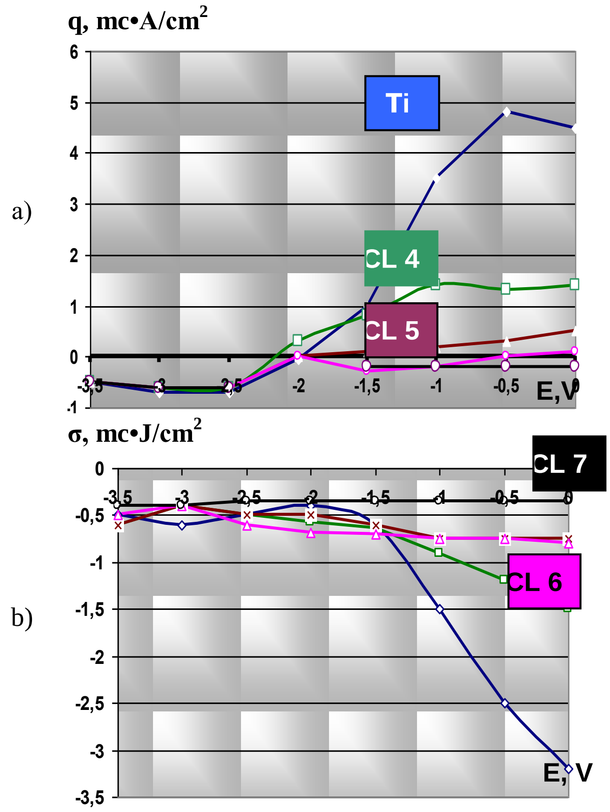


Fig. 8. Dependence of charge density of the studied samples surfaces (a) and surface tension alternation on electrode potential in physiological saline

Fig. 9. Samples of implants for interbody spinal fusion with installation tool coated by oxide-ceramics formed in activated electrolytes

The research of other features of oxide coatings on titanium alloys, created by using electrolyte activation, reveals:

1) surfaces, formed in activated solutions, do not violate the configuration and dimensional parameters of endoprostheses and implants (Figure 9);

2) not less than 70–75% of titanium dioxide with anatase and rutile structure is in the composition of such coatings;

3) the composition of the mentioned coatings do not contain harmful impurities (Al, Fe, V, N, C);

4) these coatings are of high adhesion to the substrate and minimum level tension;

5) the ultimate tensile strength of the oxide coatings, made by AMAO method, on the surface of the implants, manufactured of VIAM titanium alloy, is not less than 400–440 MPa, and for the implants, made of high-strength VIAM titanium 6 titanium alloy, is not less than 900–950 MPa;

6) the relative lengthening of the samples with oxide coatings is not less than 8–9%.

The efficiency and safety of the implants with coatings, created in accordance of the described manufacturing method, have been checked during sanitary-hygienic and animal (mice) tests. Two variants of the coatings were tested: variant 1 is coating on basis of oxide ceramics with hydroxyapatite and superdispersed diamonds; variant 2 is coating on basis of oxide ceramics with hydroxyapatite.

The mentioned samples were sent to the State Institution “Republican Scientific-Practical Center of Hygiene” for sanitary and hygienic examination. During the examination they studied:

1) <u>Organoleptic properties</u>.

Result: the product is odorless, the extract is transparent.

2) <u>Sanitary-chemical test.</u>

Result: the presence of such heavy metals as plumbum, cadmium, nickel, chromium in the offered samples was not revealed.

3) <u>Toxicological study.</u>

To test corrosion resistance the samples were carried out by the exposing it in citric acid 10% solution under temperature 20±5°C for 5 hours, then it was flushed, were boiled in distilled water for 30 minutes, and were keptin it for 24 hours.

Result: the traces of corrosion (spots, points) were not revealed.

4) <u>Definition of the extracts from the samples for hemolytic action.</u>

In vitro experiment the following was performed: isotonic solution was made of extracts by adding in them 9 g chloride sodium per 1ml to estimate the response of erythrocyte suspension. The acceptable level of hemolysis is not more than 2%.

Result: hemolytic action of the extracts is from 0.25 to 0.5%.

5) Study of acute intra-abdominal toxicity of the extracts from the samples.

Animal tests on outbred white mice by mass 18–22 g (8 individuals in each group) were performed. 50 mg per kg of extract was injected one-fold intra-abdominally. The control animals (8 individuals) got similarly physiological saline. The general habits of the animals, their behavior, mobility, appetite, coat were checked immediately after the extract injection and then in 4 and in 24 hours.

Result: clinical signs of intoxication or death of animals were not registered.

6) Cytotoxic action test in vitro.

The test was performed on the primary culture of mouse embryonal fibroplate. The density of plating is 5000 cells per $1cm^2$. The cultivation conditions are 37°C, 5% CO_2. Tests with extracts from the samples into distillate water were performed. Cells were plated into a six-socket tray. The total cell number in $30mm^2$ on the bottom of each socket was counted. The negative test is distillate water (1%), the positive test is ethanol (1%).

Result: the type of cell progression met the control series with distillate water. In case of the positive test with ethanol the lag phase of the cell enlargement discontinued in 2-5 days after ethanol introduction.

3. Conclusion

According to the performed research it is possible to conclude that standard samples of the implants with oxide-ceramic coatings for interbody spinal fusion meet sanitary-chemical, organoleptic, toxicological, requirements in the current technical statutory acts (Sanitary Rules and Codes 1.1.12-30-2006, Directions 1.1.0-12-41-2006), and can be used according to their intended purpose and specifications and are recommended for an official enregistrement in the Republic of Belarus.

It is concluded that the clinical practice implementation of the modern types of biocompatible fixators with oxide-ceramic coatings formed under the developed method will allow reducing complications related to the insufficient quality by 5–7% and also shortening the period of hospital treatment and bony union.

The product is patented No.13878 of 29.09.2010 in the Republic of Belarus.

Clinical trials were performed to check the effectiveness of the oxide coatings of the implants. They were being performed successfully for 90 days (27 operated people) in a regional clinical hospital, in the tate Institution «Republican Scientific and Practical Centre for Traumatology and Orthopedics» of the Ministry of Health of the Republic of Belarus.

The development of import replacing products allows saving on-budget expenditures, including currency, under relatively low costs of design and manufacture of modern domestic fixators.

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