ISSN 2409-9066. Sci. innov. 2016, 12(1): 36—53 doi: http://dx.doi.org/10.15407/scine12.01.036

Omelchuk, A.A., Yudenkova, I.N., Zakharchenko, M.F., and Bliznyuk, A.V.

Vernadsky Institute of General and Inorganic Chemistry, the NAS of Ukraine, Kyiv

ELECTROPOLISHING OF STAINLESS STEEL IMPLANTS FOR STABLE FUNCTIONAL OSTEOSYNTHESIS

A new method for the electrochemical polishing (ECP) of stainless steel to be used for stable functional osteosynthesis has been developed. Implants have been polished in solutions based on trinary system H_2SO_4–H_3PO_4–H_2O with a stepwise decrease in current density and increase in orthophosphoric acid concentration. The optimal polishing conditions (current density, solution composition, temperature and duration) have been determined. The developed method improves the quality and the mechanical properties of the surface polished.

Keywords: electrochemical polishing, stainless steels, implants, and functional osteosynthesis.

Analysis of the current level of development of science and technology testifies to the undoubtable fact that one of the most urgent tasks upon which contemporary medical science focuses is the creation and usage of implants [1—6]. Implants are custom-designed items that are manufactured to serve as replacements for organs which a certain human individual does not have (such as joints, teeth, bones and so on) or as auxillary components to correct and/or regenerate the said organs and also to restore their functional efficiency (osteosynthesis, also referred to as bone fusion or bone welding). The purpose of osteosynthesis is to ensure that the damaged bone tissue is firmly set into correct position while its functional capacities are retained pending completion of coalescence. The most widespread materials used to produce implants are stainless steel varieties, titanium, zirconium, and the alloys containing the above.

According to the assessments made by experts, the global implants markets had the following structure as of the year 2012, in %:

- orthopedic surgery — 20;
- vertebrology — 24;
- cardiovascular surgery — 20;
- regenerative medicine — 8;
- bone transplants — 6;
- anti-adhesion items — 2.

Between 2008 and 2010, gross global output of orthopedic segment items only amounted to USD 37 bn, including USD 2.2 bn for transplants used in joints — mostly knee and hip joints [2—5]. According to forecasts made by «Value-Added Materials» [1], European demand for regenerative medicine implants is estimated to be at USD 35 bn as of 2015, at USD 43 bn as of 2020, and USD 52 bn as of 2025. In the United States, over USD 2 bn annually is spent on surgical operations involving osteoreplacement implants and the number of American citizens having at least one implant amounts to 11 million individuals.

The most accessible and widely used ones are implants produced from special sorts of austenitic steels such as 12X18H9T, O3X17H14M3, 316L et al. These brands of steel are characterised by high durability and are relatively inexpensive (max. USD 2.5/kg). Their bioinertia characteristics are, however, insufficient. Higher degree of biocompatibility can be encountered among special alloys of titanium, zirconium (starting at USD 20/kg), cobalt, chrome (starting at USD 200/kg), and tantalum (approx. USD 1,000/kg). Specialists differentiate between mechanical polishing of implants (whereby polishing machine tools operated by numerical control software) and electrochemical polishing. Application of either of these methods ensures the same quality of surface treatment but the mechanical finishing is costlier in view of more expensive polishing equipment and software used in the polishing process. Substantial disadvantages of the mechanical polishing option include the complications emerging in the course of polishing of implants with complex surface (relief) and geometry. Apart from this, it has been ascertained that mechanical properties of the surface exacerbate through mechanical polishing due to emergence of micro-defects and dislocations that is, quite often, the cause of emergence of infiltrates.

Electrochemical polishing does not have the said disadvantages. It ensures high quality polishing of surfaces with any relief. In addition to this, by using special saline and surface active agents as components of the polishing solutions and by changing correlations between components, one is able to create conditions in which it is possible to passivate of the surface of items during the polishing and to accommodate the emergence of protective films on this surface. This will facilitate a substantial increase in the biocompatibility of implants produced from even cheap materials such as various brands of stainless steel.

As the global market of target-function implants is growing and the yearly demand on them is anticipated to increase as well, development of highly efficient technologies for finishing treatment of such items becomes a pressing matter for both scientific researchers and practical users.

This is a pressing issue for Ukraine as well, since the producers should take into account the tendencies that have established in the subject segment of the market, particularly with regard to the necessity of individual prosthetic repair medicine as well as in view of the growth and development of the implants market. All of Ukrainian citizens who have needs with regard to the matter should be able to satisfy their needs not only with expensive imported products but also with domestically manufactured items at affordable prices.

The purpose of this project is to enhance the process of electrochemical polishing of domestically produced products which would allow to achieve high quality of the surface. As the basis for the study, the authors addressed electrochemical processes taking place on the metallic surface with anodic polarisation in the solutions of mineral acids (typically, these are orthophosphoric and sulphuric acids). Exposed to electrical current, the micro relief of the surface becomes smooth and shiny at the same time. Dependent upon the composition of the polishing solution, the surface of the metal gets covered by surface active film contributing to the formation of lustre and creates conditions in which the surface is not affected by any micro-defects, micro-dislocations, and/or surface stresses. The films also prevent any ambient factors from impacting the surface and contribute to the increase of the surface biocompatibility.

THE MOST WIDESPREAD MATERIALS USED IN PRODUCTION OF OSTEOSYNTHETIC IMPLANTS

Analysis of scientific and technical works [7—12] shows that, in the orthopaedic and traumatological practice, the following are used as materials to produce implants (retaining fixtures for osteosynthesis, endoprosthetics etc) as well to produce surgical instruments: XI8H9T, XI8HI0T (ferrum-based alloys); — vitallium/comochrome (cobalt-based alloys); 95X18, 20X13, 40X13 (chrome-based and tantalum-based alloys); BT-1, BT-2, BT-5, BT-6 (titanium-based alloys).

As far as production of implants is concerned, most of the presently known brands of stainless steel have satisfactory properties in terms of long-term durability, abrasion resistance capacity, wear resisting properties, resistance to corrosion etc; it can also be processed mechanically without any particular efforts. At the same time, these brands of steel are characterised by insufficient bioinertia. If large-size retaining fixtures, endoprosthetics, and implants made from stainless steel are used, problems may emerge such as tissue metallosis and corrosion after the said items remain embedded in the human body for a long time [13].

Metallic implants made from alloys based on cobalt as opposed to stainless steel are characterised by a high degree of bioinertia. In addition to this, they are characterised by high corrosion resistance after a long period of operation and when subjected to changes in mechanical loads.

The technology of production of complex metallic implants, particularly endoprosthetics, calls for the application of the method of precision casting of the models in accordance with exact forms — that is, it is an expensive approach. Retaining fixtures and endoprosthetics made from titanium-based alloys are characterised by high degree of bioinertia and resistance to corrosion. Advantages of implants made from this type of metal include high durability in the course of long lasting maintenance, elasticity, simple and easy mechanical treatment. Disadvantages of titanium-based constructions include their insufficient resistance properties when subjected to mechanical abrasion (for instance, when they are used as endoprosthetics). However, if the implants and instruments are to be mass manufactured, one should consider the high cost of titanium as this metal costs about five times as much as the X18H9T stainless steel [9].

As far as nitinol-type alloys (Ni — 50,8%, Ti — 49,8%) with their shape memory effect are concerned, it is only reasonable to use them in order to resolve certain medical and technical challenges. The stainless steel brands H-45, H-47, H-53, and H-63 have passed the experimental and clinical approbation and its application in orthopaedics and traumatology is an object of considerable interest [14, 15].

Usage of porous alloys produced by resorting to the methodology of powder metallurgy on the basis of cobalt in endoprosthetics is regarded as advanced and promising technology but also an expensive one.

The abovementioned data convince us that it is a reasonable approach to apply certain alloys to produce implants according to their specific intended purpose — to be used for retaining fixtures for osteosynthesis (bone welding/bone fusion), endoprosthetics etc.

Application of structures from stainless steel requires complex measures to be taken in order to prevent tissue metallosis and implant corrosion.

One advanced and promising development in the clinical practice are metallic implants made from new steel brands — the METOST production batches — that are available for mass application, possess a high degree of bioinertia, decent technological properties, and necessary mechanical qualities [9, 10].

As has already been stated above, before they are introduced into human body, implants made from any sort of material must undergo the finishing treatment including polishing, oxidising, application of protective coatings and other necessary procedures, in order to prevent any formation of infiltrates (sections of living tissues characterised by foreign cell elements, increased volume and density). Emergence of such neoplasms or inflammations of the living tissue and its incompatibility with implants may be caused not only by individual features of a specific human organism but also by lack of biocompatibility of the implant material and the insufficient quality of its finishing treatment.

Due to this, in view of the above, production of implants it is necessary not only to find and create construction materials that are biocompatible with the living tissue; there is also another challenge, i.e., how to form a top quality abrasive coating layer on the surface of the implants which would ensure such compatibility. We have suggested a new method of formation of high quality protective coating: the electrochemical polishing of implants.

CERTAIN ASPECTS PERTAINING TO ELECTROCHEMICAL POLISHING OF STAINLESS STEEL

Electrochemical polishing is a set of complex electrochemical processes taking place within the thin superficial layer of electrolytic conductor [16]. The suggested method ensures fast dissolution of relief protrusions on surfaces with variable amplitude without destruction (festering) of the main array of the metal, creates the conditions necessary for the formation of lustre and the protective surface film enabling to firmly set and preserve the implant.

In order to form such surface, it is necessary to create and maintain equilibrium between the speed of formation of the superficial layer on the implant and the speed of its chemical dissolution in a way enabling the thickness to be permanent. Presence of thin superficial viscous layer of the electrolytic conductor on the interphase surface creates the necessary matter interchange mode for electrochemical polishing without festering of the array surface. The composition and thickness of the superficial layer of electrolytic conductor and its stability over time undoubtedly depend upon the composition of the electrolytic solution, upon whether it does or does not contain any complexing agents and surface active compounds [16]. Besides, the formation of the surface film is greatly impacted by the mode of polarisation of the interphase boundary subjected to direct or alternate electrical current and also by the mode of matter interchange through natural or forced convection.

It is common knowledge that, during anodic polarisation, most metals transition into passive state if dissolution of the surface layer of the electrode array, including polishing, is not taking place.

Given the above, in order to select and determine proper conditions for electrochemical polishing, one is to duly consider the data on electrochemical behaviour of metals in the solutions with various composition that are recommended to be used in polishing processes.

High quality polishing of stainless steel is only possible with potentials for repassivation (exiting the passive state). It is worth noting that in this realm of potentials, oxygen ions discharge commences. This circumstance may contribute to worsening of the polishing quality.

The first one to undertake an attempt at mathematical analysis of processes taking place in the course of electrochemical polishing of metals was made by *S. Wagner* [16], who noted that a perfect polishing process takes place if the current density corresponds to the maximum speed of diffusion of reagents through passivizing film. However, despite the substantial amount of both experimental materials and theoretical researches accumulated as of the present time [16—20], kinetics and mechanism of polishing of metals in general and of the specific group in particular have not been ascertained beyond any reasonable doubt. It has not been possible to determine what the best modes for polishing would have to be. They are being determined by a detailed analysis of current-voltage characteristics of metals that are being polished and the composition of solutions that are being used in that process.

Studies undertaken by us have shown that by changing the composition of solutions, it is possible both to deliberately shift the potential for transition into passive state (Flade potential) in the arbitrary direction and also to increase or decrease the current density of transition — and hence to manage specific heat expenditures. The smaller the potential for polarisation and the duration of treatment is, the lower the heat expenditures are. High density of current contribute to a reduction in the duration of the surface treatment. This is why, in order to optimise the conditions for polishing, it is necessary to have more detailed information on the current voltage characteristics of metals that are going to be electrochemically treated.

COMPOSTION OF BASE SOLUTIONS FOR ELECTRO CHEMICAL POISHING OF CORROSION RESISTANT STEELS

The researches [21, 22] have showed that the solutions based on orthophosphoric and sulfuric acids with corrosion inhibitors, complexing agents, and surfactants added meet the above mentioned requirements better than other ones. Rochelle salt (up to 50 g/l), acetanilide (up to 30 g/l), benzotriazole (up to 20 g/l), oxalic or citric acids (up to 25 g/l) are proposed to be used as complexing agents; the mixes consisting of condensation products with further polymerization of aniline and urotropine (up to 30 vol. %) with triethanolamine

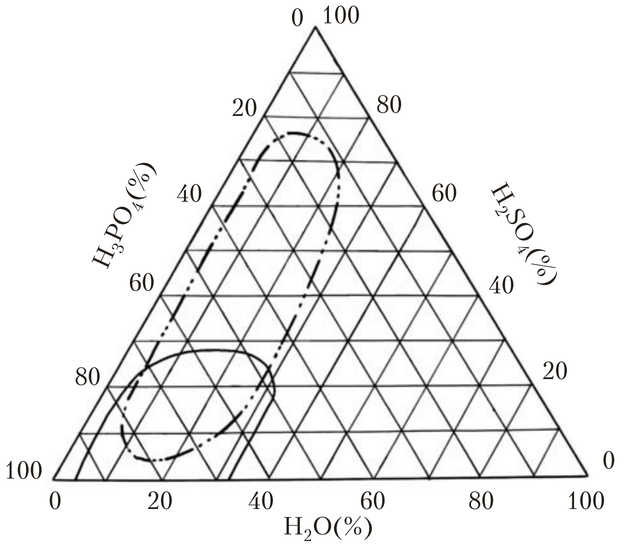

Fig. 1. The areas of trinary H_2SO_4–H_3PO_4–H_2O, system composition recommended to be used as basic polishing solutions for industrial AC polarization (solid line); the areas recommended to be used as basic polishing solutions for DC polarization (dash line)

or tribenzyl-trihydro-triazine are recommended as corrosion inhibitors. The above compounds facilitate the formation of viscous near-surface layers of solution protecting the metal surface from etching and the creation of unstable passivity mode required for homogeneous dissolution of surface layer and for chemical polishing. The recommended areas of composition of triple base system H_2SO_4—H_3PO_4—H_2O suitable for preparing the solutions to be used for finishing the high-corrosive alloys both with DC and power AC are showed in Fig. 1.

Some compositions of solutions used for electrochemical polishing of corrosion-resistant steels most frequently used for implant bone welding and modes of DC polarization in the presence of corrosion inhibitors and complexing agents are given in Table 1; the composition of the most effective inhibitors and complexing agents are presented in Table 2.

POWER AC POLISHINGИ

Power AC can be successfully used for electrochemical polishing [20, 23, 24]. The mechanism of this process has not been established yet, however, there are reasons to assume that it is associated with repassivation of electrode array surface when current polarity periodically alternates.

In the cathode half-period, the dominating process on the electrode array surface is hydrogen ion discharge with the formation of electrode array surface layers enriched with hydrogen. In the anode half-period, the metal and hydrogen atoms from the formed layer are ionized, which facilitates the surface polishing.

The *pH* of near-electrode layer is known to increase for the cathode polarization and to decrease for the anode one. Due to this, in the case of AC polarization, the components constituting the stainless steels form viscous layers of insoluble hydro-compounds. The higher is current density, the faster is the formation of these layers.

The obtained results give reasons to assume that in the case of AC polarization, the main factor facilitating the polishing of electrode array is joint discharge-ionization of hydrogen and metal in the near-electrode layer whose *pH* varies periodically.

The researches have showed (see Fig.1) that high-quality electrochemical polishing at power

Table 1

Recommended Electrolytes and Electrochemical Polishing Modes

Stainless steel grade	Composition of deactivating mixes, weight %			Content of inhibitory composite, vol. %	Current density, A/dm^2
	H_3PO_4	H_2SO_4	H_2O		
12X18H9T, 12X18H10T,	60	—	40	0.5—1.5 (D-1,D-2,C-1, C-3)	5—50
X18H10T,	60	20	20	0.5—1.5 (D-2,C-1, C-2, C-3)	15—30
95X18, 20X13, 40X13	40	20	20	0.5—1.5 (D-1,D-3, C-1, C-2)	10—50

AC can be reached in the base solutions for ECP as well. As compared with DC, the areas of polishing compositions are much narrower and in order to ensure high quality of polishing, the steels should be treated at high current density (35—50 A/dm^2).

Adding inhibitory (D-1, D-2, D-3) and saline (C-1,C-2, C-3) admixtures to the base solutions enables decreasing current density without impairment of high quality of polishing. The higher is content of inhibitory admixture the lesser is limit AC density to ensure due quality of polishing. For instance, for the acidic mix (10)H$_2$SO$_4$—(80)H$_3$PO$_4$—(10)H$_2$O containing (weight %) 5% D-2, the minimum permissible current density is 20 A/dm^2, while in the case of 10% D-2, it decreases down to 10 A/dm^2.

The addition of saline and inhibitory admixtures enables not only decreasing the polarizing current density but also widening the area of polishing mixes (towards increase in the content of sulfuric acid).

In the case of AC, the polishing effect has been established [24] to be ensured only at a frequency of 20—200 Hz. In this case, the actual current efficiency can exceed the theoretical one. As current density and frequency increase, current efficiency and quality of polishing degrade.

ECP EFFECT ON STAINLESS STEEL SURFACE PROPERTIES

The X-ray structural and micro-indentation analysis, as well as the ESM method have showed that after ECP the surface layers of 12X18H9T, 12X18H10T, X18H10T, 95X18, 20X13, and 40X13 corrosion-resistant steels get a structure differing from that of initial electrode array, as density of dislocations (ρ, cm^{-2}), and micro-distortions of the 2nd ($\Delta\alpha/\alpha$) and the 3rd ($\sqrt{\overline{U^2}}$, Å)) type shows a downward trend. The quantitative changes in the above mentioned parameters depend on the conditions and duration of polishing, composition of initial material to be treated by ECP. It should be noted that in the case of short-term treatment, when stripping a thin surface layer (up to 1 μm), where the highest number of stress concentrators and defects is accumulated, a decline in strip extension and an insignificant decrease in elastic strength are reported. In the case of stripping thicker layers (up to 10 μm), the strip extension gets enhanced.

The reported effect can be explained by dissolution of surface layer saturated with stress concentrators and dislocations during ECP. In the case of anode polarization, a more homogenous film of oxide is formed at the metallic surface. It prevents the dislocations from coming out to the surface and enhances the material's resistance to plastic deformations.

There are reasons to assume that improvement of structural elastic properties during ECP depends on the specific features of interphase processes and the formation of new surface layer.

Table 2

Marking and Composition of Recommended Saline and Inhibitory Admixtures to Electrochemical Polishing Solutions Based on Sulfurous and Orthophosphoric Acids

Marking of saline and inhibitory composites recommended to be added to the polishing solutions for stainless steels	Components and content
D-1	30 vol. % corrosion inhibitor PB-5* 70 vol. % triethanolamine
D-2	50 vol. % corrosion inhibitor PB-5 50 vol. % triethanolamine
D-3	40 vol. % corrosion inhibitor PB-5 30 vol. % TTT** 30 vol. % triethanolamine
C-1	50 g/l Rochelle salt 25 g/l benzotriazole 50 g/l acetanilide
C-2	50 g/l Rochelle salt 50 g/l aminoacetic acid 25 g/l citric acid
C-3	50 g/l Rochelle salt 30 g/l acetanilide 20 g/l benzotriazole 25 g/l oxalic acid

Note. PB-5* — corrosion inhibitor — condensation product with further polymerization of aniline and urotropine; TTT** — tribenzyl-trihydro-triazine

Not only mechanical properties but also the quality (roughness) of surface are important for implant ECP. Practically, the application of ECP to metallic products having 7—9 grade of surface roughness (arithmetic mean deviation of surface profile Ra within basic line l = 800 μm is 1.25—0.2 μm) is considered advisable [20]. As a rule, the molds for producing the implants have a higher roughness of surface. During ECP of stainless steel surfaces with large arithmetic mean R_a, the surface layer of electrode array is smoothed and gets lustrous. The appearance of luster on the surface in the case of anode ECP, first of all, is associated with a slowdown in etching [16—20]. Hence, in each case, it is necessary to know how the metal surface layer with different magnitude of micro- and macro-relief dissolves.

Effect of ECP conditions has been studied using 12X18H10T stainless steel samples. The basic solution for ECP had the following composition (weight %): H_3PO_4 — 65, H_2SO_4 — 20, H_2O — 15, inhibitory composite D-1 — 15 vol. %. The treatment was performed at a current density ranging within i_a = 15,0÷35,0 A/dm^2. The duration was 5—30 minutes. Temperature was kept by a thermostat, within the range of 20—25 °C. The profilographic study of surface was carried out using M-201 profile meter. The average height of roughness was determined as arithmetic mean of several measurements in different points on the surface. The obtained results are given in Table 3.

The data show that the quality of surface treatment depends on both duration of ECP and current density. The best parameters of ECP of 12X18H10T stainless steel are reported for current density less than 25 A/dm^2. Further increase in current density and duration of ECP is not advisable insofar as average magnitude of roughness R_a decreases very insignificantly while power consumption grows.

It should be noted that rate of polishing of 20X13 martensitic steel depends on heat treatment conditions. The steel samples of lesser hardness more easily yield to polishing as compared with the harder ones. For example, when polishing the samples with HRC = 20—27 in electrolytes of the above composition at i_a = 25—35 A/dm^2, the average duration of ECP to decrease the arithmetic mean magnitude of roughness R_a by a grade (for instance, from 1.25 to 0.80 μm) is 10 minutes. For the samples with HRC = 29—32, the ECP lasts 15—20 minutes, while the treatment of the samples with HRC = 42—49 takes 30 minutes.

At the same time, the harder samples of 20X13 martensitic steel better get lustrous as it has been showed by the results of studying the light mirror reflection from polished surfaces with the help of СФ-4 spectrophotometer within the range of wavelength from 300 to 1100 Å (Fig. 2). The samples were polished in electrolyte consisting of (weight %): H_3PO_4 — 80, H_2SO_4 — 10, H_2O — 10, with 15 vol. % inhibitory mix D-1.

Table 3

Effect of 12X18H10T Stainless Steel Electrochemical Polishing on the Surface Quality Conditions

Average roughness of the samples (R_a), μm						
Before polishing	After polishing, at current density, A/dm^2					
	15.0		25.0		35.0	
	during		during		during	
	15 min	30 min	15 min	30 min	15 min	30 min
0.76	0.60	0.52	0.51	0.23	0.48	0.25
0.90	0.70	0.59	0.52	0.22	0.54	0.30
1.25	0.83	0.72	0.71	0.49	0.79	0.48
1.89	1.21	1.01	0.91	0.52	0.93	0.54

The highest coefficients of mirror reflection (50—60%) are recorded for the samples of 20X13 heat-treated steel with a hardness of HRC = 42—49 polished at a current density ranging within 20—30 A/dm^2).

Hence, the quality of ECP of stainless steel surfaces depends not only on the polarization conditions, but also on the pre-treatment of material to be polished.

PHYSICAL AND CHEMICAL PROPERTIES OF ECP ELECTROLYTES BASED ON H_2SO_4—H_3PO_4—H_2O SYSTEM

Among the preconditions for high-quality ECP, there is the formation of viscous thin surface layer of electrolyte with a quite rapid mass transport and, respectively, a high conductivity through it [16—19, 25]. Therefore, to choose the polishing conditions it is necessary to get information on dependence of the transport properties of basic polishing solutions (density, viscosity, and conductivity) on their composition.

The acidic mix solutions were prepared from p.a. orthophosphoric and sulfuric acids, on bi-distilled water. The density of acidic mixes was measured by density gauges, at a temperature of 20 and 25 °C, having kept them in thermostat during 15 minutes. The kinematic viscosity was measured by ВПЖ-2 viscometer with a 1.31 mm diameter capillary and calculated by the formula:

$$V = \frac{0.2982 \times g_1 \times t}{g_2}, \qquad (1)$$

where V is kinematic viscosity of solution, centistoke; 0.2982 is viscometer constant, mm$^2 \cdot$ s^{-2}; g_1 — acceleration of gravity in the place of viscosity measurement, g_2 = 980.665 cm $\cdot$ s^{-2} — acceleration of gravity at a latitude of 45°; t is time of liquid discharge, s.

The conductivity was measured by the bridge method with the help of P-5021 AC bridge in thermostated electrochemical cell, at a temperature of 25 °C, on platinum electrodes using the parallel circuit of resistive and capacitive impedances at frequencies 0.6; 1.0; 2.0; 3.0; 4.0; 6.0; 10.0 kHz. To determine the cell constant, a 0.02 N KCl solution was prepared from 0.1 N fixanal.

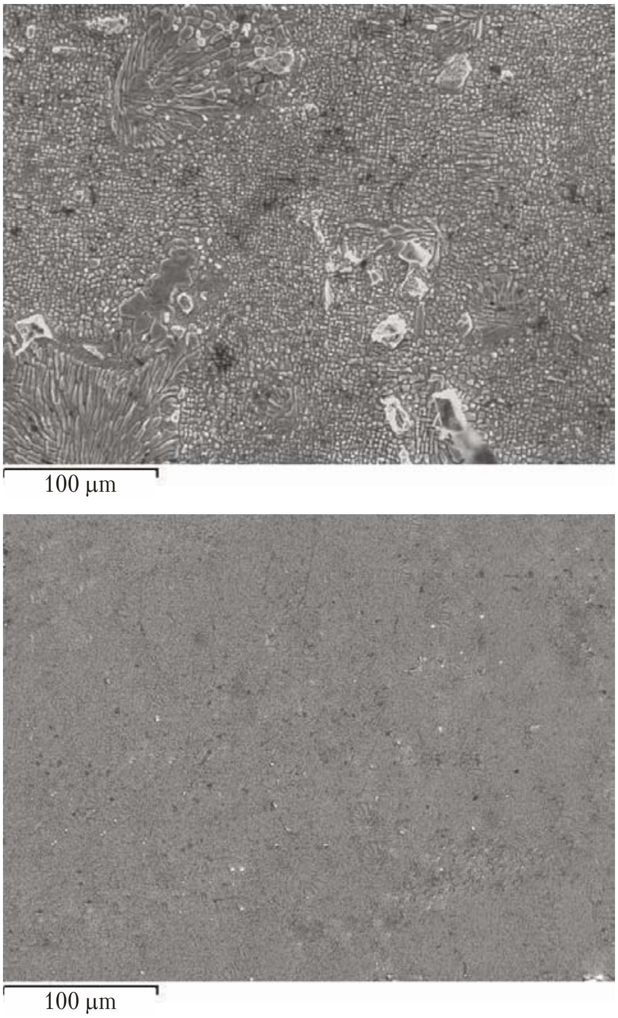

Fig. 2. Micro-pictures of X18H10T stainless steel samples before (*a*) and after (*b*) electrochemical polishing

The analysis of conductivity data has showed that they almost do not depend on current frequency. To calculate correlations the data obtained at a frequency of 10.0 kHz were used. It should be noted that the inhibitory mix added to basic polishing solutions causes a decrease in both density and conductivity, with the higher being its concentration in the solution, the more significant being the decrease. The effect of inhibitory mix on viscosity has not been unambiguously established. In the majority of cases, it leads to a

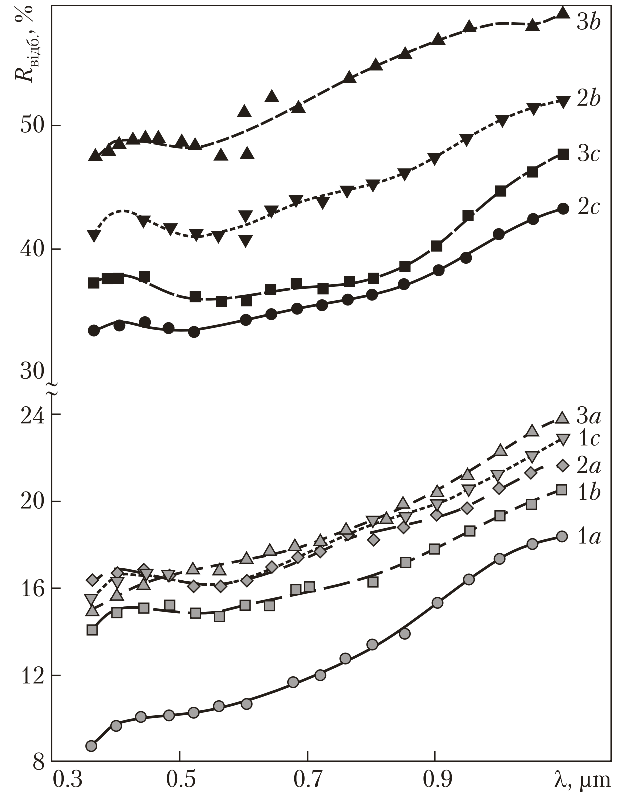

Fig. 3. Effect of ECP and heat treatment of 20X13 steel on mirror reflection factor (%): *1a, 1b*, and *1c* — initial samples before polishing; *2a, 2b*, and *2c* — samples (HRC = 29–32) polished at a current density of 5; 25; and 75 A/dm^2; *3a, 3b*, and *3c* — samples (HRC = 42–49) polished at a current density of 5; 25; and 75 A/dm^2, respectively

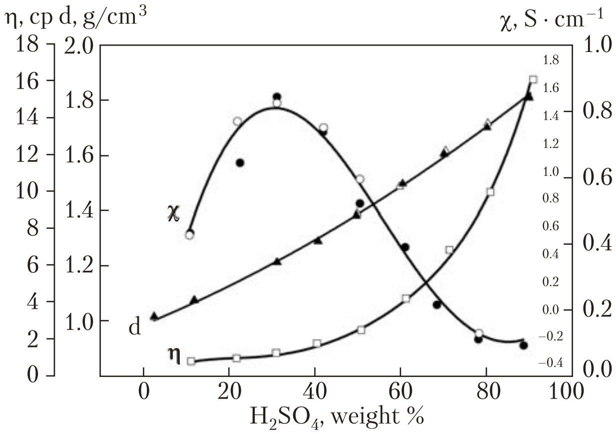

Fig. 4. Dependence of viscosity (η), density (*d*), and conductivity (χ) on the content of sulfuric acid (weight %) in the H_2SO_4—H_2O binary system, at 25 °C

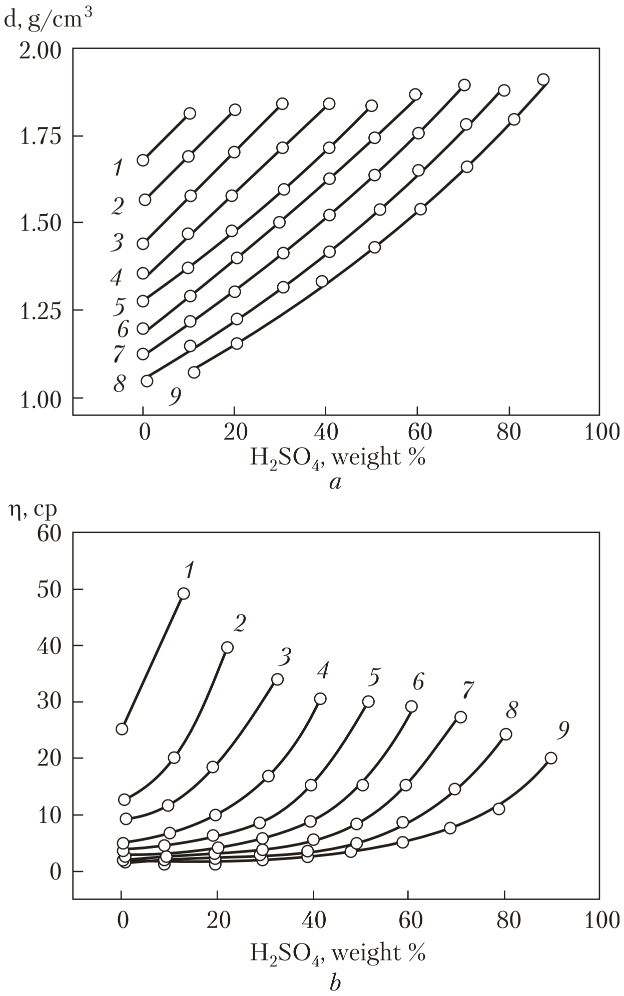

Fig. 5. Dependence of viscosity (*a*) and density (*b*) for the solutions in iso-concentration crossings of the H_2SO_4—H_3PO_4—H_2O trinary system concentration triangle by phosphoric acid (weight %): *1* — 80; *2* — 70; *3* — 60; *4* — 50; *5* — 40; *6* — 30; *7* — 20; *8* — 10; *9* — 0 on the content of sulfuric acid, at 25 °C

drop in viscosity (in the solutions with low content of orthophosphoric acid). In the solutions with high and medium content of orthophosphoric acid, viscosity can go up or down depending on the proportion between acids. Hence, in each case, it is necessary to refer to previous results.

Changes in the key properties of initial binary system for preparing ECP solutions for stainless steels are given in Fig. 4.

Figs. 5 and 6 show dependence of viscosity, density, and conductivity at the iso-concentration crossing points by orthophosphoric acid of concentration triangle (see Fig. 1) of trinary system H_2SO_4—H_3PO_4—H_2O.

From the above data (Fig. 4) one can see that both viscosity and density of the system under review vary monotonously. The dependence does not feature any specific areas that can be attributed to radical changes in the system properties. Unlike density that is low sensitive to structural transformations, viscosity, in the majority of cases, reflects molecular level changes in the multicomponent systems, which cannot be established by other methods. Thus, the monotonous viscosity at all crossing points of trinary system allows us to assume that at a temperature of 25 °C, the system structure and properties vary monotonously as well.

Fig. 6 bears conductivity dependence of basic ECP solutions under review on acid content. Figs. 5, *b* and 6 show that there is a certain correlation between viscosity and conductivity of the solution: more viscous solutions are less conductive. This fact should be taken into account when choosing and optimizing the ECP conditions.

The experiment data were processed and the correlation coefficients were calculated by the regressive analysis method [26], which has enabled estimating density (d, g/cm^3) and viscosity (η, cP) of basic solutions at 25 °C depending on the content of orthophosphoric (X_1) and sulfuric (X_2, weight %) acids:

$$d = 0.99779 + 0.004506X_1 + 0.00041X_1^2 + 0.000031X_2^2 + 0.00007X_1X_2;$$

$$\eta = 0.04062 + 0.010028X_1 + 0.08123X_2 + 0.0003664X_1^2 + 0.0002934X_2^2 + 0.000597X_1X_2.$$

It should be noted that water content in the acidic mixes of the trinary system correlates with acid content as: $\%H_2O = 100 - (\%H_3PO_4 + \%H_2SO_4)$. Therefore, it was removed from the independent variables.

The temperature effect on conductivity for some isohydric structures of trinary system H_2SO_4—H_3PO_4—H_2O is showed in Tables 4 and 5.

The given data show that as temperature and concentration of sulfuric acid grow, conductivity of basic ECP solutions significantly increases. This fact should be taken into account in order to optimize the ECP conditions.

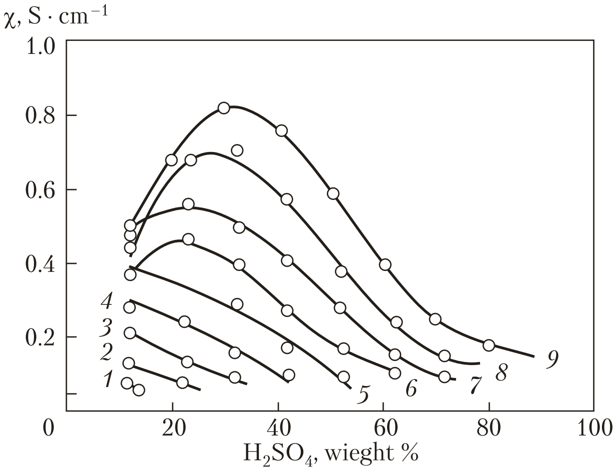

Fig. 6. Dependence of conductivity (χ) for the solutions in iso-concentration crossings of the H_2SO_4–H_3PO_4 –H_2O, trinary system concentration triangle by phosphoric acid (weight %): *1* — 80; *2* — 70; *3* — 60; *4* — 50; *5* — 40; *6* — 30; *7* — 20; *8* — 10; *9* — 0 % on the content of sulfuric acid, at 25 °C

IMPROVEMENT OF ECP OF FUNCTIONAL OSTEOSYNTHESIS IMPLANTS

Surfactants (organic compounds and their derivatives) are known [20] to be added to solutions for raising the efficiency of polishing (service life, quality, rate of surface layer dissolution, regeneration frequency, etc). Usually, polishing is made in the presence of carboxylic acids (oxalic, citric, винної, бензойної) and/or their salts, amines, and amino-alcohols. The number of solutions offered increases, but some of them cannot apply to industrial production insofar as from time to time their composition should be adjusted and insoluble compounds accumulated during polishing should be removed. In most cases, high-quality ECP requires a high current density (from 25 to 100 A/dm^2), within the temperature range 25—90 °C. In addition, often, the admixtures used for improving the polishing properties of solutions are toxic (for instance, chromic acid or methyl-tris-(oxyethyl)-ammonium methyl sulfate) [20].

One of effective techniques for ECP of stainless steels in the solutions based on orthophosphoric and sulfuric acids is the use of condensation products with further polymerization of aniline and urotropine (up to 30 vol. %) with triethanolamine or tribenzyl-trihydro-triazine as corrosion inhibitors. The content of inhibitory mix in the solutions accounts for 5—10 vol. %. Rochelle salt (up to 50 g/l), acetanilide (up to 30 g/l), benzotriazole (up to 20 g/l), oxalic or citric acid (up to 25 g/l) are recommended to be used as complexing agents. Electrochemical treatment is done at a current density of 20—30 A/dm^2, during 20—30 minutes [21, 22, 27].

Among disadvantages of the known method, there is the fact that at relatively high current density (20—30 A/dm^2) and long-term polishing (20—30 minutes) as a result of heat release, the tank temperature grows up to 50—90 °C, with effectiveness of organic admixtures and service life of polishing solution decreasing (before the first regeneration, approximately 500 A · hour/l). In addition, the used inhibitory mixes have a very ugly odor, stimulate the release of polishing solu-

Table 4

Temperature Effect on Specific Conductivity of H_3PO_4—H_2SO_4—H_2O Isohydric Structure (10 weight % H_2O)

Concentration, weight %		Specific conductivity (cm · cm^{-1}) at various temperature (°C)						
H_3PO_4	H_2SO_4	25	40	50	60	70	80	90
90	—	0.07562	0.1074	0.1473	0.1823	0.2223	0.2633	0.3026
80	10	0.07713	0.1116	0.1523	0.1871	0.2225	0.2634	0.3028
70	20	0.08202	0.1162	0.1575	0.1922	0.2303	0.2709	0.3104
60	30	0.08534	0.1195	0.1599	0.1953	0.2303	0.2702	0.3119
50	40	0.08413	0.1164	0.1560	0.1899	0.2281	0.2653	0.3063
40	50	0.07821	0.1151	0.1473	0.1806	0.2130	0.2538	0.2957
30	60	0.07350	0.1107	0.1437	0.1789	0.2167	0.2601	0.3059
20	70	0.08053	0.1227	0.1597	0.1985	0.2430	0.2910	0.3426
10	80	0.1051	0.1558	0.1973	0.2489	0.2890	0.3413	0.3968
—	90	0.1355	0.1901	0.2376	0.2923	0.3348	0.3912	0.4493

Table 5

Specific Conductivity of H_3PO_4—H_2SO_4—H_2O Isohydric Structure (20 weight % H_2O) at Various Temperature

Concentration, weight %		Specific conductivity (cm · cm^{-1}) at various temperature (°C)						
H_3PO_4	H_2SO_4	25	40	50	60	70	80	90
80	—	0.1129	0.1638	0.2005	0.2398	0.2787	0.3199	0.3614
70	10	0.1272	0.1861	0.2273	0.2696	0.3126	0.3584	0.4042
60	20	0.1439	0.2059	0.2510	0.2968	0.3437	0.3936	0.4437
50	30	0.1573	0.2268	0.2754	0.3234	0.3731	0.4262	0.4795
40	40	0.1607	0.2279	0.2761	0.3253	0.3759	0.4299	0.4854
30	50	0.1571	0.2270	0.2754	0.3255	0.3774	0.4329	0.4916
20	60	0.1479	0.2108	0.2586	0.3080	0.3605	0.4180	0.4791
10	70	0.1409	0.2035	0.2532	0.3054	0.3618	0.4245	0.4903
—	80	0.1374	0.2048	0.2581	0.3149	0.3763	0.4430	0.5158

tion from the tank, and, consequently, lead to increase in its consumption, require special equipment for flushing and recovery of solution.

As a result of research, a new composition of solution and ECP technique enabling to remove the above mentioned disadvantages, to ensure high quality of polishing, and to reduce specific consumption of power and reagents. The method and the ECP solution composition have been protected by invention patent [28].

The polishing parameters improve due to gradually decreasing current density, from 25—20 down to 15—10 A/dm^2. The electrolysis lasts, at each stage, 3—5 and 5—10 minutes, respectively, in the solutions (weight %): orthophosphoric acid (55—65), sulfuric acid (18—21), triethanolamine (0.3—1.6), glycerol (0.3—1.6), Rochelle salt (0.1—0.5), amino acetic acid (0.1—0.3), oxalic acid (0.1—0.3), Trilon B (0.01—0.1), and water.

The abandonment of the urotropine and aniline condensation products with triethanolamine or TTT and the use of the compounds in specified proportion enable improving the conductive properties and throwing power of polishing solution, as well as increasing its capacity with respect to accumulation of polishing products (soluble compounds of steel components). These factors ensure a high-quality polishing at a lower current density and a shorter duration of treatment and an extension of service life of solution before the first regeneration. The possibility of polishing at a lower current density and a shorter duration enables reducing specific power and reagent consumption.

Table 6 shows the averaged basic parameters of ECP of stainless steels X18H10T, 12X18H9T, 12X18H10T, 95X18, 20X13, and 40X13 by the known method (single stage, in the presence of inhibitory mix C-1 and saline mix Д-3 (Table 2) 10 vol. %) and by the proposed technique. The samples were polished in the basic solution of the following composition (weight %): orthophosphoric acid (65), sulfuric acid (21), triethanolamine (1.0), glycerol (1.0), Rochelle salt (0.3), amino acetic acid (0.1), oxalic acid (0.1), Trilon B (0.01), and water. The average magnitude of roughness of surfaces before treatment does not exceed 2.5 μm.

The given data show that ECP with gradual decrease in current density has better efficiency.

The proposed method enables:

- To reduce specific power consumption due to increased conductivity; to decrease the duration of polishing and current density;
- To cut specific consumption of reagents due to extended service life of polishing solution, reduced frequency and their content in the initial polishing solution;
- To raise quality of polishing and its intensity due to reduced duration and current density.

THREE STAGES OF ELECTROCHEMICAL TREATMENT OF IMPLANTS

The studies conducted have shown that, dependent upon the conditions of polarization, the speed of dissolution of the surface layer of the implant, the qualitative composition, composition of dissolution of the superficial microstructures, geometrical dimensions of the output item shall differ.

Table 6

Comparison of Techniques for Chemical Polishing of Stainless Steels

Polishing technique	i, A/dm^2	τ, min	Specific power consumption, W · hour/dm^2	Quality of surface treatment, R_a, μm	Service life of solution, A · hour/l	Specular reflection,%
One-stage	25—30	20—30	60—90	0.20—0.30	200	55—60
Two-stage						
1st stage	20—25	3—5	6—12	0.30—0.35	500	55—58
2nd stage	10—15	5—10	4.5—9.5	0.20—0.30	450	62—65

In some cases, during the polishing process, it is necessary to maintain the specified the set tolerable ranges for the changes in the geometrical dimensions of the output item. The best conditions for polishing can be created with such a polishing mode whereby high quality of the surface, minimal metal losses, and minimal change in geometrical dimensions are ensured at the same time. In addition to this, it is worth noting that, during electrochemical polishing, in the superficial layer, microstructures are being formed that enhance the surface of the implant in terms of mechanical elasticity properties. This is also assisted by the formation of an oxide layer on the metallic surface on the side of the polishing solution.

The issue of detection of interrelation between conditions for polishing, the composition of the superficial layer, and the quality of the surface after electrochemical treatment is of great interest for the optimisation of the conditions for electrochemical polishing of implants.

Table 7 shows average values of dependence between the current density and temperature. It has been stated that, at the same temperature and current density, the austenitic steel brands (12X18H10T, 12X18H9) have a higher dissolution speed than the martensitic ones (20X13). An increase in the temperature and the current density contribute to the increase of the speed of dissolution of the superficial layer.

Lower speed of dissolution of the 20X13 martensitic steel is apparently caused by higher content of iron (up to 83 mass %) able to passivize in basic polishing solutions at potentials that are almost equal to the Flade potential of the austenitic steels (about 0 V as related to the potential of a standard hydrogen electrode). Unlike austenitic steels, the potential of iron repassivation is within a more positive region (+1.9 ÷ +2.0 V) as compared with austenitic steels (+1.5 ÷+1.6 V). This is very much due to a higher content of carbon (0.2 mass %) and silicon (1.0 mass %) in the 20X13 steel brand as compared with austenitic salts. Somewhat lower dissolution speed of the 12X18H10T steel as compared with the 12X18H9 steel may be caused by the alloying titanium admixture (up to 0.7 mass %) which also very easily passivates with the formation of poorly soluble oxide compounds.

If the implants that are subject to electrochemical polishing have low tolerable limit for allowable changes in the geometrical dimensions, it is relevant to polish them at high current densities (60—80 A/dm^2) within a relatively short period of time. However, the studies we have undertaken show that, under these conditions, local iso-

Table 7

Dissolution Rate of Stainless Steels in Base Solution for Electrochemical Polishing, weight %:H_3PO_4 — 60, H_2SO_4 — 20, H_2O — 20 + salt composition C-3 — 1.5 (weight %)

Current density, A/dm^2	Dissolution Rate of Stainless Steels (μm/min) at various temperature					
	12X18H10T		12X18H9		20X13	
	25 C	60 C	25 C	60 C	25 C	60 C
5.0	0.34	0.85	0.41	0.90	0.15	0.36
10.0	0.50	1.15	0.53	1.21	0.24	0.53
15.0	0.76	1.54	0.80	1.60	0.40	0.80
25.0	1.28	2.66	1.30	2.80	0.58	1.05
35.0	2.08	3.32	2.21	3.57	1.01	1.23
50.0	3.90	4.74	4.01	4.90	1.90	2.35
75.0	7.24	7.50	7.38	7.55	3.46	3.90
100.0	8.00	9.40	8.81	9.91	3.83	4.75

lated festering is sometimes detecting that visually resembles catalyst pitting.

Using the REMMA-101M X-ray micro-scanner, it has been ascertained that in the locations of festering, the superficial layer is depleted of titanium, mangan, and nickel but enriched with silicon. In order to prevent the surface festering, it has been suggested that polishing be undertaken with gradual reduction of the current density.

On the first stage, it is best to perform electrochemical polishing at high current density (60—80 A/dm^2) within 1—3 min within a temperature range of 40—60 °C in the solutions with low (up to 40 mass %) content of phosphoric acid. The studies undertaken have shown that such solutions have a rather high conductivity (higher than the solutions with high (70—80 mass %) content of phosphoric acid have) and viscosity, which is one of the necessary requirements for electrochemical polishing. The high conductivity of solutions allows to substantially reduce the specific energy losses at the expense of reduction of voltage in the bath furnace. Values of electrochemical polishing of implants produced from the 12X18H10T stainless steel in solutions with low content of orthophosphoric acid and high current density are shown in Table 8.

The obtained results show that solutions with low content of phosphoric acid may successfully

Table 8

Parameters of 12X18H10T Stainless Steel ECP in Solutions with Low Content of Orthophosphoric Acid at 50 °C

Polishing conditions					Average roughness, µm		Specific power consumption W · hour/dm^2
Composition of polishing solution, weight %			*i*, A/dm^2	*τ*, min			
H_3PO_4	H_2SO_4	Admixture			Before ECP	After ECP	
30.0	50.0	C-3 (1.5)	80.0	1.0	1.25	0.64	21.3
35.0	45.0	—	80.0	2.0	1.54	0.31	49.5
40.0	40.0	C-1 (2.0)	60.0	3.0	1.25	0.25	42.0
30.0	50.0	C-3 (1.5)	70.0	1.0	1.61	0.32	17.5
35.0	50.0	D-1(15.0)	60.0	2.0	1.32	0.39	28.0
30.0	40.0	D-1(15.0)	60.0	3.0	1.25	0.30	39.0
35.0	45.0	—	70.0	1.0	1.15	0.43	16.3

Table 9

Element Composition of 12X18H10T Stainless Steel after Polishing at the 1st Stage in Solution, Weight %: H_3PO_4 – 30, H_2SO_4 – 50, H_2O – 20 + Saline Composite C-3 – 1.5 (weight %.); i_a = 80 A/dm^2, τ = 1 min, *t* = 50 °C

Distance from the sample surface, µm	Content of elements, weight %						
	O	Si	Ti	Cr	Mn	Fe	Ni
0	0.54	1.49	0.37	17.76	0.69	68.23	10.61
1.0		0.81	0.30	18.17	0.86	69.16	10.29
6.0		0.76	0.39	18.36	0.9	68.82	10.43
15.0		0.8	0.28	18.33	0.74	69.14	10.41
20.0		0.6	0.32	18.37	0.91	68.42	11
40.0		0.80	0.24	18.29	0.7	69.19	10.45

be applied in smoothing the macroirregularities of the implant surfaces at high current densities and increased temperature of the polishing solution.

Method of X-ray scanning microanalysis was applied to study the influence of electrochemical polishing upon the change in the composition of the surface layer of the implant (Table 9). In order to accomplish this, cross sections of the studied samples have been produced.

The aforementioned data clearly show that, following the electrochemical polishing, on the first stage, the surface and adjacent layers of the sample of stainless steel are enriched, mostly with silicon. The content of chrome and mangan is reduced. Among other elements, oxygen has been detected. This may testify to the fact that, in the process of electrochemical polishing, the oxide film is formed on the surface of the implant at the very first stage of polishing already.

It is reasonable to conduct further electrochemical polishing in solutions having higher (60—80 mass %) concentration of orthophosphoric acid. Solutions enriched with phosphoric acid have higher viscosity and density values which are beneficial to the conditions of polishing [16—18].

The results stated above testify to the fact that the suggested mode of electrochemical processing ensures high quality polishing of the 12X18H10T stainless steel. The specular reflection factor from the surface of the polished samples does not exceed 65%.

Similar results may be achieved if the solutions for polishing are used if the solutions for polishing include admixtures with compounds that are free from products of condensation of aniline and hexamethylenetetramine (corrosion inhibitor PB-5).

Both on the first stage of polishing, the forming of the surface layer containing oxygen is continuing on the second and third stages when sul-

Table 10

Parameters of Electrochemical Polishing of 12X18H10T Stainless Steel at the 2nd and the 3rd Stages in Solutions with High Content of Orthophosphoric Acid

Polishing Conditions						Average roughness, μm		Specific power consumption W · hour/dm^2
Composition of Polishing Solution, weight %			i, A/dm^2	τ, min	t, °C			
H_3PO_4	H_2SO_4	Admixture				Before ECP	After ECP	
2nd stage								
70.0	10.0	C-3(1.5)	20.0	3.0	25	0.31	0.21	3.8
60.0	20.0	C-1 (2.0)	30.0	2.0	40	0.64	0.25	5.7
80.0	10.0	C-3(1.5)	20.0	1.0	35	0.25	0.11	1.3
65.0	15.0	D-1(15.0)	25.0	1.0	40	0.32	0.16	2.0
65.0	15.0	C-3(1.5)	25.0	2.0	40	0.39	0.20	4.1
70.0	15.0	C-2(1.5)	30.0	2.0	30	0.30	0.15	6.0
75.0	10.0	C-3(1.5)	20.0	3.0	40	0.43	0.18	3.7
3rd stage								
60.0	20.0	C-1 (2.0)	15.0	3.0	25	0.21	0.10	3.3
65.0	15.0	C-3(1.5)	10.0	5.0	30	0.25	0.11	2.1
65.0	15.0	D-1(15.0)	15.0	3.0	45	0.11	0.06	3.0
70.0	15.0	C-2(1.5)	12.0	4.0	40	0.16	0.06	2.3
70.0	10.0	C-3(1.5)	10.0	5.0	25	0.20	0.07	2.4
75.0	10.0	C-3(1.5)	13.0	3.0	40	0.15	0.09	2.0
80.0	10.0	C-3(1.5)	10.0	5.0	45	0.18	0.07	2.1

fur and phosphorus are added. As the current density is gradually reduced and solutions with variable content of phosphoric acid, the polishing method which we developed allows to:

- to reduce specific energy consumptions;
- to intensify the process of polishing through the reduction of its duration;
- to reduce specific expenditures of reagents at the expense of the prolongation of the useful technical lifetime of the polishing solution, reduction of the correction frequency and their content in the output polishing solution;
- to improve the polishing quality and the mechanical properties of the surface.

CONCLUSIONS

1. A new enhanced method of electrochemical polishing of ostheosynthesis implants has been developed that have been produced firm austenitic and martensitic steel, based upon electrochemical processing of the surface in the solutions on the basis of triple system H_2SO_4—H_3PO_4—H_2O with stage-by-stage reduction of the current density and increased concentration of orthophosphoric acid in the polishing solutions. Polishing was being taken place in three stages. On stage one, the polishing in the solutions with On the first stage of polishing in solutions with insignificant content of orthophosphoric acid (up to 30—40 mass %) and high current density level (up to 80 A/dm^2), macroirregularities of the surface relief have been smoothed out and the surface was polished. Such a mode of anodic polarization contributed to the emergence of a superficial layer characterized by enhanced elastic and mechanical properties. Optimal mode has been ascertained (including current density, solution composition, temperature, processing duration) for polishing on each of the stages.

2. The method for polishing of items made from stainless steel enables to:

- avoid the necessity of surface festering;
- reduce direct electric energy expenditures;
- intensify the process of polishing at the expense of the reduction of its duration;
- reduce specific expenditures of reagents at the expenditure of prolongation of the useful technical lifetime of the polishing solution and reduce the frequencies of correction of the composition of the polishing solution;
- to improve the quality of polishing and mechanical properties of the surface.

3. Regions of the make-up of the triple system H_2SO_4—H_3PO_4—H_2O, have been ascertained that may be recommended as basic ones for electrochemical polishing of implants produced from austenitic and martensitic steel using direct and/or alternate current with industrial frequency. Optimal composition has been ascertained as well as number of inhibitory (D) and saline (C) compounds recommended to be introduced into basic solutions for electrochemical polishing in order to avoid the necessity of surface festering and passivation and also in order to ensure the emergence of a protective anti-corrosive layer. The basic components for such compounds include tri-ethanolamine, benzotriazole, potassium sodium tartrate, acetanilide, oxalic acid, trilon B.

4. Methods of X-ray electronic microscopy and microanalysis have allowed us to ascertain that electrochemical polishing contributes to the improvement of mechanical properties of the surface of implants at the expense of the reduction of concentration of microdefects and microdistortions of the second and third variety, as well as at the expense of the formation of the surface layer comprised of oxygen, sulfur, and phosphorus. It has been ascertained that martensitic steel types are a more difficult option for electrochemical polishing than austenitic ones.

5. Study has been undertaken into physical and chemical properties (viscosity, density, conductivity) of a wide range of the H_2SO_4—H_3PO_4—H_2O, triple system compounds recommended to be used as basic for preparation of solutions for electrochemical polishing of osteosynthesis implants. On the basis of the data obtained, correlation dependences have been ascertained which allow to assess the specified properties of solutions according to their composition. Solutions with a high degree

of viscosity and conductivity create the most favorable conditions for electrochemical polishing.

6. A new composition has been developed of a solution for electrochemical polishing of items from stainless steel on the basis of sulfuric and orthophosphoric acids which, unlike all of the currently known ones, does not contain condensation products of condensation of aniline and hexamethylenetetramine recommended as corrosion inhibitor. The new composition of the solution for electrochemical polishing is patent-protected as a useful model and allows to improve the electroconductive properties and the dissipating ability of the polishing solution, increase its capacity to accumulate polishing products such as soluble compounds of steel components and thus ensure high quality polishing at lower current density levels and shorter duration of treatment and also longer useful technical lifetime prior to the very first regeneration. The available option of polishing at lower current density and in a shorter period of time enables reducing specific losses of electrical energy and reagents.

REFERENCES

1. *Technology and market perspective for future Value Added Materials*, Final Report from Oxford Research AS Luxembourg: Publications Office of the European Union, 2012.
2. *The Complete Guide to the Global Orthopaedic Market 2009*, Espicom Business Intelligence (www.espicom.com), 2009.
3. *The Future of the Orthopedic Devices Market to 2012*, Global Markets Direct, Dec-2008, Report Code: GMD ME0754MR — 5 p.
4. *Global Orthopaedic Market — Focus on Hip and Knee replacement*, A&M Mind Power Solutions, Jan 2010.
5. *For Orthopedic Devices, the Future Is Still Bright*, Anthony G. Viscogliosi, Viscogliosi Bros LLC, May 2009.
6. *Hip and Knee Replacement Market: Overview of the US and European markets — growth in a mature market*, Datamonitor, Oct 2006.
7. Ankin L.N., Spasov S.A. Metally i implantaty dlja stabil'nogo osteosinteza. *Ortopedija, travmatologija i protezirovanie*. 1979, N 1: 63—68 [in Russian].
8. Bohlovitova E.N., Shahmetov V.G. Primenenie metallov v hirurgii. *Medicinskaja promyshlennost' v SSSR*. 1966, N 6: 7—11 [in Russian].
9. Moroz N.F., Muzychenko P.F. Osteosintez fiksatorami «METOST» v jeksperimente. *Izobretatel'stvo i racionalizacija na sovremennom jetape razvitija zdravoohranenija* (tezisy dokladov 1-j gorodskoj nauchno-prakticheskoj konferencii izobretatelej i racionalizatorov. g. Kiev, 27—29 oktjabrja 1988). 1988. Ch. 2: 58—59 [in Russian].
10. Muzychenko P.F., Cap Ju.P., Gercen G.I., Minaeva T.I. Korrozionnaja stojkost' nekotoryh nerzhavejushhih stalej v biologicheskih sredah. *Novye korrozionnye litejnye materialy*. Kyiv, 1984: 32—34 [in Russian].
11. Andress HJ, Braun H, Helmberger T. et al. Long-term results after posterior fixation of thoraco-lumbar burst fractures. *Injury*. 2002, N 33: 357—365.
12. Rỏhndorf H., Ziegler V., Brũckner L. Dermatologische Unvertråglichkeitsreaktionen durch X5CrNiMo 18-10 Stahl-Imlantate im Tierexperiment. *Z. Experim. Chirurgu. Chirurg. Forsch*. 1982: 125—162.
13. Gricanov A.I., Stanchic Ju.F. O korrozii metallicheskih konstrukcij i metallozah tkanej pri lechenii perelomov kostej. *Vestn. hirurgii*. 1977, N 2: 105—109 [in Russian].
14. Vytjugov I.A., Kotenko V.V., Zhuravlev B.K., i dr. Nekotorye biomehanicheskie aspekty nekostnogo osteosinteza kol'cevidnymi fiksatorami s termomehanicheskoj pamjat'ju. *Ortopedija, travmatologija*. 1984, N 2: 7—10 [in Russian].
15. Reastere J., Banamann G., Banagart F. Verwendungamẻgliehkeiten von NiTi sur Zementfrein Verankerung von Prothesen. *Med. Orthop. Techn*. 1980, 100(1): 52—54.
16. Wagner C. Contribution to the Theory of Electropolishing. *J. Electrochem. Soc*. 1954. V. 101: 225—228.
17. Jacquet P.A. Electrolytic Method for obtaining Bright Copper Surfaces. *Nature*. 1935. V. 135: 1076—1076.
18. Elmore W.C. Electrolytic Polishing. *J. Appl. Phys*. 1939. V. 10: 724—727.
19. Kolotyrkin Ja.M. K voprosu o mehanizme anodnogo rastvorenija metallov v uslovijah passivnosti. *Ser. him. nauk*. 1959, N 5: 9—22 [in Russian].
20. Grilihes S.Ja. *Obezzhirivanie, travlenie i polirovanie metallov*. pod. red. P.M. Vjacheslavovna. Leningrad: Mashinostroenie, 1983 [in Russian].
21. *Pat. Ukrai'ny 20256A, MPK S25 F 3/24, S25 F 5/34*. Elektrolit dlja elektrohimichnogo poliruvannja hromonikelevyh austenitnyh stalej. Zarubyc'kyj O.G., Judenkova I.M., Gel'man O.D., Biloshyckyj A.P. [in Ukrainian].
22. *Pat. Ukrai'ny № 61252 A MPK7 S25F 3/16*. Elektrolit dlja elektrohimichnogo poliruvannja ta dezaktyvacii' korozijnostijkoi' stali. Judenkova I.M., Zarubyc'kyj O.G., Lisogor O.I., Zaharchenko M.F., Budnik V.G. [in Ukrainian].
23. Majtak G.P., Ishhenko N.A. Jelektrohimicheskoe polirovanie stali peremennym tokom. *Zhurn. prikl. Himii*. 1965, 38(4): 840—845 [in Russian].
24. Gorodyskij A.V., Judenkova I.N., Ishhenko N.A. Vlijanie chastoty peremennogo toka na jelektrohimicheskoe polirovanie uglerodistoj stali. *Ukr. him. zhurn*. 1982, 48(10): 1105—1106 [in Russian].

25. Shivareddy S., Bae S.E., Brankovic S.R. Cu Surface Morphology Evolution during Electropolishing. *Electrochem. Solid State Lett.* 2008. V. 11: D13—D17.
26. Kolemaev V.A., Staroverov O.V., Turundaevskij V.B. *Teorija verojatnostej i matematicheskaja statistika*. Moskva: Vysshaja shkola, 1991 [in Russian].
27. *Deklaracijnyj patent Ukrai'ny 61252 MPK7 S25F3/16, S25 F5/00.* Elektrolit dlja elektrohimichnoi' dezaktyvacii' ta poliruvannja korozijnostijkoi' stali. Judenkova I.M., Zarubyc'kyj O.G., Lisogor O.I., Dmytruk B.F., Dupak L.G., Zaharchenko M.F., Kovalevs'kyj V.I., Budnik V.G. [in Ukrainian].
28. *Pat. Ukrai'ny na korysnu model' № 87509 MPK S25F 3/00; S25F5/00.* (Zajavka № U201310244 vid 20.08.2013). Sposib elektrohimichnogo poliruvannja nerzhavijuchyh i nyz'kolegovanyh stalej. Judenkova I.M., Omel'chuk A.O., Shevel' V.M., Maslo M.A., Zaharchenko M.F. [in Ukrainian].

А.О. Омельчук, І.М. Юденкова,
М.Ф. Захарченко, А.В. Близнюк

Інститут загальної та неорганічної хімії
ім. В.І. Вернадського НАН України, Київ

ЕЛЕКТРОХІМІЧНЕ ПОЛІРУВАННЯ ІМПЛАНТАТІВ З НЕРЖАВІЮЧИХ СТАЛЕЙ ДЛЯ СТАБІЛЬНО-ФУНКЦІОНАЛЬНОГО ОСТЕОСИНТЕЗУ

Розроблено новий метод електрохімічного полірування імплантатів з нержавіючих сталей для стабільно-функціонального остеосинтезу. Полірування імплантатів проводилося в розчинах на основі потрійної системи H_2SO_4—H_3PO_4—H_2O при постадійному зменшенні густини струму та збільшенні концентрації ортофосфорної кислоти. Визначено оптимальний режим полірування (густина струму, склад розчину, температура, тривалість обробки). Розроблений метод дозволяє поліпшити якість та механічні властивості поверхні.

Ключові слова: електрохімічне полірування, нержавіючі сталі, імплантати, функціональний остеосинтез.

А.А. Омельчук, И.Н. Юденкова,
Н.Ф. Захарченко, А.В. Близнюк

Институт общей и неорганической химии
им. В.И. Вернадського НАН Украины, Киев

ЭЛЕКТРОХИМИЧЕСКОЕ ПОЛИРОВАНИЕ ИМПЛАНТАТОВ ИЗ НЕРЖАВЕЮЩИХ СТАЛЕЙ ДЛЯ СТАБИЛЬНО ФУНКЦИОНАЛЬНОГО ОСТЕОСИНТЕЗА

Разработан новый метод электрохимического полирования имплантатов из нержавеющих сталей для стабильно функционального остеосинтеза. Полирование имплантатов проводилось в растворах на основе тройной системы H_2SO_4—H_3PO_4—H_2O при постадийном уменьшении плотности тока и увеличении концентрации ортофосфорной кислоты. Определен оптимальный режим полировки (плотность тока, состав раствора, температура, продолжительность обработки). Разработанный метод разрешает улучшить качество и механические свойства поверхности.

Ключевые слова: электрохимическое полирование, нержавеющие стали, имплантаты, функциональный остеосинтез.

Received 23.06.15