CORROSION RESISTANT NANOCRYSTALLINE TI-8NI-CR SYSTEM ALLOYS COATINGS

M.MIKABERIDZE, D.RAMAZASHVILI, L.AKHVLEDIANI, E.GOZALISHVILI, V.GARIBASHVILI, Z.MIRIJANASHVILI, V.GABUNIA

Nanocrystalline coatings were received by electro spark alloying of the commercial titanium alloys samples surface with application bulk and a compact Ti-8Ni-(1-3)Cr alloys electrodes. Compacting of powders was prepared by mechanical alloying, with subsequent cold pressing and high-temperature baking. The nanocrystalline coatings increase mechanical properties, wear and corrosion resistance of a substrate and can be recommended for coatings of medical tools of multiply usage.

Key words: *nanocrystalline coatings, titanium, alloys, electro spark alloying, powders, corrosion resistance, medical tools.*

Titanium, its alloys and coatings are used for manufacturing of many surgical tools. The great part of quantity of medical products are instruments and together with more than thousand tones of orthopedic and prosthetic titanium devices of various applications. Because it is biocompatible, titanium is used in a gamut of medical applications including surgical implements and implants, that can stay in place for up to 20 years. Titanium and its alloys are used to make both medical instrument, implants as well as modifications to their surface. Titanium and titanium alloys, based on their physical and chemical properties, appear to be especially suitable for dental implants and prostheses. For the construction of endosseous implant devices, titanium and its alloys have become well-accepted and can be considered the materials of choice. [1-9].

For the increase of wear and corrosion resistance, also functional properties of medical tools and implants, hardened working surfaces are developed especially by mechanical alloying. Mechanical alloying is the generic term for processing of metal powders in high-energy ball mills. Mechanically alloying describes the process when mixtures of powders (of different metals or compounds) are milled together to produce a solid solution, inter metallic or amorphous phase homogenous alloy. This compacted material is placed in an oven and sintered in a controlled atmosphere at high temperatures and the metal powders coalesce and form a solid. A second pressing operation, repressing, can be done prior to sintering to improve the compaction and the material properties. Compacting and comminuting are repeated to produce the desired extent of alloying and homogenization. [10-12].

Most of commercial titanium alloys have low hardness and insufficient corrosion resistance in aggressive washing and sterilizing media and they are expensive. In this connection, the development of new titanium alloys with high mechanical properties together with corrosion resistance represents significant interest, for coatings of medical tools and implants surfaces with the purpose of their hardening. New corrosion resistant Ti-8Ni-Cr system alloys with increased hardness and strength have been developed by us for surgical implants and medical tools of multiply usage [13,14] .

The purpose of the given work was working out of technology of reception of mechanically alloyed Ti-8Ni-Cr system alloys, which should be characterized by the increased strength and corrosion resistance for coatings of medical instruments and elaboration of the recommendations on use of powder titanium alloys for coatings of working parts of medical tools.

Preparation of the powders Ti-8Ni-Cr system alloys by mechanical alloying was carried out in the high energy ball mill of attriton type in an argon atmosphere. Mechanical alloying was achieved under the following regimes;

- **ratio of the mass spheres and workable powder was 10:1 - 30:1.**
- **frequency of the rotation of the shaft of attriton was 270 -720 turn/min**
- **duration of process was 5-25 hours.**

Compacting of powders and manufacturing of electrodes with the 5x5x35 mm size for coatings was carried out by the method of cold pressing (under loading of 4-5 tons) and high-temperature baking of mechanically alloyed powder alloys Ti-8Ni-(1-3)Cr. The pressed rods of samples were baked in vacuum electro furnace under residual pressure 10^{-3}mm of Hg, at the following temperatures: 1000^0, 1200^0, 1300^0C, during 3 hours. As the result we have obtained the following alloy samples: Ti-8Ni-1Cr; Ti-8Ni-2Cr and Ti-8Ni-3Cr.

Surface of samples of commercial titanium alloys Ti-5Al-3Sn and Ti-3Al-0,5Cr, used for manufacturing of various surgical tools, was covered with electric-spark alloying on the installation "ELITRON ". Samples of square sections of 4x4 mm alloy Ti-8Ni-(1-3)Cr were used as anodic electrodes. The surface of samples was cleaned mechanically by a glass-paper and were degreasing with acetone before coating. . Surface alloying was realized by two regimes – "soft" and "rough". Vibration frequency of a vibrator was 200 Hz. Current strength by a 'soft" regime was 1,8 – 2,0 A. Potential – 2,5-3,0 V. Volume of accumulated condensers was 210 µF. When a "rough" regime was used current strength was 5,0-6,0 A; Potential – 7.0 – 9.0 V. Volume of accumulated condensers – 630 µF. The thickness of the received coatings was 30-35µ.

For comparison electric-spark alloying has been carried out on the installation "ELFA-541" as well. Unlike from "ELITRON " where an electrode performs a vibrate movement and renders an additional intensive mechanical influence on a undercoat, under the use of the ELFA-541 a cylindrical electrode with 1-2 mm diameter rolls around its axis, removes with a permanent speed and does not touch the undercoat. Interstice between the electrode and undercoat is regulated and automatically preserved in 5-50mkm range in the process of coating. Bulk Ti-8Ni-Cr system alloys were used as en electrodes. They were manufactured by melting and casting. Coating was realized by two regimes – at first "soft" and then by a "rough" regimes. Under the "rough" regime the volume o accumulated condenser was 5 µF; under the "soft" regime -3 µF. In both cases the rotate frequency of the electrode was 2000 turn/min, when the speed of linear movement of the electrode was 1 cm/min .The thickness of coatings was 3-5µ. The coatings obtained on the installation 'Elfa-541" are considerably better than on the installation "ELITRON". They are characterized by smaller roughness and cleanliness of a surface.

Micro structural and micro-radio-spectral x-ray analyses of polished sections of Ti-8Ni (1-3)Cr alloys coatings samples were realized on the optical microscope "NEOPHOT-21" and on the micro analyzer Cameca MS-46. The crystalline structure and also the substrate were conducted on the general x-ray diffractometer DRON-2,0. During the exposure samples revolved in their plane. The studies have shown that the crystalline structure of the substrate and coatings constituted the structure of α – titanium. All coatings contain α" – martensite phase and nitride of titanium (Fig. 1,2).The grain sizes of crystals in both cases do not exceed 100 nanometers; so it is possible to make the conclusion, that received coatings have nanocrystalline structure. Investigations showed that a surface of the coating is characterized by a strong roughness. Thickness of a coating by a "rough" regime was 20-30 µ and by a "soft" regime – 10-15 µ. A surface cleanliness was better using a "soft"

regime. Using of both powder and bulk electrodes give almost the same results as regards to homogeneity and porosity of coatings.

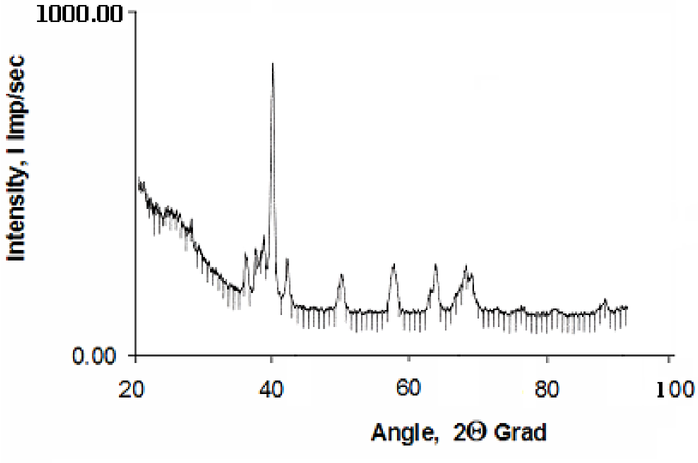


Fig. 1. X-ray diagram of Ti-8Ni-1Cr alloy coating obtained on the "ELFA-541"

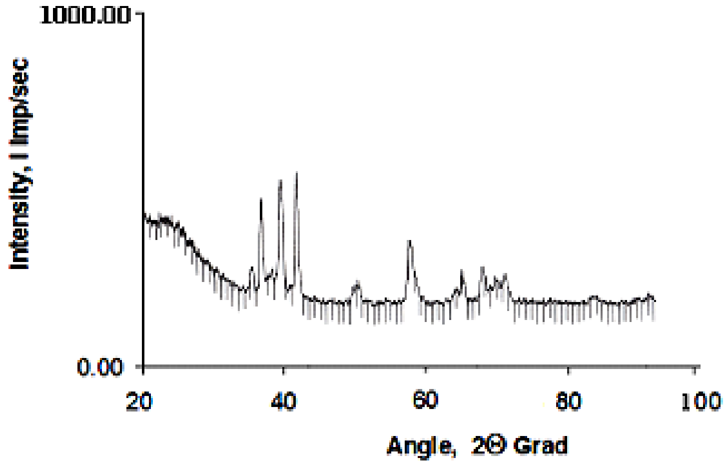


Fig. 2. X-ray diagram of Ti-8Ni-1Cr alloy coating obtained on the "EITRON"

The intensity of the reflexes of α – titanium in substrate as well as contents of titanium nitride in the coating obtained on "ELITRON" (30 - 35μ), is 2-3 times more than in coatings applied by way of electric spark alloying on the installation "ELFA" (3 - 5μ).Formation of titanium nitride is connected with conducting of the electric spark alloying process into the air. In this case the formation of the titanium oxides is not excluded. However, the reflexes corresponding of titanium oxides were not clearly fixed by x-ray structural phase analysis.

Distribution of elements – nickel and chromium were defined by a linear scanning and scanning on the area as well.
Curves of nickel and chromium distribution on a coating surface obtained as a result of a linear scanning are illustrated on the figure 3.

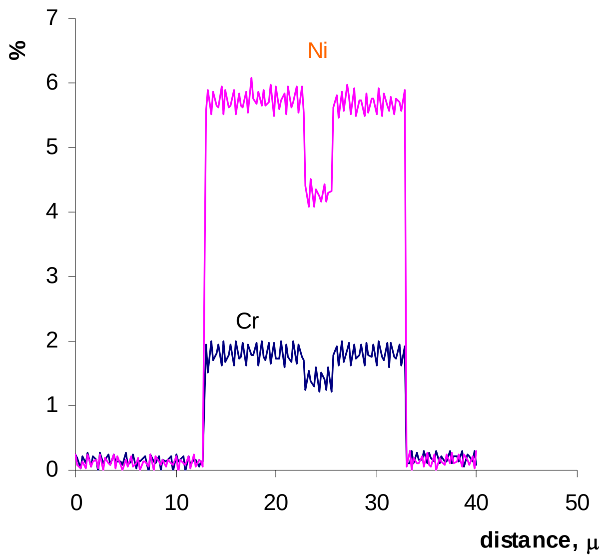


Fig. 3. Elements distribution in structure of Ti-8Ni-3Cr alloy coating

In the figure 4 are represented micro photos of a surface coating after scanning on an area as in absorbed electronic rays (a), so in characterized x-rays; b-Ni; c-Cr.

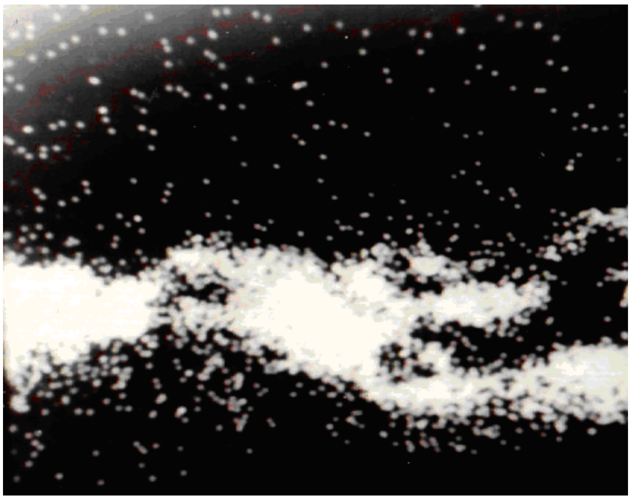
For the determination of the adhesion of Ti-Ni-Cr alloys coatings they were plated on the mushroom type sample from carbon steel at the fixed temperature. To this sample the second same sample was soldered by means of the Roze's solder (with the melting point 93-94^{0}C).The soldered samples were placed in the tension grips and subjected to breaking. Breaking was performed on the alloy Roze. It was preliminarily established that the breaking strength of alloy Roze was equal to 380 kg/sm^2. The following results have been received:

Adhesion of the alloys coatings: Ti-8Ni-1Cr F_a = 400 kg/sm^2
Ti-8Ni-2Cr F_a = 470 kg/sm^2
Ti-8Ni-3Cr F_a = 520 kg/sm^2

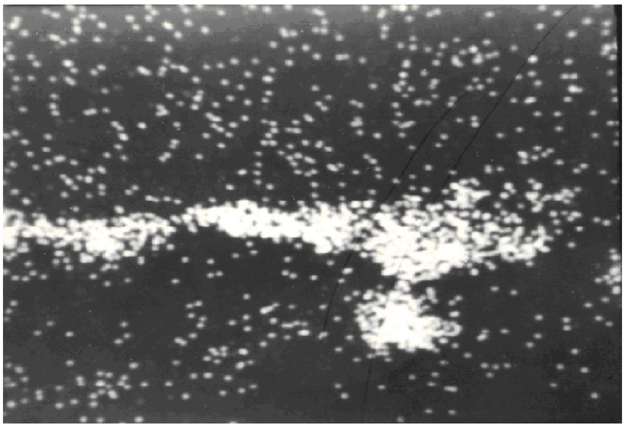
Tests on a dry wear of coatings were carried out on the device "SPTS-2". Couple of samples having the shape of rings with 50 mm diameter and 8 mm thickness, one from which was coated by an electro spark alloying and the other one – without any coatings (pure titanium) were spitted to different axes. The samples were pressed to each other under the 60 kg loading and were brought to rotation to different sides with speed ~200 turn/min. The number of revolutions of an upper axis on 10% is less than the number of revolutions of the lower axis. Thus, creeping in 10% took place. Duration of each working cycle was 10 min. All samples were weighed before and after each cycle. Wear resistance was defined towards to weight lose. The test results are shown on fig. 5. It is seen from a diagram that a surface of titanium by alloying with Ti-8Ni-1Cr alloy noticeably increases its wear resistance.

Measuring of the micro hardness of metallographic sections is carried out by device PMT-3 under 20g loading. The following results have been received:
Micro hardness of the main alloy H_1=233.6 kg/mm^2
Micro hardness of a layer H_2=343.0 kg/mm^2
Micro hardness of the coating H_3=401.7 kg/mm^2

a)



b)



c)

Fig. 4. Distribution of nickel and chromium of the surface of coatings by absorbed electron–beam scanning (a) and characteristic x-ray emission: b – Ni, c – Cr

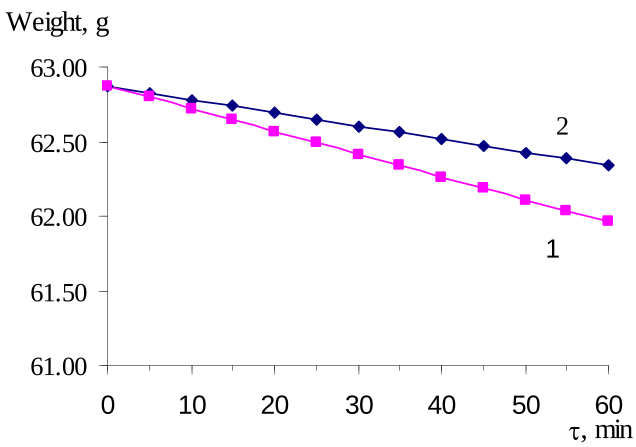


Fig. 5.Change of samples' weight in the time
1 - substrate; 2 - coating

Increase of hardness of coating and intermediate layer is, evidently, the result of change of chemical content and also strengthening caused by as mechanical so electrodynamics peening during electro spark alloying of the surface.
Thus, we can say that alloys Ti-8Ni -(1-3) Cr are quite suitable for hardening of medical tools.

Corrosion resistance of coatings, with the thickness 30 μ , was carried in preserved blood, physiological (0,9% NaCl) and tissue solutions. Corrosion rate of coatings after 120 hours tests is given on figure 6. As shown in the figure, corrosion rate of coatings in physiological solution is the smallest influence of chromium is not observed. In the tissue solution with increasing of chromium content corrosion rate coatings rises and reaches amount ~ 0,06 g/m^{2}hr. In the blood – with increasing of chromium corrosion rate of alloys coatings rise and it reaches 0,01 g/m^{2}hr.
In general, all alloy coatings revealed good corrosion resistance.

Study of corrosion resistance of coatings has been carried out also in 1% solution of hydrochloric acid. Kinetic curves are given on figure 7. Value of corrosion rate was determined after 100, 200, 300, 400 and 500 hours testing. As shown, the minimum corrosion rate of coatings is controlled after 100 hours. maximum losses are obtained after 200 hours testing: in this case by increasing of chromium in alloys content the corrosion rate increases and it reaches 0,0026 g/m^{2}h (for Ti-8Ni-3Cr alloy coating). Farther increase of testing time leads to decreasing of corrosion rate of coatings and consists amount 0,0008 g/m^{2}h (Ti-8Ni-1Cr). A decrease of corrosion rate in this case is caused by the formation of the protective titanium oxides films on the surface of coatings. Results of chemical analysis after testing of alloy coatings in HCl solution are according to their corrosion resistance. Quantity of moving ions of titanium and nickel are insignificant. With increasing of chromium content, quantity of moving ions in 1% HCl increases slightly. In general, all alloy coatings revealed good corrosion resistance in 1% HCl solution.

Corrosion tests of coatings with the thickness 5 μ has been carried out in the physiological solution (0,9% NaCl). The value of corrosion rate was determined after 100, 200, 300 and 500 hours testing. All alloy coatings revealed absolute corrosion resistance (K=0, 0000 g/m^{2}h). Corrosion rate of coatings after their testing in the solution 1% HCl during 240 hr

was 0,0007 g/m^{2}hr.After corrosion tests of Ti-8Ni-(1-3)Cr alloys coatings the best corrosion resistance revealed samples with Ti-8Ni-1Cr alloy coatings.

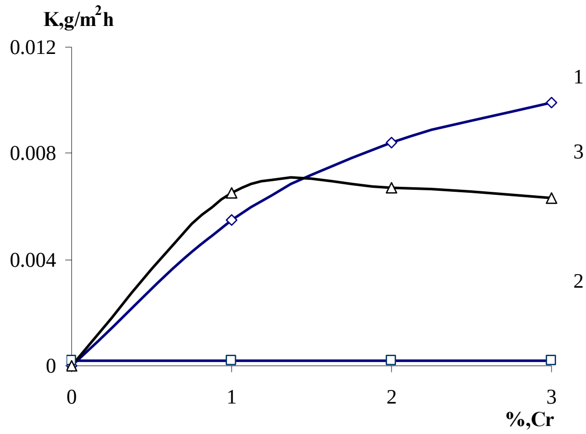


Fig. 6. Corrosion rate of Ti-8Ni-(0-3)Cr coatings (thickness 30 μ) in:
1 - blood; 2 - phiziological solution; 3 – tissue solution.

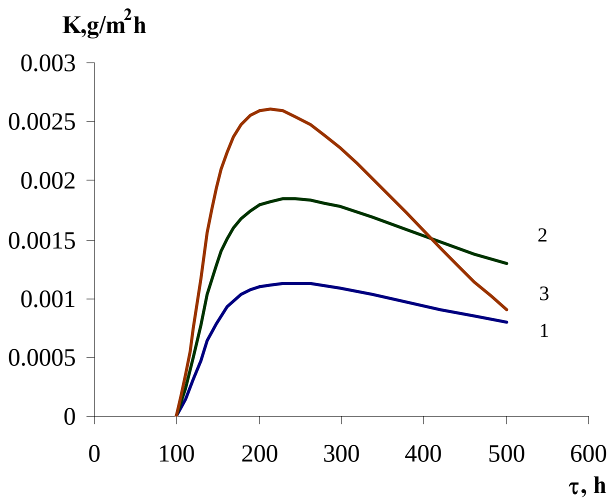


Fig. 7. Corrosion rate of Ti-8Ni-Cr system alloys coatings (thickness 30 μ) in 1% HCl solution:
1 - Ti-8Ni-1Cr; 2 - Ti-8Ni-2Cr; 3 - Ti-8Ni-3Cr

Corrosion testing of the Ti-8Ni-(1-3)Cr alloys coatings has been carried out also according to the following regime: cleaning+dezinfection+sterilization. Washing solution with addition of 0,5% hydrogen peroxide was used as cleaning solution means. Disinfection was done in boiling distilled water during 45 minutes with addition of cooling to the room temperature; Sterilization was done in 1.air-drying chamber at 180^{0}C, 45 min. and 2.Chemical sterilization in 6% solution of H_2O_2. Twenty cycles of tests have been performed. Corrosion loses of coatings increase with rising of chromium content in them and also with increasing of cycles quantity. Maximum loses are obtained after 20 cycles. For coating with 1% Cr Δm/s=0.035 g/m^2 after 20 cycles. Corrosion losses of the known alloys are ~one orders more than the losses of Ti-Ni-Cr alloys. Visual control of alloys showed that known alloys withstand 10 cycle of cleaning without surface changing. Further

the surface condition changes, spots of oxide tint appear; the surface of Ti-8Ni-(0-3) Cr alloys does not change after 20 cycles.

Electrochemical investigations of Ti -8Ni-1Cr alloy coatings received by electro spark alloying method under two regimes with the thickness 30 μ and thickness 5 μ were carried out in NaCl, HCl and NaOH solutions (Fig. 8,9).

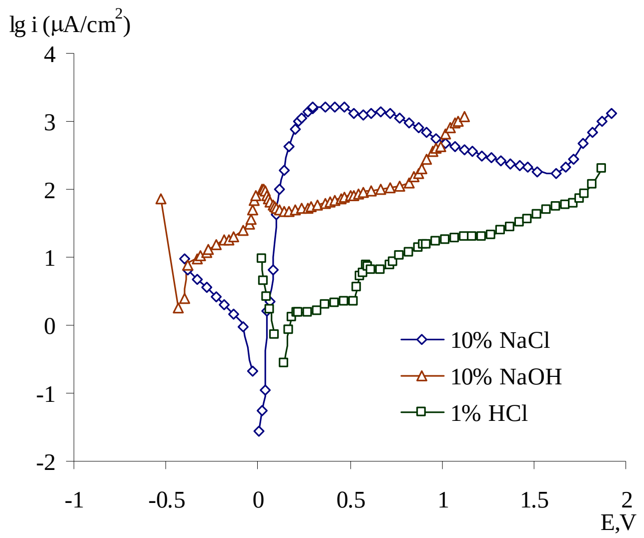


Fig. 8. Potentiodynamic curves of Ti-8Ni-1Cr coating (thickness 30 μ)

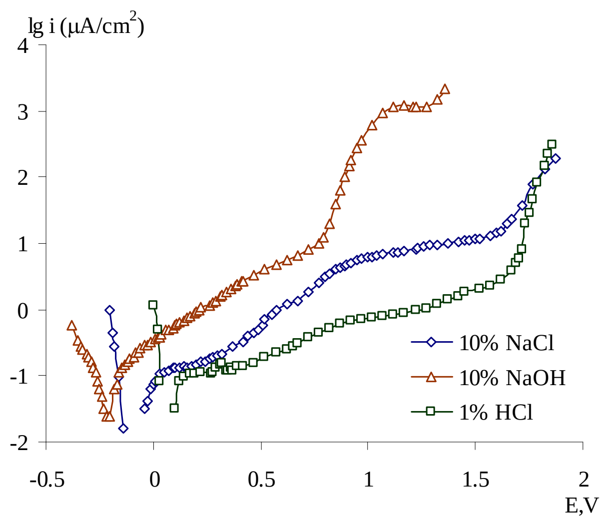


Fig. 9. Potentiodynamic curves of Ti-8Ni-1Cr coating (thickness 5 μ)

Corrosion potentials of coating with 5μ thickness in 1% HCl and 10% NaCl and NaOH solutions are accordingly equal to 0.05, -0.11 and -0.21 V. In NaCl solution two areas of self passivity in 0,07 -0,21 V and 0,9-1,52 V limits are observed. Average current density on the first stage is equal to 0.130μA/cm^2, on the second stage it is 0.008μA/cm^2. Corrosion rate calculated from Tafel extrapolation method is equal to 0,00005 g/m^{2}hr.

The most aggressive area for coatings is NaOH solution. On the anodic polarization curve unstable self passivity is observed; current density slowly, but constantly increasing and its average value is equal to 1,305μ A/cm^2, that is one order higher than in NaCl solution. Repassivation begins at 0,26 V. Corrosion rate is equal to 0,00001 g/m^{2}hr. There are two areas of self passivity in HCl, as well as in NaCl solutions: the first in the areas of 0,17-0,37V, the second one –in the section of 0,82-1,45V with the average current densities 0.124 and 0.996μ A/cm^2 accordingly. Corrosion rate does not exceed 0,00005 g/m^{2}hr. Corrosion potential of Ti-8Ni-1Cr alloy coatings with 5μ thickness in 1% HCl solution is equal to 0,12V, in 10% NaCl - -0,13, and in 10% NaOH - -0,42V. In NaCl solution coating has self passiveness in the area of potentials 0,72-1,62V, but average current density of passivity is big – 495,580μ A/cm^2. Minimum current density-,45 μA/cm^2 is observed at 1,62V potential, after which repassivation starts. Corrosion rate is equal to 0,00169 g/m^{2}hr. The pick of active dissolution is noticed in NaOH solution on the anodic polarization curve when potential is 0,02V and current density is 102,3 μA/cm^2. In the passive area within the limits of 0,14-0,72V corrosion rate is equal to 0,0148 g/m^{2}hr.Unstable self passivity has been noted in HCl solution. The first area is situated within the limits of 0,21-0,32V, average current density in which is equal to 1.58μ A/cm^2. The second stage of passivity includes the 0.72- 1.75V area. Current density in this area is 26.53μ A/cm^2. Corrosion rate does not exceed 0.0051 g/m^{2}hr. According to potentiodynamic curves, corrosion resistance of the coating with the thickness 5 μ , received on the device "ELFA" is approximately two orders higher, than coating with the thickness 30 μ, received on the device "ELITRON".

Corrosion and electrochemical investigations in 1%HCl, physiological and tissue solutions and also tests, according to the following regime: cleaning+dezinfection+sterilization shoved that all alloy coatings revealed good corrosion resistance. The best corrosion resistance revealed samples with Ti-8Ni-1Cr alloy coatings.

Thus, we can say that alloys Ti-8Ni -(1-3) Cr coatings are quite suitable for medical tools of multiply usage.

The coatings received by electro spark alloying method with application both, cast and a compact Ti-8Ni-(1-3)Cr alloys electrodes can be recommended for medical instruments to increase their strength , hardness, wear and corrosion resistance.

Conclusions:

Nanocrystalline coatings were received by electro spark alloying of the commercial titanium alloys samples surface with application bulk and a compact Ti-8Ni-(1-3)Cr alloys electrodes.

Preparation of the powders Ti-8Ni-Cr system alloys by mechanical alloying was carried out in the high energy ball mill of attriton type. Compacting of powders and manufacturing of electrodes was carried out by the method of cold pressing and high-temperature baking. Surface of samples from commercial titanium alloys was covered by electric-spark alloying method; compacted alloys Ti-8Ni-(1-3)Cr were used as anodic electrodes; the thickness of coatings was 30-35μ.

To compare electric-spark alloying has been carried out as well, where a cast Ti-8Ni-Cr alloys was used as en electrodes. The thickness of coatings was 3-5μ. Using of both powder and bulk electrodes give almost the same results as regards to homogeneity and porosity of coatings.

X-ray investigations showed that the crystalline structure of the of Ti-8Ni (1-3)Cr alloys coatings and substrate constituted the structure of α – titanium. All coatings contain α'' – martensite phase and nitride of titanium. The grain sizes of crystals in both cases do not exceed 100 nanometers; so it is possible to consider that the received coatings have nanocrystalline structure.

Measuring of the micro hardness showed that increase of hardness of coatings up to 401.7 kg/mm^2 is, evidently, the result of changing of chemical content and also strengthening caused by as mechanical so electrodynamics peening during electro spark alloying of the surface.

Wear resistance of the coatings, defined towards to weight lose, showed that a surface of titanium by alloying with Ti-8Ni-1Cr alloy noticeably increases its wear resistance.

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MANANA MIKABERIDZE

Ferdinand Tavadze Institute of Metallurgy and Materials Science
Tbilisi, Georgia

E-mail: mananamikaberidze@yahoo.com