Modification of surface films on chromium-nickel-molybdenum steel implants used in orthopaedics and traumatology

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ABSTRACT

Purpose: the paper is to characterize stainless steel of modified surface as a material used in orthopaedics and traumatology on the example of LCP (Locking Compression Plate) used in long bones treatment.

Design/methodology/approach: In order to reach the goal biomechanical analyses, both numerical and experimental, were carried out. The results of the analyses are the basis for selecting geometrical features of a plate stabiliser and biomaterial mechanical properties. The degree of stress and deformation also determines areas where corrosion can start to develop. Chromium-nickel-molybdenum steel widely applied for making implants used in orthopaedics and traumatology was selected for testing implant surface modification. Passive and passive-carbon films were formed on the implants. The structure of the created films was tested together with their susceptibility to deformation and resistance to corrosion.

Findings: It was shown that formation of passive-carbon DLC coatings is an effective method of increasing steel resistance to pitting, crevice and stress corrosion and of increasing its biocompatibility.

Practical implications: The proposed surface treatment seems to be effective method that allow to reduce the risk of post-surgical complications. The coatings can be formed by using electrolytic polishing and passivation and a final RF PACVD process.

Originality/value: The author also presents results of the coating surface topography examination, results of tests on its chemical and phase structure as well as mechanical and physicochemical properties.

Keywords: Metallic implants; Chromium-nickel-molybdenum steel; Passive carbon coatings; DLC coatings; Corrosion resistance; Biomechanical analysis of plate fixation

Reference to this paper should be given in the following way:
1. Introduction

Metal biomaterials are still the major material used for implants in orthopaedics and traumatology, maxillo-facial surgery, dentistry (prosthetics and orthodontics) as well as intravascular surgery. Each metal and alloy can be safely used for a specific period of time. The division is mainly based on biomaterial biocompatibility related to biological reactions.

As far as mechanical properties presented against biomechanical conditions are concerned, metal biomaterials reveal a full range of features required for all functional applications. There are technological solutions to shape the structure of metal biomaterials (chemical and phase composition, degree of non-metallic inclusions) and their mechanical characteristics (strength, fatigue and ductility). Most of the different types of implant constructions used for setting and stabilising fragments of fractured bones in the process of adhesion and treating bone deficiencies in intramedullary plate fixation and with external apparatuses as well as replacing bone assemblies damaged as a result of trauma or pathologically deformations (joint endoprostheses), are made of biomaterials.

Research carried out in some leading centres focuses on modifying implant surfaces with coatings with good adhesion to metallic substrate, susceptible to deformation at the stage of pre-surgical implant modelling and elastic deformation during use, and resistant to different corrosion types (pitting, crevice and stress) and hence indicating good biocompatibility. DLC (diamond-like carbon) coatings can be given as a good example. They are applied to implants used in traumatology, orthopaedics, maxillo-facial surgery and stents for intravascular surgery. No fibroblast damage or presence of macrophages was found on animals, which is evidence of a lack of a cytotoxic effect [2].

Silicon carbide coatings with amorphous structure are a different type of coating. A semi-conductive coating of carbide indicated high athrombogeneity and susceptibility to deformation. Clinical tests did not reveal any cytotoxic reactions of the abovementioned film or mutagenic effect on blood cells [3, 4].

Chromium-nickel-molybdenum steel, or steel with an addition of nitrogen, manganese and niobium is a well known and popular biomaterial. Implants used in traumatologic and orthopaedic surgery, maxillo-facial surgery and surgical cardiology are made of the steel, most often in the form of plates, screws, shafts, nails, clasps, wires, stabilisers and stents. Based on many years of clinical observations of biocompatibility of implants made of this steel, its qualitative and quantitative chemical and phase composition were identified to minimise the risk of complications and safety only in a limited period of time [5, 6].

The possibility to adjust mechanical properties of the Cr-Ni-Mo steel within a wide range fully secures the required scope of mechanical properties due to biomechanical conditioning of bone fragment stabilisation and tissue reconstruction. Therefore researchers focus on physical and chemical properties of the implant surface, aimed at improving biocompatibility and reducing post-surgical complications. Literature data indicates that this can be achieved by forming a surface layer with surface engineering methods [6, 7].

Breakdown potentials of implants made of Cr-Ni-Mo steel in a ground or mechanically polished steel are low, about 400-420 mV. Implants have to be polished at the final technological operations since the maximum surface roughness (Ra ≤ 0.16 μm) is limited. It can be obtained by grinding and mechanical and electrolytic polishing. The traditional polishing technology is made in H3PO4 and CrO3 based electrolyte and followed by chemical passivisation in a HNO3 solution. Breakdown potentials for such conditions are between 550 and 600 mV [8].

In relation to the abovementioned issues, making barrier coatings increasing implant resistance to corrosion and biocompatibility is intentionally considered [8-16].

The coatings can be obtained with different methods, which results in their different structure and properties. The coating structure may contain hydrogen (a-C:H) but equally it may not contain hydrogen (a-C). Coatings without hydrogen are obtained through graphite cathode spraying (magnetron or arch spraying, laser ablation) [10]. Hydrogen coatings are in turn obtained by hydrocarbon decomposition with PACVD methods [11]. Depending on the parameters of DLC type film formation, diamond, graphite or polymer groups CHn=1,2,3 can be found in the a-C:H structure. Their amount finally determines the coating properties. Results of tests on the structure of coatings obtained with various methods on the surface of implants made of this steel and their relationship to physicochemical properties can be found in the literature [12-16]. However, there is no full presentation of the relationship between the structure and coating properties in relation to specific functional use of implants.

Results of tests referring to structure and physicochemical properties of implants made of Cr-Ni-Mo steel, with passive or passive-carbon films for various uses in reconstruction surgery have been recently published in literature. However, the publications do not present a complete relationship of mechanical properties against biomechanical analysis, which is the basis for selecting geometrical properties of implants as well as their mechanical properties and physicochemical characteristics of surface [1-16].

2. Material and methods

Prior to testing the structure and properties of implants made of Cr-Ni-Mo steel, different forms of implants used for stabilising fragments of fractured bones were selected. Typical implants used in osteosynthesis, such as plate stabilisers, intramedullar nails and spine stabilisers, were analysed. The paper presents a sample biochemical analysis of tibia osteosynthesis using a stabiliser with a limited contact plate (LCP). The plate shape corresponds to the natural anatomic curve of the bone. The plate is fixed to the bone with bone screws.

A geometric model of a tibia was developed based on data obtained from the real bone computer tomography. A geometric model of the plate was made based on technical documentation. For the needs of the analysis, material properties corresponding to Cr-Ni-Mo steel were acquired: Young’s modulus of elasticity E = 2·1010 MPa, and Poisson’s ratio ν = 0.33. Figure 1 presents a geometric model of the analysed tibia - LPC plate assembly. Recommendations for surgery technique were also taken into consideration.

Finite element meshes were generated based on geometric models. Finite elements of SOLID95 type, used for spatial
analyses of solids were used for model discretisation. This type of element is identified by 20 nodes with 3 degrees of freedom in each node (displacement in direction x, y and z).

During tests, the displacement and stress ratio in the assembly elements, depending on the acquired mechanical properties of the plate material were determined. In order to make calculations it was necessary to identify and set initial and boundary conditions that reflected the phenomena occurring in the real assembly, with appropriate precision.

The following assumptions were acquired for the analysis needs:

- the lower part of the bone was immobilised by taking away all degrees of freedom from the nodes located on the plane, which made displacement of epiphysis in the bone axis impossible and hence blocked its possible rotation,
- the lower epiphysis of the tibia was loaded axially with forces ranging from between 100 N and 2000 N, with the load gain every 100 N.

The scope of analysis covered determination of the stress and displacement rate in the elements of the tibia - plate assembly.

The values of stress and deformation obtained in the analyses were equivalent ones according to the Huber - Misses hypothesis. The results of displacement and stress analyses carried out for the tibia - LCP assembly are presented in Figures 2 and 3. Based on the analysis it was discovered that the maximum reduced stress created as a result of applying the maximum force of 2000 N was observed in the screw located closest to the fracture gap (tibia shaft in the proximal section). They were not distributed evenly on the whole surface. The maximum values were observed in the area of the plate direct impact on the screw - Figures 2 and 3. The value of stress reduced in the plate, while loading the model with the force of 2000 N, did not exceed 175 MPa. Loading the assembly with 2000 N force did not cause exceeding the yield point of the material the bearing plate was made of. Maximum displacement in the fracture cleft, identified while loading the assembly with 2000 N force did not exceed 0.56 mm. The value of stress reduced in the bone while loading the model with 2000 N force did not exceed 280 MPa – Fig. 2. A biomechanical analysis of the suggested solution shows that this type of external osteosynthesis can be successfully used for treating tibia fractures.

Experimental tests on LCPs were also carried out. Dependence of displacement in the function of load from the range F = 100 - 2000 N for a tibia - LCP assembly was identified - Fig. 4. Characteristics of a bone not broken in the sagittal and frontal planes were identified in the first stage. Next, tests on models simulating transverse fracture, located at 1/3 of the distal part of tibia were carried out.

After installing the test stand, Mitutoyo displacement measuring sensors allowing for recording details with 0.01 mm accuracy were mounted and appropriately set. The sensors were set to measure displacement in two planes. Sensor 1 and 3 were used for assessing the carbon coating thickness.

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The presented analysis based on anatomic and physiological conditions and the applied surgical technique is the basis for selecting both the material hardening as well as the geometrical features of elements of the bone fragment stabilising assembly. The revealed stress and deformation zones indicate areas that have to be considered due to corrosion processes.

Material technology tests covering different forms of implants subject to specific stress and deformation were carried out next. Based on biomechanical analyses a wider range of mechanical properties of steel used for implants was determined. The structure and properties of the formed passive-carbon coatings were analysed for the selected implant substrate material hardening (supersaturated and strain hardened).

Cr-Ni-Mo steel, D grade in a hardened (Rm -1036 MPa, Rp 0.02 - 827 MPa, A 5 - 19 %) and annealed (Rm - 715 MPa, Rp 0.02 - 330 MPa, A 5 - 45 %) state was used. The steel structure met all requirements of the abovementioned standard for degree of pollution with non-metallic intrusion (not higher than model number 1.5) and austenite grain size (higher than model No. 8).

Imploins were subject to electrolytic polishing in a solution containing sulphuric and phosphoric acid as well as acetonilide, glycerine, oxalic acid and corrosion inhibitors, and after the required roughness Rq ≤ 0.16 µm was achieved, the surface was passivised in a nitric acid solution. At the next stage a film of carbon was applied to the passive layer in a RF PACVD process, in CH4 atmosphere. The described technology has been protected by patent [17].

To solve the issues, the following complimentary test methods were used:
• testing mechanical properties of the substrate material and coatings,
• metallographic tests of the substrate material and coating structure with a Transmission Electron Microscope (TEM),
• coating examination with the following methods: Auger electron spectroscopy, Raman spectroscopy and photoelectron spectroscopy (XPS),
• surface topography examination with an Atomic Force Microscope (AFM) and SEM,
• testing resistance to corrosion: pitting, crevice and stress,
• biological evaluation of implants in vivo and in pre-clinical and clinical conditions.

A static elongation test, according to ISO 6892 recommendations was performed to identify mechanical properties. The elongation test was conducted with INSTRON, model 1195, testing machine, at room temperature.

Tests on nanocrystalline carbon adhesion to the surface were done on steel implants with different hardening. The carbon film adhesion was evaluated with a scratch test. A CSEM REVETEST device was used for adhesion tests. The loading rate was 101 N/mm.

A CSEM nanohardness meter was used for measuring the nanohardness of the nanocrystalline carbon film. Additionally, Young's modulus of elasticity was identified for the coating.

Atomic Force Microscopy (AFM) was used for testing the topography of the carbon film surface, formed on the surface of the samples. A NanoScape E microscope from Digital Instrument was used for the tests. The film structure was evaluated both before and after corrosion tests. Ellipsometric spectroscopy was used for assessing the carbon coating thickness.
The chemical composition of the passive film formed on the implants was examined with an Auger spectrometer from Varian, model 981-2807.

Photoelectron spectroscopy of passive and passive-carbon coatings on implants was carried out with a Physical Electronics PHI 5700/660 multi-function electron spectrometer. XPS - X-ray Photoelectron Spectroscopy was applied with a mono-chromatic Al Kα radiation with 1486.6 eV power.

The tested steel structure was observed with a LEICA MEF4A light microscope, within the magnification range 100 - 1000 times.

To determine the structure of passive and passive-carbon coatings formed on the implant surface, tests were carried out in a transmission, high-resolution electron microscope JEOL JEM 3010. The microscope was equipped with Energy Dispersion Spectrometers (EDS) and a high-resolution slow scan camera for electronic image recording. The obtained high-resolution images were processed electronically with the Digital Micrograph programme. FFT images were obtained from the selected high-resolution images and then analysed just like classic electronograms.

Electrochemical tests of the steel resistance to pitting corrosion were conducted by recording anode polarisation curves with a potential dynamic method. The tests were carried out in a Tyrode's physiological solution, at 37°C and pH = 6.8-7.4.

Tests on steel resistance to crevice corrosion of implants were made for the hardened and annealed state, including different degrees of surface preparation. Ground, polished and passivated samples and samples with a carbon coating were subjected to the tests. Tests on resistance to pitting corrosion were carried out according to the requirements of ASTM F-746-81 and ASTM G-

The samples were bent on rolls with diameter D = 20, 30, 40, 60 mm.

The samples were polarised to the maximum potential value of +0.8 V. If corrosion did not occur during the first 20 seconds, which was indicated by low values of anode current, sample polarisation was continued at +0.8V potential for 15 minutes. After that time the measurements were stopped and the sample material was considered resistant to pitting corrosion in the testing environment when the anode current did not increase at +0.8V potential. When an increase in the anode current was observed at potentials lower than E Kor = + 0.8 V, the result was considered negative and not meeting the standard requirements. In such cases, the potential value of E Kor < E Kmax was assumed as the value corresponding to pitting corrosion critical potential.

After tests, the samples cleaned in an ultrasonic washer in ethyl alcohol, were examined with a Scanning Electron Microscope.

Resistance of Cr-Ni-Mo steel to stress corrosion was tested on implants in an annealed and hardened state:
- ground, electrolytically polished and passivated,
- ground, polished and passivated with a deposited carbon coating.

The tests were carried out in a neutral environment - glycerine and corrosive environment - Tyrode's solution. Directly before the tests the samples were degreased with ethyl alcohol by means of an ultrasonic disintegrator and then placed in corrosion vessels. The test was carried out with the sample elongation method, at a constant speed of 4.95 × 10⁻³ mm/min.

Indicators Kδ and Kτ, were assumed as the criterion of steel resistance to corrosion (1) and (2). The indicators represent respectively the relationship between the maximum elongating stress σmax in a corrosive environment (Tyrode’s solution) and the maximum elongation stress σmax in a corrosively neutral environment (glycerine) and the relationship between time of breaking the sample in a corrosive τδ and neutral ττ environment.

\[
K_\delta = \frac{\delta_{K_{\text{max}}}}{\delta_{O_{\text{max}}}} \quad (1)
\]

\[
K_\tau = \frac{\tau_K}{\tau_O} \quad (2)
\]

where:
- δKmax – maximum elongating stress in a corrosive environment,
- δOmax – maximum elongating stress in a neutral environment,
- τK – time to break samples in a corrosive environment,
- τO – time to break samples in a neutral environment.

Fractography of the implant surface after tests, was made with a Scanning Electron Microscope. The passive and passive-carbon coating resistance was tested with bending tests with a pitting corrosion control.

Resistance corrosion was tested on the samples in laboratory conditions, simulating a physiological fluid environment and deformation made during pre-surgical modelling. Samples prepared this way were subject to deformation – Fig. 6. The samples were bent on rolls with diameter D = 20, 30, 40, 60 and 80 mm.

The developed method of electrolytic polishing and chemical passivisation of Cr-Ni-Mo steel allows for obtaining the required roughness R_a ≤ 0.16 µm from the initial R_a = 60-40 µm. It is a more favourable method of final surface treatment than the traditionally used one in a bath containing H₃PO₄ + H₂SO₄ + CrO₃, which allowed for implant surface modification within the range R_a = 0.20-0.16 µm. The initial surface roughness R_a = 60-40 µm could be modified with strenuous mechanical polishing [8, 9]. The new polishing and passivisation method also allowed for
a more intense solubilisation of iron and nickel from the surface film. As a result, an increase in chromium concentration of about 4.8% and molybdenum of about 2.3% was observed against concentration of these elements in the surface, in the passive film structure about 12 - 15 nm thick, with Auger spectroscopy.

The XPS was used for identifying that chromium was mainly present in a Cr₂O₃ and CrO₂ form, and molybdenum in an oxidised MoO₂ and MoO₃ form. Based on the observation of the film structure with a High-Resolution Transmission Electron Microscope it was shown that nanocrystals with a size between 4 and 8 nm are present in the amorphous structure. The nanocrystalline phase analysis was carried out by making a Fourier transform, based on which distances between planes and angular values were calculated. They were also used for identifying each oxide crystallite - Fig. 7.

The obtained results of the passive film structure tests also substantiate the good corrosion resistance of steel. Corrosion potentials Eₚ₉₀ were between -140 and -110 mV for mechanical polishing state, while breakdown potentials Eₚ₉₀ were from +390 to +457 mV. After polishing and passivation the values increased in the applied conditions: Eₚ₉₀ = -16 - +37 mV and Eₚ₉₀ = +943 - +1020 mV.

Polishing in a traditional H₃PO₄ +H₂SO₄+CrO₃ based electrolyte allows only obtaining Eₚ₉₀ = -40 - -60 mV and Eₚ₉₀ = +560 - +650 mV potentials – Fig. 8.

The passive coating on the Cr-Ni-Mo steel, enriched with chromium and molybdenum, also makes a good surface for applying a carbon coating in an RF PACVD process. The good carbon coating adhesion to the passive one was connected with the conditions of its formation. The conditions were selected so that the concentration of these elements does not decrease in the process of passive surface (enriched with chromium and molybdenum) ion etching.

The passive-carbon coating showed good adhesion to the steel surface. The scratch-test method showed that substrate hardening did not have a significant impact on the mean value of force causing the film destruction (Fₚ = 115.2 N for the supersaturated state and Fₚ = 114.6 N for the hardened state). The obtained thickness of the passive-carbon film was between 40 and 60 nm. Such film properties as nanohardness (2409 HV for the supersaturated state and 2474 HV for the hardened state) and Young's modulus (701 GPa for the supersaturated state and 705 GPa for the hardened state) were also similar.

The film structure revealed a different degree of crystallinity – Fig. 9. The top part of the film mainly consisted of homogenous (as far as size is concerned) areas of coherent dispersion – Fig. 9a. These areas are composed of nanocrystalline phase in an amorphous base – Fig. 9b. The crystalline phase share increases towards the substrate material. Areas with amorphous structure were also found at the substrate surface, in the coating structure.

Ramann spectroscopy was used to show the presence of sp³ type phase coating (diamond with wave number ν=1356 cm⁻¹) and sp² type (graphite with wave number ν = 1591.7 cm⁻¹). The quotient of peak intensity in both phases Iₚ₃/Iₚ₆ was 0.98.

The chemical composition of the coating was determined with XPS examination – Fig. 10. A deep profile analysis showed that etching did not change the passive coating significantly during electrolytic polishing and chemical passivation.
The formed thin passive-carbon coating with a favourable amorphous-nanocrystalline structure and good adhesion to steel substrate also provides good characteristics. Both coating potentials are higher: corrosion ($E_{\text{cor}} = +66 \text{ mV}$) and breakdown ($E_{\text{bp}} = +1250 \text{ mV}$) for the hardened state as well as corrosion ($E_{\text{cor}} = +109 \text{ mV}$) and breakdown ($E_{\text{bp}} = +1160 \text{ mV}$) for the supersaturated state.

It was generally discovered that a passive-carbon coating made with this method is susceptible to significant deformation during which it is not subject to decohesion and maintains its resistance to pitting corrosion – Figs. 11 and 12. It is also resistant to pitting corrosion (Fig. 13), crevice corrosion (Fig. 14) and stress corrosion (Fig. 15) in the physiological fluid and tissue environment of the body. Moreover, implants with the coating are susceptible to significant deformations. This is shown by a stable value of corrosive potentials before and after deformation on different implant types (with a circular and non-circular cross-section) and a lack of corrosion damage on the surface of implants checked after light and scanning microscopy examination.

**Fig. 10.** XPS spectrum of CrNiMo steel surface with passive-carbon film

**Fig. 11.** Resistance of implants with passive-carbon coatings to pitting corrosion after deformation

**Fig. 12.** Topography of passive-carbon coating surface before and after deformation

**Passive-carbon film quality assessment (AFM)**

**Fig. 13.** Resistance of implants with passive-carbon coatings to pitting corrosion, for different hardening

**Fig. 14.** Resistance of implants with passive-carbon coating to crevice corrosion

**Deformability of passive-carbon film**

<table>
<thead>
<tr>
<th>Deformation angle</th>
<th>Corrosion potential, mV</th>
<th>Transpassivation potential, mV</th>
</tr>
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<tbody>
<tr>
<td>$0^\circ$</td>
<td>$-56 \pm 159$</td>
<td>$-506 \pm 3150$</td>
</tr>
<tr>
<td>$10^\circ$</td>
<td>$-20 \pm 159$</td>
<td>$+129 \pm 3150$</td>
</tr>
<tr>
<td>$30^\circ$</td>
<td>$-53 \pm 159$</td>
<td>$+192 \pm 3150$</td>
</tr>
<tr>
<td>$60^\circ$</td>
<td>$-61 \pm 159$</td>
<td>$+298 \pm 3150$</td>
</tr>
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**Corrosion resistance**

**Pitting corrosion**

- Annealed breakdown potential $E_{\text{bp}} = 956 \text{ mV}$
- Hardened breakdown potential $E_{\text{bp}} = 1046 \text{ mV}$

**Crevice corrosion**

- Ground surface: $E_{\text{corr}} = -350 \text{ mV}$, $E_{\text{ocp}} = -200 \text{ mV}$
- Surface with passive coating: $E_{\text{corr}} = -300 \text{ mV}$, $E_{\text{ocp}} = -150 \text{ mV}$
- Surface with passive-carbon coating: $E_{\text{corr}} = -250 \text{ mV}$, $E_{\text{ocp}} = -100 \text{ mV}$
Corrosion resistance

\[
\begin{align*}
K_r &= \frac{\sigma_{K_{\text{max}}}}{\sigma_{O_{\text{max}}}} \\
K_t &= \frac{\tau_{K}}{\tau_{O}}
\end{align*}
\]

- annealed
- hardened

\[
\begin{align*}
K_r &= 0.96 & K_r &= 0.99 & K_r &= 0.96 & K_r &= 1.00 \\
K_t &= 0.93 & K_t &= 1.00 & K_t &= 0.98 & K_t &= 0.97
\end{align*}
\]

Fig. 15. Resistance of implants with passive-carbon coating to stress corrosion

Passive-carbon coatings were also examined for susceptibility to sterilisation. The examination basically aimed at evaluating the effectiveness of sterilisation of implants with passive-carbon coatings. The presence of aerobic and anaerobic bacteria was evaluated in the examination. After bacteriological tests, sterilisation impact on the implant surface quality was assessed. Microscopic observations of the surface were made and corrosion resistance of the final implant form identified to determine any potential changes in the implant surface [18]. Sterilisation was carried out on chemically passivised Cr-Ni-Mo steel samples and on samples with passive-carbon coating under clinical conditions, i.e. in an autoclave with saturated water vapour at 121°C, for 20 minutes.

Implant surface sterilisation in the suggested conditions provides an effective surface protection against bacterial flora development (both aerobic and anaerobic bacteria).

After bacteriological examination, the impact of sterilisation on the final implant surface quality was evaluated with a potential dynamic method. Anode polarisation curves were recorded during the tests. The tests covered evaluation of Cr-Ni-Mo steel samples (chemically passivised and with passive-carbon coating) resistance to pitting corrosion.

Fig. 16. Sample of anode polarisation curves for implants: a) with passivised surface, b) with passive-carbon coating

The measurements indicated that the corrosion potential value was \(E_{\text{corr}} = +137 \text{ mV}\). Polarisation of the tested implants caused an increase in the anode current density at potential range \(E_{\text{np}} = +396 \text{ mV} \rightarrow +467 \text{ mV}\). The mean value of corrosion potential for implants with passive-carbon coating was \(E_{\text{corr}} = +221 \text{ mV}\), while the mean transpassivation potential was \(E_{\text{np}} = +1063 \text{ mV}\) – Fig. 16.

The final verification of quality and usefulness of the passive-carbon coating formed on the implants was made with \textit{in vitro} [18] and \textit{in vivo} pre-clinical and clinical tests [18]. The results of tests were positive. The number of recorded reactive complications was far lower.

3. Conclusions

A method of forming passive-carbon coatings in a two-stage process of electrolytic polishing and chemical passivisation and RF PACVD was developed. The process allows for forming coatings on different forms of Cr-Ni-Mo steel implants used in bone surgery (including bone screws), maxillofacial and intravascular surgery. The coatings with amorphous-nanocrystalline structure show good adhesion to the metallic surface and the susceptibility to deformation necessary for elastic osteosynthesis.

One of the key distinctive features of the coating is its resistance to typical corrosion mechanisms (pitting, crevice and stress) that implants in the physiological fluid and tissue environment are subjected to. This fact was confirmed in testing procedures following the effective normative recommendations. The usefulness of this method of finishing the surface of implants made of Cr-Ni-Mo steel was demonstrated by \textit{in vitro} and \textit{in vivo} tests. The coating application opens new prospects for surgery. It allows for preoperative implant modelling or its elastic deformation during use, but mainly reduces post-surgical reactive complications, which results from higher biocompatibility and resistance to corrosion.

Passive-carbon coatings can be subject to sterilisation in conditions required and used in hospital practice. Mechanical and physicochemical characteristics of the coatings do not change after the treatment.

Acknowledgements

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