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# Influence of hardening and surface modification of endourological wires on corrosion resistance

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Guide wires with suitable functional characteristics are of crucial importance for proper urological treatment. This study presents an analysis of the effect of work hardening taking place in the process of wire cold drawing and the effect of surface modification by means of electrochemical polishing and chemical passivation on the resistance of wires made of X10CrNi18-8 steel used in urology. Corrosion resistance was evaluated on the grounds of the registered anodic polarisation curves by means of potentiodynamic method. The tests were made in solution simulating human urine. Anodic polarisation curves were presented for selected wire diameters. Mechanical properties were tested in a static uniaxial tensile test. The course of flow curve as well as mathematical form of flow stress function were determined. Curves presenting the relation of polarisation resistance as a function of strain applied in the drawing process are given. The tests carried out show that surface modification by means of electrochemical polishing and then chemical passivation of wires used in endourological treatment is fundamental.

*Key words*: *endourology, guidewires, stainless steel, flow stress and flow curve, corrosion resistance*

## 1. Introduction

The main direction in modern urology development related to urolithiasis treatment was the need for treatment invasiveness limitation. New treatment methods were introduced to clinical practice at the turn of the 1970's and 1980's. Nowadays for majority of cases where uroliths have to be removed, so called low-invasive treatment is used – uroliths are crushed with shock waves (ESWL), and endourological treatment is also applied – percutaneous nephrolithotripsy (PCNL) and ureterorenoscopy (URS). Propagation of those methods eliminated almost entirely the need for surgical intervention in order to remove uroliths from kidney or ureter [1]–[5].

Endourology is a branch of urology that deals with diagnostics and treatment applied within urinary system by means of endoscopic equipment (optical visors), without the need for surgical access to the organ (kidney, urinary system) containing uroliths. The point of endourological treatment in urolithiasis is to gain access to uroliths by means of special instruments, make the uroliths visible in the optical system of the instrument and remove them in the whole or crush them and remove their fragments. ESWL and endourological methods of urolithiasis treatment were introduced in Poland in the second half of the 1980's. Currently, they are widely used in the more developed urological centres in our country.

Percutaneous nephrolithotripsy (PCNL) consists in the removal of uroliths from kidney pelvicalyceal

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system or the upper part of ureter through fistula created by means of puncture. Prior to creation of this renal fistula, cystoscopy is applied and urinary catheter is inserted to the renal pelvis in order to inject contrast medium. The aim is to make the pelvicalyceal system visible on the TV screen coupled with X-ray tube. When the patient is placed on his belly, his selected renal pelvis is pricked and puncture channel is widened. Nephroscope is inserted through this fistula. Deposits are crushed and little fragments are removed. URS takes place by means of a device called ureterorenoscope, which is inserted to the ureter through the urethra and bladder (ascending ureterorenoscopy) or through percutaneous renal fistula (descending ureterorenoscopy). Ureterorenoscopy is performed on urological table where the patient can be placed in gynaecological position and which enables urinary system to be shown by means of X-ray apparatus. To perform this treatment, it is necessary to have a cystoscope, various kinds of urinary catheters and a set of urinary guide wires [1].

A great role in the development of endourological methods is played by improvements in equipment that is applied, auxiliary materials for treatment and miniaturization of instruments. Obtaining medical instrumentation with the functional characteristics required is connected with proper characteristics of biomaterial it is made of, proper construction of the product and proper execution of production process. Among the instruments used in modern endourology, one must distinguish guide wires [1], [5]. Thanks to their application in the treatment, it is possible to insert endoscopes, catheters or urological stents efficiently. Guide wires are made of stainless steel [6]–[8].

Among numerous properties that guide wire used in endourology should feature, the ones that should be listed first of all are: proper for each application selection of mechanical characteristics and high resistance to electrochemical corrosion in the environment of tissues and saline solutions. These properties depend, among other things, on chemical composition of material, its metallurgical purity, parameters of technological process of wire production. It must also be highlighted that an important issue in the process of determination of functional characteristics of wires and wire products (e.g., guide wires and stents) used in urology is the selection of physical and chemical characteristics of their surface [9]–[12]. They should be accommodated to the features of human tissue environment.

An important role in the selection of optimal parameters of wire production process is played by proper characteristics of technological plasticity of the material. They condition both obtaining a structure that is good for cold drawing process as well as obtaining a product featuring the functional characteristics required (among other things, mechanical characteristics and corrosion resistance). Plastic strain is accompanied by strain hardening that is connected with the increase in flow stress $\sigma_p$. Proper determination of plastic working parameters and obtaining proper final characteristics of products is connected with the analysis of function course $\sigma_p = f(\varepsilon)$, where $\varepsilon$ is the strain expressed as logarithm. The curves of the flow stress change as a function of strain (so called strain hardening curves) enable us to predict the reaction of material in the plastic working process. Strain applied in the drawing process also influences substantially wire corrosion characteristics [13], [14].

Production engineers, who design wire production technology, make use of flow curves in order to select drawing parameters in such a way that they can obtain wires featuring mechanical characteristics required for the respective applications. This study suggests similar attitude in order to predict corrosion characteristics of wire in relation to strain applied in the drawing process.

Guide wires used in endourology are mostly made of stainless steel of X10CrNi18-8 grade. This study presents the course of flow curve of wires made of such steel and mathematical form of flow stress function. Corrosion resistance was evaluated on the grounds of registered anodic polarisation curves by means of potentiodynamic method. The tests were made in the solution simulating human urine on samples that were electrochemically polished and polished and then chemically passivated. Exemples of anodic polarisation curves are given as well as the curves presenting the relation between polarisation resistance as a function of strain applied in wire drawing process.

## 2. Materials and methods

Steel rod made of X10CrNi18-8 steel with a diameter of 5.65 mm, annealed, was used as the initial material for tests. Wire rod was drawn up to the diameter of 1.5 mm. Total logarithmic strain in the drawing process was $\varepsilon = 2.65$. In the cold drawing process, strain hardening of wire took place. During drawing process, samples for mechanical and corrosion tests were cut off. Next, wire surface was modified. Wires with electrochemically polished and polished and then chemically passivated surface were selected for the tests. Thanks to such preparation of wire surface it was possible to determine the influence of both strain hardening as well as the way of surface modification on electrochemical corrosion resistance in artificial urine.

Pitting corrosion resistance was evaluated on the grounds of registered anodic polarisation curves by means of potentiodynamic method, with the employment of electrochemical tests system VoltaLab® PGP 201. Tests were performed in alternative solution simulating human urine. The solution featured molar concentration of chloride ions of 0.46. Chemical composition of artificial urine is presented in table 1. Both solutions, A and B, the components of artificial urine, were mixed together in the proportion 1:1. Solution temperature during the test was 37.0 ± 1.0 °C, and pH = 7.0 ± 0.2. Saturated calomel electrode (NEK) of KP-113 type was used as a reference electrode. Platinum electrode of PtP–201 type was used as an auxiliary electrode.

Table 1. Chemical composition of artificial urine

| Component | Amount of distilled water, g/l |
|---|---|
| Solution A | |
| $CaCl_2 \cdot H_2O$ | 1.765 |
| $Na_2SO_4$ | 4.862 |
| $MgSO_4 \cdot 7H_2O$ | 1.462 |
| $NH_4Cl$ | 4.643 |
| KCl | 12.130 |
| Solution B | |
| $NaH_2PO_4 \cdot 2H_2O$ | 2.660 |
| $Na_2HPO_4$ | 0.869 |
| $C_6H_5Na_3O_7 \cdot 2H_2O$ | 1.168 |
| NaCl | 13.545 |

The tests started with determination of initial potential OCP, and then anodic polarisation curves were registered at the rate of potential change of 1 mV/s in anodic direction. Based on the curves registered, typical parameters describing pitting corrosion resistance were determined, i.e., breakdown potential $E_b$, polarisation resistance $R_p$, corrosion current density $i_{corr}$, and also corrosion rate corr.

Mechanical properties, including proof stress, were determined in static uniaxial tensile tests on the testing machine Instron type 1116. Next, the course of strain-hardening curve $\sigma_p = f(\varepsilon)$ was determined. For proper determination of flow stress $\sigma_p$, precise determination of actual stress $\sigma_{r0.2}$, that the samples are subject to during tensile test, becomes an important issue. For the load corresponding to proof stress, the value of real stresses $\sigma_{r0.2}$, may be calculated with the following formula:

$$\sigma_{r0.2} = \frac{R_{p0.2}}{\left[\sqrt{\frac{1}{1.002}} - \frac{\nu \cdot R_{p0.2}}{E}\right]^2}, \tag{1}$$

where:

$\sigma_{r0.2}$ – effective stress corresponding to conventional yield stress,

$R_{p0.2}$ – proof stress,

$\nu$ – Poisson's ratio,

$E$ – Young's modulus.

Precise methodology of procedure when determining strain-hardening curve has been described in the literature [15], [16].

# 3. Results

The results of strength properties of wire made of X10CrNi18-8 steel are shown in table 2.

Table 2. Strength properties of wire made of X10CrNi18-8 steel

| Wire diameter $d$, mm | Logarithmic strain in the drawing process, $\varepsilon$ | Tensile strength $R_m$, MPa | Yield point $R_{p0.2}$, MPa |
|---|---|---|---|
| 5.65 | 0 | 604 | 252 |
| 3.0 | 1.27 | 1607 | 1403 |
| 2.0 | 2.22 | 1827 | 1507 |
| 1.5 | 2.65 | 2178 | 1653 |

Real stresses that correspond to the flow stress $\sigma_{r0.2}$ (formula (1)), which were determined by means of tensile test, were used to draw a flow curve of the wire tested and to determine a mathematical form of the flow stress function. The curve was approximated by means of $\sigma_p = \sigma_{p0} + C\varepsilon^n$ type function that allows for stress at the initial condition (i.e., for annealed wire for drawing). The mathematical form of the flow stress function for the test steel X10CrNi18-8 is as follows:

$$\sigma_p = 253.1 + 894.6\varepsilon^{0.51}. \tag{2}$$

Figure 1 presents a flow curve for test wires made of X10CrNi18-8 steel ($\varepsilon$ presents strain in the drawing process expressed as a logarithm).

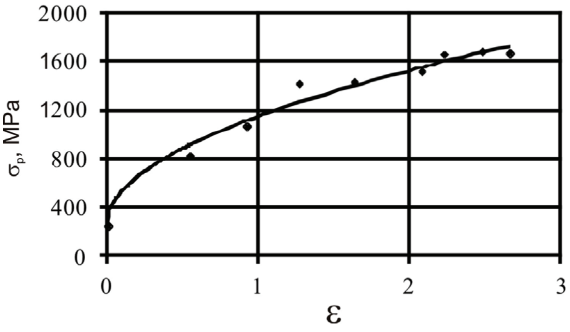

Fig. 1. Flow curve of wire made of X10CrNi18-8 steel

Potentiodynamic tests in artificial urine enabled changes of resistance to electrochemical corrosion of wire to be determined, depending on both strain applied in drawing process and the way the wire surface was prepared. OCP potential for all the samples tested would set after 60 minutes. The results of corrosion tests are shown in table 3. Figures 2 and 3 illustrate the selected anodic polarisation curves, namely those of the test wire with 5.65 and 1.5 mm in diameter.

Then, the results of potentiodynamic tests went through statistic analysis. It was determined

Table 3. Test results of pitting corrosion resistance of wire made of X10CrNi18-8 steel

| Diameter of wire *d*, mm | Logarythmic deformation in drawing process *ε* | Breakdown potential $E_b$, mV | Polarization resistance $R_p$, kΩcm$^2$ | Corrosion current density $i_{\mathrm{corr.}}$, μA/cm$^2$ | Corrosion rate, μm/year |
|---|---|---|---|---|---|
| Wires electropolished | | | | | |
| 5.65 | – | +607 | 3220 | 0.008 | 0.09 |
| 3.0 | 1.27 | +494 | 2260 | 0.012 | 0.13 |
| 2.0 | 2.22 | +250 | 1340 | 0.013 | 0.15 |
| 1.5 | 2.65 | +225 | 468 | 0.016 | 0.24 |
| Wires electropolished and passivated | | | | | |
| 5.65 | – | +969 | 6870 | 0.004 | 0.04 |
| 3.0 | 1.27 | +890 | 2810 | 0.011 | 0.09 |
| 2.0 | 2.22 | +790 | 1540 | 0.012 | 0.13 |
| 1.5 | 2.65 | +728 | 1410 | 0.015 | 0.21 |

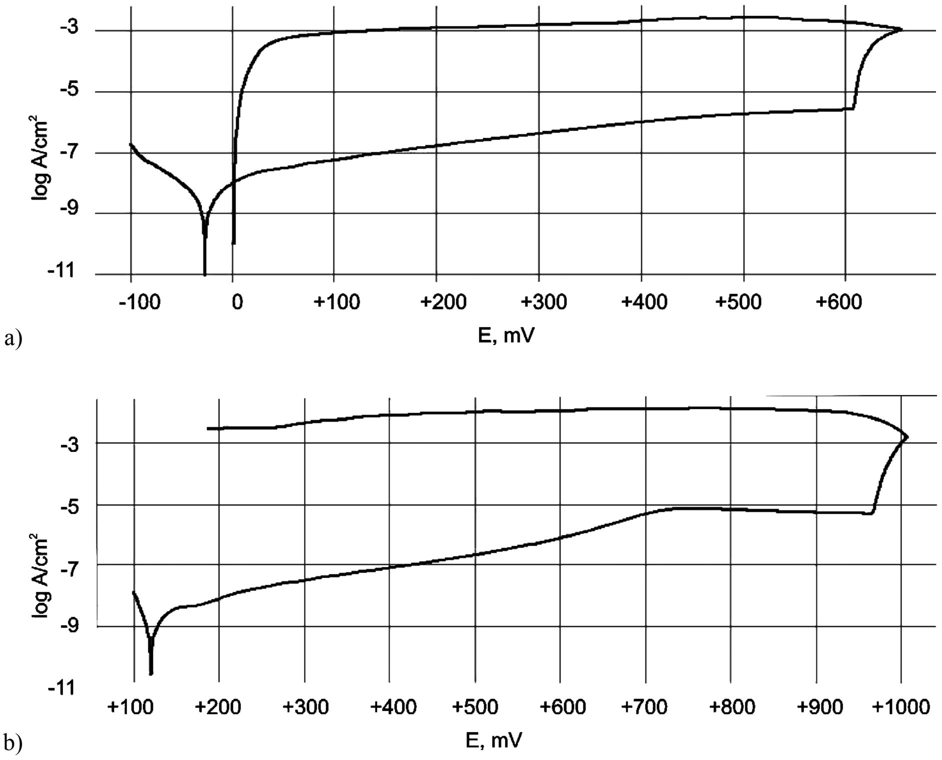

Fig. 2. Anodic polarisation curve recorded for wire rod (*d* = 5.65 mm), electropolished (a) and passivated (b)

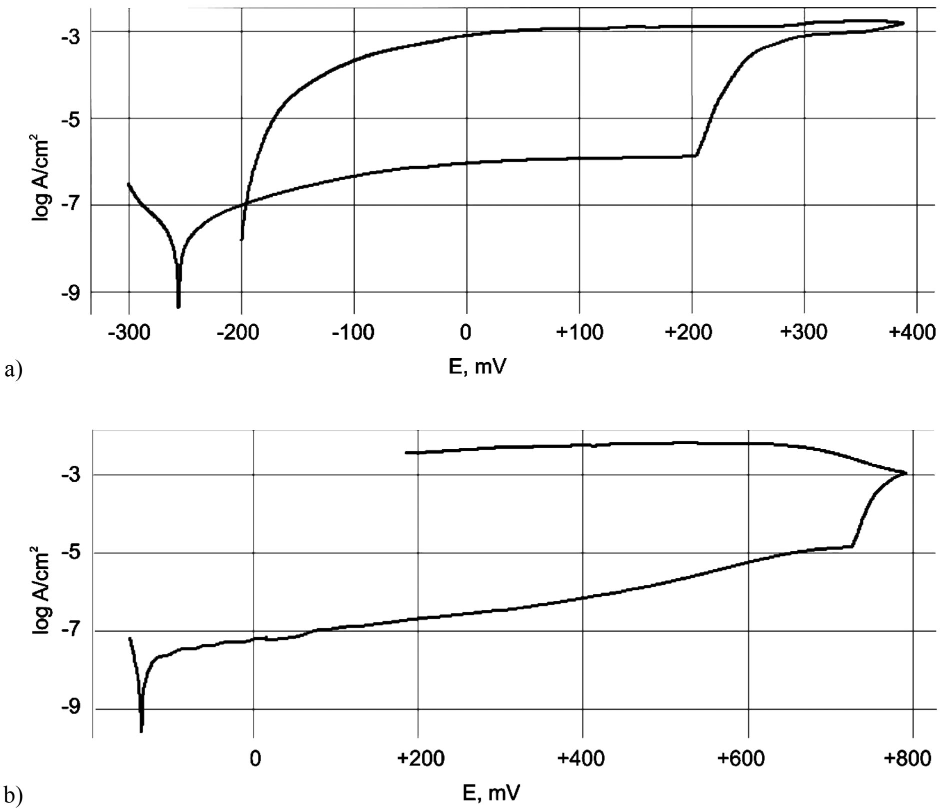

Fig. 3. Anodic polarisation curve recorded for wire $d = 1.5$ mm, electropolished (a) and passivated (b)

whether there is a significant relation between corrosion characteristics and strain applied in drawing process.

Figure 4 shows curves obtained on the basis of selected corrosion test results, namely the change of polarisation resistance as a function of strain applied in drawing process. The tests performed enabled functions that present the relation $R_p = f(\varepsilon)$ to be selected. They have the following form:

$$R_p = -1109.1\varepsilon + 3498.7 \quad \text{(electropolished wire)}, \qquad (3)$$

$$(R^2 = 0.9681;\ S_e = 186.32),$$

$$R_p = -1826.6\varepsilon + 5497.1 \quad \text{(polished and chemically passivated wire)}, \qquad (4)$$

$$(R^2 = 0.8555;\ S_e = 694.48).$$

In both cases, the level of significance $p < 0.05$.

Coefficients of regression function in accordance with Pearson's linear model were estimated using the least squares method. The matching of the model to empirical points was evaluated by means of the coefficient of determination $R^2$. $S_e$ is a residual standard deviation of matching. Calculations connected with regression and correlation analysis were made in the Statistica 7.1.Pl package by StatSoft.

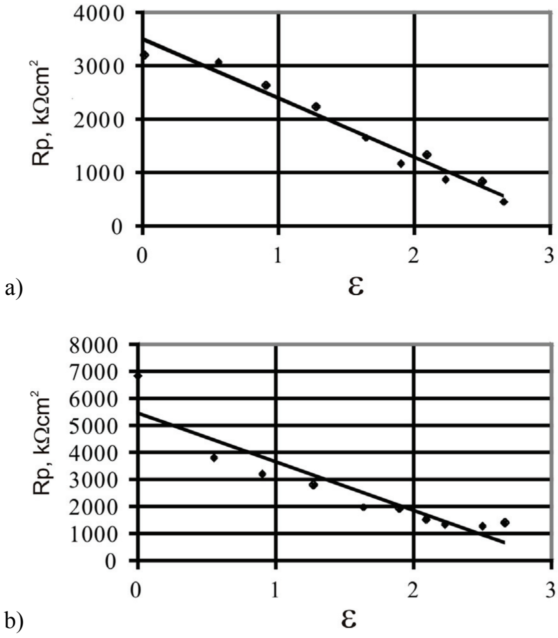

Fig. 4. Relation between polarisation resistance and strain in wire drawing process
(a) electrochemically polished
(b) electrochemically polished and chemically passivated

# 4. Discussion

The tests of mechanical properties allowed the course of flow curve to be determined and flow stress function of drawn wires made of stainless steel X10CrNi18-8 to be selected. Strain hardening taking place as a result of drawing process caused an increase of mechanical properties of wire and a decrease of corrosion properties.

The analysis of potentiodynamic test results proved that an increase of strain applied in wire drawing process caused a decrease of corrosion potential, breakdown potential and polarisation resistance. At the same time corrosion current density and corrosion rate increased. These tendencies refer both to electropolished and polished and then chemically passivated wire.

The highest corrosion resistance, irrespective of the condition of the surface, was observed for wire rod in annealed state. Breakdown potential of polished wire rod was $E_b$ = +607 mV, and passivated $E_b$ = +969 mV. With the increase of strain in drawing process, breakdown potential decreased. For wire with diameter of 3 mm it was $E_b$ = + 494 mV (polished surface) and $E_b$ = +890 mV (passivated surface). Breakdown potential for wire with a diameter of 2.0 mm that was polished and passivated, in turn, was $E_b$ = + 250 mV and $E_b$ = +790 mV. The lowest breakdown potential was observed for wire with a diameter of 1.5 mm ($E_b$ = +225 mV for polished wire, $E_b$ = +728 mV for passivated wire).

With the increase of strain, polarisation resistance decreased. Polarisation resistance for polished wires was respectively $R_p$ = 3220 kΩcm$^2$ (wire rod) and $R_p$ = 468 kΩcm$^2$ (wire with a diameter of 1.5 mm). Polarisation resistance of passivated wire rod equalled $R_p$ = 6870 kΩcm$^2$, and for passivated wire with a diameter of 1.5 mm – $R_p$ = 1410 kΩcm$^2$.

Plastic strain in drawing process brought about an increase of corrosion current density and corrosion rate. This tendency was observed both for polished as well and for polished and passivated wire. Corrosion current density for polished wire rod was $i_{\text{corr}}$ = 0.008 μA/cm$^2$, and polished and passivated $i_{\text{corr}}$ = 0.004 μA/cm$^2$. The highest corrosion current density was observed for wire with a diameter of $d$ = 1.5 mm. It equalled $i_{\text{corr}}$ = 0.016 μA/cm$^2$ for polished wire and $i_{\text{corr}}$ = 0.015 μA/cm$^2$ for passivated wire.

Corrosion rate of wire rod with a diameter of 5.65 mm was respectively corr = 0.09 μm/year (polished surface) and corr = 0.04 μm/year (passivated surface). Together with an increase of strain, corrosion rate increased and it was biggest for wire with a diameter of 1.5 mm.

The tests carried out prove without any doubt a substantial increase of wire corrosion parameters as the result of polishing and chemical passivation in comparison with the process of polishing as such.

Static analysis proved that there is a significant dependence between corrosion properties (polarisation resistance) and strain applied in drawing process. Given the curves as well as functional relations we can draw conclusions about polarisation resistance of wire after surface treatment. The value of polarisation resistance proves that it is essential to make use of chemical passivation in the case of guide wires made of stainless steel X10CrNi18-8 used in endourology.

The curves represent in a proper way the results obtained in the experiments. The biggest differences in polarisation resistance may be observed for wire with initial diameter.

# 5. Summary

Corrosion tests showed that in each case, irrespective of the strain hardening taking place, and of differences in the way of surface preparation, wires are subject to pitting corrosion. This proves that wires made of X10CrNi18-8 steel are not resistant to this type of corrosion. Pitting corrosion is fostered by, among other things, an increase in chloride ion concentration as a result of their migration with corrosion current leading to creation of corrosion cell inside the pit (chloride ions are included in urine solution), acidification of the solution inside the pit as a result of hydrolysis of metal ions and high conductivity of metal ions as well as high conductivity of concentrated saline solution inside the pit [9]. The results show that application of protective layers on wires that are to be used in urological treatment is indispensable.

The results of electrochemical corrosion resistance tests also enabled functional relations to be obtained showing the influence of strain in drawing process on the change of polarisation resistance. It must be stated that the given functional relations are not of universal character and are only related to wires made of X10CrNi18-8 steel tested in artificial urine solution. In applications either on wires made of other material, or with other product destination, it is necessary to carry out analogical tests for wires made of that material in other environment simulating saline solutions of human body. It must also be highlighted that functions presented in the article were developed for one type of melt. To transform them into universal relations for stainless steel X10CrNi18-8, it is necessary to repeat the tests for a bigger number of biomaterials.

The issues presented are extremely important for production engineers dealing with designing drawing processes, as the problem of correct description of materials workability is tightly coupled with the selection of optimal parameters of technological process of wire production. This issue is also important for manufacturers of guide wires, as having quoted curves or functions at disposal you can predict in advance corrosion characteristics of wire with the required strength drawn with the required strain.

We cannot forget that the correct description of flow stress function is one of the elements determining the acquisition of correct characteristics of materials technological plasticity. These characteristics make at present the grounds for databases used in computer simulation of plastic working. Such bases could be supplemented with functional relations $R_p = f(\varepsilon)$ determined for various metallic biomaterials accommodated to the features of human tissue environment in the environment of various saline solutions. They could then be used by production engineers and manufacturers of goods produced by means of cold working for various medical applications. For example, in the production of products (strips, rods, wire, etc.) with the mechanical characteristics required, it would be possible to read from such a database both the value of the necessary strain applied in processing as well as polarisation resistance corresponding to this strain, that this biomaterial will feature. This innovative offer of creation of databases including corrosion characteristics of metallic material for medicine would be an extremely useful tool in designing technological processes of biomaterials.

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