



Potentiodynamic studies of stainless steel wire for endourology

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ABSTRACT

Purpose: The purpose of the study is to evaluate resistance to electrochemical corrosion of wire made of Cr-Ni stainless steel, designed for use in endourological treatment. The influence of strain formed in the process of drawing and methods of wire surface preparation to corrosive resistance in artificial urine solution were analysed.

Design/methodology/approach: Wire corrosion tests were carried out in the solution of artificial urine with the use of the system for electrochemical tests VoltaLab®PGP201. Resistance to electrochemical corrosion was evaluated on the ground of recorded curves of anodic polarization by means of potentiodynamic method. Mechanical properties of wire were tested by means of static uniaxial tension test.

Findings: Potentiodynamic tests carried out in artificial urine enabled to determine how the resistance to pitting corrosion of wire changes, depending on strain formed in the drawing process as well as on the method of wire surface preparation. Deterioration of corrosive properties of wire along with the increase in the formed strain hardening was observed.

Research limitations/implications: The obtained test results proved the suitability of the applied research methodology for evaluation of electrochemical corrosion resistance of wire made of stainless steel designed for use in endourology.

Practical implications: Test results are of significant utilitarian value because they can determine the relation between pitting corrosion resistance and the volume of strain formed in the wire drawing process, and consequently their mechanical properties.

Originality/value: The analysis of the results of electrochemical corrosion resistance tests showed positive impact of wire surface treatment by means of electrolytic polishing and chemical passivation method on improvement of its corrosive properties. It must be emphasised that despite the increase in corrosion resistance, obtained thanks to surface treatment, it is necessary to use protective coating on wire used in urology.

Keywords: Metallic alloys; Biomaterials; Corrosion; Wires for endourology

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MATERIALS

1. Introduction

Within the last several years of the previous century, a great development of curative treatment of both urinary tract lithiasis, regarded as a social disease, as well as several other urological diseases, took place. Previously, uroliths from kidneys and ureters could be removed only by means of a surgery. New methods of lithiasis treatment were introduced into clinical practice on the turn of the 70s and 80s of the XX century.

Currently, endourology takes the leading place in clinical urology. It is one of urology fields, that is mainly based on endoscopy, carried out in the area of urinary tract. At present it is the leader in clinical urology, covering diagnostic and curative treatment performed under visual control by means of endoscopic equipment (optical visors), without the need to carry out a surgery in order to access the organ (kidney, ureter). A noticeable boom of endoscopic urology took place in the XX century, mainly due to the considerable improvements in the area of the equipment. In 1929 Hugh Hampton Young constructed the first ureterorenoscope, in 1953 Mulvaney discovered that ultrasonic wave can crush uroliths, in 1955 Goodwin performed the first percutaneous nephrostomy, in 1976 a method of percutaneous nephrolithotripsy was introduced - PCNL, and in 1983 Lithotripter Dornir HM-3 was used commercially for the first time. Endourological treatment character requires the use of specially adopted equipment, appliances and instruments. They may include catheters and ureter dilators, cystoscopes or pephroscopes, electroresectoscopes, lithotriptors as well as urethrotomy [1-7].

Diagnostic and medical endourological treatment performed in the area of urinary tract by means of endoscopic equipment requires the use of guide wires. They enable trouble-free insertion of endoscopes, catheters or urological stents.

Endourological treatment eliminated to a great extent the necessity of reaching the organ (kidney, ureter) by means of a surgery. Minimally invasive surgery treatment is used to perform e.g. electrotomy of prostate cancer, bladder neoplasms or cervix vesicae cirrhosis, as well as electrotomy per urethra. Endourological treatment also includes endopyelotomy, that is cutting of the connection between renal pelvis and renal duct, which is caused by congenital or acquired hydronephrosis; as well as treatment of urethra contraction [1].

Nowadays, apart from the aforementioned treatment, partial nephrectomy is successfully performed, kidneys are collected from alive donors, kidney cysts are cured, kidney biopsy, renal pelvis reconstructive operation, pyelolithotomy, ureterolithotomy, adrenalectomy, ureterolysis are performed. Some urological operations can be modified by means of mixing laparoscopic surgery technique with classical one. Endoscopic methods are low-invasive, non-destructive to organs, they reduce the time of hospitalisation and reduce the cost of treatment [1-6].

The essence of endourological treatment in nephrolithiasis is to access the calculus by means of special devices and to remove it as the whole or to crush it and remove the pieces. Traditional surgical treatment of nephrolithiasis has been almost completely replaced by crushing the deposits with waves generated extracorporeally (ESWL) and by endourological methods: percutaneous nephrolithotomy (PCNL) and ureterorenoscopy (URS) [7]. Percutaneous nephrolithotomy is preceded by the creation of a renal fistula. This procedure is carried out under control of USG or RTG.

Fistula canal is widened by means of special telescopic wideners. Opening prepared in such a way is used to insert nephroscope to renal pelvis. Large calculi are crushed by means of electric-hydraulic waves, whereas smaller ones are crushed by means of ultrasonic probe and sucked out simultaneously. Small particles of deposits are removed with special pliers [8].

Ureterorenoscopy takes place with the employment of a device called ureterorenoscope, which is inserted to the renal duct through urethra and bladder (ascending ureterorenoscopy) or through percutaneous renal fistula (descending ureterorenoscopy). Ureterorenoscopy is performed on the urological table that enables to arrange the patient in gynaecological position and to view urinary tract by means of X-ray apparatus. To carry out this operation, it is necessary to use a cystoscope, various types of ureteral catheters and a set of ureteral guide wires [9].

The success of performed endourological treatment is connected, among other things, with manufacturing of guide wires with the required effective properties. Guide wires were previously manufactured to vascular application, but in time they became indispensable also in other areas of medicine. Currently they are also used in almost all endourological treatment. They serve two purposes: 1) they provide access to the desired parts of the urinary system, 2) they serve as guides on which catheters and stents may be passed.

Complicated construction of wire involves the necessity to master various production techniques, including: drawing, flattening and heat treatment of wire, spring winding together with insertion of the core. In medical practice many types of guide wires are used, that differ in e.g. structure, length, diameter properties as well as destination. Most of them are equipped with an elastic, flexible tip and a stiff or semi-stiff body. The elastic tip enables to avoid tissue damage and perforation. The body is often made in the form of a spring inside which a core, made of round wire, and in some cases of flat wire, is placed.

When testing commercial wires it was determined that one of the wires, generally used in endourology, consisted of three sections [8,9]:

- J-shaped elastic spring 55 mm long,
- straight, stiff wire 345 mm long,
- spring 400 mm long, made of round wire.

The first section (flexible spring) is inserted to kidney fistula. It is connected with straight wire (stiff) by means of tin solder. The connection between straight wire and spring 400 mm long is made analogically. Tests proved that inside the flexible spring one can find two wires – round and flat. In consideration of small dimensions of measured objects the measurement of wires was made by means of computer-aided quantitative metallography. It was determined that the diameter of the round wire was 392 μm , whereas the dimensions of the flat wire were as follows: width 278 μm and thickness 58 μm . Figure 1 shows respectively the connection between straight wire and the spring, section of stiff wire, 400 mm long spring and the same spring with flux-cored wires.

Qualitative and quantitative analysis made by means of electron scanning microscope proved that all elements used for PCNL were made of chrome-nickel steel type 18-8.

Another wire used in endourological treatment, 1500 mm long, is made as a spring with a core, consisting of two wires: round and flat. Initial section of the wire is elastic spring (90 mm long), the core of which consists of the same flat wire and round wire that was made thinner. This part of wire can be safely inserted into urethra.

Figure 2 shows elastic spring used in endourology. Visual inspection proves that the spring is made of flattened wire. Inside the spring there are two wires: round one and flat one. Wire measurement made by means of computer-aided quantitative metallography showed that the diameter of core round wire was ~484 μm , whereas flat wire dimensions were: 261x75.8 μm .

Also for this wire it was established that all its parts were made of chrome-nickel stainless steel.

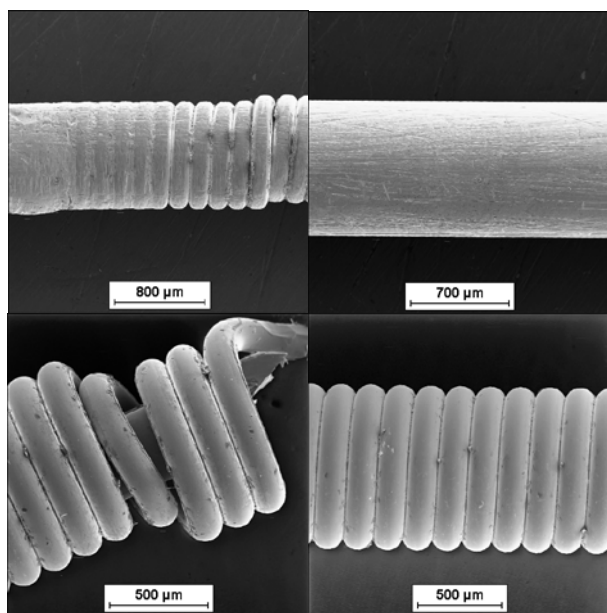


Fig. 1. Elastic wire used in endourology

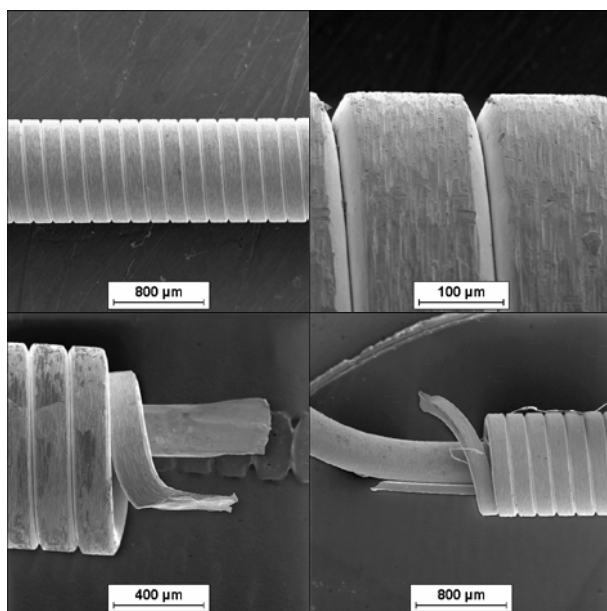


Fig. 2. Elastic wire used in endourology

Next of tested wire consisted one by one of J-shaped spring, 105 mm long, made of round wire with diameter of 0.18 mm, a section of straight wire with diameter of 0.88 mm and length of 300 mm, weave made of 7 wires (wire diameter – 0,2 mm) 510 mm long, flat wire 195 mm long. Respective parts were connected together by means of solder made of 80Sn-20Au alloy. Selected parts of guide wire are shown in Figure 3.

All presented examination of commercial wire were made on scanning electron microscope with field emission FE SEM S-4200 HITACHI collaborating with spectrometer Voyager 3500 NORAN INSTRUMENTS.

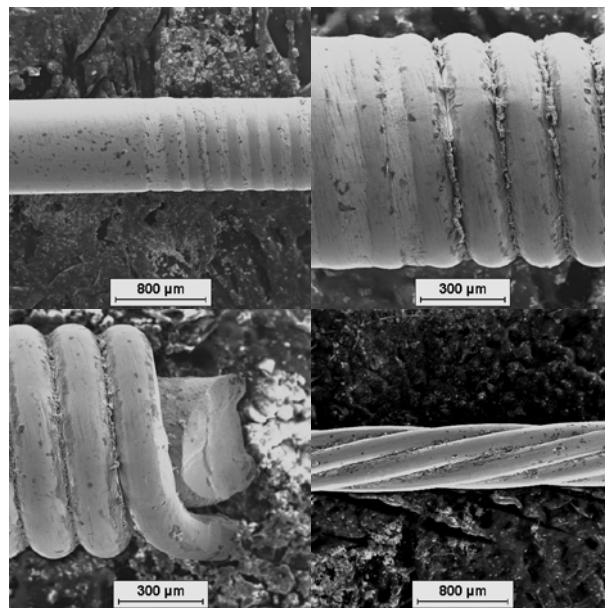


Fig. 3. Wire used in endourology

As mentioned before, tests have shown that widely used commercial guide wires are made of stainless steel [9,10]. As wire corrosion resistance depends to a great extent on material structure, created during plastic forming and heat treatment, it is necessary to establish the relation between strain in the drawing process and corrosive properties.

The purpose of the study is to evaluate resistance to pitting corrosion of wire made of Cr-Ni stainless steel in artificial urine. Research into determination of the influence of strain formed in the process of wire drawing on its corrosion resistance was started. The relationship between strain hardening and electro-chemical corrosion resistance was determined. Also the relation between wire surface preparation and corrosive properties was analysed.

2. Materials and methods

Initial test material was wire rod in supersaturated condition, diameter $d=5.65$ mm, made of stainless steel grade X10CrNi18-8 (steel 1.4310). Chemical composition of tested materials is given in Table 1.

Table 1.
Chemical composition of steel X10CrNi18-8

C	Mn	Si	P	S	Cr	Ni
0.08	0.91	0.68	0.028	0.001	17.96	8.42

Table 2.
Chemical constitution of artificial urine

Component	Amount of distilled water, g/l
Solution A	
CaCl ₂ · H ₂ O	1.765
Na ₂ SO ₄	4.862
MgSO ₄ · 7H ₂ O	1.462
NH ₄ Cl	4.643
KCl	12.130
Solution B	
NaH ₂ PO ₄ · 2H ₂ O	2.660
Na ₂ HPO ₄	0.869
C ₆ H ₅ Na ₃ O ₇ · 2H ₂ O	1.168
NaCl	13.545

Wire rod was drawn up to the diameter of $d=1.5$ mm. After each drawing samples were cut off, for both – strength tests and corrosive tests. Samples for potentiodynamic tests were subject to grinding, electrolytic polishing and chemical passivation.

Resistance to electro-chemical corrosion was evaluated on the ground of registered anodic polarization curves by means of testing system VoltaLab@PGP201 made by Radiometr [10-16]. Tests were performed in alternative solution simulating human urine. Chemical composition of the urine is shown in Table 2. Both solutions A and B, the components of artificial urine, were mixed in the proportion of 1:1. The solution was characterised by chloride ions molal concentration in the amount of 0.46. The temperature of the solution during the test was $37\pm 1^\circ\text{C}$, and $\text{pH}=7.0\pm 0.2$. Saturated mercurous chloride electrode (NEK) type KP-113 was used as a reference electrode. Auxiliary electrode was platinum electrode type PtP-201.

Prior to test commencement, all samples were cleaned in 96% ethanol in ultrasonic washer. The tests started with determination of initial potential OCP, and then anodic polarization curves, with the rate of potential change of 1 mV/s in the anodic direction, were recorded. On the ground of recorded curves the following typical parameters, characterising pitting corrosion resistance, were determined: breakdown potential E_b , polarisation resistance R_p , corrosive current density i_{corr} , and also corrosion rate corr . The tests were performed for ground, polished and passivated samples.

Mechanical properties were determined by means of static test of uniaxial tension on testing machine Instron type 1116.

3. Results

Cold plastic strain during drawing is accompanied by the phenomenon of strain hardening that is connected with the increase in strength properties of wire. Selected results of static tension test are given in Table 3.

Table 3.
Strength properties of wire

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

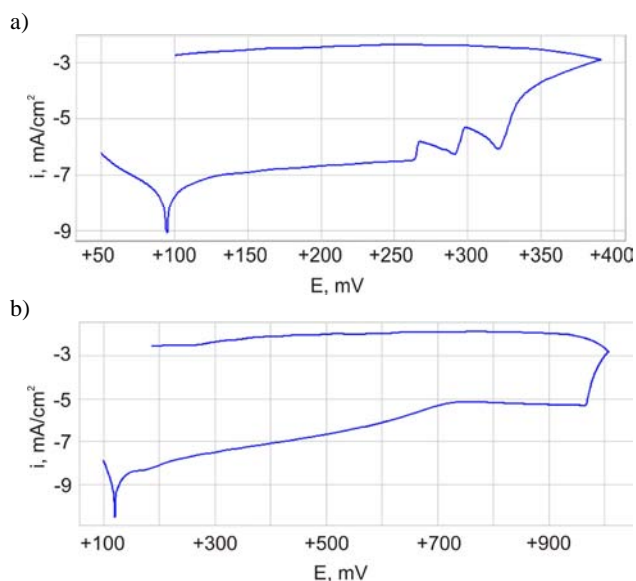


Fig. 4. Anodic polarisation curve recorded for wire rod ($d=5.65$ mm) ground (a) and passivated (b)

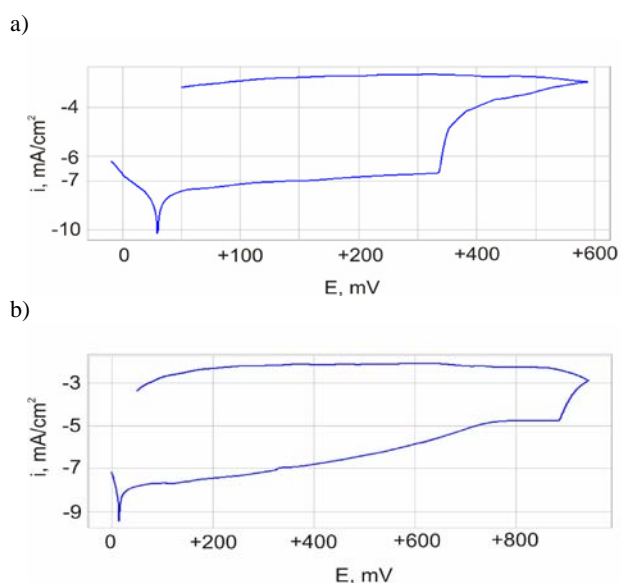


Fig. 5. Anodic polarisation curve recorded for wire $d=3.0$ mm ground (a) and passivated (b)

Potentiodynamic tests in artificial urine enabled to determine how wire resistance to pitting corrosion changed both – depending on strain formed on the drawing process as well as on the way wire surface is prepared. OCP potential for all tested samples established after 60 minutes.

Figure 4 shows exemplary anodic polarization curves set for wire rod $d=5.65\text{mm}$ with ground and passivated surface. Figure 5 shows exemplary anodic polarization curves set for wire rod $d=3.0\text{ mm}$ with ground and passivated surface.

Figure 6 shows anodic polarisation curves for wire with diameter $d=2.0\text{ mm}$, and Figure 7 shows anodic polarisation curves for wire with diameter of $d=1.5\text{ mm}$.

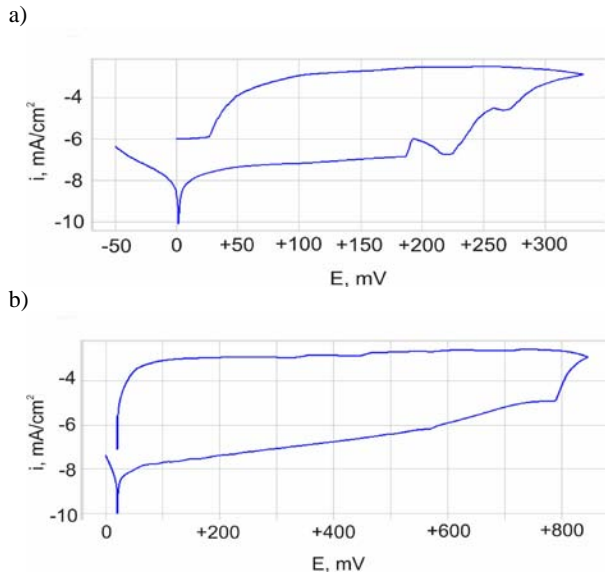


Fig. 6. Anodic polarisation curve recorded for wire $d=2.0\text{ mm}$ ground (a) and passivated (b)

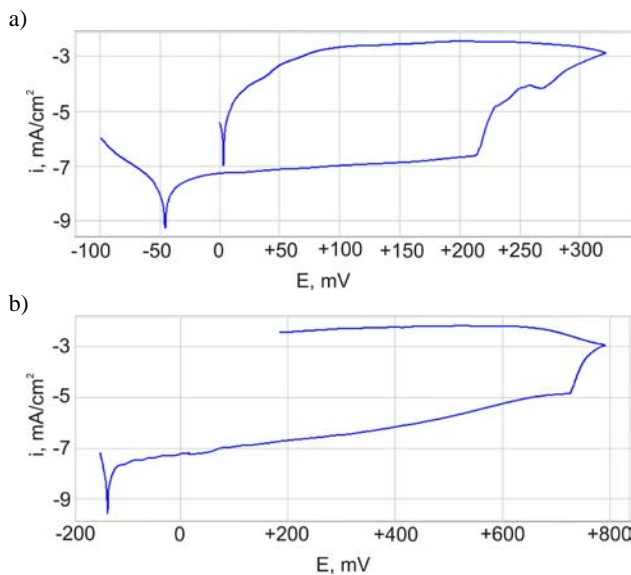


Fig. 7. Anodic polarisation curve recorded for wire $d=1.5\text{ mm}$ ground (a) and passivated (b)

The highest corrosion resistance, and despite the condition of the surface, was typical for wire rod in supersaturated condition. Breakdown potential of ground wire rod was $E_b=+321\text{ mV}$, polished: $E_b=+607\text{ mV}$, and of passivated: $E_b=+969\text{ mV}$. Together with the increase in strain in the drawing process, breakdown potential decreased. For wire with diameter of $d=3.0\text{ mm}$ it amounted to $E_b=+272\text{ mV}$ (ground surface), $E_b=+494\text{ mV}$ (polished surface) and $E_b=+890\text{ mV}$ (passivated surface). Breakdown potential for wire with diameter of 2.0 mm that was in turn ground, polished and passivated, was $E_b=+225\text{ mV}$, $E_b=+250\text{ mV}$ and $E_b=+790\text{ mV}$. The lowest breakdown potential was observed for wire diameter 1.5 mm ($E_b=+214\text{ mV}$ for ground wire, $E_b=+225\text{ mV}$ for polished wire, $E_b=+728\text{ mV}$ for passivated wire).

Together with the increase in strain, polarisation resistance decreased. Thus, for ground wire rod it equaled $R_p=334\text{ k}\Omega\text{cm}^2$, and for ground wire of diameter 1.5 mm $R_p=244\text{ k}\Omega\text{cm}^2$. These values for polished wire were respectively $R_p=3220\text{ k}\Omega\text{cm}^2$ (wire rod) i $R_p=468\text{ k}\Omega\text{cm}^2$ (wire with diameter of 1.5 mm). Polarisation resistance of passivated wire rod was equal to $R_p=6870\text{ k}\Omega\text{cm}^2$, and of passivated wire with diameter of 1.5 mm - $R_p=1410\text{ k}\Omega\text{cm}^2$.

Plastic strain during drawing caused the increase in corrosive current density and corrosion rate. This tendency was observed for ground and polished wire as well as for polished and passivated wire. Corrosive current density of ground wire rod was $i_{\text{corr}}=0.078\text{ }\mu\text{A/cm}^2$, polished wire rod: $i_{\text{corr}}=0.008\text{ }\mu\text{A/cm}^2$, and polished and passivated: $i_{\text{corr}}=0.004\text{ }\mu\text{A/cm}^2$. Wire with diameter of $d=1.5$ was characterised by the highest corrosive current density. It amounted $i_{\text{corr}}=0.106\text{ }\mu\text{A/cm}^2$ for ground wire, $i_{\text{corr}}=0.016\text{ }\mu\text{A/cm}^2$ for polished wire and $i_{\text{corr}}=0.015\text{ }\mu\text{A/cm}^2$ for passivated wire.

The rate of corrosion for wire rod with diameter of $d=5.65\text{ mm}$ amounts respectively $\text{corr}=0.89\text{ }\mu\text{m/year}$ (ground surface), $\text{corr}=0.09\text{ }\mu\text{m/year}$ (polished surface), $\text{corr}=0.04\text{ }\mu\text{m/year}$ (passivated surface). Together with the increase in the strain, the rate of corrosion increases and it is the highest for wire with diameter of 1.5 mm .

Selected results of wire corrosion tests are presented in Table 4.

4. Conclusions

Corrosion tests carried out in artificial urine solution enabled to obtain information regarding how electrochemical corrosion resistance of wire made of stainless steel X10CrNi18-8 (1.4310) changes under the influence of strain in the drawing process.

Comparative analysis of anodic polarisation curves showed that strain influences the course of those curves to a great extent. Wire rod in supersaturated condition is characterised by the highest corrosion resistance. Together with the increase in strain in the drawing process within the range of $\epsilon_d=0-2.65$, decrease in the value of breakdown potential and polarisation resistance was observed, as well as increase in corrosive current density and corrosion rate (Figures 8–10). These results explicitly indicate deterioration of corrosion resistance together with the increase in wire strength properties, and consequently - strain hardening that takes place.

Table 4.
Test results of pitting corrosion resistance of wire

Test results of pitting corrosion resistance of wire Diameter of wire d, mm	Logarythmic deformation in drawing process ϵ_d	Breakdown potential E_b , mV	Polarization resistance R_p , $k\Omega cm^2$	Corrosive current density $i_{corr.}$, $\mu A/cm^2$	Corrosion rate $\mu m/year$
Wires ground					
5.65	-	+321	334	0.078	0.89
3.0	1.27	+272	324	0.080	0.92
2.0	2.22	+225	303	0.086	0.98
1.5	2.65	+214	244	0.106	1.22
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

Wire resistance corrosion also depends on the way of surface preparation. Research proved that wire surface treatment, resulting in the improvement of physico-chemical properties of the upper layer of wire, was purposeful. Presented results show that further stages of surface processing (grinding, electrolytic polishing, chemical passivation) result in substantial improvement of electrochemical corrosion resistance of tested materials.

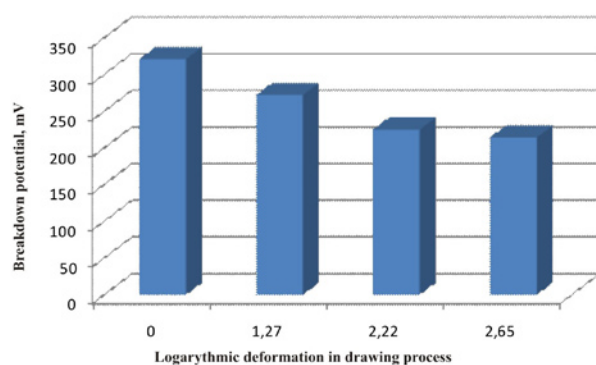


Fig. 8. Change in breakdown potential together with the increase in plastic strain in drawing process (ground wire)

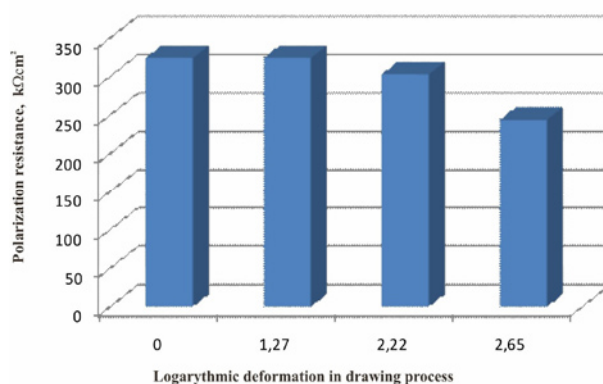


Fig. 9. Change in polarisation resistance together with the increase in strain in the process of drawing (ground wire)

Wires with chemically passivated surface are characterised by the highest corrosive properties in artificial urine. Electrochemical polishing and then chemical passivation, increased the value of perforation potential (Figures 8 and 11) and polarisation resistance (Figures 9 and 12), but decreased the value of corrosive current density (Figures 10 and 13).

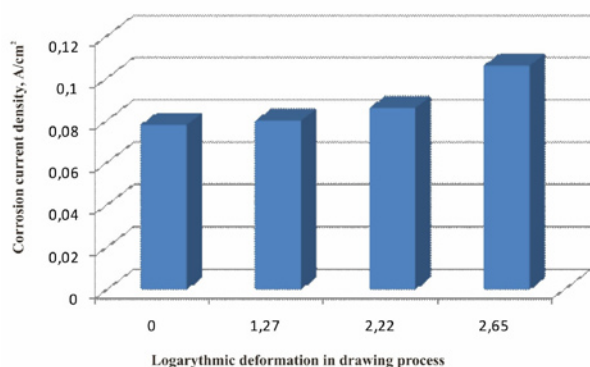


Fig. 10. Change in current density together with the increase in strain in the process of drawing (ground wire)

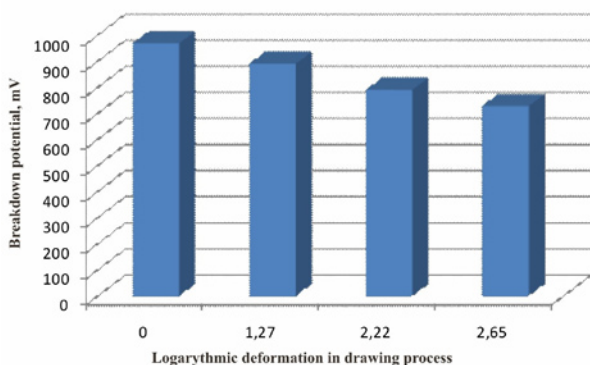


Fig. 11. Change in breakdown potential together with the increase in plastic strain in drawing process (polished and passivated wire)

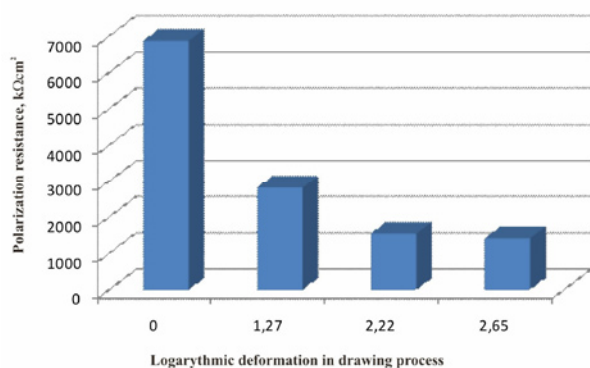


Fig. 12. Change in polarisation resistance together with the increase in strain in the process of drawing (polished and passivated wire)

It must be emphasised in the conclusions that in every case, regardless of formed strain hardening and differences in surface preparation, pitting corrosion takes place. It proves that wire made of X10CrNi18-8 steel is not resistant to this type of corrosion. Pitting corrosion is fostered among other things by

the increase in chloride ionic concentration due to their migration with corrosive current, which leads to the occurrence of corrosive cell inside the pit (chloride ions are the part of urine solution), acidification of solution inside the pit as the result of metal ion hydrolysis, (as the result of acidification, passivation potential increases locally) and great conductivity of concentrated saline solution within the pit [17].

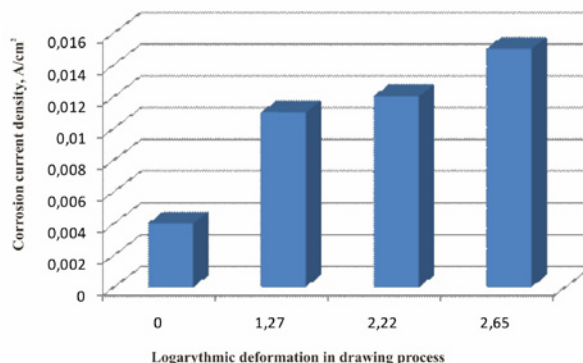


Fig. 13. Change in current density together with the increase in strain in the process of drawing (polished and passivated wire)

Test results show the necessity to use protective layers on wire used in urological treatment.

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