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STUDIES OF THE CORROSION RESISTANCE PROPERTIES OF BONE SCREWS MADE FROM 316L STAINLESS STEEL IN RINGER'S SOLUTION

Stainless steel 316L is one of the most common metallic biomaterials used for implants. Its passive surface provides a good corrosion resistance in the body environment, which can be reduced by surface mechanical damages. This is the reason why the bone screws made of stainless steel 316L were subjected to laboratory analysis in the initial state, after diversified implantation period and after mechanical damage of the surface. The mechanical damages were estimated on the basis of stereoscopic and scanning electron microscope (SEM). In order to estimate the pitting and crevice corrosion resistance, potentiodynamic and potentiostatic examinations were performed. On the basis of obtained results it can be stated that despite the visible damages on the surface, the investigated screws present a good pitting corrosion resistance. However, the way the screws were fastened caused frictional corrosion and existing cavities led to crevice corrosion. Moreover, clear correlation between magnitude of mechanical damages of the surface, implantation time and screws corrosion resistance was observed.

Keywords: bone screw, 316L steel, pitting corrosion, crevice corrosion, SEM

1. Introduction

Human health and life are dependent on the proper operation of the implants. Therefore, the biomaterials used for implants are expected to meet the highest standards. AISI 316L stainless steel is one of the metallic biomaterials which are commonly used for implants such as: intramedullary nails [1], plates and bone screws, spine implants in fields such as orthopaedics [2], thoracic surgery [3] and in cardiology. The reasons why stainless steel became widely applied are its mechanical properties and good corrosion resistance in body fluids environment, which is directly connected with biocompatibility [5,6]. Additionally, stainless steel 316L implant production is much cheaper comparing to implants made of other metallic biomaterials [7,8]. Among all its properties, corrosion is the most important matter, especially regarding to close contact between implant and physiological environment. Corrosion is a progressive material degradation, which is caused by electrochemical phenomena.

Furthermore, corrosion causes chromium, ferrite and nickel metal ions release, which leads to disturbances of natural chemical elements decomposition on different structure levels and different processes in human body [9-11]. Local influence of metal ions or implant corrosion products on body tissues leads to the intoxication of organs and was named by Nicole as metallosis. Among metal oxides which can be formed on the surface of 316L stainless steel, chromium oxide is responsible for corrosion resistance of the material due to its low diffusion constant [13,14]. What is more, in the 1980s Steinmann tried to find a correlation between biocompatibility and corrosion resistance expressed as polarization resistance [15]. Corrosion is caused by thermodynamic forces both by oxidation or reduction and kinetic barrier such as: oxide layer on the surface, which prevents from corrosion in a physical way [16].

To ensure a good corrosion resistance and to avoid proceeding reactions in the contact with implant, their surfaces are subjected to electrochemical polishing and passivation processes [14,17,18].

Passivation process of steel depends on stimulators or anodic dissolving process inhibitors presence in the solution. Moreover, the stimulators for steel are mainly depassivation substances, for example chloride ions and complexing compounds. Inhibitors are substances which are characterized by strong oxidation properties, for example substances that form not easily soluble chemical compounds with anodic metal such as phosphate ions. These ions are responsible for iron phosphate presence in a passive layer which leads to the increase of its ion conductivity. If the current flow is interrupted, the metal surface loses its passive properties in a short period of time. Furthermore, the presence of chloride ions in the solution causes the decay of passive properties or disables passive layers formation on iron, chrome, nickel, cobalt and acid resistant steel. Small microanodic areas surrounded by big cathodic areas of passivated metal

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can be observed on the alloys surfaces. Moreover, because of mechanical damage of the layer which can occur during implant modelling (prebending), on the undeformed surfaces, numerous pits can be noticed. Such pits usually appear in the areas where carbides or non-metallic inclusions are released. Deformed parts corrode equally [19].

Therefore, in the process of bone anastomosis using screws, mechanical damage to the surfaces of screws and plates can occur, leading to a local destruction of the passive layer and the development of local sources of corrosion. The Authors' research works [14,17,20] indicate that electrochemical polishing enables obtaining a surface with good corrosion resistance.

Corrosion of metallic implants is very complex due to use of different materials of diversified chemical and phase composition, which enables to produce geometrical forms of the implants. The mechanical damages of the implant surface can be formed as a result of local defects of passive film. The corrosion initiation can also be caused by the size of cavity between implant and bone or between bone and implants' elements. During investigation of corrosion damages of the screws and bone plates made from 316L stainless steel, the authors noticed electrochemical, pitting, cavity, stress and fatigue corrosions. The type of corrosion depends on the chemical composition of the steel which is specified by manufacturer. The corrosion breakdown potentials are precisely correlated with the amount of chrome and molybdenum concentration in 316L stainless steel. In not loaded areas the pitting corrosion predominates [18], whereas in places where head of the bone screw meets the surface of the socket, fretting [21] and crevice corrosion [16] are the most visible ones. On the other hand, loaded implants are subjected to stress [22] and fatigue corrosions [23]. Consequently, despite of the steel chemical composition, the corrosion development depends also on the defectiveness of the construction, the defects of shapes, the quality of passive layer and also on the insufficient material resistance. Thus, the implant mechanical damage causes the decrease of corrosion resistance [24,25]. In order to increase the corrosion resistance it is possible to use alternative biomaterials e.g. titanium and its modified alloys [26-28].

Therefore, the principal aim of this work was to evaluate the physiochemical properties of the bone screws surfaces in initial state and after implantation.

2. Materials and methods

For this study, screws used for various types of stable, internal osteosynthesis were chosen. Screws were composed of metal biomaterial AISI 316L corrosion resistant steel with the chemical composition (C < 0,03%, Cr – 17%-19%, Ni – 13%-15%, Mo – 2,25%-3%, Mg < 2%, P < 0,025%, S < 0,01%, Si < 1%, N < 0,1%, Cu < 0,5% Fe – balance), structure and mechanical properties consistent with the recommendation of ISO 5832-1 [29]. The surfaces of the screws were subjected to electrochemical polishing processes in a solution composed of phosphoric acid, sulfuric acid, oxalic acid, acetanilide and corrosion inhibitor and chemical passivation in nitric acid for 1 hour. The acid solution temperature was adjusted to 60 ±2°C. Based on the duration of implantation, screws were divided into three groups:

- Group I – four screws (1_1, 1_2, 1_3, 1_4) implanted into small bones for three months, with outer thread diameter d = 3.5 mm and screw length L = 26 mm (Fig. 1a)
- Group II – four screws (2_1, 2_2, 2_3, 2_4), implanted in cortical bone for six months, with outer thread diameter d = 4.5 mm, and screw length L = 18 mm (Fig. 1b)
- Group III – four screws (3_1, 3_2, 3_3, 3_4), intended for cortical bone but never implanted because of signs of visible mechanical damage and other production defects, with outer thread diameter d = 4.5 mm and screw length L = 40 mm (Fig. 1c).

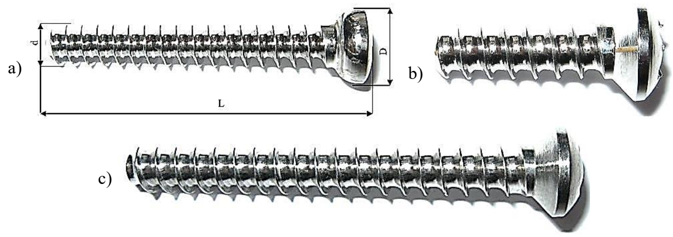

Fig. 1. Examples of bone screws from each tested group: a) I, b) II, c) III [30]

In the first stage of the analysis, a macroscopic evaluation of the surface of the screws was performed by means of a stereoscopic microscope (SteREO Discovery V8, Zeiss) with the AxioVision software at 10x magnification. Whereas for a more detailed analysis of the surface state (at magnifications of 37× and 3000×) and the approximate chemical analysis, studies were carried out using a scanning electron microscope (SEM; Zeiss Supra 35) with an EDS detector. The SEM acceleration voltage was 20 kV. Electrochemical testing was then conducted in order to evaluate corrosion resistance. For corrosion tests, area of about 1 cm^2 which had direct contact with the bone tissue of the patient during implantation was tested. For non-implanted screws (Group III), a corresponding area was chosen. Tests on pitting corrosion resistance were performed by potentiodynamic methods based on the registration of polarization curves, using the laboratory station. This stand consists of a system for laboratory examination VoltaLab PGP201 from Radiometer company, the reference electrode (saturated calomel electrode SCE type KP-113), the auxiliary electrode (platinum electrode type PtP-201), the anode (the tested sample) and a PC with VoltaMaster 4 software. Before the test, the screws were cleaned in an ultrasound bath. Corrosion testing started with the setting of opening potential E_{ocp} under no current condition. Polarisation curves were registered from the value of initial potential $E_{init} = E_{ocp} - 100$ mV. The potential changed along the anode direction at the rate of 1 mV/s. Once the anodic current density reached the value of 1 mA/cm^2, the polarization direction was changed. On the basis of the charts (Fig. 6), the following parameters were determined: corrosion potential E_{cor}, breakdown potential E_b, repassivation potential E_{cp}, polarization resistance R_p calculated with the use of Stern-Geary equation [31].

During the macroscopic observation, corrosive changes were observed under the bolt head of some screws after implantation. Therefore, the resistance to crevice corrosion was examined with the use of potentiostatic method according with the ASTM F746 – 04 standard [32]. The same device as for the test of resistance to pitting corrosion was used. The chosen screw was from the group I. In the first step, the curve of opening potential was recorded. The initial corrosion potential occurred after 40 minutes. Then, anodic polarization curves were recorded at a potential value of 800 mV for 900s. An increase in the current density at 900 seconds indicated no resistance to this type of corrosion.

Potentiostatic and potentiodynamic studies were performed in Ringer's solution (the chemical composition and concentration are shown in Table 1) at temperature $T = 37 \pm 1°C$. This solution simulates human's body fluids. The specialist electrochemical cell with double walls maintained constant temperature equal to 37°C due to warm water flow.

TABLE 1

The chemical composition of Ringer's solution

Ingredients of the solution	**NaCl**	**KCl**	**$CaCl_2 \cdot 2H_2O$**
Ingredients concentration, g/dm^3 distilled water	8.9	0.3	0.48

3. Results and discussion

All the performed macroscopic observations of the damage of the bone screws enabled the division of samples according to the following criteria: size of mechanical damage, duration of implantation and visible signs of corrosion.

Macroscopic observations of screws implanted in the body for three months (Group I) showed visible cracks and damage to the screws and to the screw heads at the point of the contact with the plates and in the area of the screw sockets. This damage probably resulted from the implantation procedure and/or during removal of the screws due to the impact of surgical instruments or fitting of the stabilization system into the patient's bone. In Group I screws, signs of corrosion and mechanical damage were observed on following parts of the implants:

- on the surface of the screws under the head at the point of contact with the plate of the thread visible,
- the distortion of the thread contour on the whole length of the screw.

Very similar damages were observed by authors [21], which investigated the plate-screw arrangement in case of fretting corrosion resistance. It was found that in place where head of the screw meets the plate, there was corrosion damage, while the rest remained intact. Probably it resulted from passive film damage and implant contact with agressive environment in several areas. The surface defects located next to the contact point of the screw increase local fretting corrosion. What is more, surface faults may cause cavities which lead to crevice corrosion.

In Group II, we observed minor visible mechanical damage to the thread around the screw head, considerable damage to the end face of the screw, but no signs of corrosion. In Group III (non-implanted screws) we observed many small decrements and defects, distributed over the entire length of the screws (Fig. 2).

On the basis of observations carried out with the use of the SEM images, various degrees of clear distortion were noticed. On the screws from Group I and II, the thread contour deformation, jagged and irregular surfaces were observed. Considerable wear of the front surface was also observed for the screws from Groups I and II. The screws from Group III were characterized both by defects on the surface and the unfinished ending of the screw. The above mentioned defects might have been caused by wrong machining parameters applied during finishing process. An approximate analysis of the chemical composition of the surface of the screws after implantation showed the presence of calcium on the screws from Groups I (example Fig. 3c) and II, which confirms the use of these implants in the patient's body. Whereas the chemical elements, such as Cr, Ni, Mo confirm the application of corrosion resistant steel type 316L. The chemical analysis was not carried out for the screws from Group III because of economic reasons. The SEM results are shown in Figs. 3-5.

Based on the results of the surface observation and potentiodynamic testing (Fig. 6 and Table 2) it can be determined that the damage of the thread causes the decrease in the corrosion resistance of the screws from Groups II and III. The values of breakdown potentials E_b did not exceed +741 mV and +804 mV for Groups II and III respectively. For screws from Group I, the largest value of E_b was +1004 mV which indicates a permanent interruption of the passive film on the surface due to extensive mechanical damage. After reaching the breakdown potential, the electromagnetic field intensity in areas, where passive film is the thinnest is so big that chloride ions penetrate through the film and form oxide chloride compounds with increased solubility. This formation results in local damage of oxide layer. Further pits development is caused by autocatalitic processes with returnable coupling. In pitting corrosion there are three stages of expansion:

Fig. 2. Examples of screw surfaces from studied groups: a) I b), II c) III, stereoscopic microscope mag. 10× [30]

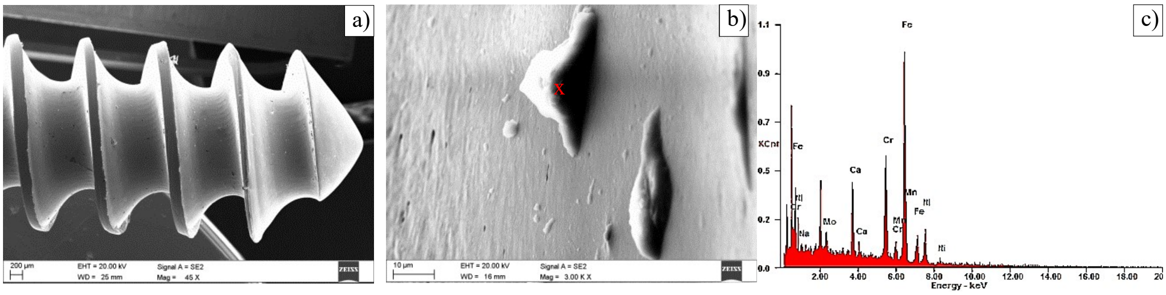

Fig. 3. Results of SEM test for Group I bone screws: a) irregular thread contour and mechanical damage to the surface of the screw, mag. 45×, b) a single molecule of calcium, the residue of bone of the patient, mag. 3000×, c) EDS spectrum of the elemental composition

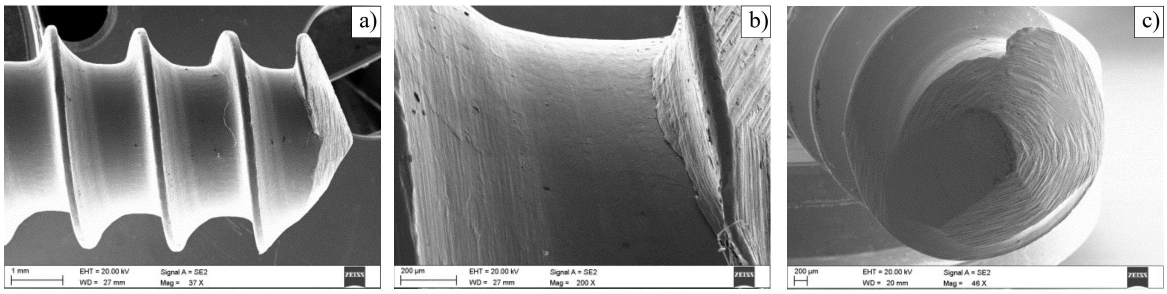

Fig. 4. Results of SEM test for Group II bone screws: a) thread contour is regular, visible minor damage, mag. 37×, b) the surface of the screw with a small number of calcium molecules, mag. 200×, c) Visible considerable wear of screw front surface, mag. 46×

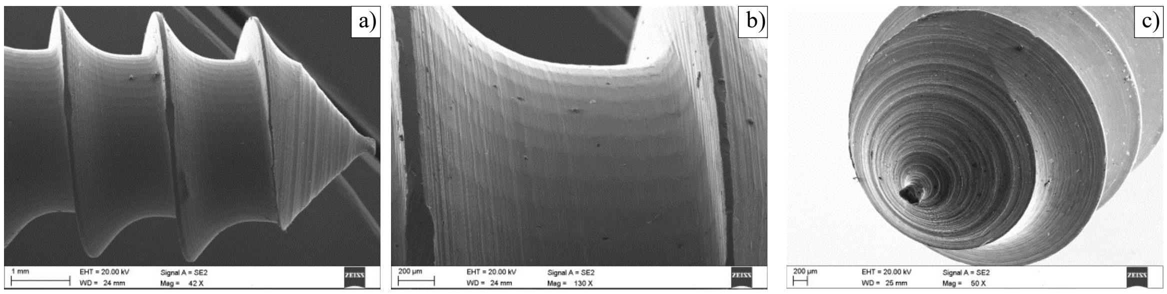

Fig. 5. Results of SEM test for Group III screws: a, c) an outline of the irregular thread contour, visible poorly finished tip, mag. 42× and 500×, respectively, b) surface coated with precipitates and visible decrements, mag. 130×

pit nucleation, initial growth state (depending on conditions, can be ended by pit overpassivation or transition to the thrid stage) and the last one is stable pit growth. For Group I of screws, the highest value of polarization resistance was recorded R_p = 2.24 kW×cm^2, in comparison to the highest value of R_p = 1.47 kW×cm^2 for the screws from Group III and R_p = 2.22 kW×cm^2 for the screws from Group III. It was observed that the highest value of the corrosion potential E_{cor} = +11 mV occurred in Group II of screws. On the basis of potentiodynamic research, the obtained hysteresis loops (Fig. 6d) confirm the presence of corrosion pits (example for the Group I) as verified by the SEM study.

The increase in the corrosion resistance of 316L steel was determined by Yazici M. et al. [33]. The authors of above mentioned publication compared the corrosion resistance and pitting corrosion on a grinded and electropolished steel surface which was modified in the process of plasma nitriding at different temperatures. For samples prepared this way, the polarization resistance increased from R_p = 1.76 kW×cm^2 for electropolished surfaces up to 68.8 kW×cm^2 for nitrided surfaces produced at 350°C and 33.7 kW×cm^2 at 400°C. Very comparable values of breakdown potential E_b were obtained by authors [34]. For steel 316L the values of E_b were around 400 mV for polished surface and for steel with 0.01% of La addition the value was equal to 900mV. The modification of chemical composition by adding 0.01% of La caused the increase in pitting corrosion resistance.

The authors [10,35] also showed, that the conditions of electrochemical polishing of 316L stainless steel have an effect on corrosion resistance, thereby on the biocompatibility of metallic implants. The diversified corrosion resistance for electrochemically polished 316L stainless steel surface in solution with 60% phosphoric acid, 20% sulfuric acid, 10% glycerol and 10% DI water in differences potential: 2.5V, 4.0 V and 10.0 V was observed. On the basis of electrochemical research carried out in 0.16 M NaCl solution, the highest value of breakdown potential E_b for polished surface was observed at 2.5V (290 mV) and lowest value for surface polished at 4 V (E_b = 180 mV) [35]. Therefore, it can be stated that chemically passivated screws in reference only to eletropolished steels prove better pitting

TABLE 2

Test results of pitting corrosion

Group number	I				II				III			
Sample number	1_1	1_2	1_3	1_4	2_1	2_2	2_3	2_4	3_1	3_2	3_3	3_4
Corrosion potential E_{cor}, mV	–39	–47	–52	–53	+11	–20	+11	–89	–57	–76	+9	–12
Breakdown potential E_b, mV	+768	+890	+470	+1004	+596	+715	+417	+741	+770	+566	+602	+804
Repassivation potential E_{cp}, mV	+86	+79	+137	+56	+128	+164	–11	+51	+98	+213	+49	+139
Polarization resistance R_p, kWcm^2	2.24	1.78	1.38	1.53	2.12	1.69	1.60	2.22	0.25	1.47	0.58	0.96

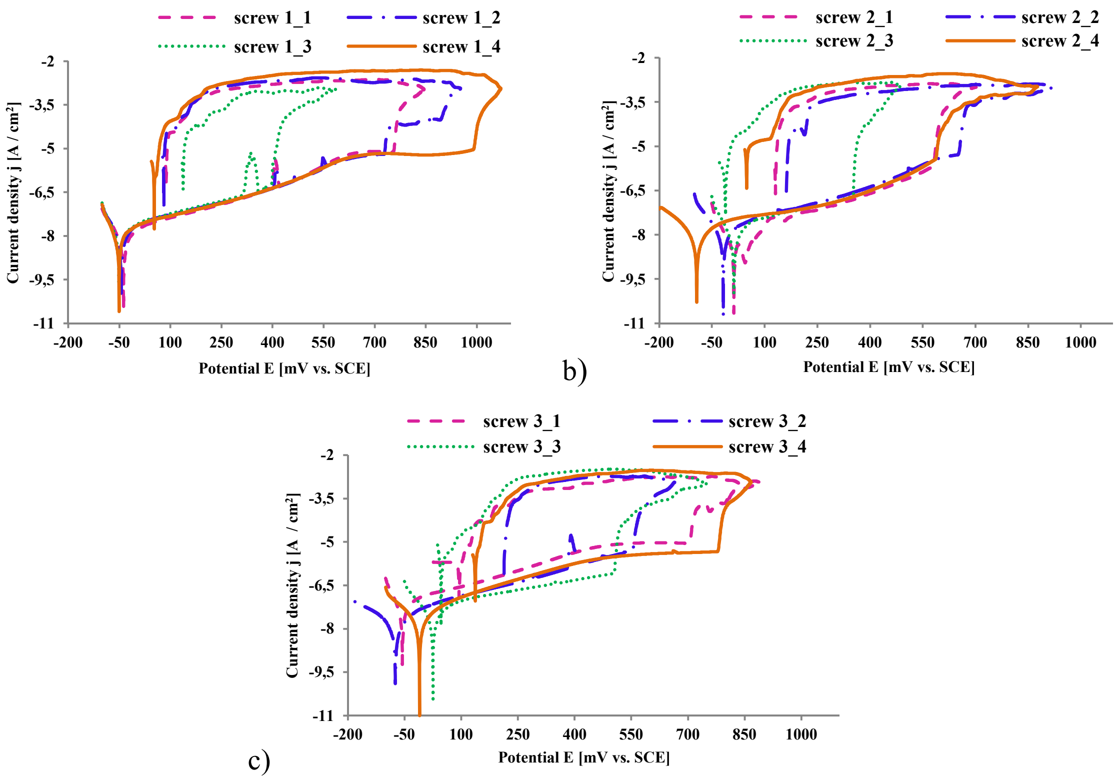

Fig. 6. Polarization curves: a) Group I, b) Group II, c) Group III

corrosion resistance. Latifi et. Al [20] observed that the reason for increased corrosion resistance of eletropolished steel in an electrolyte solution composed of 60% phosphoric acid and 40% sulfuric acid might be the time of immersing it in solution mixture of hydrofluoric acid, nitric acid and deionized water. The beneficial increase of corrosion potential E_{cor} with the increase of immersion time was observed. From E_{cor} = –343 mV for not immersed steel to +25 mV for steel immersed in acid after 1200s. was observed. During fixing the bone plate with bone screws and during the stabilization, local strengthening might occur, which can have influence on corrosion resistance. Influence of local strain hardening during cumulative strain 316L of mechanically polished steel by alumina was presented by authors [36]. Breakdown potential was changed from E_b = +200 mV to E_b = +436 mV with the increase of degree of strain hardening.

The potentiostatic curve of the study of crevice corrosion resistance is shown in Fig. 7.

The curve shows a significant increase in current density which confirms that the analyzed screw made from 316L steel is not crevice corrosion resistant. It can be concluded that corrosion damage at the point of contact between the screw head and the bone plates may have been caused by a corrosion cell in the screw – implant system due to the occurrence of the crevice corrosion [21,37-39].

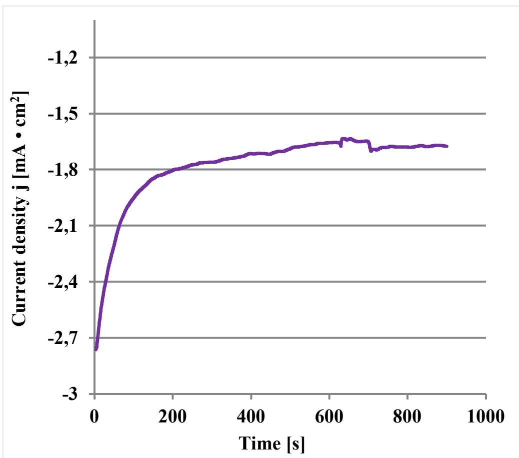

Fig. 7. Potentiostatic curve obtained from crevice corrosion

4. Conclusions

One of the main criteria for the evaluation of a bone implant is its corrosion resistance in an environment consisting of bodily fluids, which is determined by the physico-chemical properties of the implant surface. Based on the results of this study, it was concluded that the surfaces of the bone screws implanted for three or six months show typical signs of wear due to their presence in a tissue environment and the process of surgical insertion and/or removal. The tested screws showed signs of damage done during implantation, and the resulting mechanical damage decreased their resistance to pitting corrosion, and increased tissue adhesion to the implant substrate as compared to undamaged areas. This was confirmed through SEM analysis which demonstrated the presence of calcium on the surface of the implanted screws. Corrosion resistance of non-implanted screws with production defects was comparable to those introduced to the body for a period of six months. In addition, crevice corrosion was observed between the bottom part of the screw heads (from Groups I and II) and the plate.

To sum up, the corrosion resistance of bone screws can be influenced by biomaterial used, the duration of the implantation and the size of the mechanical damage to the surface of the screw. An increase in the resistance to both pitting corrosion and crevice corrosion can be achieved by using alternative biomaterials, such as titanium or titanium alloys, and surface of the screws modification technique such as nitriding and anodization polymer counting.

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