Corrosion Resistance of Stabilizers for Funnel Chest Treatment

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Abstract. The paper presents results of physicochemical properties of the plates used for the treatment of pectus excavatum after implantation. Within the research, chemical analysis, macroscopic evaluation of the surface, electromechanical analysis, wettability and surface energy tests were conducted. On the basis of obtained results, it can be stated that the reduction of corrosion resistance is influenced by mechanical damage of the surface and laser marking, as well as by producing stabilizers made of various types of steel. This caused the decrease of corrosion resistance of the plate with reduced content od Cr, Ni and Mo. It was also stated that the analysed surfaces were hydrophilic with an average surface wettability, on which overgrowth of the tissue was not observed, which is an essential condition for short-term implants.

Keywords: Corrosion resistance · Wettability · Stainless steel · 316LVM

1 Introduction

The development of implantology is connected with numerous accomplishments of interdisciplinary fields of science and technique; with the increased knowledge about the anatomy of the organs and physiological processes, as well as with introducing innovative processes of treatment, diagnostics and therapy. Therefore, it is extremely important to place great demands on the used implants at all of the stages of design, production and exploitation. Only complying all the requirements and demands will guarantee correct stabilization and will ensure health and safety of the patients. One of many very important subspecialties of surgery, in which metal materials are priority, is thoracic surgery. It includes surgical treatment of chest deformations. The deformation of anterior surface of the chest causes many cardiovascular disorders. Left-sided heart displacement is also connected with the disclosure of the right hilum and the change of the

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heart shape which becomes similar to mitral heart. It is difficult to state how far cardiovascular disorders are dependent on the location of a heart and large blood vessels, and how far on the asthenic physique [1–4].

In order to minimize complications and postoperative pain in the treatment of chest deformations, minimally invasive Nuss technique is used [5]. In this method, a plate appropriately profiled to the anatomical curvature of the chest is introduced. Due to the fact that stabilization lasts up to 2 years, for this type of stabilizers steel CrNiMo [6] with good corrosion resistance in the tissue environment is used. Corrosion resistance is a result of precise selection of the amount of alloy elements. Above chrome concentration, within 13 %, we can observe a sudden change in electrochemical potential of steel from negative $(-0,6V)$ to positive $(0,2V)$. As a result, corrosion resistance increases in oxidizing areas and material itself gains ability of passivation similar to chrome. Nickel is responsible for stabilization of austenite phase. This results in the increase of stacking-fault energy and more persistent passive layer. In addition, due to presence of molybdenum, corrosion resistance is increased [7]. Mechanical damage of the surface which occurs during the process of implantation can cause interruption in the passive layer and at the same time, decrease of corrosion resistance, which as a consequence, leads to inflammations in the implant area [8,9]. Improvement of corrosion resistance can be obtained by applying surface layers [10] or using alternative steel biomaterials with higher biocompatibility, eg. titanium alloy [11–13]. Taking implantation technique into consideration, it is extremely important to conduct tests of physiochemical properties, both before and after implantation, in order to evaluate if the implant, which is present in the body from 12 to 24 months, fully ensures correct stabilization without reactions and inflammations. Therefore, in the research we conducted the analysis of the influence of mechanical surface damage on physiochemical properties on two plates used for the treatment of pectus excavatum, – PG1 and PG2, removed from the body after 28 months from the surgical procedure.

2 Materials and Methods

In order to conduct the tests, 2 plates used for the treatment of pectum excavatum were selected. The implants were placed in the body of a patient (male) for 28 months. During clinical observations periosteal reactions we observed. Such reaction of periosteum is most frequently caused by inflammation in the bone area. The plates were produced from austenitic stainless steel 316LVM with mechanical properties in the line with ISO 5832-1 recommendations [6]. As a surface treatment, electrochemical polishing, chemical passivation and steam sterilization were used. The plates were marked appropriately: PG1 – 320 mm long and PG2 – 360 mm long. Next, the plates were subsequently cut into samples with the use of Discotom – 6 mechanical cutter produced by Struers – Fig. 1.

The material for testing was divided into three groups of samples: containing mechanical damage in the form of numerous scratches – group 1, with undamaged surface – group 2 and with an engraving on the surface made for identification – group 3. From each group, 3 samples were selected for tests. Prior to

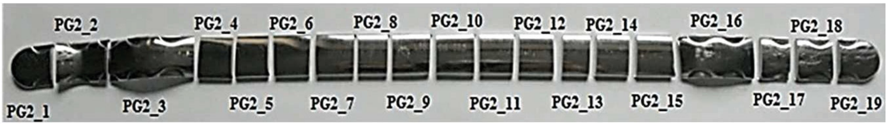


Fig. 1. The plate selected for the tests

the tests, the samples were cleansed in 96 % ethyl alcohol in ultrasonic baths BANDELIN Sonorex Digitec for 10 min.

2.1 Chemical Compostion Test

Researches of chemical composition of the implants were made using LECO GDS500A emission spectrometer. As a result of the glow discharge of studied areas of samples were obtained recording of complete emission spectrum from 165 nm to 460 nm using photosensitive Charge Coupled Device (CCD). Next, by using the method of comparison with reference standards appropriate for a group of stainless steel and NWA Quality Analyst software was determined from three measurements for each sample, the average concentration of the individual elements in the chemical composition of the implants. During the researches, the following work parameters of the spectrometer are used: voltage $1250V$ voltage, current intensity $45mA$, pressure of argon 2 Tr and vacuum 0,1 Tr.

2.2 Wettability Test

In order to determine the surface wettability of the selected samples, the wetting angle and surface free energy were evaluated with the use of Owens-Wendt method. The wettability angle measurement were performed with two liquids: distilled water (θ w) (by Poch S.A.) and diiodomethane (by Merck). Measurements with a drop of liquid and diiodomethane spread over the sample surface were carried out at room temperature ($T = 23°C$) at the test stand incorporating SURFTENS UNIVERSAL goniometer by OEG and a PC with Surftens 4.5 software to assess the recorded drop image. 10 drops of distilled water and diiodomethane each, 1.0 μl volume, were placed on the surface of each of the samples. Duration of a single measurement was 60 seconds at the sampling frequency 1 Hz. The mean values of the wetting angle θ_{av} and the surface free energy γ_S were presented in tabular form.

2.3 Potentiodynamic Test

The tests were carried out as recommended by ISO 10993-15 standard. The test stand comprised of the VoltaLab PGP201 potentiostat, the reference electrode (saturated calomel electrode SCE), the auxiliary electrode (platinum wire), the anode (test sample) and a PC with VoltaMaster 4 software. The corrosion tests started with determination of the open circuit potential E_{OCP} during the first

120 min. The polarization curves were recorded starting with the initial potential value, $E_{init} = E_{OCP} - 100\,mV$. The potential changed along the anode direction at the rate of 3 mV/s. Once the anodic current density reached the value of $1mA/cm^2$, the polarization direction was reversed. On the basis of the curves the corrosion potential E_{corr}, the breakdown potential E_b, the repassivation potential E_{cp}, were determined along with the value of the polarization resistance R_p, calculated with the use of Stern method. Electrochemical test were carried out in the environment of 250 ml Ringer solution supplied by Baxter at the temperature $T = 37 \pm 1$°C and pH $= 7 \pm 0.2$.

2.4 Macroscopic Observation

Evaluation of the surface using a stereomicroscope SteREO Discovery V8 from Zeiss with software AxioVision was carried out. Observations before and after the pitting corrosion resistance test were performed with total magnification: $9,6x$ and $25x$.

3 Results and Discussion

3.1 Chemical Composition Test

Results of chemical composition test are presented in (Table 1).

On the basis of obtained results it can be stated, that due to the differences in percentage participation of individual alloy elements, the plates were produced from 2 different steel alloys. The diversified content of individual elements can influence on various properties of the implants. Steel with chrome concentration above 13 % proves better passivating properties, which is connected with the increase of corrosion resistance. Higher content of nickel fosters the increase of resistance to stress corrosion. Furthermore, molybdenum content of 2 %–4 % improves resistance to pitting corrosion. Comparing both plates in relation to all the described elements, less of their content was observed in steel used to produce plate PG1. For this steel higher concentration of carbon was observed in comparison to implant PG2.

3.2 Wettability Test

The results of wettability and surface energy calculations and examples of drops dripped in the surface of samples are presented in (Table 2). Higher average value

Table 1. The content of chemical elements

Elements	C%	Cr%	Ni%	Cu%	Mo%	S%	Si%	P%
Plate PG1	0.039	16.7	13.0	0.062	2.65	0.001	0.394	0.033
Plate PG2	0.029	17.1	13.4	0.057	2.72	0.00	0.373	0.029
ISO 5832-1	0.030 max	17.0-9.0	13.0-5.0	0.50 max	2.25-3.0	0.010 max	1.0 max	0.025 max

Table 2. Results of the wettability and surface energy

Plate number	Contact angle, θ°_{avr}		Surface energy $\gamma_s, mJ/m^2$
	Distilled water	Diiodomethane	
PG1	40.23 ± 3.73	42.40 ± 3.90	56.61 ± 2.10
PG2	36.10 ± 1.72	40.28 ± 2.80	59.49 ± 1.61

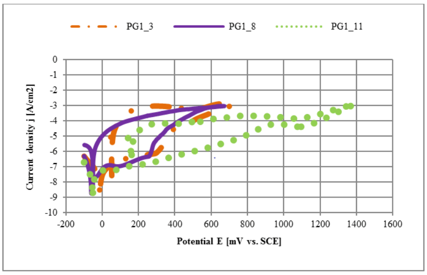
of contact angle was observed for PG1 plate. Obtained results for both plates were not significantly different from each other. On the basis of obtained values of wetting angles θ, hydrophylic character of the surface of the plate of average wettability was stated. The values of surface energy γ are comparable for both implants.

Obtained results of wetting angles are lower in comparison to the literature [9,14]. Therefore, it can be stated, that the contact of the stabilizer made of CrNiMo steel with body fluids influenced the increase of the surface wettability. The authors of the paper obtained the following results for steel CrNiMo: [14] value $\theta = 73.67°$ for distilled water and value $\theta = 39.48°$ for diiodomethane. On the other hand, the authors of the paper [9] state, that the average values of wetting angles change in the range of 76.44° to 81.95°. It can also be stated that there are insignificant differences in the values of surface energy for both plates with regards to the paper of the authors [15,16] in which for the analysed steel they were accordingly: $\gamma_s = 53.2\ mJ/m^2$ and $\gamma_s = 44.1\ mJ/m^2$.

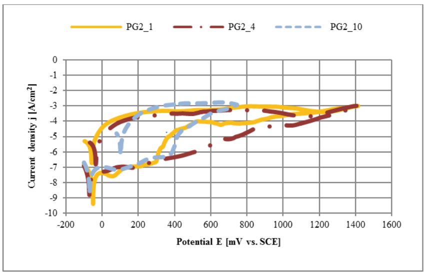
3.3 Potentiodynamic Test

Results of potentiodynamic tests carried out to evaluate the pitting corrosion resistance are presented in (Table 3) and Fig. 2(a) and (b).

The values of selected parameter for both plates are different. The biggest differences were observed for breakdown potential E_{np}. Analysing appropriate



(a)



(b)

Fig. 2. Examples of polarization curves: (a) PG1_3 - mechanical damage, PG1_11 - undamaged, $PG1_8$ - engraving, (b) PG2_2 – mechanical damage, PG2_4 – undamaged, PG2_8 – engraving

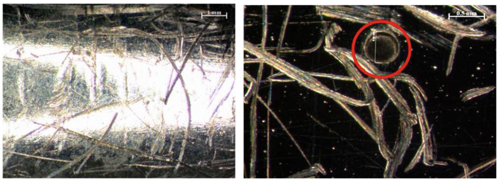
groups of samples, it can be stated that the value of E_{np} is dependent on in the tested surface. The highest values were obtained for the samples from group 2 - with minor or complete lack of mechanical damage. Average values are: $E_{npav} =$ +1023 mV for PG1 plate and $E_{npav} = +1318$ mV for PG2 plate. On this basis, it can be stated that passive layer in the areas of the least damage is the best protective barrier. The presence of mechanical damage in the form of scratches and burrs influences the decrease of the average value of breakdown potential, which for the samples from group 1 amounts to: $E_{npav} = +919$ mV for PG1 plate and $E_{bsr} = +1214$ mV for PG2 plate. However, the biggest influence on the decrease of corrosion resistance was noticed for laser marking. The layer was damaged, as a result of which the average value E_b in the group of 3 samples is the lowest in comparison to the rest of the samples and for the plate PG1 is +919 mV and for the plate PG2 +831 mV. It can be concluded that on the basis of the course of polarizations curves, the analysed material has the ability to repassivate in the body fluids environment. What is more, the highest average value of polarization resistance R_p was observed for the samples without any mechanical damage, which for plate PG1 came to $R_{pav} = 592\,k\Omega cm^2$ and for plate PG2 - $R_{pav} = 1128\,k\Omega cm^2$. The values reviewed differ, depending on the discussed plate. This is connected with the diversified content of alloy elements in both plates. In the previous paper of the authors [9] a negative influence of the surface damage on the corrosion resistance of the implants in comparison to the samples taken from implants in the initial state was also observed. The increase of corrosion resistance of steel CrNiMo was obtained by the authors of the paper [17] who covered the steel with SiO_2 layer. For the surface prepared in such way, the values of breakdown potential E_b ranged from +1543 mV +1518 mV for the samples subjected to ethylene oxide sterilization.

Table 3. The results of pitting corrosion tests

Surface condition	E_{corr}, mV	E_b, mV	E_{cp}, mV	$R_p, k\Omega cm^2$
PG1 plate				
Surface damage	-20 ± 16	$+919 \pm 318$	-19 ± 101	437 ± 38
Undamaged	-78 ± 46	$+1023 \pm 247$	$+60 \pm 89$	592 ± 224
Engraved	-83 ± 33	$+919 \pm 269$	$+57 \pm 94$	373 ± 116
PG2 plate				
Surface damage	-2 ± 40	$+1214 \pm 39$	$+129 \pm 302$	355 ± 123
Undamaged	-42 ± 24	$+1318 \pm 61$	-21 ± 37	989 ± 185
Engraved	-56 ± 14	$+831 \pm 234$	$+92 \pm 15$	323 ± 96

3.4 Macroscopic Observation

In the result of macroscopic evaluation, deep mechanical damage was observed for both PG1 plate (Fig. 3a) and PG2, in the end area of the implant, in the



(a) (b)

Fig. 3. Sample of surface: (a) before corrosion test – stereomicroscop mag. 9.6x and (b) after corrosion test with example of pitting – stereomicroscop mag. 25x

point of locking. Samples taken from the middle part of the plates had few or no damage. In case of both implants, no corrosion processes were observed. After pitting corrosion resistance tests, another macroscopic evaluation of the surface was carried out. Corrosion changes in the form of pitting were observed (Fig. 3(b).

4 Conclusion

On the basis of macroscopic the biggest number of damage was observed in the end area of the implant, at the point of locking with bars. This is the area, where the plates were modelled in order to adjust the geometry to the anatomical shape of the chest. Numerous mechanical damage on the surface of the implants but, above all, laser marking technique had a huge impact on the decrease of the pitting corrosion resistance. As a result of the analysis of the obtained polarization curves, it can be concluded that for the samples with numerous mechanical surface damage hysteresis loops are wide. This proves slow repassivation. What is more, reduced breakdown potential can be observed for these samples. The decreased resistance in the places of frequent mechanical damage was probably caused by periosteal reactions in the tissues surrounding the implant, which was proved by clinical tests. In the most damaged areas, as well as in the areas of laser marking, changes in the form of corrosion pittings were observed. Furthermore, as a result of conducted tests of wettability and surface energy, the values of wetting angles of the plates PG1 and PG2 were similar. The higher the value of the wetting angle, the more hydrophobic the analyzed material. The values of wetting angles for plates PG1 and PG2 always reach the result below 90°. On this basis, hydophylic but averagely wettable surface is observed. The wettability is determined by the level of absorption and aggregation of the material. During the observation of the implants no tissue adhesion was observed. This indicates beneficial for short-term implants low ability to adhesion and reaction of the surface to the osteoblasts activity [14,18].

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