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CORROSION RESISTANCE, EIS AND WETTABILITY OF THE IMPLANTS MADE OF 316 LVM STEEL USED IN CHEST DEFORMATION TREATMENT

The paper presents the influence of mechanical surface damage on the physicochemical properties of plates after implantation made of CrNiMo stainless steel, used in the treatment of anterior surface deformity of the chest. Analysis of the data allowed us to investigate the effect of implant design and condition of their surface on the results of chest deformation treatment. Results of electrochemical, impedance and surface wettability tests and SEM observations were compared with clinical observations. When removing the plates we found only slight inflammatory-periosteal reactions. On the basis of obtained results, it can be stated that plates, in spite of mechanical damage of the surface, were characterized by good corrosion resistance, a fact which is confirmed by the results of clinical evaluation.

Keywords: stainless steel, corrosion resistance, wettability, plate

1. Introduction

The anterior surface deformity of chest has been a significant treatment problem since years and in more than 90% of cases it includes pectus excavatum and pectus carinatum types of deformations [1]. To treat these types of deformations most frequently Nuss technique is used in which plates stabilizers are introduced to restore the appropriate shape of the chest. This technique proves that it is possible to perform a surgical procedure correcting this defect in a way less traumatic for patients, and to accelerate the healing and rehabilitation processes. However, in some observed cases the plate rotated during the process of stabilization, which caused pain and the necessity to reoperation [2, 3]. Therefore, the solution to the problem required numeric analysis and experimental studies carried out on different age groups of patients [4, 5].

The most popular metallic biomaterial used for this type of implants is austenitic stainless steel [6]. Plates which stabilize chest are short-term implants. Their implantation time is up to two years. While bending the implant to the anatomical curvature of the chest, mechanical damage in the form of scratches of varying depth and width occur on the surface of the plates, which may cause decreased biocompatibility in these areas and may initiate inflammation in the place of the contact with the tissue [7].

Therefore this paper presents the results of a physicochemical surface study and clinical observation of a new generation of plates for the treatment of pectus excavatum and carinatum.

2. Materials and methods

Tests were carried out on 5 plates removed from the body made of stainless steel which met the recommendations of the ISO 5832-1 standard. The obtained values were compared with results concerning the plate at the initial state electromechanically polished and chemically passivated without laser marking on the surface.

The first plate GA, developed to treat pectus carinatum, was removed from the body after 27 months. Fibrous reaction was observed in the area where the plate was attached to the ribs. Another plate, PA was used in the treatment of pectus excavatum. Fibrous reaction was also observed just like in case of in spite of the GA plate. The plate was removed after 24 months. RA plate was used to treat symmetrical pectus excavatum. The treatment proceeded as planned and no inflammation or implant damage were observed. The plate was removed after 20 months. At the same time, RK plate used to treat unsymmetrical pectus carinatum (type 8 in Willital classification [8]) was removed after 12 months.

Next, the plates were subsequently cut into samples with the use of Discotom - 6 mechanical cutter produced by Struers. The material for testing was divided into three groups of samples: with undamaged surface, containing mechanical damage in the form of numerous scratches and with an engraving on the surface made for identification (Fig. 1).

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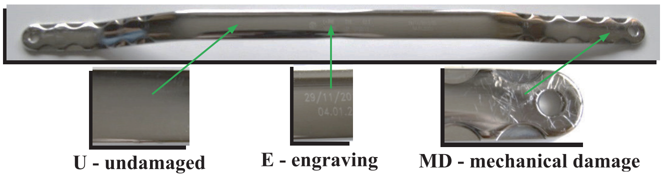


Fig. 1. Sample plates selected for the tests

Next, in the areas of laser marking, observations were made with the use of scanning electron microscope Supra 25 produced by Zeiss, with an X-rays energy dispersive spectrometer EDX for chemical analysis. The analysis resulted in diffractogram presenting spectra of identified elements and their percentage content in particular point.

To determine the wettability we analyzed contact angles and surface energy (SEP) with the Owens-Wendt method. Contact angle measurements were performed using two liquids: distilled water (θw) (manufactured by Poch S.A.) and diiodomethane (θw) (manufactured by Merck Sp. z o.o.), each with a capacity of 1.5 µl. Measurement was made at room temperature T = 23 °C on a test bench consisting of a SURFTENS UNIVERSAL manual goniometer manufactured by OEG and computer with Surftens 4.5 software for the analysis of the recorded drops' image.

Next, pitting corrosion test using the potentiodynamic method consisting of registration of polarization curves were conducted [7]. The measurement set up consisted of VoltaLab's PGP201 potentiostat and of a PC with VoltaMaster 4 software. Corrosion testing was 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 3 mV/s. Once the anodic current density reached the value of 1 mA/cm^2, the polarization direction was changed.

In order to obtain additional information on physiochemical properties of tested samples surfaces further research with the use of electrochemical impedance spectroscopy (EIS) was conducted. Studies were performed using the AutoLab PGSTAT 302N test set with a FRA2 module (Frequency Response Anlyser) in the frequency range $10^4 \div 10^{-3}$, with the voltage of 10 mV. All electrochemical tests were carried out in Ringer solution at the temperature T = 37 ± 1° C and pH = 7.2 ± 0.2. The reference electrode was the saturated calomel electrode (SCE), anode (tested sample) and as the auxiliary electrode platinum wire was used.

3. Results and discussion

Conducted chemical analysis of the microsite revealed the presence of Cr, Ni, Mo on the surface which is connected with chemical composition of the implant (Fig. 2). Moreover, an increased concentration of calcium and phosphorus compounds were also observed, which has an adverse influence on short-term implants as the overgrowth of a tissue to the substrate complicates the process of removing the implant from the body of a patient.

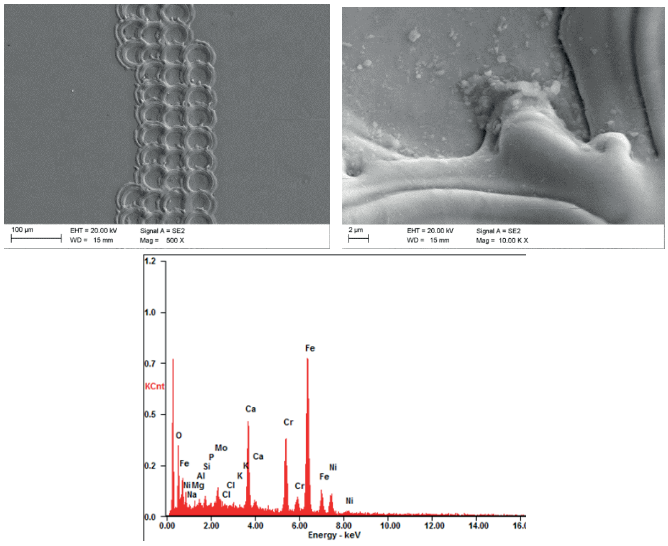


Fig. 2. Results of SEM test – engraving area of RK plate

The values of contact angle prove the hydrophylic character of the surface of the plates with low wettability θ_{avr}є58.1°–64.2° (Table 1), which is beneficial for short-term implants [9]. The values of surface energy for all the tested surfaces were comparable. It can be stated that there is no dependence between the change of contact angle and the time of presence in the body or type of treated disease.

The tests of wettability were conducted by the authors [10] who put siliceous layers on the steel samples using sol-

TABLE 1

Results of wettability

Plate		Initial state	GA	RA	PA	RK
Contact angle, θ_{avr},°	Distilled water	58.1(2.4)	60.6(4.9)	64.2(3.4)	59.6(3.9)	65.1(3.4)
	Diiodomethane	48.4(1.8)	56.6(1.2)	53.8(1.8)	54.6(1.4)	57.3(1.7)
Surface energy γS, mJ/m^2		19.9	15.8	18.8	14.9	16.9

TABLE 2

Results of pitting corrosion test

Plate	Initial state	GA	RA	PA	RK
E_{corr}, mV	+0.3(33)	-34(29)	-29(47)	-83(31)	-66(17)
E_b, mV	+1285(32)	+1145(126)	+1219(105)	+1136(151)	+1089(137)
E_{cp}, mV	-41(24)	+11(51)	-9(28)	-6(37)	-4(28)
R_p, kΩ·cm^2	1566(310)	215(33)	482(224)	283(187)	271(118)

gel method and stated increased wettability of all the tested types of surfaces in comparison to the samples in polished state, which in case of biomaterials used in orthopaedics is not beneficial.

The samples of the plates without mechanically damaged surface and the samples of the plate in the initial state showed in majority the breakdown potential above +1200 mV. For the samples with numerous scratches, burrs etc (areas of peri-implantive reaction) characteristic were breakdown potential values ranging from +850 mV to +1285 mV. Whereas for samples with laser marking, the values ranged from +1080 mV to +1180 mV (Fig. 3, Table 2).

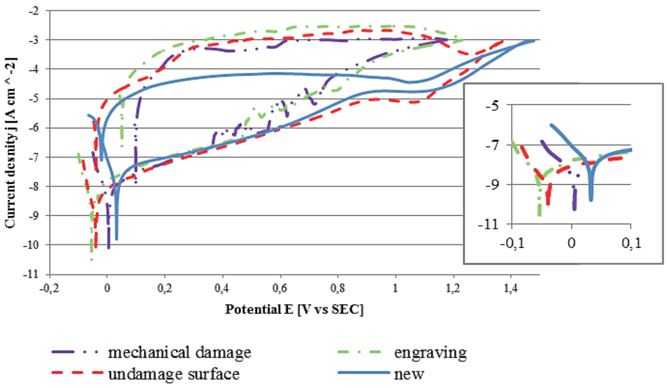
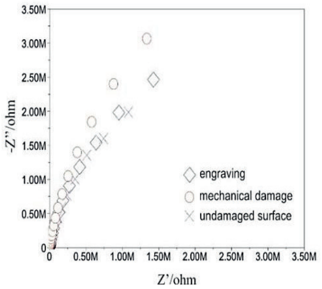


Fig. 3. Representative logarithmic curves

Among all the tested implants, the highest values of both, polarization resistance R_p and corrosion potential E_{corr}, were observed for the plate in the initial state. The negative influence of surface damages on the corrosion resistance of the implants in comparison to the samples taken from the implants in the initial state was also stated in the previous paper of the authors [9]. The improvement of the corrosion resistance and increased resistance to the mechanical damage of the implants can be achieved by using alternative metal biomaterials such as Ti6Al4V or Ti6Al7Nb alloys and different types of protective coatings [11-15].

Obtained sample impedance spectra for GA, PA plates are shown on (Figs. 4 and 5).

a)



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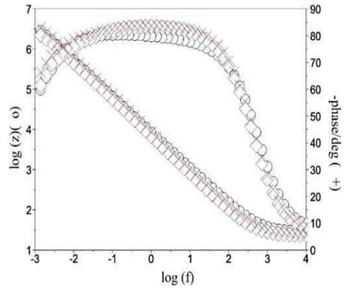
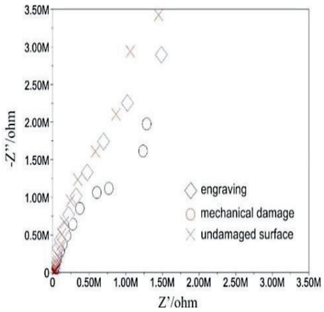


Fig. 4. Sample diagrams for GA plate: a) Nyquist, b) Bode

a)



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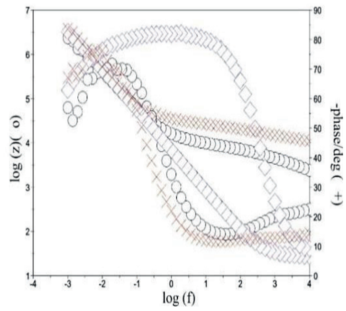

Fig. 5. Sample diagrams for PA plate: a) Nyquist, b) Bode

Registered impedance spectra obtained for the plates denoted appropriately as GA, PA, RA and RK, were referred to the equivalent electrical circuits which indicates the presence of single layer (Table 3) for (GA – U, MD, E, PA – E, RA – U, RK – MD) and participation of 2 sublayers: compact inner and porous outer (demonstrated on the diagram two time constants: PA – U, MD, RA – MD, E; RK – U, E) (Fig. 6, Tab. 3). On the

TABLE 3

The EIS results

Plate	Surface	R_s, Ωcm^2	R_{pore},	CPE_{pore}		R_{ct},	CPE_{dl}		E_{OCP}
				Y_0,	n		Y_0,	n	
			$k\Omega cm^2$	$\Omega^{-1}cm^{-2}s^{-n}$		$k\Omega cm^2$	$\Omega^{-1}cm^{-2}s^{-n}$		mV
GA	MD	26	-	-	-	8180	0.2261E-04	0.91	-62
	E	26	-	-	-	5820	0.2754E-04	0.92	+1
	U	26	-	-	-	11380	0.2145E-04	0.92	-26
PA	MD	26	13	0.8615E-04	0.34	5200	0.2563E-04	0.85	-86
	E	27	-	-	-	8580	0.2735E-04	0.91	-33
	U	26	69	0.1091E-04	0.16	14530	0.2325E-04	0.90	-27
RA	MD	27	26	0.2041E-05	0.66	7410	0.1943E-04	0.77	59
	E	27	28	0.2054E-04	0.71	6660	0.1886E-04	0.90	-41
	U	27	-	-	-	15510	0.1924E-04	0.93	1
RK	MD	26	-	-	-	6400	0.2928E-04	0.91	-62
	E	26	26	0.2308E-04	0.15	15670	0.2545E-04	0.91	-114
	U	26	146	0.1611E-05	0.44	13500	0.2144E-04	0.85	-17
U – undamaged, MD – mechanical damage, E – engraving									

(Fig 6). Rs stands for electrolyte resistance (Ringer's solution), CPE_{pore} - capacity of porous layer and R_{pore} - resistance of solution in the porous layer sphere, whereas R_{ct} and CPE_{dl} stand appropriately for resistance and capacity of oxide layer.

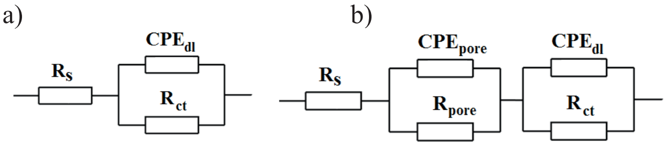

Fig. 6. Equivalent circuit for corrosion system: steel - Ringer's solution

The impedance tests proved that areas, where there was no surface damage, either caused by mechanical interaction or by deliberate sample marking, demonstrated the highest value of ions transition residence R_{ct}, which proves good properties of passive layer protecting the steel from the influence of the corrosion environment (Table 3).

The obtained results also seem to be confirmed by the research carried out by Baron [16]. Baron confirms a positive influence of the chemical passivation on the improvement of steel corrosion resistance in Tyrod's solution due to the change of chemical composition of the surface layer. This layer, enriched mainly with chromium oxide Cr_2O_3, contributes to a better electrochemical stability in the environment of body fluids.

4. Conclusions

The obtained results prove increased susceptibility to the corrosion of the plates removed from the body mainly from the areas where damage of the surface occur. This also refers to the samples taken from the areas where peri-implantive reaction occurred. Therefore, it can be stated that corrosion resistance is not dependant on the time of implantation but on the type and character of mechanical surface damage, marking the implant in a way which should not influence the adhesion of the tissues to the substrate and on the patient's individual reactivity. It was also stated that marking using the laser method caused the decrease of breakdown potential, which indicates interruption of the passive layer. Tested samples demonstrate hydrophilic surface of low wettability. The authors [9] proved that the surface which demonstrates low wettability reduces significantly the adsorbtion of proteins to the metallic substrate. The energy value of the analyzed surfaces stabilizers indicates their athrombogenicity, which eliminates the overgrowth of the bone tissue to the surface. The obtained results were confirmed by clinical observation. The plates provided a very good treatment results. However, minimal inflammatory-periosteal reactions could have been caused by a "cell" at the fixing of the plate to the ribs with a cross-bar following the occurrence of crevice corrosion. They also could have been a result of fretting caused by a friction between cooperating elements of the stabilizer [17, 18].

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