



HAL
open science

Chemical, Corrosion and Topographical Analysis of Stainless Steel Implants after Different Implantation Periods

Wojciech Chrzanowski, David Andrew Armitage, Jonathan Campbell
Knowles, Jacek Szade, Wojciech Korlacki, Jan Marciniak

► **To cite this version:**

Wojciech Chrzanowski, David Andrew Armitage, Jonathan Campbell Knowles, Jacek Szade, Wojciech Korlacki, et al.. Chemical, Corrosion and Topographical Analysis of Stainless Steel Implants after Different Implantation Periods. *Journal of Biomaterials Applications*, 2008, 23 (1), pp.51-71. 10.1177/0885328207083728 . hal-00570787

HAL Id: hal-00570787

<https://hal.science/hal-00570787>

Submitted on 1 Mar 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chemical, Corrosion and Topographical Analysis of Stainless Steel Implants after Different Implantation Periods

WOJCIECH CHRZANOWSKI, DAVID ANDREW ARMITAGE
AND JONATHAN CAMPBELL KNOWLES*
Division of Biomaterials and Tissue Engineering
UCL Eastman Dental Institute, University College London
256 Gray's Inn Road, London WC1X 8LD, UK

JACEK SZADE
University of Silesia, Institute of Physics, ul.
Uniwersytecka 4,40-007 Katowice, PL

WOJCIECH KORLACKI
Department of Pediatric Surgery, Silesian Medical University
Minimally Invasive Surgery Center for Adults and Children
University Hospital No. 1, 3 Maja 13-15, 41-800 Zabrze, PL

JAN MARCINIAK
Biomedical Engineering Centre, The Silesian University
of Technology, ul. Akademicka 2a, 44-100 Gliwice, PL

ABSTRACT: The aim of this work is to examine the corrosion properties, chemical composition, and material-implant interaction after different periods of implantation of plates used to correct funnel chest. The implants are made of 316L stainless steel. Examinations are carried out on three implants: new (nonimplanted) and two implanted for 29 and 35 months. The corrosion study

*Author to whom correspondence should be addressed.

E-mail: j.knowles@eastman.ucl.ac.uk

Figures 2-7 appear in color online: <http://jba.sagepub.com>

JOURNAL OF BIOMATERIALS APPLICATIONS Volume 23 — July 2008

51

0885-3282/08/01 0051-21 \$10.00/0 DOI: 10.1177/0885328207083728

© SAGE Publications 2008

Los Angeles, London, New Delhi and Singapore

reveals that in the potential range that could occur in the physiological condition the new bar has the lowest current density and the highest corrosion potential. This indicates that the new plate has the highest corrosion resistance and the corrosion resistance could be reduced during implantation by the instruments used during the operation. XPS analysis reveals changes in the surface chemistry. The longer the implantation time the more carbon and oxygen are observed and only trace of elements such as Cr, Mo are detected indicating that surface is covered by an organic layer. On some parts of the implants whitish tissue is observed: the thickness of which increased with the time of implantation. This tissue was identified as an organic layer; mainly attached to the surface on the areas close to where the implant was bent to attain anatomical fit and thus where the implant has higher surface roughness. The study indicates that the chest plates are impaired by the implantation procedure and contact with biological environment. The organic layer on the surface shows that the implant did not stay passive but some reactions at the tissue-implant interface occurred. These reactions should be seen as positive, as it indicates that the implants were accepted by the tissues. Nevertheless, if the implants react, they may continue to release chromium, nickel, and other harmful ions long term as indicated by lower corrosion resistance of the implants following implantation.

KEY WORDS: 316L stainless steel, implants corrosion, funnel chest (*pectus excavatum*) implants, XPS of implant surface, implants examination, AFM of implant surface, post implantation examination of the funnel chest plate.

INTRODUCTION

Stainless steel has a long history as a metallic material for medical implants. The wide range of applications of the material includes bone implants (intramedullary nails, bone plates, clamp), cardiovascular implants (stents) urologic, and dental implants. Since the material was introduced numerous technologies have been applied to improve its biomedical performance. These technologies have primarily been targeted at improving the corrosion resistance [1–5]. However, due to relatively high chromium and nickel concentration the stainless steel is not without biological risks. High concentration of these elements can cause adverse, toxic, or carcinogenic reactions in the harsh body condition when the implants are exposed not only to an aggressive chemical environment but also to different forces that accelerate corrosion and wear processes [6–8]. Implants made of stainless steel tend to be used as temporary implants which help to restore body function. Nonetheless, there are few papers that analyze any implant changes after removal from the body. The removed implant examination can reveal changes in terms of chemical composition, topography, and alteration of corrosion properties. Corrosion products on the surface can show potential ability of the material to resist corrosion in the body

environment. Topographic examination can illustrate changes in roughness, the structure of any organic layer which may be formed in the body, changes in the material structure which appears on the surface after deformation, and finally can reveal wear effects.

One of the implants that is commonly made of stainless steel and which is used with a high success rate is the Nuss plate for funnel chest correction (*pectus excavatum*). Clinical practice showed low rates of adverse body reaction on the material. However, some cases were reported where patients reacted negatively to the stainless steel [9,10].

Because the funnel chest plates have direct contact with both soft and hard tissues and are in close proximity to the heart and surrounding associated tissues, they should exhibit high biocompatibility and have a very low rate of degradation. For this reason examination of the implants after implantation is important to assess *in vivo* interaction of the material with different tissues, and potential degradation of the material [11].

The purpose of the paper was to establish any relationship between implant residence time and corrosion resistance, surface chemistry, and topography changes of the chest plates.

MATERIALS AND METHODS

In the examination plates made of stainless steel AISI 316 LVM were used. Three plates of the same type were used in the tests. The brand new plate was used as a reference sample. The plate was not implanted, but it was prepared according to the clinical procedure under clinical conditions – deformed and sterilized. The shape of the plate was adjusted to the typical shape of the chest of patients of age 12–15 (Figure 1). The plate was then sterilized in steam at 120°C for 60 min. Two other plates were implanted in the same patient with a six months time interval. The first plate was implanted in 01.2003 and then due to its rotation and insufficient stability in 07.2003 the second plate was implanted. In 12.2005 both plates were removed. After implant removal they were carefully cleaned in propanol and then sterilized in the steam. Therefore, there were three implants:

- (1) nonimplanted new plate prepared according to the clinical standard procedure,
- (2) after 29 months being in the body and,
- (3) after 35 month being in the body.

Due to the fact that the implanted plates came from the same patient, the results were minimally influenced by different environment, age,

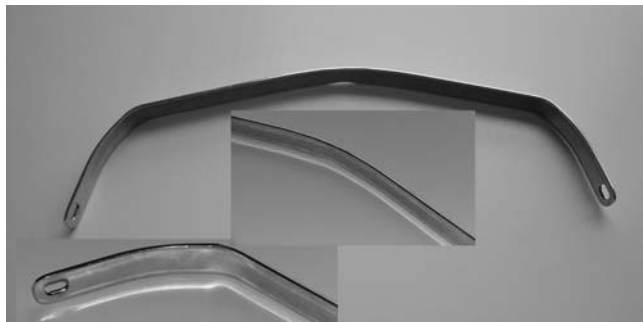


Figure 1. Geometrical presentation of the plate after shape adjustment.

different patient activity, genetic features, and diet or used medicines that normally would take place when comparing implants from different patients. The patient was monitored for the whole treatment period. All medication given was recorded.

The examinations of the new plate and those removed from the patient were carried out in different regions: deformed and non-deformed. Additionally, it was seen that some parts of the removed implants were macroscopically altered – on the surface a whitish layer was observed. These were mainly in the areas where the implant had contact with bone. The analysis was performed for both sides of the plate – upper and lower.

For the implants, the following analyses were carried out:

Topography of the Surface

The roughness measurements of different implants parts were performed by laser profilometry (Proscan 1000, Scantron, UK). In these examinations the R_a parameter was recorded.

The topography of the surface was further examined using an atomic force microscope (XE-100, PSIA, Korea). Non contact mode was used in the investigation to produce $45 \times 45 \mu\text{m}$ images. The examination was carried out for the selected areas on samples:

- (1) the new plate: deformed area, and straight part,
- (2) the plate after 29 month from implantation: deformed areas, straight parts, and areas with altered surface topography (macroscopically),
- (3) the plate after 35 months from implantation: as above.

Chemistry of the Surface

To assess chemical composition of the surface X-ray photoelectron spectroscopy (XPS) was carried out. The examination was done using VG Escalab 220i-XL spectrometer using an monochromated Al-K α X-ray source and the large-area XL electrostatic lens mode. Quantification was performed using CasaXPS software with Shirley background removal and Wagner sensitivity factors. In the examination dull, shiny, deformed, and nondeformed implants regions were examined.

Corrosion Resistance

The corrosion tests were carried out in SBF solution [12–14] using a Voltmaster 21 electrochemical set. The tests were carried out at $36.6 \pm 1^\circ\text{C}$ and $\text{pH} \in (7.9-8.2)$. At the beginning of the experiment the corrosion potential (E_{cor}) was measured for 60 min. Following this the potentiodynamic curves were recorded. The potential was increased from $E_{\text{cor}} - 100$ mV up to the potential for which the current density was equal to 1 mA/cm^2 . Then the direction of polarization was reversed and the return curves were recorded. In the tests, the following parameters were established: corrosion potential – E_{cor} , polarization resistance – R_p , breakdown potential – E_B , corrosion current density – i_{cor} and area under the potentiodynamic curve that represents the amount of charge that was used to transfer the ions from sample to the liquid – C .

RESULTS

Results of Topography Examination

The roughness measurements revealed variations of the R_a values with both location on the implant and time of implantation (Table 1).

The roughness measurement and AFM observations of the straight part of the implant surface before implantation showed that surfaces were smooth and well polished. The roughness of that part was $R_a = 0.74 \mu\text{m}$. Observations did not reveal any significant change along the straight fragments. Parts of the implant that were deformed according to the clinical procedure (that was done by an experienced surgeon) were dull. The AFM observation revealed numerous deformation slide bands along many grains (Figure 2(a, c)). The roughness of these regions increased to $R_a = 12.47 \mu\text{m}$. Macroscopic examination of the implants revealed numerous of scratches on the surface. These scratches resulted from the implants shape adjustment to the patient's

Table 1. Results of AFM roughness measurements for different areas of the samples.

Sample	Non implanted plate		Plate that stayed in the body for 29 months				Plate that stayed in the body for 35 months					
			Nondeformed parts		Deformed parts		Parts covered with tissue layer		Nondeformed parts		Deformed parts	
	Nondeformed parts	Deformed parts	Nondeformed parts	Deformed parts	Nondeformed parts	Deformed parts	Parts covered with tissue layer	Parts covered with tissue layer	Nondeformed parts	Deformed parts	Parts covered with tissue layer	Parts covered with tissue layer
Mean R_{a} , μm	0.74	12.47	0.88	1.66	1.06	2.49	1.06	1.06	1.07	2.49	1.21	1.21
SD	0.314	0.823	0.414	0.296	0.124	0.339	0.124	0.124	0.158	0.339	0.058	0.058

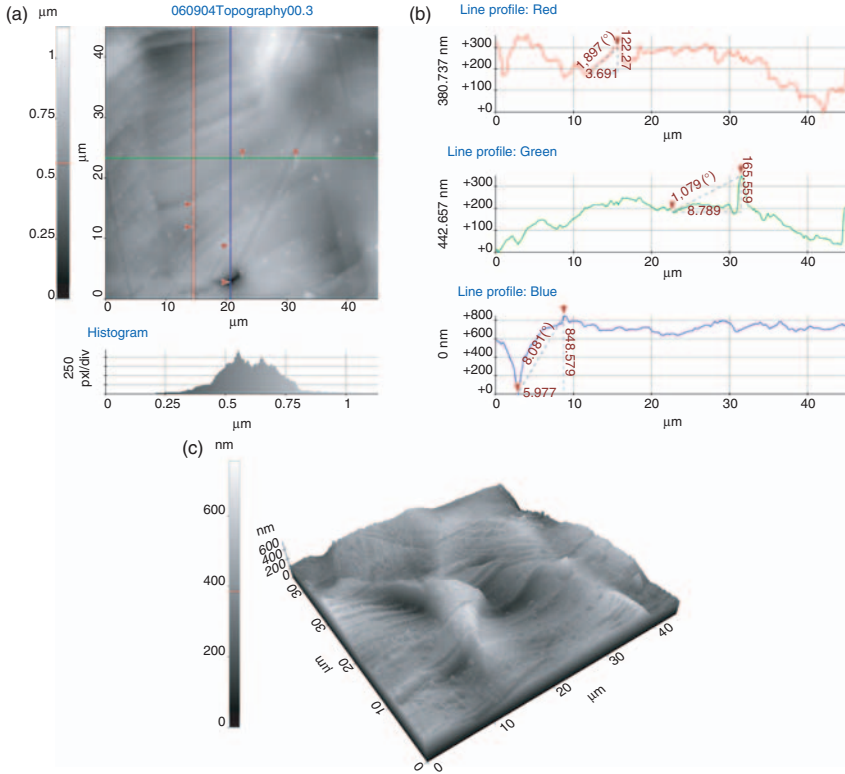


Figure 2. AFM images of deformed part of not implanted bar (a) surface topography, (b) line profiles, (c) 3D topography.

chest shape that was done by metallic instruments – according to manufacturer requirements.

The implant that was taken out of the patient after 29 months possessed regions that were covered with a dull, whitish film. These areas were observed on both upper and lower parts of the implant. Additionally, on the surfaces numerous scratches were observed (these were preoperative, occurring during implant shape adjustment). The roughness examination carried out for the regions that were nondeformed and not covered with a whitish layer showed that the roughness was not significantly greater ($R_a = 1.06 \mu\text{m}$) compared to the uncovered regions of the same implant ($R_a = 0.88 \mu\text{m}$), while R_a value for the deformed parts was $1.66 \mu\text{m}$. The deformed surface had a similar topography to the reference (not implanted) plate. The parts that

were covered with the whitish film part were observed either on inside and outside part of the implant. The AFM observations did not reveal any topographical differences between the different sides. The whitish film on the surface was relatively thick and cracked (Figure 3(a), (b)). The depth of the cracks was about 0.65–0.94 μm which suggests the thickness of the layer is at least this value (Figure 4(b)).

The analysis of the implant that stayed for 35 months showed a roughness for noncovered parts of the plate of $R_a = 1.07 \mu\text{m}$ and that the surfaces were smooth and shiny without any significant impairment except for scratches that appeared due to operative procedure. The roughness of the parts covered with the whitish layer was $R_a = 1.2 \mu\text{m}$. The film was cracked, but cracks were more regular and their number and size was greater compared to the shorter duration implant. The depth of the cracks was about 1.35 to 1.72 μm . This suggests that thickness of the layer increased with implantation time.

Results of XPS Examination

The XPS examination for the new plate revealed the following elements on the top layer: O, C, Cr, Ni, Fe, Mo, and N (Table 2 and Figure 5(a)). The carbon peak at the energy 284.9 eV indicates that this element originated from contamination. The carbon was single bonded with hydrogen and other carbon atoms: C–H, C–C. There was also some amount of carbon bound to oxygen; peak at the energy 288.7 eV (C=O). The chromium peak at the energy 576.7 eV corresponded to Cr_2O_3 . The nitrogen energy peak 400.7 eV correlated with N_2 . The molybdenum peak 227.4 eV corresponded to metallic state of this element. The iron and nickel peaks at the energies 706.7 and 852.7 eV agreed with metallic iron and oxidized nickel – NiO.

The plates that remained in the body for 29 and 35 months and which were not covered with the whitish layer had analogous chemical composition to the nonimplanted plate (Table 2). However there were differences in oxygen peak shape (Figure 6(b)). Oxygen component fitting showed that for the nonimplanted plate, water and hydroxyl group amounts were significantly lower than for plates staying for 35 months in the body. The oxygen components for plates that stayed for 29 months were similar to the nonimplanted plate (Figure 7(a)).

The chemical composition of the parts of the implants (after 29 and 35 months) that were covered with whitish layers was significantly different from the noncovered parts. In general the carbon concentration was almost twice as high as for the nonimplanted plate. Due to relatively thick tissue layer which covered the surface the concentration

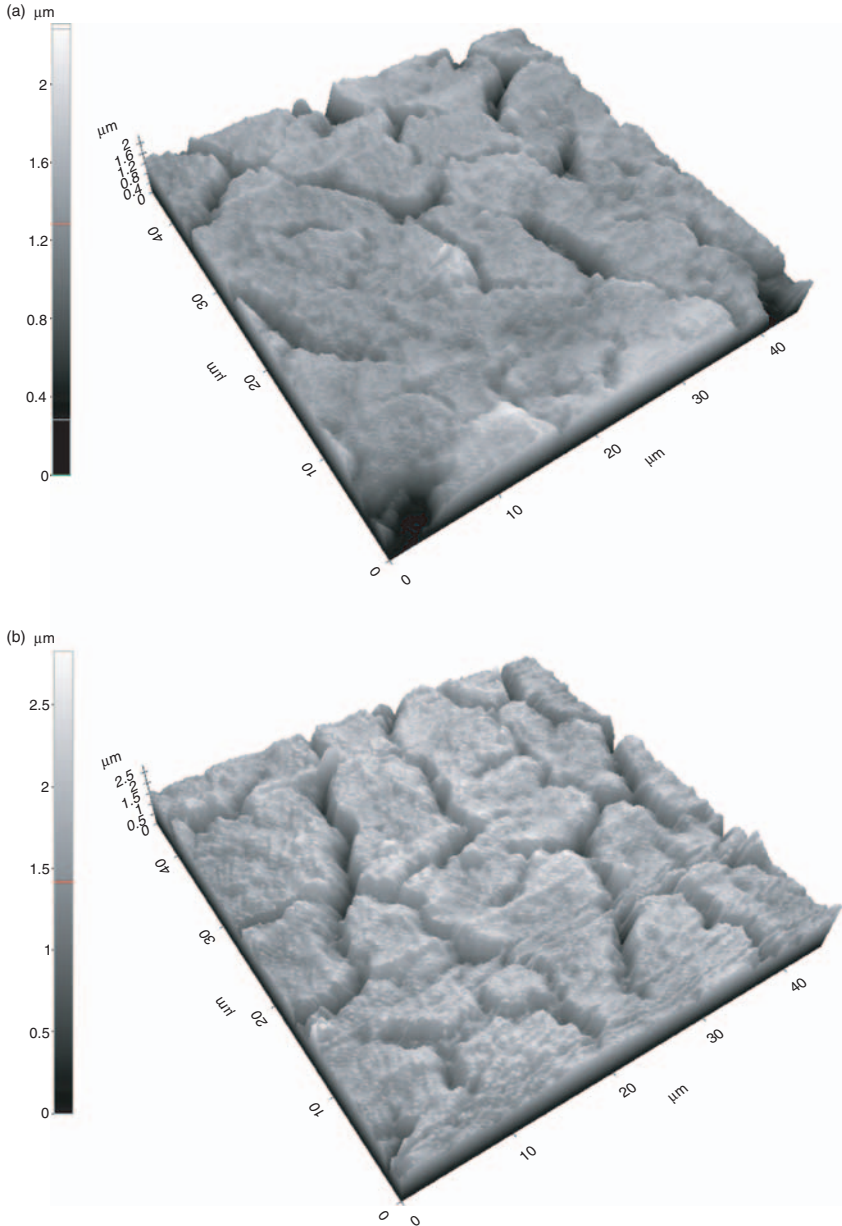


Figure 3. 3D topography images of the implant surface that were covered with film: (a) implant that stayed 29 months, (b) implant that stayed 36 months in the body.

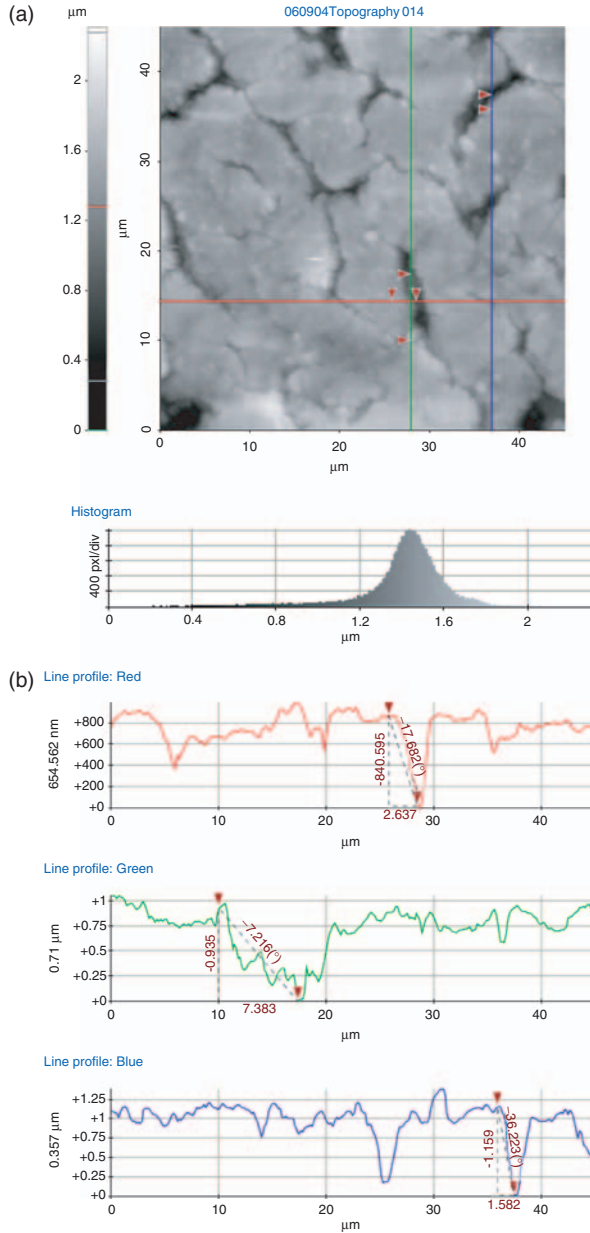


Figure 4. AFM image of the implant surface that stayed in the body for 29 month, covered with film; (a) topography image, (b) profile lines.

Table 2. Chemical composition of the examined plates.

	C	Cr	Fe	Mo	N	Ni	O
35 months without tissue							
Atomic concentration,%	29.96	12.35	3.84	0.86	5.70	1.38	45.91
SD	0.96	0.47	0.15	0.05	0.21	0.04	0.14
Binding energy of the main peak, eV	285.1	286.6	576.6	706.6	227.3	400	852.5
35 months with tissue							
Atomic concentration,%	64.92	0.19	0.34		8.57		25.98
SD	0.65	0.26	0.26		1.83		1.70
Binding energy of the main peak, eV	284.7	285.9	288.8	577.30	708.90	399.8	532.10
29 months without tissue							
Atomic concentration,%	35.47	11.33	2.93	0.38	3.40	1.67	44.44
SD	3.95	0.38	1.13	0.04	0.24	0.47	2.23
Binding energy of the main peak, eV	284.8	286.2	288.2	576.60	706.60	227.1	399.70
29 months with tissue							
Atomic concentration,%	66.64	0.46	0.24		8.66		24.00
SD	1.54	0.32	0.17		1.00		1.04
Binding energy of the main peak, eV	284.8	286	288	580.20	710.00	400.00	531.90
New plate							
Atomic concentration,%	33.46	9.79	4.02	0.53	4.16	1.56	46.47
SD	1.51	0.40	0.81	0.20	2.53	0.06	4.59
Binding energy of the main peak, eV	284.9	286.3	288.7	576.70	706.70	227.4	397.2

of iron and chromium was below 0.5%. The elements such as molybdenum and nickel were not observed on these parts of the surface. Additionally, the concentration of oxygen was reduced by about 20%. However, 3% greater concentration of nitrogen was observed for these regions. The chemical composition was very similar for both plates staying in the body for the different periods of time of the study. The increase in carbon and nitrogen indicates an organic origin to the layer. The binding energies of the carbon indicated single and double bonds of carbon to the oxygen in addition to carbon-carbon and carbon-hydrogen. Carbon-nitrogen bonds are also likely. For the samples with the tissue layer the amount of double bonded carbon increased compared with noncovered parts, but was similar for both 29 and 35 month

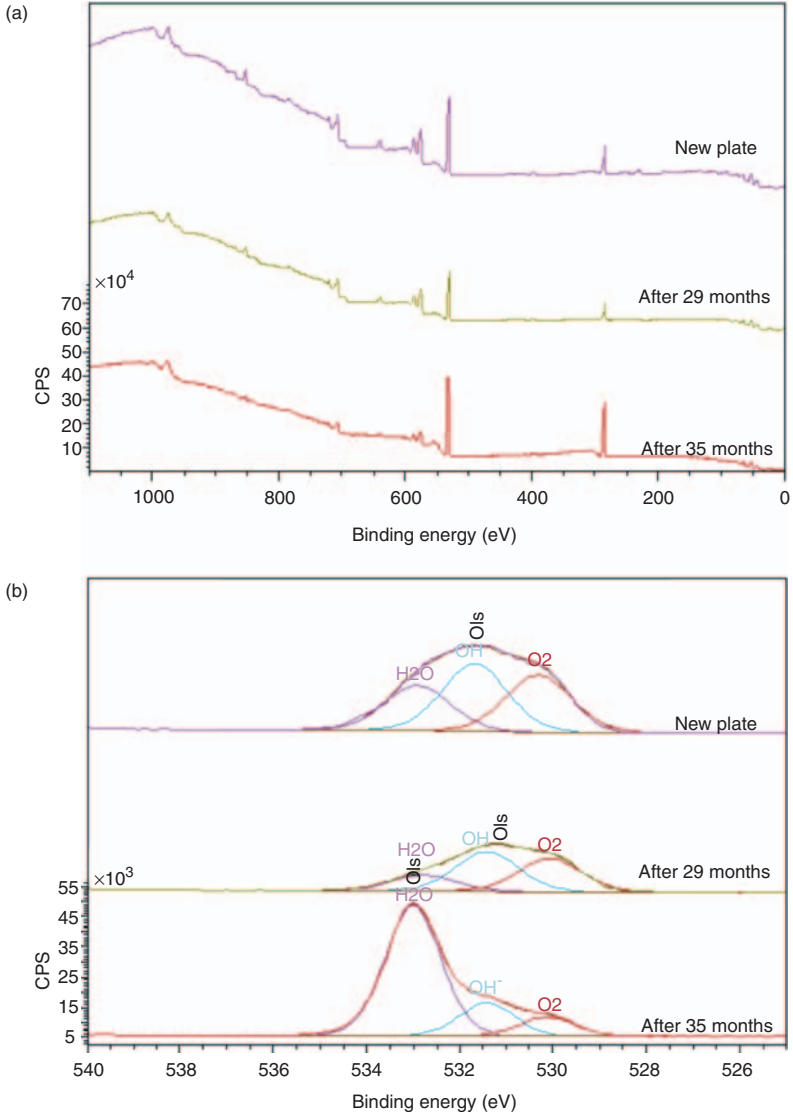


Figure 5. XPS results for the implant: (a) Survey spectra and (b) oxygen 1s spectra for new implants and implanted for 29 and 35 months.

implants (Figure 5(b)). The nitrogen had one dominant peak at the 400 eV energy level, which corresponded to C-N (Figure 6).

No significant differences in terms of chemical composition were observed for the parts of the implants covered with tissue regarding the time of implantation. However, the amount of water and hydroxyl groups was significantly lower for the longer implantation time (Figure 7(b)). Nevertheless this difference could be a result of cleaning and post operation procedure conducted for the implants after retrieving them from the body.

Results of Corrosion Examination

The results of corrosion tests are compiled in Table 3. The results for each of the plates in the deformed and nondeformed zones were analysed first. The corrosion potentials for the new, nonimplanted plate were in the range 41–48 mV. Some differences between the outside and inside surfaces of the implant were observed. The breakdown potential of the outside part was 1153 mV while for the inside part was 766 mV. The breakdown potential for the deformed part of the implant was 864 mV (Table 3). Mean deviation of the breakdown potential for the nonimplanted plate was 154 mV. The deformed area exhibited much higher polarisation resistance of $R_p = 1760 \text{ k}\Omega \text{ cm}^2$ compared to the nondeformed parts (461 and $700 \text{ k}\Omega \text{ cm}^2$).

The differences in the corrosion potentials were observed for the plate that stayed in the body for 29 months when outside and inside parts were analysed. The deformed outside part had lower corrosion potential (–105 mV) compared with the inside part (6 mV). The mean value of the breakdown potential was 1062 mV (Table 3, Figure 8). The polarization resistance was in the range 429–1090 $\text{k}\Omega \text{ cm}^2$, mean value was $711 \text{ k}\Omega \text{ cm}^2$. The straight parts showed higher polarization resistance than the deformed part.

The bars after 35 months implantation had slightly lower corrosion potentials and their level was not dependent on the part of the implant examined. The mean corrosion potential for the bar was –29 mV. The breakdown potentials were in the range 986–1140 mV. The polarization resistance oscillated in the range of 508–930 $\text{k}\Omega \text{ cm}^2$.

DISCUSSION

Stainless steel implants can cause adverse body reactions due to their chemical composition. From this point of view, examination explanted devices removed from the body can bring detailed information about

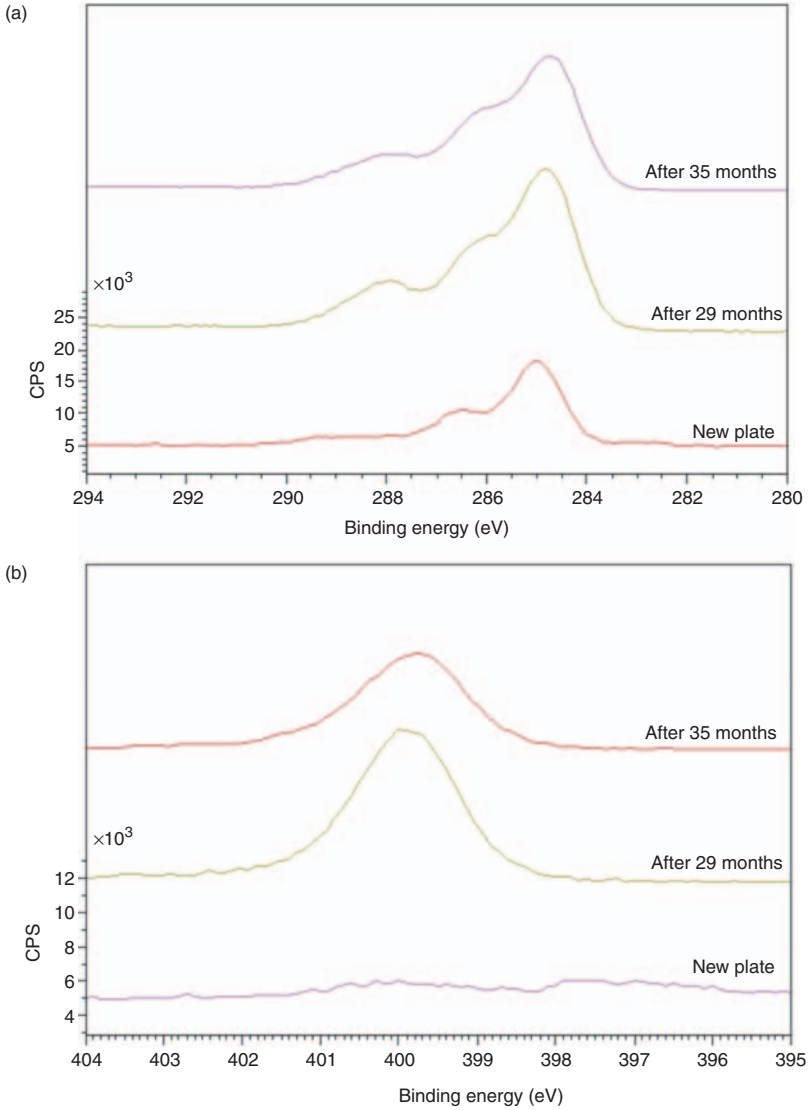


Figure 6. Detail spectra for new plates and after 26 and 35 months in the body: (a) carbon 1s and (b) nitrogen 1s.

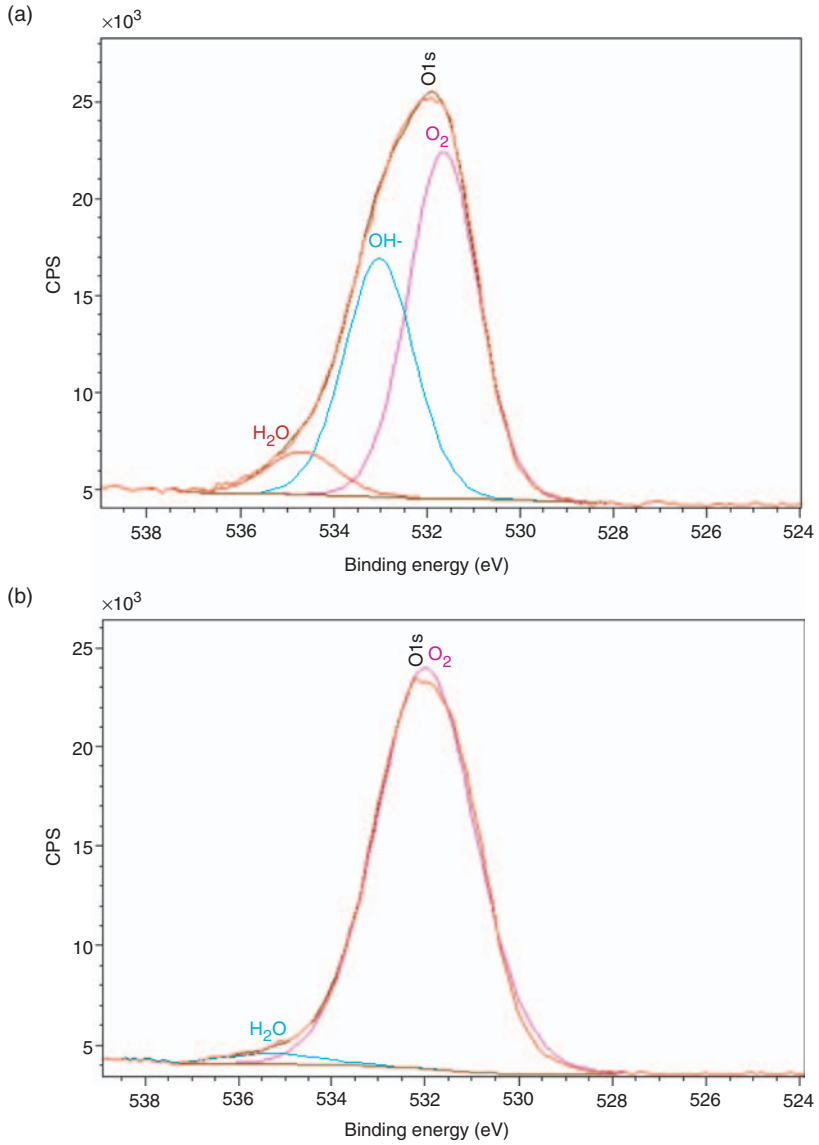


Figure 7. Oxygen spectra for parts of the implants covered with tissue after: (a) 29 months and (b) 35 months.

Table 3. Corrosion test results.

	C (C/cm ²)	E _{cor} (mV)	R _p (kΩ cm ²)	E _B (mV)	i _{cor} (nA/cm ²)
35 months in the body					
Non deformed area close to middle of the bar	4.379	-20	570	1090	11.72
Deformed inside surface	2.048	-28	508	1140	5.9
Deformed outside	1.355	-26	626	1002	19.8
around the hole, outside part	1.032	-42	930	986	16.04
29 months in the body					
Deformed – inside	1.008	6	528	1022	28.4
Deformed – outside	1.454	-105	439	1160	7.8
Straight – 2 cm off the middle part	5.759	-14	1060	1121	13.5
Straight – 2 cm off ear	0.683	-5	817	946	7.1
New plate					
No deformed outside	0.947	45	461	1153	27.6
Deformed – out part	0.553	48	1760	846	8.0
Straight	0.577	41	700	766	22.5

corrosion, topography, and chemical composition changes. Implants used to correct funnel chest were examined after different times of implantation. It is worth noting that implants prior to implantation are deformed to adjust their shape to the patients' anatomy. The typical shape of the bar which is implanted to the body (was established by the Prof. Dzielicki's [9,10] team after many years of using the technique) is shown. Because the plate is deformed to an angle of almost 90° increased stress in the plate could result in material failure but certainly results in surface alteration of the implant.

The plates after 29 and 35 months of implantation and new plate prepared according to the clinical procedure (shape adjusted) were examined. In the first stage the roughness of the surface was examined. The roughness measurements of the new plate showed that R_a values were significantly greater for the deformed regions. The deformed parts were visually dull, the AFM examination revealed numerous slide bands that had an impact on the change in roughness (Table 1, Figure 2). On the surface, texture was observed. The roughness differences between deformed and nondeformed regions were less significant for the implants after implantation. It could be the result of an organic layer that covered the surface after implantation, which gives the same roughness for both types of implants. It could also be caused by the contact with body tissues that roughens the surface resulting in no

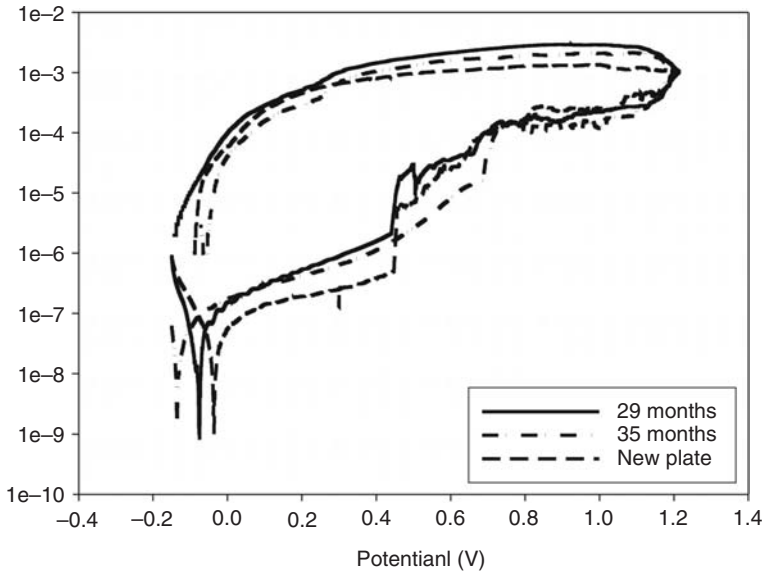


Figure 8. Potentiodynamic curves for the chest plates before and after implantation.

difference in the deformed region. For the nondeformed regions the increase of R_a with time of implantation was observed. A similar increase was observed for deformed regions but only in respect to the implanted plates. Some parts of the implants were covered with whitish layer. This appeared on both sides of the implants, especially in the areas where the implant had contact with bone. The roughness of the regions covered with the whitish film increased to $0.15 \mu\text{m}$ with time of implantation. At the same time the organic film thickness increased, which is stated on the basis of the crack depth measurements Figure 4(b).

The XPS examination was done for three types of implants: new and two implanted (remained in the body for 29 and 35 months). The examination was carried out for both types of the regions covered and noncovered with the layer.

The surface chemical composition of the new plate was very close to the composition of the steel, but higher carbon contamination lowered the concentration of the chromium, iron, molybdenum, and nickel. The chromium and molybdenum were identified as oxides. The parts of the implants taken from the body, which were not covered with layer showed similar composition to the new plate, but concentration of

chromium was 2 and 4% higher respectively for the plate stayed in the body for 29 and 35 months. The chromium had also slightly higher binding energy for implanted plates that could suggest some amount of potentially carcinogenic CrO_3 , Cr^{3+} and $\text{Cr}(\text{OH})_3$ was present. The parts which were covered with the whitish layer had different chemical composition. Concentrations of the main components of the steel were significantly lower while carbon and nitrogen concentrations were higher. This indicates a layer of organic origin.

The chemical composition was not greatly affected by the time of the implantation. Analysis of the carbon, oxygen, and nitrogen binding energies showed that the top layer of the implant were quite similar. For the implants that stayed in the body for 29 months analysis of the oxygen peaks showed that the amount of water and hydroxyl groups was higher compared to the longer implantation time. However, the amount of double bonded carbon with oxygen was very similar. It shows that these differences could be caused by post operative preparation of the samples rather than longer implantation time. Nitrogen was identified mainly as an oxide. For the implant that stayed in the body for 29 months a greater concentration of chromium was detected compared with 35 months. This may suggest a smaller layer thickness. This result was in agreement with AFM results which showed an increase in thickness of the layer with implantation time.

It is worth noting that implants before placing into the body are deformed to adjust them to the chest shape. During this procedure the surface can be scratched and abraded by the instrumentation used. Surface damage can influence the corrosion resistance. The implants were passivated and thus possess a thin protective oxide film which could be removed by the implantation procedure. On the implants numerous deep abrasions were observed.

One of the crucial factors for stainless steel that influences the biocompatibility and body reaction to the material is corrosion resistance. A low rate of corrosion ensures a low rate of ion release and therefore lower risk of adverse reactions. The corrosion resistance for the three implants and their different areas were very varied. The new plate had generally the highest and most stable corrosion potential (mean $E_{\text{cor}} = 45 \text{ mV}$) along the plate; however, the breakdown potentials were varied for different regions. The highest ($E_{\text{B}} = 1153 \text{ mV}$) was observed on the nondeformed parts, while initiation of the corrosion for deformed regions was observed at the potential 846 mV . The lowest values of the breakdown potential were observed in the inside nondeformed parts of the plate. The 29 month implantation period decreased the corrosion potentials, which were the lowest for deformed

regions ($E_{\text{cor}} = -105 \text{ mV}$). The breakdown potentials for this implant were greater than for the nonimplanted plate and were not significantly divergent along the implant. The corrosion current was generally lower for implanted plate compared with non-implanted. The longer implantation time can cause further changes in corrosion resistance. The corrosion and breakdown potentials were almost identical along the implant. E_{cor} values were greater for the implant that was implanted for 35 months in the body compared to the implant that was implanted for 29 months. However, the breakdown potentials and corrosion currents remained at the same level.

The analysis of the charge that was used to transfer ions to the electrolyte that corresponds with area under polarization curve does not give additional information about corrosion resistance for stainless steel. In general, it is observed that when the surface of the material is enhanced by surface treatment it causes an increase in the breakdown potential and decrease in the current density in the passive area. But when the breakdown potential is exceeded a very fast rise of the current is observed, thus a high corrosion rate is observed. The hysteresis loop is greater the higher breakdown potential is. The repassivation potential is the same for the material. It means that when we uncover the subsurface, i.e., by corrosion, the material repassivates without reference to surface preparation at the same potential value. When we are at higher potentials and the thin protective film breaks down then it causes a higher corrosion rate. It seems to be reasonable to compare that kind of material up to breakdown potential and not to utilize data from area under the curve measurements. We could also analyze area under the forward part of the curve that could represent charge that was used to transfer ions, change the oxidation state, or to dissolve some elements from the surface.

The corrosion resistance results indicated that implants did not remain fully passive in the body. The general increase of the breakdown potentials and changes of the corrosion potential showed that some chemical reaction took place at the surface. However, the breakdown potential increase indicates that the surface was being passivated when in the body. The analysis of the potentiodynamic curves showed that in the potential range that could occur in the physiological condition the new bar had the lowest current density and the highest corrosion potential. It indicated that the new plate had the highest corrosion resistance and the corrosion resistance was impaired during implantation.

The roughness, AFM, and corrosion results indicated that the chest plates were impaired by the implantation procedure and when in contact

with harsh physiological environment. It decreased the corrosion properties of the plates. However, an organic layer on the surface showed that the implant did not stay passive but underwent some reactions at the implant-tissue interface. These reactions should be seen rather positively, as it indicates that the implants were accepted by the tissues. Nevertheless, if the implants continue reacting they could continue to release chromium, nickel, and other ions.

The limited number of the samples specific to a single patient may not be generally applicable. To verify the results additional examinations should be carried out on samples from a greater number of patients.

CONCLUSION

- (1) Preoperative adjustment of the implant causes damage to the surface which impaired the corrosion resistance.
- (2) Preoperative bending of the implant caused stress accumulation and appearance of slide bands on the surface that increased roughness of the surface.
- (3) In some parts of the implants, a rough organic layer was detected. The thickness of the layer was the higher the longer the time of implantation.
- (4) The corrosion resistance was lower the longer time of implantation.
- (5) The chemical composition of the adhered tissues were not significantly dependent on the implantation time

ACKNOWLEDGMENTS

The authors would like to thank the EU for the Marie Curie Fellowship for Wojciech Chrzanowski.

REFERENCES

1. Marciniak, J., Paszenda, Z., Kaczmarek, M., Ziebowicz, A., Szewczenko, J., Chrzanowski, W., et al. (2007). Structure and Physical Properties of Passive-Carbon Coating on Stainless Steel Implants, *Material Engineering* (In Polish) 5(147): 440–443.
2. Smolik, J., Paszenda, Z., Walkowicz, J., Marciniak, J. and Chrzanowski, W. (2003). Carbon Coatings on Implants for Traumatology Made from the Cr–Ni–Mo Steel. *18th European Conference on Biomaterials*, Stuttgart, Germany, p. 098.
3. Szewczenko, J., Marciniak, J. and Chrzanowski, W. (2000). Corrosion Investigation of Stainless Steel Implants During Electro Stimulation Union

- Bone Using Sinusoidal Wave Form (In Polish). *Proceedings of the 9th International Scientific Conference Achievements in Mechanical and Materials Engineering 2000*, Gliwice-Sopot-Gdańsk, S. 511–514.
4. Kurella, A. (2005). Review Paper: Surface Modification for Bioimplants: the Role of Laser Surface Engineering, *Journal of Biomaterials Applications*, **20**(1): 5–50.
 5. Singh, R. (2006). Laser Surface Modification of Ti-6al-4v: Wear and Corrosion Characterization in Simulated Biofluid, *Journal of Biomaterials Applications*, **21**(1): 49–73.
 6. Perez, N. (2004). *Electrochemistry And Corrosion Science*, Kluwer Academic Publishers, Boston.
 7. Roher, P.R. (2000). *Handbook of Corrosion Engineering*, The Mcgraw-Hill Companies, Inc., New York.
 8. Fernandes, M.H. (1999). Effect of Stainless Steel Corrosion Products on *In Vitro* Biomineralization, *Journal of Biomaterials Applications*, **14**(2): 113–168.
 9. Dzielicki, J., Korlacki, W. and Sitiewicz, T. (2000). Maloinwazyjna Metoda Nussa W Leczeniu Lejkowatej Klatki Piersiowej (In Polish), *Pol. Przegl. Chir.*, **72**(6): 524–530.
 10. Dzielicki, J., Korlacki, W., Janicka, I. and Dzielicka, E. (2006). Difficulties and Limitations in Minimally Invasive Repair of Pectus Excavatum - 6 Years Experiences With Nuss Technique, *Eur. J. Cardiothorac Surg.*, **30**: 801–804.
 11. Kannan, R.Y. (2006). Review Paper: Principles and Applications of Surface Analytical Techniques at the Vascular Interface, *Journal of Biomaterials Applications*, **21**(1): 5–32.
 12. Kokubo, T., Miyaji, F. and Kim, H.M. (1996). Spontaneous Formation of Bonelike Apatite Layer on Chemically Treated Titanium Metals, *J. Am. Ceram. Soc.*, **79**(4): 1127–1129.
 13. Kokubo, T. (1998). Apatite Formation on Surfaces of Ceramics, Metals and Polymers in Body Environment, *Acta Materialia*, **46**(7): 2519–2527.
 14. Kokubo, T. (2005). Design of Bioactive Bone Substitutes based on Biomineralization Process, *Materials Science And Engineering*, **C25**: 97–104.