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Behavior of anodic layer in Ringer's solution on Ti6Al4V ELI alloy after bending

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ABSTRACT

Purpose: Characterization of the electrochemical behavior of anodized implant rods made of the titanium alloy Ti6Al4V ELI after immersion in air-saturated Ringer's solution was presented in the paper.

Design/methodology/approach: The anodized and deformed by bending at angle 20º specimens (dia 6 mm) were characterized electrochemically in two zones: the max tensile (I) and the max. compressive stress (II). Impedance spectra (EIS) and corrosion potential measurements were performed on 1, 6, 10 and 16th day after immersion in Ringer`s solution.

Findings: Bending caused an apparent decrease of the protective properties of the anodic layer, but the characteristic two-layer anodic film and the values of corrosion potentials were restored due to immersion in Ringer's solution. The regions of the compressive stresses show much stronger tendency to regenerate surface properties.

Research limitations/implications: The electrochemical tests in Ringer's solution performed only in static conditions will be followed by fatigue tests in SBF.

Practical implications: Results of the work are of great importance for surgical practice in the pre-operative stage of spinal surgery procedures. The explanation of the observed phenomena is proposed.

Originality/value: Different stress zones formed on implant alloy during bending were described electrochemically. Results of studies evidenced that changes in the electrochemical behaviour in vitro in Ringer's solution are advantageous with regard to the protective properties of the investigated alloy.

Keywords: Biomaterials; Bending; Titanium alloy; Behavior in vitro

METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

Ti6Al4V ELI alloy was originally developed for aerospace application but due to superior corrosion resistance to other implant materials like stainless steel and alloys based on cobalt–chromium it has been also extensively used as a human body implant material from the 1950s. The passive film behavior on this alloy plays a crucial role for its suitability as implant material. The anodic oxides on the surface of Ti6Al4V significantly reduce dissolution currents making Ti6Al4V more resistant to corrosion, but they are also susceptible to fracture due to scratches, and fretting resulting from mechanical shaping, treatments and loading. If not mechanically disturbed, titanium alloys exhibit an excellent combination of high mechanical properties and biocompatibility. However, plastic deformation, which occurs during the pre-operative surgery shaping process induces changes in the structure of surface layer and their electrochemical behavior in biological environment, which may change the biocompatibility of these materials. In a bending process four characteristic stress zones can be determined on the surface of the deformed material [1, 2]: max tensile (I), max compressive and cold work (II), compressive (III) and tensile and cold work zone (IV). Only some workers have considered the influence of bending/rebending process on the susceptibility of surface layer on implants made of Ti6Al4V to localized corrosion and their behaviour in biological media [3-5] and the cyclic deformation behaviour of the binary titanium alloy TiAl6Nb7 under rotating bending in physiological media [6]. It has been shown [7] that protective properties of the passive layer on implant stainless steel depends on its integrity and the extent of the deleterious effect produced during pre-operative procedure. It was observed that the process of degradation *in vivo* was related to the state of stresses and deformation of steel implants. Other authors showed that the passive film formed in a tensile stress field [8] was richer in oxygen, poorer in molybdenum in the outer part and thicker than it is on the unstrained sample. Assumption that the deleterious effect of the tensile stress might be explained by the increased number of vacancies in surface layer of the deformed 316 steel was also presented [9]. On the other hand, the observed beneficial effect of a compressive stress was attributed to the increasing chromium enrichment and the decreasing thickness of the passive film. Some authors [10, 11] indicated also the importance of negative electric charges in activating titanium surfaces and stimulating apatite growth. To characterize the properties of surface layers on implant alloys the electrochemical tests are performed in Tyrode`s [4], Hank's [12], Ringer's [13] solution and simulated body fluid – SBF [14, 15].

The purpose of this study was, therefore, to investigate the influence of plastic deformation and characterize the electrochemical behaviour of the anodized implant rods made of the Ti6Al4V ELI alloy in Ringer's solution. As the bending process causes the decrease of corrosion potential [2] to study the electrochemical behaviour of the surface layers in stress zones: the tensile (I) and the compressive (II), which had been activated during shaping in the pre-operative procedures, was of particular interest for surgical practice and the performance of the deformed material after implantation.

2. Materials and methodology

Cylindrical specimens were prepared from cold drawn and annealed rods (dia 6mm) of the titanium implant alloy Ti6Al4V ELI matching the ASTM F136-84, of chemical composition given in Table 1.

Table 1.
Composition wt.% of Ti6Al4V ELI alloy

Al	V	Fe	O	C	N	H	Ti
%							
6.2	3.95	0.2	0.2	0.08	0.04	0.015	balance

The test specimens were anodized with galvanostatic mode in phosphoric acid (PL Patent filled 185176, 2003). Plastic deformation of specimens was performed according to the pre-operative procedure of shaping the spinal rods (Fig.1). Notations (I) and (II) show the tensile and compressive zones in samples of tested material after their bending at 20º.

To characterize the electrochemical behavior of the deformed passive layers in the tensile (I) and the compressive (II) stress zones, the corrosion potential measurements and impedance tests were performed during immersion of bent specimens in Ringer's solution. In the present study, the aerated Ringer's solution at pH=7.4 was applied for all test examinations. Chemical composition of Ringer`s solution is given in Table 2.

a)

b)

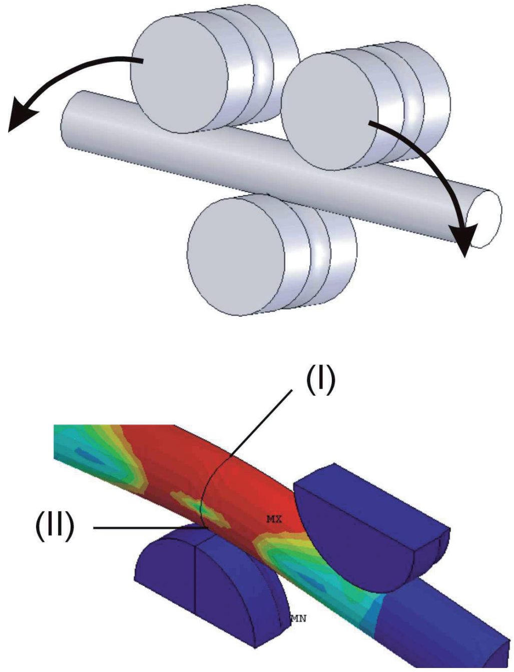

Fig. 1. Pre-operative bending of spinal rods, a) scheme of tool material arrangement, b) zones of surface stresses due to bending: (I)-max tensile and (II)-max compressive stress on tested specimens

Table 2.
Composition of Ringer`s serum

Composition	g / l	Ion	mmol / 100 ml
Natrium chloride	8.6	Na^+	14.72
Potassium chloride	0.3	K^+	0.4
Calcium chloride	0.243	Ca^{++}	0.22
Water	-	Cl	15.56

Specimens for electrochemical studies were prepared using the procedure reported earlier [2]. The specimens were then washed with distilled water followed by ultrasonic cleaning with acetone. To reduce background noise, acrylic nail polish was used to seal test samples into the sample holder and cover most of the sample surface. An area of approximately 0.3 cm^2 of the alloy surface was left uncovered for tests. Before immersion to Ringer's solution the surface of specimens were observed by optical microscopy with camera (AVT-HORN). Prior to the beginning of the impedance tests, samples were kept in the solution for at least 15 min in order to establish the free corrosion potential (E_{corr}). Then EIS measurements were performed by applying a sinusoidal potential perturbation of 5 mV at the open circuit potentials. The impedance spectra were measured with frequency sweep from 10^5Hz to 0.18Hz in logarithmic increment after the 1,6,10 and 16th day of immersion. The impedance data were gathered and analyzed using the 9831 FRA Frequency Response Analyzer and IMP 99 Software (ATLAS, Poland). The impedance data were fit to appropriate equivalent electrical circuit using a complex nonlinear least-squares fitting routine, using both the real and imaginary components of the data. The quality of fitting was judged by the error (of less than 5%) distribution vs. the frequency comparing experimental with simulated data for the model. Parameters obtained from the best fit equivalent circuit were tabulated and analyzed.

3. Results and discussion

3.1. Surface examination

Changes of the surface stereometry after bending [16, 17] and the surface deformation can be observed by simple optical methods at low magnification (Fig. 2).

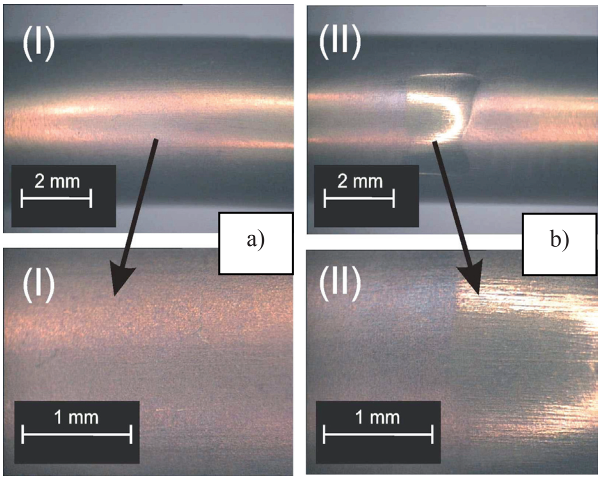

Fig. 2. Surface appearance after bending (angle 20º): a) zone (I) and b) zone (II) before immersion in Ringer's solution

As it has been described presented earlier [2] in zones presented in Fig.2 the increase of roughness parameters was noticed in the tensile stresses zone (I), whereas in the compressive stresses zone and in the region affected by an indirect cold work, the values of roughness parameters were lower. Microcracks are developed during bending and the actual contact surface enlarges, which leads to the increase of susceptibility to corrosion [2].

3.2. Corrosion potential

Values of corrosion potential can give an indication of an active/passive transformation behavior of material. After anodizing all specimens were characterized by high values of corrosion potential. In contrary to non-anodized specimens for which negative values of corrosion potential were noticed after bending [2], the anodized specimens showed only their decrease. However, in our studies the bigger decrease of E_{corr} values was noticed for the tensile stress zones (I) than for the compressive stress (II) ones. Moreover, the variation of corrosion potential with immersion time in Ringer's solution was not similar for all the specimens. The potential values moved towards noble potentials for bent samples whereas they shifted to slightly lower values for non-bent specimens with immersion time. Eventually after about 16 days all samples acquire similar potential values ranging from about 427±10 to 475±10 mV (SCE) (Fig.3).

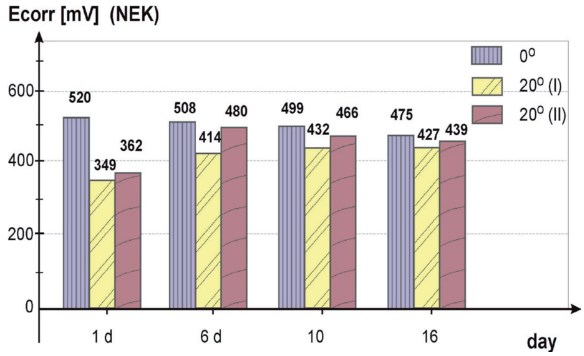

Fig. 3. Corrosion potential E_{corr} values for samples after bending recorded on 1, 6, 10 ,16th day in Ringer's solution

The changes of corrosion potential shown in Fig.3 are typical behaviour for the titanium materials. According to [18] the values of the corrosion potential of most titanium materials immersed in saliva steadily increase with time over 7 days, except for the alloy Ti6Al4V, the potential of which start to decrease from the sixth day of immersion. For CP titanium after electrochemical treatment the values of the corrosion potential still remain in the negative domain, contrary to Ti6Al4V alloy which shows the highest positive corrosion potentials decreasing with time of immersion.

3.3. Electrochemical impedance spectroscopy

Impedance spectra have been presented as Bode phase plots in Fig. 4 for non-deformed specimens and in Figs. 5 for deformed specimens, respectively. From the Bode phase plots shown in Fig. 4 it can be noted that with immersion time, for all specimens, the phase angle drops towards zero degree at very high frequencies, indicating that the impedance is dominated by solution resistance in this frequency range (no phase shift between current and potential results due to presence of a resistor in AC circuit). Moreover, it can also be noted that the phase angle remains constant and close to about -65° in the low frequency region indicating constant contribution of surface film resistance to the impedance. Bode phase plots were characterized by two distinct regions (two time constants) indicating double layer structure of the surface film.

As can be seen in Fig. 4, apart from the Bode phase plot recorded after 1 day, the phase angles are similar in nature over a wide range of frequency indicating a near capacitive response for all the specimens. This behavior is indicative of a thin passive oxide film present on the surface [19].

Bode phase plots for bent specimens (Fig.5) reveal significant differences between the behaviour of anodic passive layer in the tensile and compressive stress zones. Bode phase plots recorded after 1 day of immersion for both zones: the tensile and compressive show one time constant of a low value in a high frequency region indicating one layer of a low solution resistance. Bode phase angles increase, while plots show two-time constants with time of immersion.

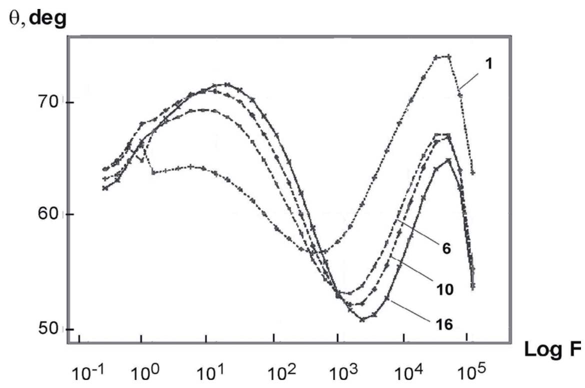

Fig. 4. Impedance spectra (Bode`a diagram) for anodized and non-deformed specimens of the Ti6Al4V alloy recorded during immersion in Ringer's solution, temp. 298 K

Particularly, the substitution of one-time constant Bode phase plots into the two- time constants curves and the increase of phase angles by the higher frequency clearly show that the surface films change with exposure time into a double-layer film of lower porosity. It confirms the gradual decrease of porosity due to coating the microcracks by deposits of a new phase. All observed changes were more significant in case of the compressive stress zones in Fig. 5b.

Phase angle plots for deformed specimens clearly show also the increase of values in high frequency region with the immersion time in Ringer's solution. This was due to changes in solution resistance R_s. Although, the solution resistance values were not high (within 18÷33 ohms cm^2), the changes for the tensile stress zone were zone better revealed on Bode diagrams and higher than in the compressive stress zone.

The phase angle increased also in the low frequency region after 10 days (Fig. 5a and 5b) and becaming less porous, which is indicative of film acquiring higher capacitance. This observation suggested improvement in nature of surface film with immersion time in Ringer's solution.

The EIS data could be well fitted with the equivalent circuit given in Fig. 6, based on the consideration of a layer model for the surface film. The circuit represents the electrochemical behavior of a metal covered with a barrier film [12, 20]. The equivalent circuit consists of the following elements: a solution resistance R_s of the test electrolyte, the capacitance C_{bl} of the barrier and the polarization resistance of the substrate R_{bl}. The resulting impedance parameters fitted with the equivalent circuit shown in Fig. 6, are given in Table 3. The quality of fitting judged by the error (of less than 5%) distribution vs. the frequency decreased with time elapsing. From their comparison it can be observed that a decrease of the resistance values (R_s and R_{bl}) for the new coating, which are one order of magnitude lower for R_{bl} than those determined for both kind of specimens at the immersion, is noticed. The same observations apply for both kind of specimens (the tensile stress zone and the compressive stress zone). The drop of R_s may indicate less electrolyte between the pores and microcracks of the surface layer and confirm a beneficial effect of the immersion the sample into the Ringer's solution.

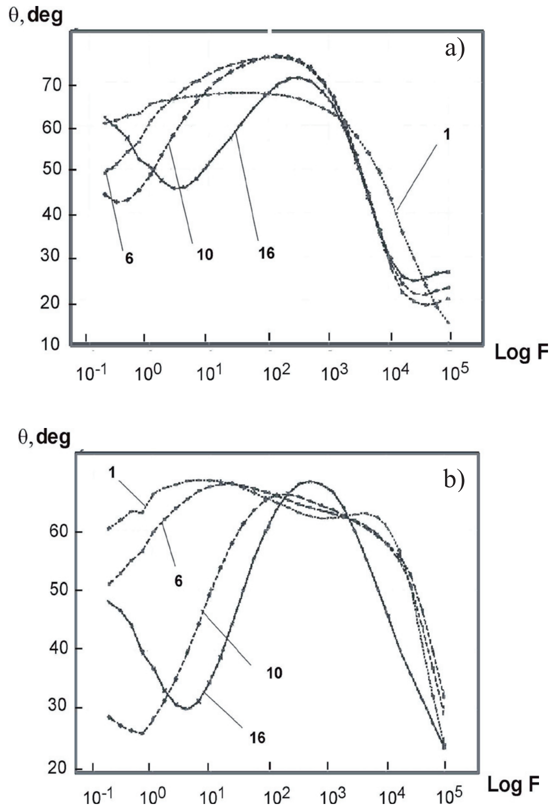

Fig.5. Impedance spectra for a) the tensile (I) and b) compressive (II) zones of the Ti6Al4V alloy sample; bending angle 20°

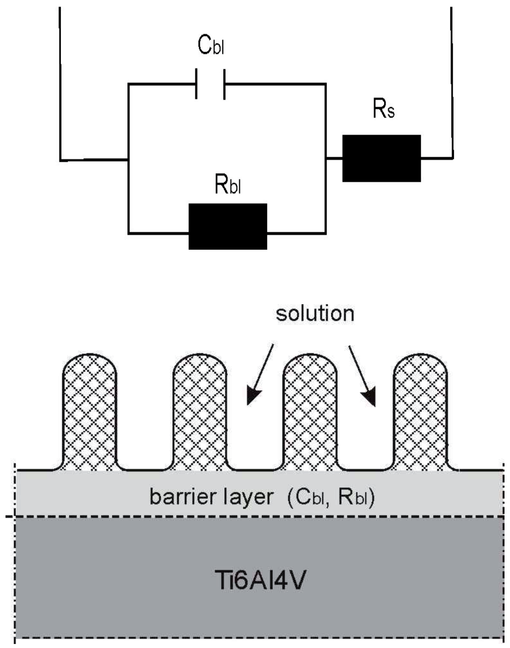

Fig. 6. Equivalent circuit and model of surface layer on the Ti6Al4V ELI alloy [12, 20]

It can be observed that anodic film resistance R_{bl} for tensile stress zone of plastically deformed Ti6Al4V ELI alloy increased initially and then decreased (Table 3). The changes in the passive film resistance of the materials can be attributed to structural changes in the film or changes in the ionic or electrical conductivity of the film. The decrease of R_{bl} may indicate the change of the chemical nature of the layer and its ionization due to the deposition of a new coating. It had been reported in the literature [20,21] however that in the case of Ti6Al4V ELI the vanadium oxide formed on the surface of Ti6Al4V ELI alloy dissolves. Its dissolution results in the generation and diffusion of vacancies in the oxide layer of Ti6Al4V ELI [21]. The change in passive behavior of Ti6Al4V ELI alloy with immersion time in Ringer's solution may be attributed to same phenomena. Hence, vanadium as an alloying element could not contribute to the observed changes of electrochemical properties of the surface film on Ti6Al4V ELI alloy. This is a desired feature of the process under investigation as vanadium is well known toxic element in orthopedic applications [7].

Table 3.
The parameters of EIS analysis for the tensile (I) and compressive (II) zones of the Ti6Al4V ELI alloy bent samples (bending angle 20°)

angle/zone	day	R_s [Ωcm^2]	$C_{bl} \cdot 10^{-6}$ [$F \cdot cm^{-2}$]	$R_{bl} \cdot 10^5$ [$\Omega \cdot cm^2$]
0º	1	$4.11 \cdot 10^{-9}$	1.41	509
	6	5.68	1,84	$155 \cdot 10^9$
	10	13,9	1,98	$105 \cdot 10^9$
	16	11,4	2,16	$6,51 \cdot 10^9$
(I) 20º	1	28.9	4.44	9.28
	6	33.3	3.57	2.43
	10	32.4	3.53	1.13
	16	23.5	12.2	1.43
(II) 20º	1	20.5	2.68	27.00
	6	19.5	2.76	7.44
	10	15.6	3.10	0.54
	16	18.0	6.96	0.15

The highest recorded values of R_s correspond to the tensile stress zones, which is the evidence that the specimens of the highest roughness [2] consist more electrolyte penetrating into the microcracks of the layer. The decrease of C_{bl} (the capacity of barrier layer) values observed yet after the 1st day indicated initially the tendency to coat the surface layer by the deposits from the electrolyte (and filling up the microcracks), both in the tensile and the compressive zones. However, after longer soaking (after the 10th day) the increase of C_{bl}, was noticed, which might be the symptom of dissolution of the barrier layer. The corresponding values for the non-deformed specimens increased in the same time from $1.46 \cdot 10^{-6}$ (on the 1st day) to $3.06 \cdot 10^{-6}$ [$F \cdot cm^{-2}$] (on the 8th day). In comparison, the anodic layer on non-deformed specimen manifests the best protective properties.

It is evidenced by the lowest values of R_s and the highest resistance R_{bl}. The latter further increases due to the immersion in Ringer's solution. The lowest values of C_{bl}, confirm the greatest thickness of the layer on non-deformed materials. A slight increase of this value may indicate that the diffusional processes on anodic layer/electrolyte interface were initiated.

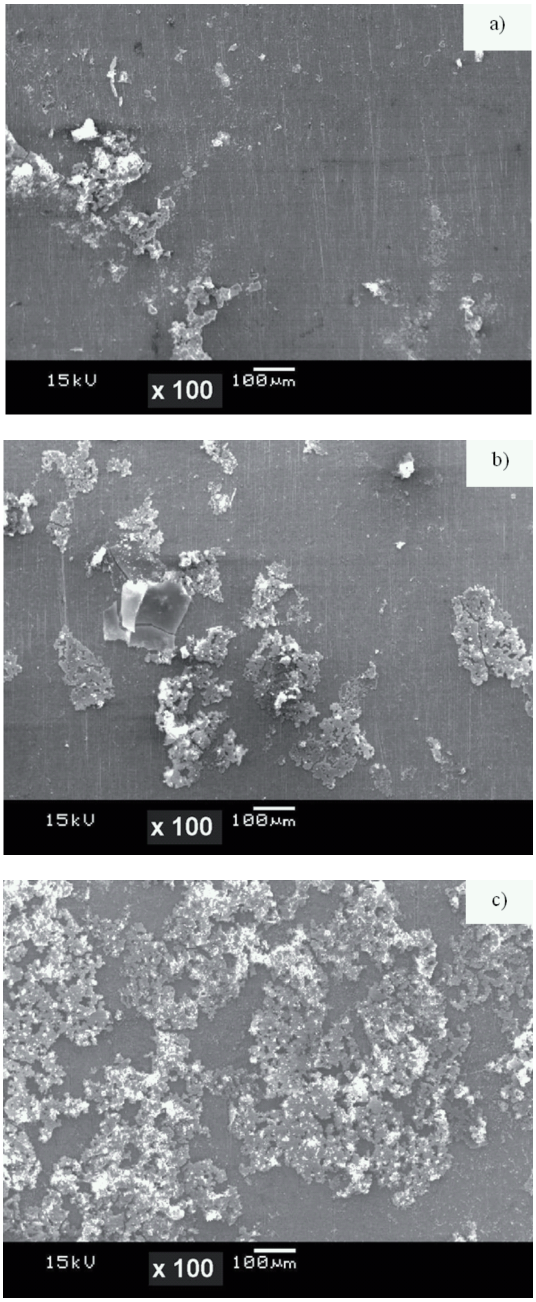

Fig. 7. SEM microphotograph of the tensile stress zone (I): a) non-bent, b) bent and c) rebent (angle 20º) after 30 days in SBF solution (100x)

Results of this work may confirm that deformed titanium alloy in the tensile and compressive zone is covered after immersion in the Ringer's solution by Ca-P-O deposits [3]. Due to the new coating the deleterious effect of the deformation of the implant titanium on its corrosion resistance is hindered by blocking the pores by precipitated Ca-P-O salts. In the experiments described earlier [3] (Fig. 7, 8 and 9) SEM and EDS analyses showed a new coating formed in the max tensile stress zones in simulated body solution (SBF). It consisted of deposits of the electrolyte components, mainly Ca and P, covering microcracks. These observations agree with the results of the impedance spectroscopy analysis in the present studies and confirm the stimulating effect of deformation in enhancing the apatite deposition on the surface layer of titanium material.

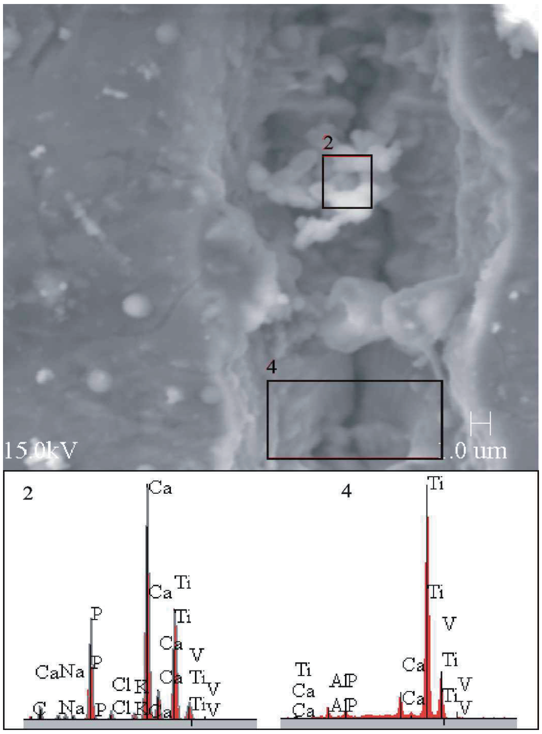

Fig. 8. SEM microphotograph and EDS results of EDS analysis for Ca-O-P deposits in the tensile stress zone of rebent specimen (bending angle 20º) after 30 days in SBF solution (5500x) [5]

When immersed in SBF solution for at least 3 days the samples showed the recovery of the layer structure and numerous Ca-P-O deposits on the surface. The number and localization of the deposits showed the stimulating effect of the surface polarization (more negative) and topography on the deposition of SBF components and formation of hydroxyapatite on the mechanically activated surface of the alloy. However, though the deposition of a new coating was at first enhanced in the SBF solution, eventually the stimulating effect disappeared. It is worth to mention that Ca-P-O coating is not an effective anticorrosion layer. It hinders to some extent the electrochemical processes occurring at the implant metal interface, thus contributing to a decrease in the metal ion release from the implant system, but the more important is its bioactivity and stimulation of bone in growth.

All surface deformation processes and finishing treatments (polishing and anodizing with electrochemical polishing) change the surface energy of the alloy. After immersing in SBF the exchange of ions at electrolyte/biomaterial interface in two opposite processes: the oxide layer dissolution and the deposition of electrolyte components, form the equilibrium of the system. Depending on the prevailing process during the first days of immersing, the decrease of the appropriate corrosion parameters are observed in case of the less deformed specimens, for which the anodic layers were not broken. As the result of breaking of anodic layer at higher bending angles, microcracks and naked metal appear, giving rise to the deposition of the electrolyte components [2]. Thus, deformation of anodic layer on implant titanium alloy induces the increase of bioactivity *in vitro* and enhances the coating of deformed area by SBF components, which form porous hydroxyapatite and stimulate faster growth bone tissue [22, 23].

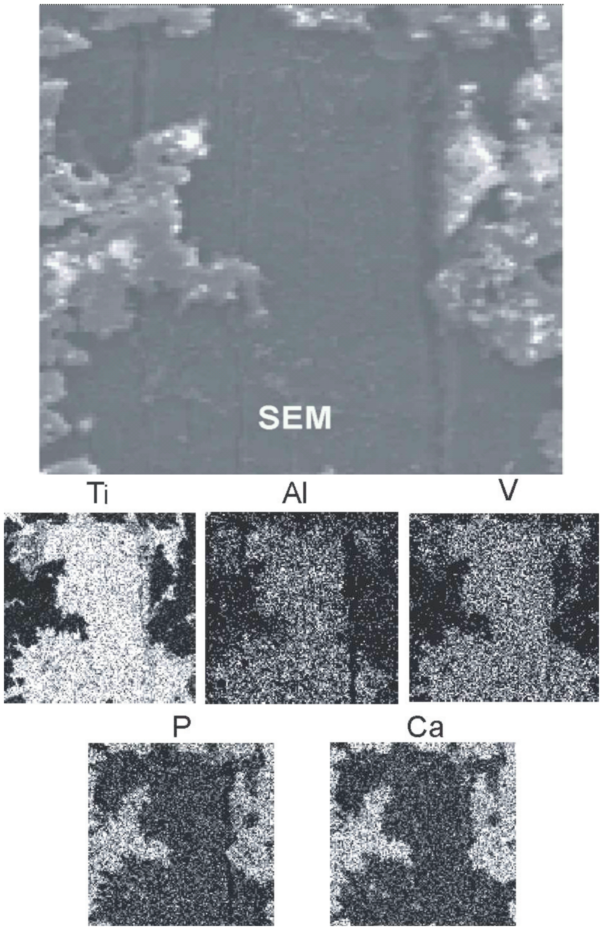

Fig. 9. Distribution of elements (SEM+EDS) in the tensile stress zone of rebent specimen (bending angle 20º) after 30 days in SBF solution (1000x) [5]

Results of the present studies indicate the initial decrease of protective properties of the layer, which was caused by plastic deformations and observed both in the tensile and the compressive zones of the investigated samples. It was evidenced by the disappearing of the two-layer structure of the surface film, which is characteristic for non-deformed anodic layer, by the decrease of potential corrosion values and the corresponding changes of impedance parameters (resistance of R_s and R_{bl} and capacity C_{bl}). However, the immersion of deformed samples into the Ringer's solution leads to the „repair" of the surface oxide layer during 10 days. The characteristic two-layer structure is restored, while the corrosion potentials maintain the similar values ranging from 427 mV to 475 mV after 16 days for all specimens. More destructive influence of the tensile stresses in comparison to the compressive stresses was revealed due to rebending/bending treatment procedure applied in the pre-operative stage of the surgical procedure.

4. Conclusions

The electrochemical behavior of plastically deformed anodic layer film formed on Ti6Al4V ELI alloy in Ringer's solution was studied as a function of immersion time using corrosion potential measurements and impedance spectroscopy (EIS) technique. EIS data were analyzed by assuming the presence of a single passive and a double surface layer. The analysis revealed that although the potential corrosion values of anodic layer decreased due to bending they never reached the active state of the material. The resistance of the anodic layer also decreased with immersion time for Ti6Al4V ELI alloy, contrary to values of the values of its capacitance.

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Additional information

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