Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 17
ISSUE 1-2
July-August
2006

Effect of bending on anodized Ti6Al4V alloy: II. Behavior in vitro

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Received 15.03.2006; accepted in revised form 30.04.2006

Materials

ABSTRACT

Purpose: Evaluation of the influence of plastic deformation and characterization of the electrochemical behaviour of anodized implant rods made of the titanium alloy Ti6Al4V after immersion in air-saturated Ringer's solution was presented in the paper.
Design/methodology/approach: The specimens (dia 6 mm) were anodized and deformed by bending at angle 20º. The comparative characteristics of two zones: the max tensile (I) and the max. compressive stress (II) was based on the determination of electrochemical properties. Impedance spectra (EIS) and corrosion potential measurements were performed on 1, 6, 10 and 16th day after immersion in Ringer`s solution.
Findings: Although bending caused an apparent decrease of the protective properties of the anodic layer, 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 the much stronger tendency to restore.
Research limitations/implications: The electrochemical tests in Ringer's solution were performed only in static conditions. Fatigue tests in SBF are in progress.
Practical implications: The explanation of the observed phenomena is proposed. Results of the work are of great importance for surgical practice in the pre-operative stage of spinal surgery procedures.
Originality/value: Various stress zones formed on implant alloy during bending were described. The results of studies presented in the paper evidenced that changes noticed 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; Behaviour in vitro

1. Introduction

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 behaviour 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 a few workers have analyzed 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] and Ringer’s [13] solution.

The purpose of this study was, therefore, to investigate the influence of plastic deformation and characterize the electrochemical behaviour of anodized implant rods made of the Ti6Al4V alloy in Ringer’s solution. As the bending process causes the decrease of corrosion potential [2] to study the behaviour of stress zones: tensile (I) and compressive (II), 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

Specimens were prepared from cold drawn and annealed rods (dia 6mm) of the titanium implant alloy Ti-6Al-4V matching the ASTM F136-84 (chemical composition: C: 0.08, O: 0.2, H:0.015, V: 3.95, Al: 6.20, other elements 0.3 wt.%, Ti: balance). The test specimens were anodized in phosphoric acid [14, 15]. Plastic deformation of specimens was performed according to the pre-operative procedure of shaping the spinal rods. (I) and (II) means tensile and compresive zones as bending at 20º angles.

Impedance spectra (EIS) measurements were used to determine the electrochemical characterization with ATLAS 9831 (Poland). In the present study, the aerated Ringer’s solution (composition of Ringer`s serum: Na^+ - 8.6, K^+ - 0.3, Ca^{++} - 0.243 g/l and Cl^-) at pH=7.4 was applied for all test examinations.

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. Prior to the beginning of the polarization, the samples were kept in the solution for 15 min in order to establish the free corrosion potential (E_{corr}). The measurement of the EIS was performed at the open circuit potential applying of 5mV (rms) wave in 10^5Hz ÷ 0.18Hz frequency range across the cell. The impedance spectra were performed on 1,6,10 and 16th day after immersion. Before immersion to Ringer’s solution the surface of specimens were observed by optical microscopy with camera (AVT-HORN).

The EIS data could be well fitted with the equivalent circuit given in Fig. 1, 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 [15, 16]. 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 quality of fitting was judged by the error (of less than 5%) distribution vs. the frequency comparing experimental with simulated data for the model.

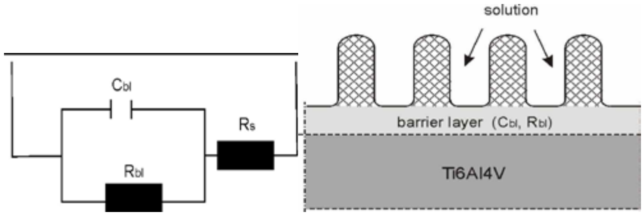

Fig. 1. Equivalent circuit and model of surface layer on the Ti6Al4V alloy [12, 16]

3. Results and discussion

The surface deformation and changes of the surface stereometry after bending [17,18] can be observed by simple optical methods also at low magnification (Fig. 2). The increase of roughness parameters was noticed in the tensile zone stresses (I), whereas in the compressive stresses zone and in the region affected by an indirect cold work the values of roughness parameters were lower, as it had been presented earlier [2]. Due to bending microcracks are developed and the actual contact surface enlarges, which leads to an increase of susceptibility to corrosion [2].

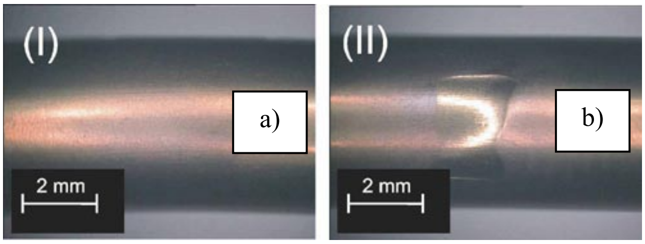

Fig. 2. Surface appearance after bending (angle 20º): a) zone (I) and b) zone (II) before immersion in Ringer’s solution

Changes in corrosion potential can give an indication of active/passive behavior of material. In our studies the bigger decrease of E_{corr} values was noticed for the tensile stress zone (I) than for the compressive stress ones. It is interesting that during soaking in Ringer’s solution the values of E_{corr} increase (contrary to the reverse tendency for non-deformed samples). Eventually both samples acquire the similar values 427÷475 mV (SCE) after about 16 days.

The impedance Bode spectra obtained at different exposure times during the immersion of the non-deformed and deformed samples in Ringer’s solution are shown in Fig. 3-4. Particularly, the substitution of one-time constant curve into the two- time constants curves and the low values of phase angles by the higher ones clearly show that the surface film changes with exposure time into a double-layer film of lower porosity. It confirms the gradual decrease of porosity due to coating the microcracks by a new phase of deposits.

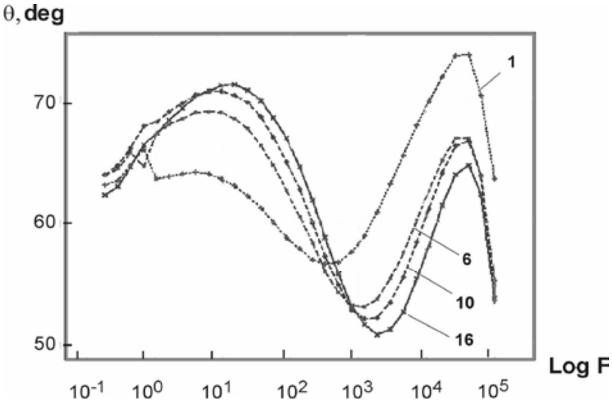

Fig. 3. Impedance spectra (Bode`a diagram) for anodized Ti6Al4V alloy non-deformed specimens recorded during immersion in Ringer's solution, temp. 298 K

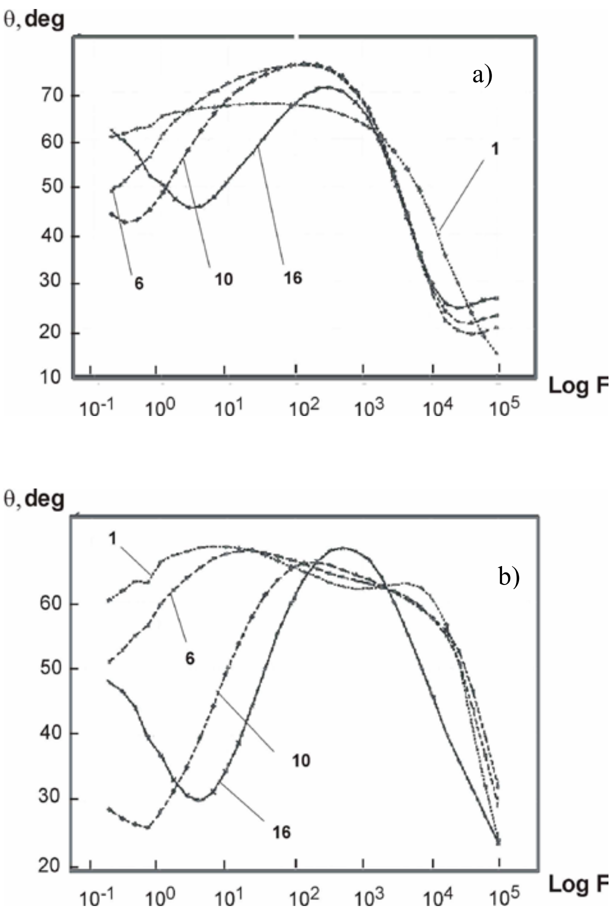

Fig. 4. Impedance spectra for a) the tensile (I) and b) compressive (II) zones of the Ti6Al4V alloy sample; bending angle 20°

All observed changes were more significant in case of the compressive stress zones in Fig.4, where some curves (recorded on the 2nd and the 8th day) are not presented.

The resulting impedance parameters fitted with the equivalent circuit shown in Fig. 3-4, are given in Table 1. 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).

Table. 1.
The parameters of EIS analysis for the tensile (I) and compressive (II) zones of the Ti6Al4V alloy bent samples (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 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. 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. The highest recorded values of R_s correspond to the tensile stress zones, which is the evidence that the specimens of the highest roughness [18] consist more electrolyte to penetrating into the microcracks of the layer. The decrease of C_{bl} (the capacity of barrier layer) values observed after the 1st day indicated initially the tendency of coating 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 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).

Anodic layer on non-deformed rod manifests the best protective properties. It is confirmed by the lowest values of R_s

and the highest resistance R_{bl}. The latter further increases due to the immersion in the Ringer's solution. The lowest values of C_{bl}, confirm the greatest thickness of the layer on non-deformed materials.

The interesting observations were made in the experiments described earlier [3] (Fig. 5). SEM and EDS analyses presented there showed that in the max tensile stress zones a new coating was formed in SBF solution. 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 and confirm the stimulating effect in enhancing the apatite deposition on the deformed surface layer of titanium material.

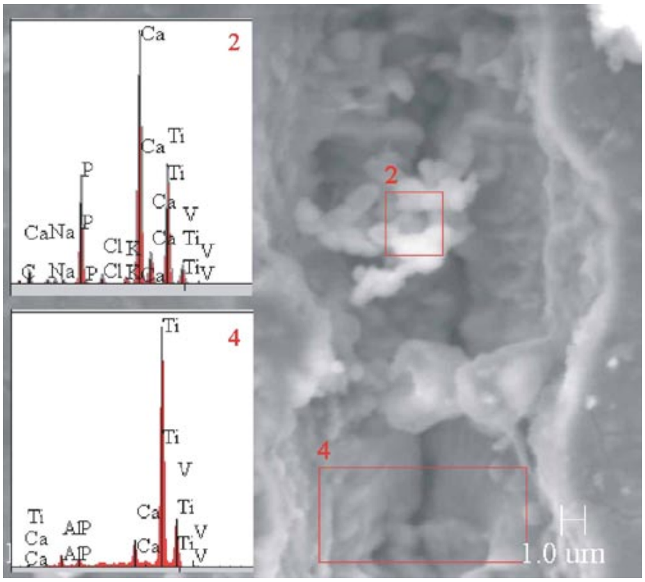

Fig. 5. SEM microphotograph and EDS results of EDS analysis for Ca-O-P deposits in the tensile stress zone of rebent specimen (bending angle 20º) after 30 days in SBF solution (5500x) [3]

4. Conclusions

Results of studies indicate the initial worsening of protective properties caused by plastic deformations, both in the tensile and the compressive zones of the investigated samples. It is shown by the disappearing of the two-layer structure of the surface film, which is characteristic for non-deformed anodic layer, 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 in the solution. 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.

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