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Effect of bending on anodized Ti6Al4V alloy: I. Surface layers characteristics

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Materials

ABSTRACT

Purpose: The plastic deformation behaviour of the anodized binary titanium alloy Ti6Al4V was characterized in mechanical and electrochemical tests.

Design/methodology/approach: The effect of tensile and compressive stresses on properties of different clinically relevant surfaces of the deformed by bending implant rods was investigated. The deformation behaviour was characterized by FEM analysis. Relevant surfaces in tensile and compressive zones were characteristics by microhardness and roughness measurements, and electrochemical testing (Ecor, anodic polarization, EIS) in oxygen-saturated Ringer's solution.

Findings: It was concluded that bending influenced mostly the properties of material in the tensile zone of the specimen, whereas the properties of surface layer in the compressive zone and the properties of surface layer in tensile zone after rebending are comparable and not so severe.

Research limitations/implications: Studies were performed in static conditions, fatique studies are planned in the future.

Practical implications: Results are of great importance in for surgical practice in the in the evaluation of the influence of shaping process applied during pre-operative procedures on the performance of spinal implant systems.

Originality/value: In the paper a typical pre-operative procedure of shaping was applied to anodized titanium implants in order to evaluate its influence on the characteristics of the surface layer. Studies were focused on the safety their application in vivo.

Keywords: Biomaterial; Titanium alloy; Bending; Surface characteristics

1. Introduction

In comparison with other metals, titanium alloys exhibit an advantageous combination of high mechanical properties and excellent biocompatibility, which qualifies them as materials for load-bearing implants. If not mechanically disturbed, the anodic oxide on the surface of Ti6Al4V significantly reduces dissolution currents at a wider range of potentials making Ti6Al4V more resistant to corrosion. However, anodic films are susceptible to fracture due to scratches, dents, and fretting resulting from mechanical loading. Plastic deformation, which occurs during the intra-surgery shaping process induces changes in the structure of surface layer and in the electrochemical behaviour after implantation, which may change the biocompability of these materials. In a bending process four characteristic stress zones can be determined on the surface of the material (Fig. 1). max tensile (I), max compressive and cold work (II), compressive (III) and tensile and cold work zone (IV).

Only a few workers have attempted to analyze the effects of a prebending/rebending process on the susceptibility of surface layer (native and anodic) on implants made of Ti6Al4V to localized corrosion and on their behaviour in biological media [1,2,3]. In [4,5] authors present the cyclic deformation behaviour of the implant alloy TiAl6Nb7 in SBF. It has been shown [6] 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. Authors showed that the passive film formed in a tensile stress field [7] was richer in oxygen, poorer in molybdenum in the outer part and thicker than it is on the unstrained sample. On the other hand, the beneficial effect of a compressive stress was both attributed to the increasing chromium enrichment and the decreasing thickness of the passive film. Assumption that the deletorious 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 [8].

The purpose of this study was, therefore, to inspect and characterize the stress zones: tensile (I) and compressive (II), activated during shaping (bending and rebending) of anodized implant rods made of the Ti6Al4V alloy according the the typical procedures applied in the pre-operative stage of implantation and determine their electrochemical behaviour *in vitro*.

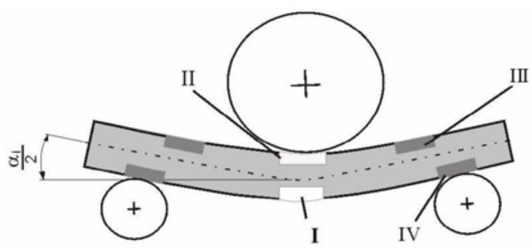

Fig.1. Zones of surface stress due to bending: (I)-max tensile, (II)-max compressive and cold working, (III)-compressive, (IV)-tensile and cold working stresses [1]

2. Materials and methodology

2.1. Specimens and methods

Specimens (dia 6mm) were prepared from cold drawn and annealed rods of the binary titanium implant alloy Ti-6Al-4V matching the ASTM F136-84. The test specimens were anodized according to patented method [9, 10]. Plastic deformation of specimens was performed according to the pre-operative shaping of spinal rods by bending and rebending with angles 20º and 20º×2, respectively. The comparative characteristics of two zones: the max tensile (I) and the max compressive stress (II) was based on the determination of mechanical and electrochemical properties. The finite element method (FEM) was used to evaluate and compare the stress profiles in both zones, whereas the mechanical properties determined in microhardness tests. In the present study, aerated Ringer's solution at pH=7.4 was used for all test procedures. 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}). Subsequently, the potentiodynamic polarization curves were obtained with a scan rate of 1 mV/s from E_{corr} to 5500 mV (SCE). The investigations of the EIS spectra were performed at the open circuit potential applying of 5mV (rms) vawe in 10^5 Hz÷0.18 Hz frequency range across the cell.

2.2. FEM

The analysis of stress and deformation in the plastic deformed samples of the Ti6Al4V alloy was performed according to Von Misses method using the ANSYS of 64.000 nodes software system. Because of the symmetry of the sample the analysis was applied only a half of the system. To achieve the desired bending angle the loading tools were forced to move along the determined trajectory. Results were expressed as Von Misses stresses (combined effect of the different stresses) and compressive and tensile stress in the x- and y-axes The elastic-plastic model of material alloy was adopted with the elastic parameters for the Ti6Al4V as follows: Young's modulus E=108 GPa and Poisson's coefficient ν=0.3. Analysis was performed for the yield strength $R_{0.2}$ = 820 MPa of material [11,12].

2.3. Microhardness

In order to compare the hardening of the tensile and compressive zones microhardness tests (according to PN-EN ISO 6507) were conducted using a tester PMT-3 and microhardness (HV) was determined using 0.196 N (0.02 kG) load. The distribution of the measurement points are illustrated in Fig. 2.

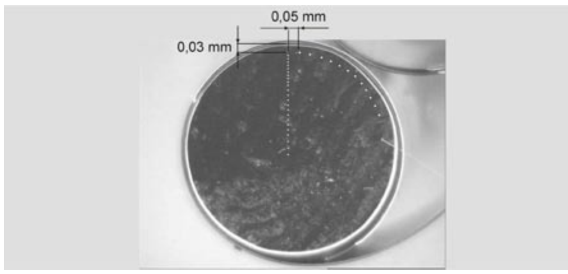

Fig. 2. Microhardness measurement points on cross section of the samples

3. Results and discussion

3.1. FEM

The finite element method (FEM), has the advantage of being applicable to solids of irregular geometry that contain heterogeneous material properties. It is, therefore, ideally suited to evaluate the structural behavior of the anodized rod (dia. 6mm), made of the Ti6Al4V alloy during bending (angle 20º).

In this case stresses extent to the rod core and reach the largest values in zones (I) and (II). The maximum value expressed as Von Misses stress (combined effect of the different stresses), which was noticed in the tensile zone exceeded 860 [MPa]. Results presented in Fig.3 show that according to Von Mises in the tensile zone (I) also the highest plastic deformation occur, which influence the structure and properties of surface layer.

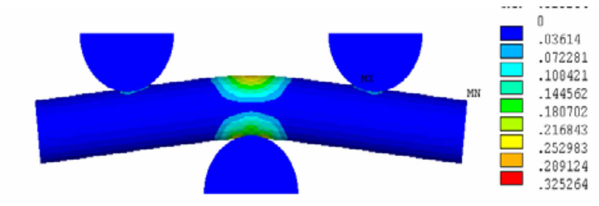

Fig. 3. Strain distribution in rod made of Ti6Al4V (bending angle 20º) Von Mises

3.2. Microhardness tests

The results of the microhardness testing of all samples indicate that the areas of the tensile stress (I) are characterized by lower values of microhardness (<350 μHV) in comparison to the microhardness of the compressive areas (~400 μHV) and non-deformed zones (~430μHV). The characteristic feature of tested areas is the non-homogenity of microhardness observed when rebending is applied (Fig.4). Values of microhardness decrease towards the core of the rod. Hardening of material caused by compressive stress (II) is observed to the depth of 1 mm and disappear below 0.33 mm from the surface.

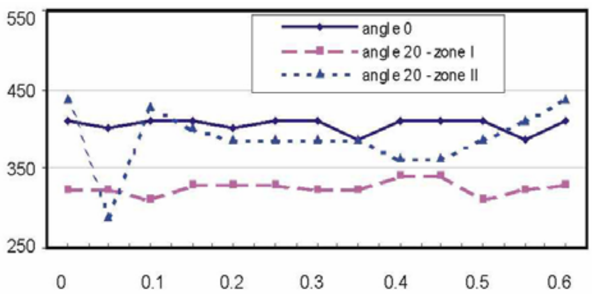

Fig. 4. Distribution of microhardnes values along perimeter sample in zone (I) and (II) for bent and non-deformed samples (bending angle 20°)

3.3. Electrochemical testing

Electrochemical tests clearly indicate the relantionship between values of corrosion potential E_{corr} and both the type of stress and bending condition. Deformation of surface layers, results in decrease of E_{corr} in both zones from 520 mV (SCE) to 362÷349 mV (SCE) for bent samples and to 338÷316 mV (SCE) for rebent samples. In both cases the tensile zones (I) are also characterized by lower E_{corr} values in comparison to the compressive ones.

In order to compare the susceptibility to corrosion of the anodised samples deformed by bending in relation to the non-anodised and non-deformed samples, the anodic polarization potentiodynamic curves of all samples in Ringer's solution were recorded. The polarization curves in Fig.5 show the same passivity region for all examined samples.

When the open circuit potential is reached, the samples quickly enter the passive region, without exhibiting well-defined active or active/passive transition regions. Some differences can be observed when considering the potential dependence of the passive currents of deformed samples. As the applied potential is made more positive both deformed samples show small peaks at about 1800 mV (SCE) and an increase of current in the whole measuring potential window. The passive current is almost one order of magnitude higher for the tensile zone (I) than for the compressive zone (II). These currents continued to increase linearly and did not exhibit a breaking potential or a transpassive behavior within the range of potentials up to 5.5 V (SCE).

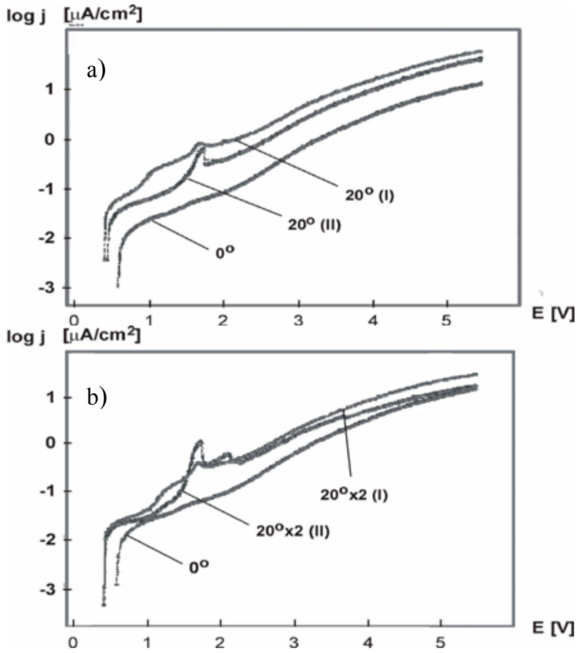

Fig. 5. Anodic polarization curves for tensile (I) and compressive (II) zones on the surface of the Ti6Al4V alloy anodized samples: a) after bending, b) after rebending (angle 20º); curves for non-deformed sample included for comparison

The impedance spectra (Fig.6) vary in relevant parameters of the surface layers of different stress zones. Spectra for compressive (II) stress zones exhibit two time constants, whereas spectra for tensile (I) zones one time constant, respectively. Moreover, both spectra for the tensile zones (I) show lower values of R_s from ohmic resistance due to the electrolytic solution and the impedance characteristics resulting from the penetration of the electrolyte through a porous film to uncovered metal under deformed anodic layer. Such a behavior is typical of a metallic material covered by a porous film which is exposed to an electrolytic environment. Both observations indicate breaking of surface films in tensile zones of the samples. The values show that the deformation of material due to bending causes the change of R_s values (the resistance of the electrolyte in pores). The corresponding values of R_s are the highest in the tensile zones of twice bent samples. Due to bending the values of R_{bl} (the resistance of a barrier layer on the surface of material) decrease, whereas both capacities the C_{bl} (the capacity of the barrier layer) and the C_{pl} (the capacity of porous layer) increase. Comparing the zones of the tensile (I) and the compressive (II) stresses in the investigated samples it is clear that the former show much lower protecting properties, whereas compressing does not influences so evidently the barrier effect of anodic layer. All these changes indicate that large bending stresses lowers the corrosion resistance of material and confirm that damages caused by bending influence the barrier properties of surface layer.

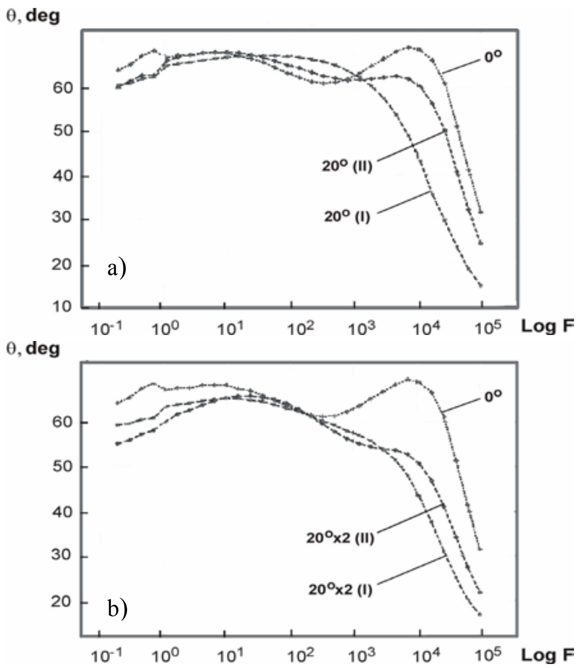

Fig. 6. Impedance spectra for the tensile (I) and compressive (II) zones of the Ti6Al4V alloy sample: a) bending, b) rebending

4. Conclusions

Results of the work confirm that the areas of different mechanical and electrochemical properties are formed on the surface of the Ti6Al4V sample during bending.

The change of surface properties depend on the kind of stresses produced in the deformed material. The most deleterious effect of bending was observed in the zone of the largest tensile stresses and the corresponding deformations assigned by FEM analysis, where also the lowest microhardness and the lowest corrosion potential values were determined. The results of electrochemical examinations revealed that during bending in the zone of tensile stresses the surface anodic layer breaks and its the characteristic two-layer structure turns into a one layer porous film with pores (microcracks) reaching the metal. However, titanium alloys are susceptible to passive layer regeneration in media and show higher susceptibility of being hydroxyapatite [1]. Thus, the question of the influence of external loads the "self-repairing" processes of anodic layers on titanium alloys is still open and studies on this issue are in progress [13].

As the plastic deformations may decrease the fatigue strength, particularly in the presence of the tensile stresses [14, 15], also the multicyclic tests with physiological loads are planned.

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