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Fatigue and cyclic deformation behaviour of surface-modified titanium alloys in simulated physiological media

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Abstract

In this investigation, the cyclic deformation behaviour of the binary titanium alloys Ti-6Al-4V and Ti-6Al-7Nb was characterized in axial stress-controlled constant amplitude and load increase tests as well as in rotating bending tests. The influence of different clinically relevant surface treatments (polishing, corundum grit blasting, thermal and anodic oxidizing) on the fatigue behaviour was investigated. All tests were realized in oxygen-saturated Ringer's solution. The cyclic deformation behaviour was characterized by mechanical hysteresis measurements. In addition, the change of the free corrosion potential and the corrosion current during testing in simulated physiological media indicated surface damages such as slip bands, intrusions and extrusions or finally microcracks. Microstructural changes on the specimen surfaces were examined by scanning electron microscopy (SEM).

Keywords: Titanium alloys; Surface modification; Titanium oxide; Surface roughness; Corrosion fatigue

1. Introduction

The fatigue strength, the low specific weight and the corrosion resistance of titanium alloys are important properties for their use as aerospace materials as well as for medical applications as implant materials. In comparison with other metals, titanium alloys exhibit an advantageous combination of excellent biocompatibility and high mechanical properties, which qualifies them as materials for load-bearing implants. Their excellent biocompatibility is assumed to be due to the formation of a dense and stable TiO_2 layer, which rebuilds spontaneously after being damaged, even in solutions with low oxygen contents [1–4]. In order to improve the bioadhesion and the corrosion behaviour, titanium implants are often surface modified, for example by surface roughening, oxidation or coating techniques [5–7]. These surface treatments can influence the mechanical properties of the implant alloy [8–10]. The integration behaviour can be influenced by structural and morphological changes of the implant surface. Thus, the in situ detection and characterization of mechanically induced surface damages such as fatigue cracks is of major interest to satisfactorily predict the long term in vivo behaviour of implant materials.

Despite their physiological and mechanical relevance a possible influence of the highly complex in vivo loading conditions on the cyclic deformation behaviour of these alloys has hardly been considered yet. In particular, work on the fatigue behaviour of titanium implant alloys with clinically relevant surface conditions is rather scarce. Former work dealt mainly with different aspects limited to fatigue life and crack growth [11,12], whereby the measurement of the free corrosion potential allowed the detection of surface damage in axial or rotating bending fatigue tests of passivating metals, such as stainless steels or titanium alloys in saline solutions [13,14]. In addition, current measurements are often used to study local

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corrosion effects on metallic materials such as crevice or pitting corrosion [15–17]. In some cases, potentiostatically controlled current measurements were used to gain information on fatigue-induced surface damages on stainless steels in corrosive media [18,19]. Load increase tests in combination with mechanical hysteresis measurements allow to determine the endurance limit of a material with a very limited number of specimens [20]. In this work, the cyclic deformation behaviour of the implant alloys Ti-6Al-4V and Ti-6Al-7Nb with different clinically relevant surface conditions was characterized in rotating bending tests as well as in axial constant amplitude tests and load increase tests in Ringer's solution.

2. Materials and methods

2.1. Materials

Cylindrical specimens were machined from hot and cold drawn rods of the binary titanium implant alloys Ti-6Al-4V and Ti-6Al-7Nb, which corresponded to the requirements of DIN ISO 5832 parts 3 and 11. Two batches of each alloy with slightly different mechanical properties supplied by different manufacturers, designated (C) and (E), respectively, were considered. The chemical composition and the monotonic properties are listed in Tables 1 and 2. Both alloys show very high yield and tensile strengths, $R_{p0.2}$ and R_m, and ductility, A_5. The (C)-batches were used for axial fatigue specimens. Rotating bending specimens were taken from the (E)-batches.

2.2. Surface preparation

In order to compare different surface conditions, the specimens were mechanically polished (pol), corundum grit blasted (cgb) or thermally (to) and anodically (ao) oxidized. The mechanically polished surfaces were finally polished with 0.25 μm SiO_2 suspension, whereby surface roughness values of $R_a = 0.03$ μm were achieved. The machining and mechanical polishing-generated surface-compressive residual stresses of approximately −406 MPa (Ti-6Al-4 V) and −340 MPa (Ti-6Al-7Nb), respectively, as determined with the $\sin^2\psi$-method (cf. Table 3). Grit-blasted surfaces on Ti-6Al-4 V specimens were produced using an air shot peening device and Al_2O_3 (corundum) shot with a mean particle size between 0.5 and 1 mm. Oxide films were generated on Ti-6Al-7Nb specimens. Thermal oxidation was performed on the polished specimens in a laboratory furnace in air at 675 °C for 180 min. Anodically oxidized specimens were produced after polishing under galvanostatic conditions in 1 M H_2SO_4 at room temperature. During the oxidation, the constant current density of 10 mA/cm^2 resulted in a permanently increasing potential. The power supply was immediately switched off at a final potential of 40 V.

Table 1
Chemical composition of the investigated Ti-6Al-4V and Ti-6Al-7Nb alloys

[wt.−%]	C	*N*	Al	O	Fe	V/Nb	H
Ti-6Al-4V (C)	0.012	0.005	5.88	0.11	0.12	3.97/—	0.0019
Ti-6Al-4V (E)	0.02	0.01	6.04	0.105	0.18	4.02/—	0.0047
Ti-6Al-7Nb (C)	0.01	0.008	5.85	0.185	0.125	—/6.90	0.003
Ti-6Al-7Nb (E)	0.01	0.004	6.03	0.175	0.13	—/7.17	0.0022

Table 2
Monotonic properties of the investigated Ti-6Al-4V and Ti-6Al-7Nb alloys

Alloy	$R_{p0.2}$ (MPa)	R_m (MPa)	A_5 (%)
Ti-6Al-4V (C)	880	960	18.5
Ti-6Al-4V (E)	865	1020	15
Ti-6Al-7Nb (C)	875	967	16.5
Ti-6Al-7Nb (E)	882	1070	16.6

2.3. Experimental techniques and loading parameters

2.3.1. Surface characterization

The chemical composition at the specimen surfaces was characterized by Auger electron spectroscopy (AES, Perkin Elmer SAM 600). Element depth profiles could be determined by solid state sputtering using an Ar^+-ion gun with a maximum accelerating voltage of 5 kV. Fourier transformation infrared spectroscopy (FTIR) was used to characterize the structure of oxidized specimens (IFS 66 v/s, Bruker). The measurements were carried out in the reflection mode at an angle of 70° with p-polarized light. A Philips XPert X-ray diffractometer (Philips Analytical B.V.) was used to measure surface residual stresses on specimens with different surface conditions. All measurements were performed using Cr-K_α radiation ($\lambda = 0.229$ nm). The surface residual stresses were determined by the $\sin^2\psi$-method. The elastic lattice strains were measured for the (10–13) plane ($2\theta = 118.52°$) in the range $116° \leqslant 2\theta \leqslant 122°$ in the positive and negative ψ-direction between +60° and −60°.

2.3.2. Fatigue tests

The axial fatigue tests were performed on a Schenck servo-hydraulic testing system. Data were recorded by means of a software based on LabView programmed at the Institute of Materials Science and Engineering, University of Kaiserslautern. The axial stress-controlled constant amplitude tests were performed at a frequency of 5 Hz and a load ratio of $R = -1$. Furthermore, the cyclic deformation behaviour was investigated in stepwise load increase tests. The initial stress amplitude of 300 MPa was increased by 25 MPa every 20,000 cycles over a period of 1000 cycles. Single-step rotating bending tests at a frequency of 10 Hz were performed on a Schenck PUP Simplex rotating bending machine. All fatigue tests were performed in oxygen-saturated Ringer's solution at 37 °C. At the beginning of the tests the pH-value was set to 7.4.

The cyclic deformation behaviour was characterized by the evolution of the plastic strain amplitude versus the number of cycles. Fatigue-induced surface changes were detected and characterized by corrosion potential and current measurements. The free corrosion potential is measured between the working electrode (WE, specimen) and the reference electrode (RE, Argenthal Ag/AgCl, +207 mV to standard hydrogen electrode (SHE)). To determine the free corrosion current, the WE is connected with a counter electrode (CE) via a low noise multimeter. The CE is a specimen consisting of the same material with the same surface condition as the working electrode. Consequently, both electrodes are on the same electrochemical potential versus the RE while the surface of the loaded specimen is undamaged. This experimental setup allows the simultaneous detection of the corrosion current and potential in open circuit conditions. The principles of the electrochemical techniques have been described elsewhere in greater detail [13,14]. Fig. 1 shows schematically the experimental setup for axial fatigue tests. All testing parameters are summarized in Table 4.

3. Results

3.1. Surface conditions

3.1.1. Corundum grit blasted specimens

The SEM micrograph in Fig. 2(a) shows the coarse surface structure of a grit-blasted specimen. Due to their