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Wear behaviour of NiTi shape memory alloy after oxygen-PIII treatment

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Abstract

Super-elastic Nitinol (NiTi alloys) is predestined for major biomedical applications as its mechanical properties are more closely matched to those of living bones than titanium alloys. Using suitable surface modifications, it is possible to form pure titania (rutile) surface layers, thus prohibiting the outdiffusion of toxic nickel cations. The wear behaviour and the lifetime of such surface layers, produced by oxygen plasma immersion ion implantation (PIII) at 25 kV and 250–550 °C sample temperature, are measured and compared to that of untreated NiTi. Ball-on-disc tests with intermittent impact loading revealed a specific wear volume of the treated samples comparable to that of the base material, slightly lower and higher depending on the process conditions. An increased fatigue lifetime was found for lower temperatures and higher oxygen fluences, indicating that the layer thickness is not the decisive factor. Instead, internal stress relaxation and atomic rearrangement are proposed as the dominant mechanism.

Keywords: PIII; NiTi; rutile; wear; biocompatibility

1. Introduction

Biocompatibility is a concept which is very easy to understand while it is rather difficult to provide a succinct definition. In the regard of the osseointegration of metallic implants, several different features are identified to have an influence on the biocompatibility: (i) surface topography on the micrometer- and nanometer-scale, determining the adhesion of cells and receptor molecules [1,2]; (ii) the electronic density of state at the surface responsible for electron transfer and the distribution of the electrical potential, both effects which may interrupt normal cell behaviour [3]; (iii) the outdiffusion of metallic cations leading to toxic effects and apoptosis in the surrounding tissue, especially critical for Ni-containing metals [4,5] and (iv) the generation of wear particles and their transport, e.g. in macrophages towards a final agglomeration in the lung and spleen [6,7].

Using oxygen plasma immersion ion implantation (PIII), it has been shown that the surface topography [8,9], chemical composition and cation outdiffusion [10] can be beneficially controlled for NiTi alloys, leading to a much better biocompatibility than for untreated material. The effect of the treatment is the formation of a pure titanium oxide layer, facilitated by radiation enhanced diffusion, either of titanium towards the surface or of nickel towards the bulk. NiTi (or Nitinol) has superior mechanical properties as the elastic modulus and elastic strength are quite closely matched to those of cortical bone [11]. Additionally, displays of super-elastic behaviour resemble the hard tissue response [12], while the shape memory effect provides a natural fixation force. However, no data on the wear behaviour of such surfaces are available up to now. In this presentation, ball-on-disc tests with intermittent impact loading are presented to simulate a more realistic wear mode encountered by fixation elements in fracture surgery. This allows to derive the specific wear volume of the titania surface layers and a corresponding lifetime of these layers before failure as a function of PIII treatment parameters.

2. Experiment

The base material were flat NiTi coupons, grade SE-508 with a composition of 50.8 at.% Ti and 49.2 at.% Ni, polished to a mirror-like finish. Besides a thin oxide layer of less than 2 nm, a bulk oxygen content below 0.08 at.% is present in this material. Oxygen-PIII experiments were performed in a HV chamber

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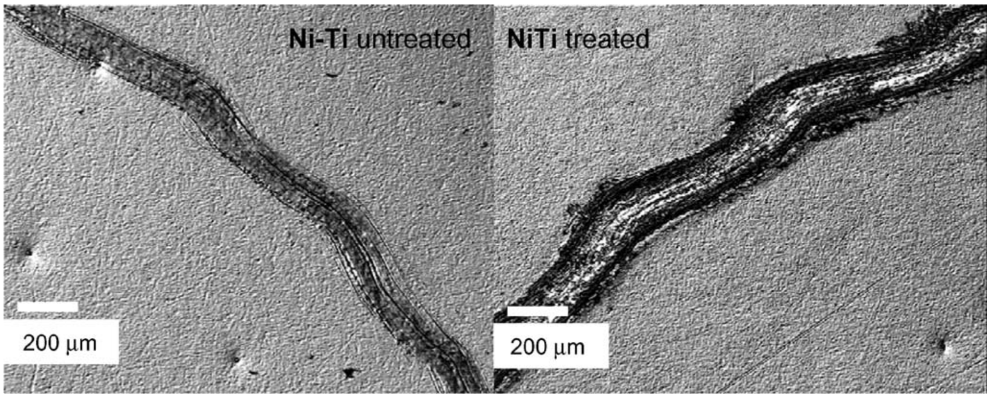

Fig. 1. Representative viewgraphs of wear tracks for an untreated and a treated NiTi sample.

equipped with an RF helix plasma source operating at a frequency of 40.68 MHz and a power of 150 W. The base and working pressures were 1×10^{-5} and 0.2 Pa, respectively.

Negative high voltage pulses of 25 kV with a rise time of 10 ns/kV and total length of 15 μs were applied to the sample at incident fluences between 7 and 21×10^{17} oxygen atoms/cm^2, as determined from the total number of pulses in a separate experiment [13]. The process temperature was between 250 and 550 °C, resulting in a total implantation time between 12 min and 1 h. A constant pulse repetition frequency was used for the initial heating phase up to the process temperature, while the process temperature was maintained by adjusting the repetition rate.

Elemental depth profiles were measured using elastic recoil detection analysis (ERDA) using 200 MeV $^{197}Au^{15+}$ ions at 19° incident angle and a detector placed at a scattering angle of 37° [14]. Additionally, spectroscopic ellipsometry was used to determine the thickness of the surface oxide layer. The phase composition was studied by X-ray diffraction (XRD) in Bragg–Brentano geometry using Cu K_α radiation, while the surface morphology was investigated by atomic force microscopy.

The wear tests were performed using a modified rotating ball-on-disc configuration with an alumina ball, diameter of 0.476 mm, in continuous sliding contact. A track diameter of 0.65 mm and a rotation speed between 50 and 200 rpm translates into a speed of 1.7–6.8 cm/s. The applied loads were between 0.66 and 9.07, corresponding to contact pressures of 0.42–1.0 GPa. The lateral intermittent loading was realized by mounting the load-bearing arm onto a spring so that a resonance of the mechanical system would be excited and a lateral deflection from a circular path, occurring several times in each rotational cycle, is present. Corresponding wear tracks are presented in Fig. 1 for an untreated and a PIII-treated NiTi sample. No influence of the sample on the oscillatory motion was found at constant speed and load. Special care was used to determine the specific wear volume from these data.

The fatigue lifetime was defined as the time when the progressive volume loss of the surface layer due to sliding friction changed into an abrupt film failure followed by a drastically increased wear rate as hard flakes were ploughed into the soft substrate. This transition was accompanied by an audible cracking sound and an increased friction coefficient, thus allowing a clear and distinct definition of this value. Despite the ion implantation process below the surface, a distinct layer system of TiO_2/Ni_3Ti/NiTi is present, thus validating the use of Griffith's [15] criterion of localized strain energy exceeding the adhesion energy at the layer interface in the present experiment.

3. Results

Fig. 2 presents ERDA data for one sample implanted at 400 °C with an incident fluence of 7×10^{17} O/cm^2. A deep oxygen profile at a Ti/O ratio of 1 : 2 followed by a sharp decay is observed in conjunction with a Ni depletion at the surface, followed by a Ni-enriched layer with a Ni/Ti ratio of 3 : 1. Near the end of the profile, limited by the depth range of the method, the original Ni/Ti ratio is observed again [10]. It has to be kept in mind that the width initial transition from TiO_2 towards Ni_3Ti is close to the depth resolution of the method. XRD data confirm this phase assignment from the chemical composition.

Supplementary secondary ion mass spectrometry investigations indicate a decay length, respective a rise length for oxygen and nickel near 5–15 nm/decade [16], so that an abrupt interface between these two regions cannot be excluded, thus allowing the use of a simple three-layer model (air–titania–substrate) to evaluate the spectroscopic ellipsometry data. The derived layer thickness as a function of implantation temperature and oxygen fluence is depicted in Fig. 3. A gradual increase of the layer

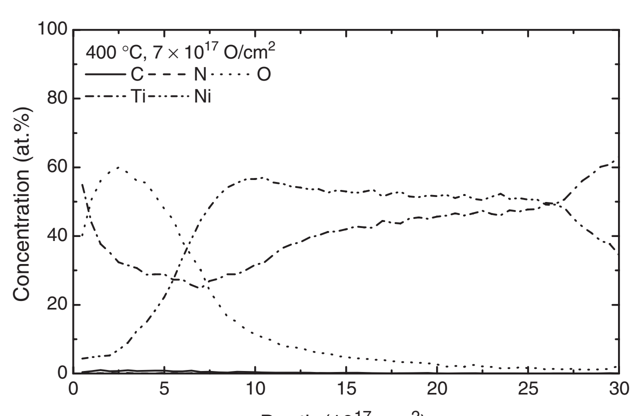

Fig. 2. ERDA depth profile of a sample implanted at 400 °C.