Influence of nanoscale surface modifications on the mechanical properties of medically relevant metals

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Introduction:

Metal implants used for various clinical conditions are relatively effective but they still need significant improvement with respect to their capacity to secure rapid and long-lasting integration in tissues. To address these challenges, different strategies have been developed to design metal surfaces in ways to directly affect the cellular events at the material-host tissue interface that ultimately determine the outcome of a biomedical implant. Chemical treatments such as oxidative nanopatterning and anodization proved to be very effective tools to endow metals (in particular titanium and Ti6Al4V, the gold standards in implantology) with the ability to guide *in vitro* and *in vivo* cellular events. This unique capacity results from the creation of distinctive nanoporous surfaces (sponge-like structures in the case of oxidative nanopatterning, nanotube arrays in the case of anodization) capable of exerting advantageous physicochemical signaling to adhering cells. To date, the majority of studies on these subjects focused on the biological response. Only a few, however, concentrated on mechanical aspects, fundamental prerequisites to ensure that such chemical approaches do not weaken mechanical properties of treated metals. Nanoporous structures could in fact act as surface defects and/or stress-raisers responsible for initiating crack nucleation and ultimately increasing the probability of premature failure under typical *in vivo* cyclical loads. To elucidate this aspect, we have assessed the effects of oxidative nanopatterning and anodization on the fatigue resistance of titanium and Ti6Al4V. In particular, we aimed at investigating the fatigue performance of treated metals and compared it to that of mechanically polished controls, from both a quantitative (i.e. cyclic stress (S) - cycles to failure (N) curves) and qualitative (i.e. morphological Scanning Electron Microscopy analysis) perspective. Results from our study highlight the importance of mechanical considerations in the development and evaluation of nanoscale surface treatments for metallic implants.

Materials and Methods:

Titanium (CpTi, grade 2) and Ti6Al4V 0.125"×3'rods were utilized for this study. As received samples were then machined in order to meet the international standards of the American Society for Testing and Materials (ASTM) (E466-07 Standard, Practice for Conducting Force Controlled Constant Amplitude Axial Fatigue Tests of Metallic Materials). Successively, a 3-step mechanical polishing was carried out first by 1200 and subsequently 4000 grit silicon carbide sandpapers and lastly by a cloth soaked in a mixture of 0.05 μm colloidal silica suspension and hydrogen peroxide (H_2O_2). Polished CpTi and Ti6Al4V according to previously published experimental protocols. For oxidative nanopatterning, samples were immersed in a solution of concentrated (96%) sulfuric acid (H_2SO_4) and H_2O_2 for 2 hours and 30 minutes under moderate stirring. In the case of anodization, samples (anode) were immersed in a stainless steel beaker (cathode) containing a 0.5% hydrofluoric acid (HF) solution, and connected to DC power supply operating at 20 Volts for 30 minutes. Fatigue tests were carried out by using an Instron All-Electric ElectroPuls E3000 with the maximum dynamic capacity of ±3KN and maximum frequency of 100Hz. Morphological investigation of pristine and modified samples prior and after fatigue testing was carried out by Scanning Electron Microscope (JEOL, JSM-7500F).

Results:

Quantitative fatigue tests revealed that mechanical polishing, oxidative nanopatterning and anodization did not affect the S-N curves of cpTi. The logarithmic interpolation of the stress and number-of-cycles-to-failure values showed in fact no significant differences among these three surface treatments. However, in the case of the Ti6Al4V alloy, the S-N curves showed that, compared to polished samples, both oxidative nanopatterning and anodization impacted negatively the fatigue resistance. Lower number-of-cycles-to-failure values at a given stress were recorded for anodized alloy samples. Although S-N curves provided valuable information about the fatigue behavior, morphological and fractographical analyses were required to better understand the characteristics and mechanisms of the fatigue failure, such as crack nucleation and propagation. To this end, SEM investigation allowed to identify crack initiation sites and propagation paths on the fracture surface. Beachmarks and striations at the fractured surfaces were also imaged, providing additional evidence of fatigue nature of the failure. Morphological analysis also permitted to assess the effects of cyclic loads on the integrity of the superficial nanostructured oxide layers. Samples subjected to oxidative nanopatterning were characterized by micrometric cracks which initiated and propagated across the oxide and the metal. No evidence of damages of the oxide layer only was observed. The nanotubular oxide layer resulting from anodization exhibited however cracks. As approaching the fracture surface, isolated cracks joined together to generate bigger crevices, ultimately yielding significant exfoliation of the oxide layer, with islands of intact nanotubes surrounded by the bare metal. Stress analysis revealed that the first cracks formed at about 2.1±0.48 mm (corresponding to 241±29 MPa) and 1.4±0.35 mm (corresponding to 638±50 MPa) from the fracture surface, for nanopatterned cpTi and Ti6Al4V, respectively. In the case of anodized cpTi and Ti6Al4V, the initiation of cracks on the oxide occurred at 2.3±0.26mm (corresponding to 237±28 MPa) and 1.25±0.52 mm (corresponding to 658±28 MPa), respectively. The surface fraction of delaminated nanotubes from the surface of the metal was quantified by image analysis. While delamination did not appear to be a function of the position/stress along the axis of Ti6Al4V samples, in the case of cpTi, the fraction of delaminated nanotubes increased from the site where the first cracks were observed towards the fracture surface.

Discussion:

In this work, we have investigated the effects of surface treatments (i.e. mechanical polishing, oxidative nanopatterning and anodization) on the response of CpTi and Ti6Al4V to cyclic loads. Results from this study show that surface modification approaches do not impact the fatigue resistance, assessed by S-N curves, of CpTi. However, in the case of the Ti6Al4V, samples subjected to oxidative nanopatterning and anodization showed lower number-of-cycles-to-failure values at a given stress. This is likely related to the biphasic structure of the alloy, characterized by α-phase grains (richer in Aluminum) surrounded by smaller β-phase ones (richer in Vanadium). The latters showed a higher susceptibility to chemical treatments, which resulted in the creation of micrometric cavities which likely acted as stress raisers or crack initiation sites, ultimately deteriorating the fatigue resistance of the material. We have also determined that while the nanoporous oxide layer resulting from oxidative nanopatterning did not exhibit evident damages, the one resulting from anodization underwent significant exfoliation, likely because of its greater thickness. In conclusion, our investigation suggests that chemical treatments aimed at generating surface nanostructures on Ti6Al4V should be applied with care in order not to decrease the fatigue life of the material. In addition, the thickness and physical properties of nanostructured oxide layers should be carefully designed to avoid exfoliation and therefore the production of potential dangerous debris.