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Corrosion resistance and mechanical properties of titanium with hierarchical micro-nanostructure

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ABSTRACT

The hierarchical micro-nanostructure has been proved to endow titanium (Ti) surface with good biological properties. However, to achieve satisfied osseointegration, good corrosion resistance and mechanical properties are also necessary. Therefore, in this paper, the corrosion resistance and mechanical properties of the Ti implant with hierarchical micro-nanostructure were investigated. The corrosion resistance was detected by polarization curve test, and the mechanical properties were evaluated by friction-wear experiment and nano indentation test. The results showed that the micro-nanostructured Ti surface showed increased corrosion potential, and it also showed decreased friction coefficient, stiffness and Young´s modulus, similar to that of the cortical bone. The improved corrosion resistance and mechanical properties might endow the micro-nanostructured Ti implant with good osseointegration and promising application in clinic.

1. Introduction

Titainium (Ti) is the most widely used orthopaedic and dental implant material due to its mechanical strength and biocompatibility. However, problems with their surface that lack sufficient osseointegration have also been gradually realized and need to be solved. The unsatisfied osseointegration of Ti usually results from its poor bioactivity, corrosion resistance and mechanical mismatch problems with bone tissues [1–3]. The bioinertness of Ti usually leads to the formation of fibrous tissue between implant and bone, raising the potential risk of loosening in the long-term usage. The poor corrosion resistance leads to the dissolution of Ti into the human body, which not only adversely affect the healing of bone tissues, but also can intensify the release of inflammatory cytokines, and sometimes even lead to the acute or chronic inflammation and implant loosening [4]. And the mechanical force interaction at the cell-implant interface is a critical indicator for implant stability and longevity. The mechanical mismatch (e.g. high Young's modulus of Ti) cannot provide proper mechanical stimulus for sensor cells such as bone lining cells of osteoblastic origin and osteocytes, resulting in that the cells cannot generate sufficient biochemical signals to transduce the obtained mechanical signal and modulate bone formation and resorption [3]. Therefore, improving the bioactivity, corrosion resistance and mechanical mismatch problems of Ti to enhance osseointegration are basic and indispensable demands in clinic.

The surface morphology is known to play key role in determining the osseointegration of biomedical implants. In our previous work, different structures (micro-structure, nanostructure, micro-nanostructure) have been prepared on Ti surface by acid etching and anodic oxidation, and the hierarchical micro-nanostructure is proved to have the optimal bioactivity and biocompatibility when compared with the other surface structures [5]. In this study, the influence of the hierarchical micro-nanostructure on corrosion resistance and mechanical properties of Ti was also investigated and compared with that of the other surface structures, with an aim of shedding light on how the surface structure influence osseointegration, achieving the satisfied Ti implant material.

2. Materials and methods

2.1. Sample preparation

Samples were prepared according to the procedure previously reported [5]. Briefly, pure Ti (TA1, 10 mm × 10 mm × 1 mm) was used as the substrate. After polished by #1000 SiC sandpapers, the

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Ti substrates were immersed in 3 wt% HF solution for 2 min to dissolve the air-formed oxide film on their surface (referred as polished Ti). The polished Ti samples were then etched in a 66% H_2SO_4 solution for 5 min at 80 °C to form microstructures on the surface (referred as Micro-Ti) and then, the Micro-Ti was treated by anodic oxidation in the electrolyte of ethylene glycol containing 0.4 wt% NH_4F to achieve the hierarchical micro-nanostructure (referred as Micro-nano-Ti). For comparison, the nanostructured Ti surface was also prepared and used as a control group (referred as Nano-Ti, prepared by anodization of the polished Ti). The experimental details can be found in our previous papers [5,6].

2.2. Wear resistance measurements

The friction and wear properties of the disk specimens of 60 mm in diameter were investigated on a Universal Micro-Tribometer tester (SFT-2M, China) using pin-on-disk contact configuration. The experiments were carried out at room temperature under dry sliding conditions using an HV-750 microsclerometer (Gr15) in diameter of 3 mm. The rotating speed and radius were separately set at 200 rpm and 5 mm, and a normal load of 10 N and rotating time of 2 min were applied during the experiment. The friction coefficients were continuously recorded with sliding distance and directly displayed on the tester.

2.3. Nanomechanical test

Mechanical properties of the Ti samples with different surface structures were performed in a TriboIndenter instrumented nanoindenter (from Hysitron, Minneapolis, MN) using a diamond Berkovich indenter. Indentations were made with applied loads up to 10 mN, and hardness was determined by the Oliver–Pharr method [7], with the instantaneous contact area determined using the calibrated area function of the Berkovich tip. The Young's modulus of the surface was calculated from nanoindentation tests through the Sneddon's equation [8].

2.4. Corrosion resistance evaluation

The corrosion behavior of the sample surfaces were examined by potentiodynamic polarization tests [9]. Polarization measurements started after the samples were immersed in the simulated body fluid (SBF) for 30 min under open-circuit conditions. The ionic concentrations in SBF are nearly equal to those in human blood plasma. It was prepared according to the reference [10]. The potential scan started with a potential that was 100 mV more cathodic than an open-circuit potential (OCP), which then increased towards the anodic values at a constant rate of 10 mV/s and stopped when the breakdown potential (Ebr) was achieved.

3. Results and discussion

Fig. 1 showed the surface morphologies of the Ti samples with different surface structures. It can be seen that, the polished Ti showed a smooth and flat surface without obvious topographic features (Fig. 1a). After anodization, the surface was roughened and the tubular structures can be obviously observed, as shown in Fig. 1b. While, for the Micro-Ti samples which was only treated by acid etching, micro-sized topographic features (ridges and valleys) appeared on their surface (Fig. 1c). And for the Micro-nano-Ti samples, the characters of nanotubes, ridges and large valleys were all presented on the surface (Fig. 1d), confirming that the structure of Nano-Ti was superimposed on the structure of the Micro-Ti.

To evaluate the effects of surface structure on the wear resistance of Ti samples, we measured the friction coefficient of the different Ti samples using Micro-Tribometer tester and the results were displayed in Fig. 2. Compared with the polished-Ti and Micro-Ti samples, the Micro-nano-Ti and Nano-Ti samples have a relatively lower friction coefficient, indicating the positive influence of the anodization on the wear performance of the Ti. Yetim et al. [11] has reported that the anodic oxidation at lower temperatures produced oxide film with higher hardness, and the wear rate of Ti significantly decreased in all wear conditions since oxide film acted like a solid lubricant. In fact, the stresses due to the volume change accompanying the anodic oxidation might also play key role in the improvement of wear resistance. Our research results are in good agreement with the literature.

The stiffness values and Young's modulus of the cortical bone and Ti samples with different surface structures were summarized in Fig. 3. It can be seen that, the stiffness values and Young's modulus of the polished Ti are far from those of cortical bone, confirming the mechanical mismatch between cortical bone and Ti implant. After acid etching and anodic oxidation, the Micro-Ti and

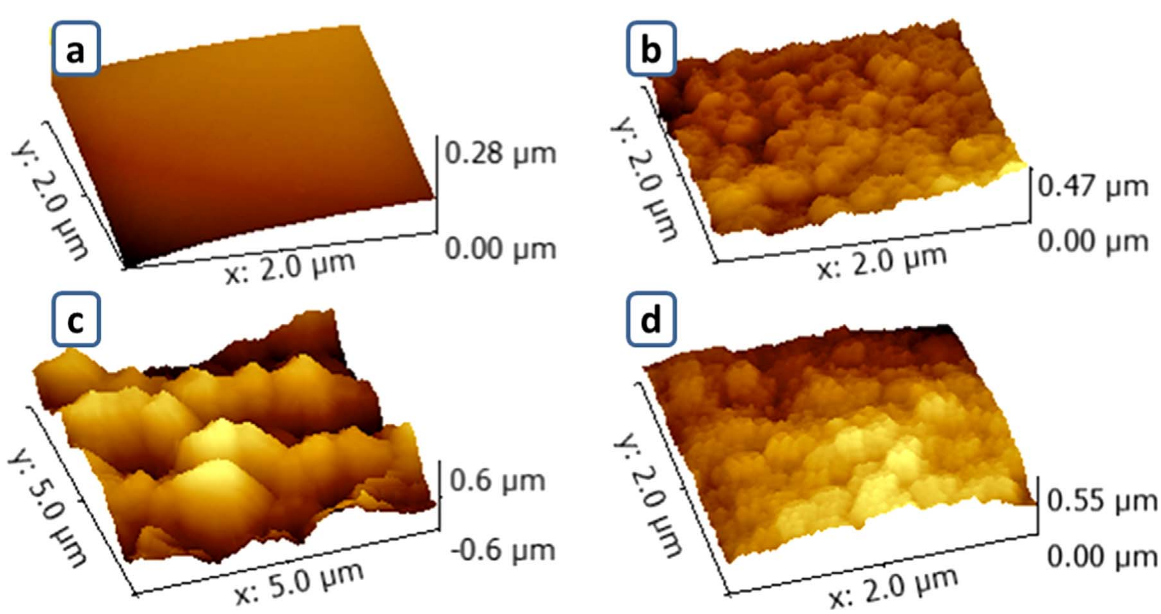

Fig. 1. Surface morphologies of the polished Ti (a), Nano-Ti (b), Micro-Ti (c) and Micro-nano-Ti (b).