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Morphology and chemical characterization of Ti surfaces modified for biomedical applications

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Abstract

The aim of the present work is to characterize in detail the chemical composition and morphology of titanium surfaces subjected to various environments. Modifications consisted of exposure of Ti to acidic, alkaline or polymer solutions. Such modifications result in chemical and/or morphological changes in the Ti surface. Special attention has been given to identifying the factors influencing cell adhesion and growth.

SEM examinations provided morphological characterization of the Ti samples. Surface analytical techniques such as AES or XPS combined with Ar^+ ion sputtering allowed examination of the chemical properties of the Ti surface after chemical pretreatments and investigating the chemical composition of the Ti oxide layer. Raman spectroscopy investigations allowed determination of the crystalline phases of the Ti-oxide layers and characterization of the dextran-modified surface.

The results show large differences in the morphology of Ti pretreated with different procedures whereas only minor differences in the chemistry of the surfaces were found. High-resolution Auger investigations have revealed that all the chemical modifications of Ti surfaces resulted in the formation of a titanium oxide layer. XPS confirmed that TiO_2 is the main component of the chemically modified Ti surface. The Raman spectroscopy investigations showed that the titanium surface with a dextran coating is rich in hydroxyl groups. All the surfaces investigated exhibit a hydrophilic character. The possible influence of various surface features on surface biocompatibility is discussed.
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1. Introduction

Titanium is known as a good biomaterial for various medical applications. In bulk form, it is used for the fabrication of implants (Pohler, 2000), whereas in the form of porous structures, it serves as a support for living cells (Spoerke et al., 2005). Biomedical applications of pure titanium are possible due to certain properties, such as relatively high mechanical strength and fatigue resistance (Rack and Qazi, 2006), good corrosion resistance and biocompatibility (Kasemo, 1983). Some of these properties, in particular the biological response of titanium, are strongly determined by the surface characteristics—its morphology, chemistry and physical properties. Surface properties may be changed by applying various surface modifications while the crucial bulk properties such as tensile strength and fatigue resistance remain unchanged.

There are many physical and chemical methods that can be used in the functionalization or activation of a surface; a relevant review can be found elsewhere (Liu et al., 2004). Among these methods, chemical modifications seem to be relatively simple and inexpensive. In addition, they may control the surface characteristics over a broad range. It has been discovered that the contact of cells with materials of different morphology and chemistry results in a modification of their shape and bioactivity of the cells (Anselme, 2000; Boyan et al., 1996). However, the morphological and chemical factors responsible for the stable growth of cells are still not well known. Bearing this in mind, the aim of the present work is to compare various chemical modifications of a titanium surface in terms of chemical composition and morphology.

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2. Experimental

For the investigations a pure titanium (Grade 2) was used in the form of a 6 mm rod cut into cylinders 2 mm in thickness. The samples were polished, degreased with detergent and rinsed in distilled water. Next, they were subjected to four different chemical surface modifications: (1) etching in a ''piranha'' solution (98% H_2SO_4 + 30% H_2O_2 mixture, the volume ratio 1:1) at room temperature for 4 h (this pretreatment is assigned as PRT), (2) etching in ''piranha'' boiling solution (PBS) for 10 min, (3) soaking in 5.0 M NaOH aq. at 60 °C for 24 h, washing in deionized water at 40 °C for 48 h, heating with a rate of 5 °C/h up to 600 °C, annealing at this temperature for 1 h, and then cooling with a furnace (this pretreatment is assigned as SH, standing for sodium hydroxide), and (4) immersing in a water dextran solution (0.05 wt.%) for 10 min (assigned as D, standing for dextran). An unmodified titanium surface was used as a reference.

Morphology of the modified titanium surfaces was examined by a scanning electron microscope (SEM, S-3500N, Hitachi). The chemical compositions of the modified surface layers were analyzed by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) (Briggs and Grant, 2003). For this purpose an Auger microprobe analyzer, a Microlab 350 (Thermo Electron) with XPS optional function was applied with a lateral resolution of about 20 nm for AES and several mm for XPS. The chemical state of the surface species was identified using the high-energy resolution of the Auger spectrometer (the energy resolution of the spherical sector analyzer is continuously variable between 0.6% and 0.06%) and of the XPS spectrometer (the maximum energy resolution is 0.83 eV). Appropriate standards for AES and XPS reference spectra were also used. XPS spectra were excited using Al Kα ($h\nu$ = 1486.6 eV) radiation as a source. The measured binding energies were corrected referring to the energy of C 1s signal at 285 eV. An Avantage based data system was used for data acquisition and processing. The crystalline phases of the layers were identified by Raman spectroscopy. Spectra were recorded on a Nicolet Almega XR apparatus (laser: 532 nm; exposure time: 30 s; laser power: 25 mW; spectrograph aperture: 50 μm pinhole). In order to evaluate the wettability of the modified titanium surfaces, contact angle measurements were carried out at a constant room temperature. A given volume of DMEM (Dulbecco's Modified Eagle Medium) was placed on the surface in order to form a drop. Then, the contact angle was measured on both sides of the drop using the goniometric method.

3. Results

Fig. 1 shows SEM images of titanium surfaces. In the as-received state characteristic, oriented grooves resulting from grinding can be seen (Fig. 1a). The morphology of the polymer-coated surfaces (Fig. 1b) is similar to that in the as-received state. The soaking in NaOH aq. solution (SH) results in a developed morphology similar to a ''honeycomb'' (Fig. 1c). The surface layer seems also quite porous. Pores of diameter 0.1–0.2 μm are well visible in the ''honeycomb'' islands, surrounded by elongated depressions and cracks, several μm long and about 0.5 μm wide. After etching in ''piranha'' solution at room temperature (PRT) or in boiling ''piranha'' solution (PSB) the morphology is quite different and less developed than that produced in the SH pretreatment. However, sub-microporosity effects on the ''piranha'' treated surfaces can also be seen, e.g. in boiling ''piranha'' solution a high population of shallow depressions about 0.5–1 μm in diameter is formed (Fig. 1d).

In order to determine the chemical composition of the titanium surfaces before and after modification, an AES study was performed. The AES survey spectra taken from the surface

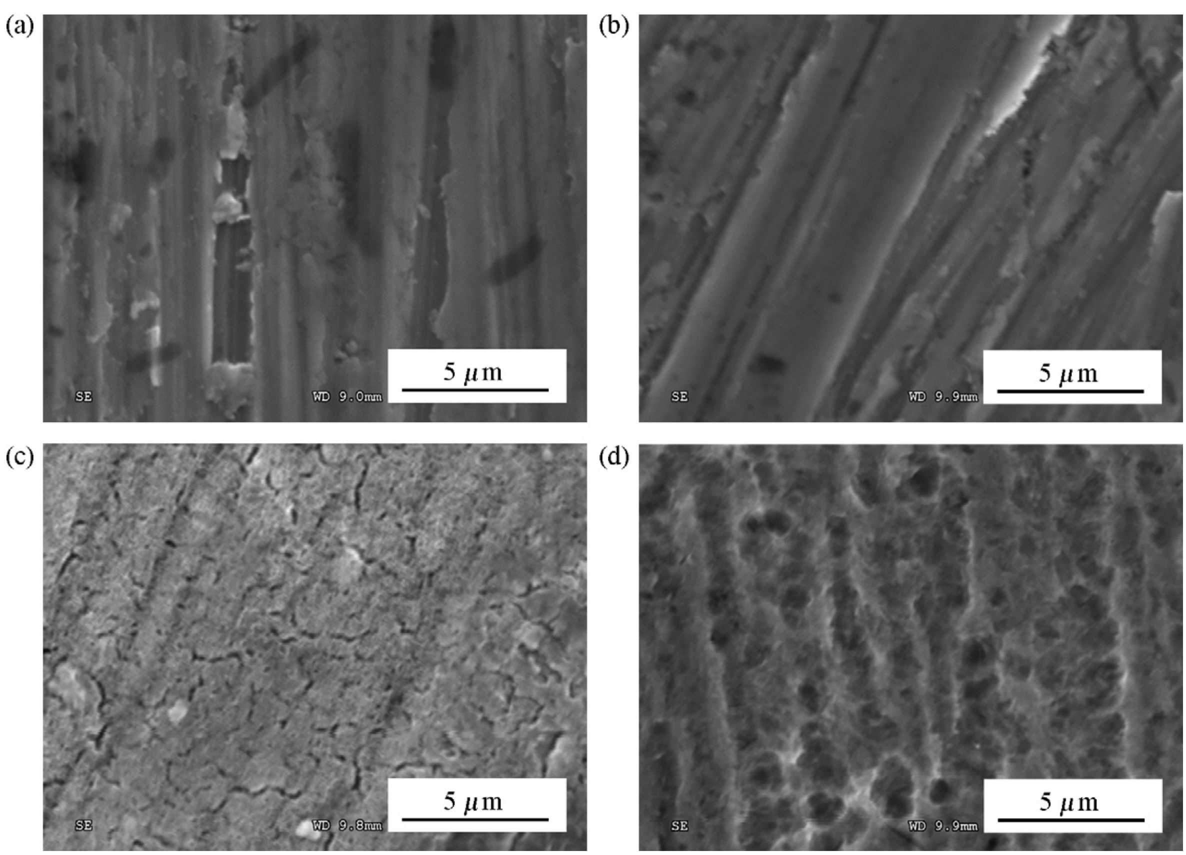

Fig. 1. SEM images of typical morphologies of Ti surface subjected to different chemical modifications: (a) as-received, (b) after immersing in water dextran solution (D), (c) after NaOH and heat pretreatment (SH), and (d) after ''piranha'' pretreatment in boiling solution (PBS).

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