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SCIENCE DIRECT
Biomaterials 26 (2005) 6129–6135
Biomaterials
www.elsevier.com/locate/biomaterials

Improvement of surface bioactivity on titanium by water and hydrogen plasma immersion ion implantation

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Received 18 January 2005; accepted 23 March 2005
Available online 10 May 2005

Abstract

We have investigated the surface bioactivity of titanium after water and hydrogen plasma immersion ion implantation. Plasma immersion ion implantation (PIII) excels in the surface treatment of components possessing a complicated shape such as medical implants. In addition, water and hydrogen PIII has been extensively studied as a method to fabricate silicon-on-insulator (SOI) substrates in the semiconductor industry and so it is relatively straightforward to transfer the technology to the biomedical field. In our investigation, water and hydrogen were plasma-implanted into titanium sequentially. Our objective is that water PIII introduces near-surface damages that trap hydrogen implanted in the subsequent step to improve the surface bioactivity while the desirable bulk properties of the materials are not compromised. Ti–OH functional groups can be detected on the (H_2O+H_2)-implanted titanium surface by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. After incubation in simulated body fluids (SBF) for cytocompatibililty evaluation in vitro, bone-like hydroxyapatite was found to precipitate on the (H_2O+H_2) implanted samples while no apatite was found on titanium samples plasma implanted with water or hydrogen alone. Human osteoblast cells were cultured on the (H_2O+H_2)-implanted titanium surface and they exhibited good adhesion and growth. Our results suggest a practical means to improve the surface bioactivity and cytocompatibility of medical implants made of titanium.

Keywords: Titanium; Plasma immersion ion implantation; Bioactivity; Cytocompatibility; Water; Hydrogen

1. Introduction

Titanium and its alloys are widely used in biomedical implants such as artificial hip and knee joints because they possess favorable properties such as good ductility, tensile and fatigue strength, and modulus of elasticity matching that of bones. Much attention is being focused on improving the bioactivity of the materials using techniques such as plasma spraying, plasma implantation, and chemical treatments. For instance, plasma-sprayed hydroxyaptite coatings are being used in the biomedical industry [1–3]. Bioactive glass, wollastonite, and dicalcium silicate coatings have also attracted much attention due to their high bonding strength with titanium substrates [4–6]. However, the possibility of fracture and delamination at the coating–substrate interface or within the coatings in a physiological environment as well as inadequate corrosion resistance affect the long-term performance and reliability. Functionalization of the titanium surface is an alternative method to enhance the bioactivity. Kokubo [7] and Kim et al. [8] reported that NaOH-treated titanium had good bone conductivity. Takadama et al. [9] studied apatite formation on NaOH-treated bioactive titanium metal. Unfortunately, destruction of the oxide film on the titanium surface caused degradation of the corrosion resistance properties. Implantation of biologically interesting elements such as Ca, Na, and P into titanium to improve the surface bioactivity has been proposed [10–14]. Hanawa et al. [10,11] found that calcium ion implantation improved the ability of titanium to induce

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0142-9612/$ - see front matter
doi:10.1016/j.biomaterials.2005.03.032

the formation of calcium phosphate precipitates and their in vivo experiments demonstrated that calcium-ion-implanted titanium was superior to unimplanted titanium from the perspective of bone conduction. Krupa et al. [12] investigated the effects of dual implantation of calcium and phosphorus on the structure, corrosion resistance, and biocompatibility of titanium. It was found that the (Ca + P)-implanted titanium possessed improved corrosion resistance and biocompatibility.

Plasma immersion ion implantation (PIII) as a nonlineof-sight process is particularly suitable for biomedical implants possessing a complicated shape. Thermal deformation of the materials can also be minimized as it is nominally a low-temperature treatment process and sample cooling can be easily implemented [15]. Oxygen plasma implantation into titanium has been conducted to fabricate titanium oxide in order to improve the biocompatibility and related properties of titanium [16–18]. Yang et al. [19] found that the non-stoichiometric titanium oxide film possessed a much higher blood compatibility compared to LTIC (low-temperature isotropic carbon) because of its surface and interfacial energy properties and interactions with adsorbed proteins. Loinza et al. [20] reported that the surface hardness increased by 100% and wear resistance also improved significantly after the treatment.

In this work, we investigated the surface bioactivity and cytocompatibility of titanium after water and hydrogen PIII. Water PIII has been employed to fabricate separation by plasma implantation of oxygen (SPIMOX), silicon-on-insulator (SOI) substrates for microelectronics [21–24]. In water plasma, the dominant species are H_2O^+, HO^+, and O^+, and so the net implantation energy of the oxygen atom in each ionic species is quite similar. This is in contrast to an oxygen plasma in which the dominant species are O^+ and O_2^+. The oxygen atom in O^+ will have twice the net implantation energy as the oxygen atom in the molecular O_2^+ ion, thereby broadening the elemental depth distribution and reducing the efficacy of the SPIMOX process [25]. In our experiments, H_2O and H_2 PIII were conducted sequentially in titanium. The microstructure and composition of the implanted titanium surfaces were investigated by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR). The bioactivity of the implanted titanium was evaluated by immersion tests in simulated body fluids as well as cell culture.

2. Experimental details

Titanium discs 10 mm in diameter and 1 mm thick were polished on one side to a mirror finish before inserting into the plasma immersion ion implanter. Water vapor was bled into the vacuum chamber to maintain a working pressure of 5×10^{-4} Torr. The PIII parameters were: sample voltage $= -30$ kV, repetition frequency $= 60$ Hz, and RF power $= 1000$ W. After implantation under a water plasma to achieve an implantation fluence of about 5×10^{16} ions cm^{-2}, the water vapor was shut off and H_2 was introduced into the chamber to perform hydrogen PIII at a sample bias of -5 kV without breaking vacuum. The hydrogen implantation fluence was $\sim 0.8 \times 10^{16}$ ions cm^{-2}.

AFM and XPS were performed to study the surface characteristics and chemical states. FTIR spectra were acquired using the reflection mode and background subtracted based on a freshly polished untreated titanium disc.

The specimens were ultrasonically washed in acetone and rinsed in deionized water before incubating in simulated body fluids (SBF) [26] for bioactivity evaluation. Samples were immersed in 50 ml SBF solution for, respectively, 14 and 28 days at 37 °C without stirring. The structure and phase composition of the surface were analyzed by scanning electron microscopy (SEM), thin film X-ray diffraction (TF–XRD), and FTIR.

A modified human osteoblast (HOB) cell line (OPC-1) was used to evaluate the cytocompatibility of the implanted samples. Approximately 10^5 cells/cm^2 OPC-1 were cultured on Φ1 cm autoclaved titanium discs. The cells were maintained at 37 °C under an atmosphere of 5% CO_2 and 95% air. The culture medium was changed every other day. After culturing for 4 or 7 days, the samples were fixed in 2.5% glutaradehyde in a 0.1 M sodium cacodylate buffer (pH = 7.4) for 1 h. After rinsing with phosphate-buffered saline (PBS) (3 × 10 min) and dehydrating in a grade ethanol series, the degree of cell spreading and propagation was determined employing SEM.

3. Results and discussion

Fig. 1 depicts the AFM images of the untreated and ($H_2O + H_2$)-implanted titanium surfaces. After sequential water and hydrogen implantation, the surface is rougher and bodes well for cell attachment [27]. The chemical states of Ti and O before and after implantation were studied by XPS and the corresponding Ti 2p and O 1 s spectra are shown in Figs. 2a and b. The metal Ti 2p peaks are at 454.1 eV (2p3/2) and 460.2 eV (2p1/2) [28]. Pham et al. [29] have reported that TiO_2 is the main component on the virgin Ti surface. Healey et al. [30] have further measured the native TiO_2 layer thickness to be about 4 nm. In this work, about 5 nm was pre-sputtered to clean the surface before the XPS measurements and small TiO_2 peaks at 458.7 eV (2p3/2) and 464.6 eV (2p1/2) [31] could be detected on the untreated