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Structure and properties of Ca-plasma-implanted titanium

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Abstract

Plasma immersion ion implantation and deposition (PIII-D) has been proven to be an effective approach to enhance the surface properties of various types of materials and applied in many industrial areas, such as semiconductor and biomaterials. In this work, calcium ions were implanted into and deposited onto titanium using PIII-D to improve its surface bioactivity. Based on secondary ion mass spectrometry (SIMS) results, the Ca implantation depth increases with higher bias voltages. After exposure to air, the outermost surface is found to comprise calcium hydroxide and calcium carbonate. The bioactivity of the implanted titanium was evaluated using a simulated body fluid (SBF) soaking test. After the sample was soaked in the simulated body fluid for a period of time, the calcium hydroxide on the surface dissolved gradually into the solution. At the same time, hydroxyapatite formed on the surface indicating the implantation of calcium into titanium indeed improves the bioactivity of the surface.

Keywords: Plasma immersion ion implantation and deposition; Calcium; Titanium; Bioactivity

1. Introduction

Titanium and its alloys are generally the preferred materials for orthopedic and dental applications due to their relatively low modulus, excellent fatigue strength, excellent formability, good machinability, superior biocompatibility, and reasonable corrosion resistance. However, titanium also has relatively poor wear resistance and bioactivity [1]. Ion implantation has been used to harden the surface and reduce the friction coefficient of titanium in tribological applications, but the metal surface still requires further modification in order to achieve enhanced bioactivity or bone conductivity [2]. Many methods have been used to coat titanium on bioactive materials. For instance, hydroxyapatite and bioactive glasses provide both good bone conduction and mechanical strength. However, the possibility of fracture and delamination at the coating–titanium interface or in the coating may occur. To overcome this hurdle, a functional titanium surface that is inherent to the materials and has good bone conduction is needed. This functional surface can be accomplished by surface modification such as chemical treatments. It has been reported that NaOH-treated titanium has good bone conduction [3,4]. Unfortunately, the thin oxide film on the surface that provides the good corrosion resistance to titanium in the body is destroyed during the chemical treatment.

Hanawa et al. [5] investigated early bone formation on calcium-ion-implanted titanium inserted into rat tibia. Their results reveal that Ca^{2+}-implanted titanium is superior to unimplanted titanium from the perspective of bone conduction. As an alternative to conventional ion implantation, there are advantages of using plasma immersion ion implantation and deposition (PIII-D) to produce the functional titanium surface for better bone conduction. PIII-D has been demonstrated to be an effective approach to enhance the surface properties of materials, such as corrosion resistance, wear resistance and hardness. It is also a non-line-of-sight process as opposed to conventional beam-line ion implantation. Therefore, under the proper conditions, samples with a complicated shape can be treated with good conformality and uniformity without the need to resort to ion beam scanning and special target

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manipulation. In addition, since PIII-D is usually conducted at low temperature and the target can be cooled, thermal deformation of the specimens can usually be minimized [6].

In this work, calcium ions were implanted into and deposited onto titanium using PIII-D. The structure and composition of the surface of the implanted materials were investigated by various means, and the bone conductivity of the calcium-ion implanted titanium was evaluated using a simulated body fluid (SBF) soaking test.

2. Experimental

The material examined was pure commercial titanium (grade 2). The titanium specimens in the form of discs 10 mm in diameter and 1 mm thick were polished on one side to a mirror finish. By applying a pulsed high voltage to the specimens, calcium ions were implanted. During the high-voltage off-cycle, deposition of Ca was accomplished. Implantation and deposition thus occurred consecutively in each cycle and the cycle was repeated many times to achieve a thick deposited and implanted layer.

To examine the bioactivity, the Ca-implanted and control (unimplanted) samples were ultrasonically washed in acetone and rinsed in deionized water. They were then soaked in a simulated body fluid for 14 days. The SBF solution was buffered at pH 7.4 with trimethanol aminomethane–HCl. The ionic concentrations in the solution are nearly equal to those in human body blood plasma [7].

Secondary ion mass spectrometry (SIMS) was utilized to determine the elemental depth profiles in the Ca-implanted titanium. A primary O^{2+} ion beam was rastered over an area of 200×200 μm in a CAMECA IMS-4f. The ^{40}Ca, ^{16}O, $^{40}Ca^{48}Ti$, ^{16}O and $^{48}Ti^{16}O$ ion profiles were acquired. X-ray photoelectron spectroscopy (XPS) was performed on the Ca-implanted titanium after 14 days of immersion in the SBF solution to investigate the surface elemental composition and chemical state. Scanning electron microscopy (SEM) was used to investigate the surface morphology of the samples.

3. Results

The SEM pictures of the titanium surface before and after Ca ion implantation are depicted in Fig. 1. The unimplanted titanium surface is quite smooth, whereas the implanted titanium samples possess a rough surface. Ball-like protuberances can be observed on the surface of the titanium sample implanted at 10 kV, as shown in Fig. 1b. The titanium sample implanted at 20 kV is different from that implanted at 10 kV and exhibits more salient features (Fig. 1c). It can be observed that a new layer has formed on the surface on these two implanted titanium samples and a higher bias (implantation) voltage creates more surface features possibly due to the higher amount of deposited energy and thicker calcium-containing layer.

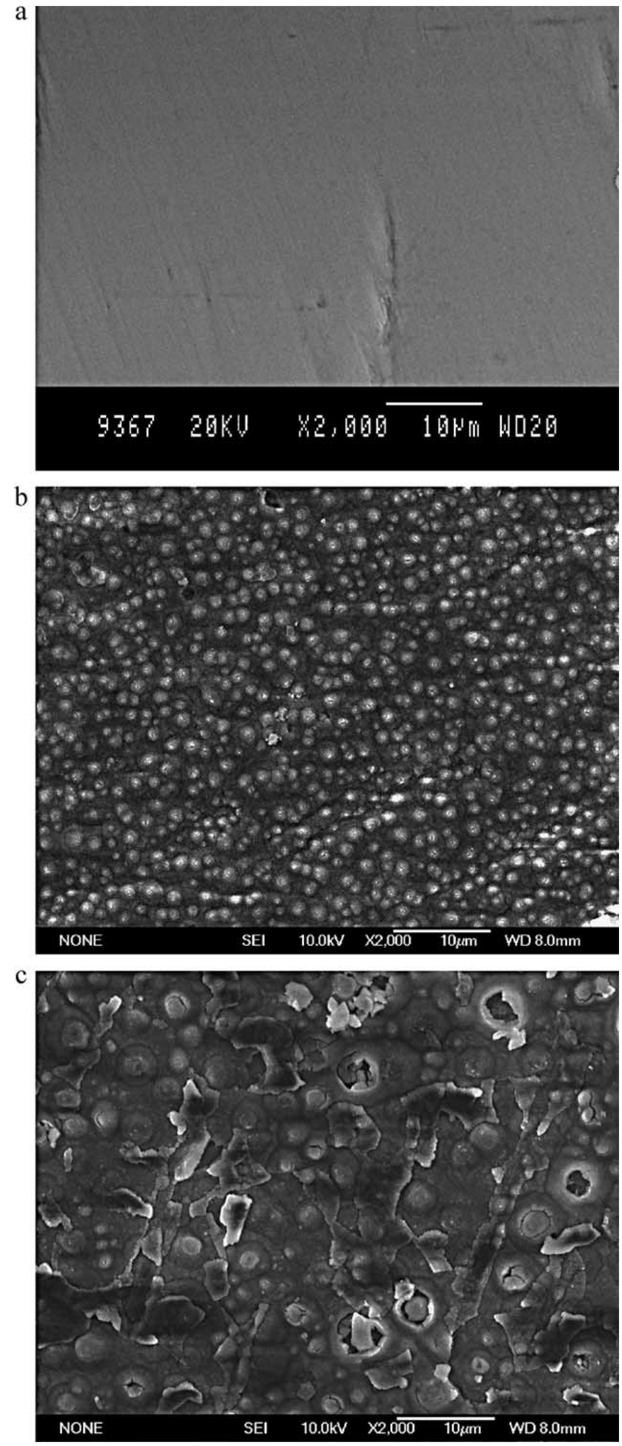

Fig. 1. SEM micrographs of titanium: (a) before implantation; (b) after Ca ion implantation at 10 kV of bias voltage; (c) after Ca ion implantation at 20 kV of bias voltage.

The elemental depth profiles acquired by SIMS are plotted in Fig. 2 as ion counts per second versus depth.