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

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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\textsubscript{2}O+H\textsubscript{2})-implanted titanium surface by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. After incubation in simulated body fluids (SBF) for cytocompatibility evaluation in vitro, bone-like hydroxyapatite was found to precipitate on the (H\textsubscript{2}O+H\textsubscript{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\textsubscript{2}O+H\textsubscript{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 hydroxyapatite 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
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 \( \text{H}_2\text{O}^+ \), \( \text{H}_2\text{O}^+ \), and \( \text{O}^+ \), 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 \( \text{O}^+ \) and \( \text{O}_2^+ \). The oxygen atom in \( \text{O}^+ \) will have twice the net implantation energy as the oxygen atom in the molecular \( \text{O}_2^+ \) ion, thereby broadening the elemental depth distribution and reducing the efficacy of the SPIMOX process [25]. In our experiments, \( \text{H}_2\text{O} \) and \( \text{H}_2 \) 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 \( 5 \times 10^{-4} \text{Torr} \). The PIII parameters were: sample voltage \( = -30 \text{kV} \), repetition frequency \( = 60 \text{Hz} \), and RF power \( = 1000 \text{W} \). After implantation under a water plasma to achieve an implantation fluence of about \( 5 \times 10^{16} \text{ions cm}^{-2} \), the water vapor was shut off and \( \text{H}_2 \) was introduced into the chamber to perform hydrogen PIII at a sample bias of \( -5 \text{kV} \) without breaking vacuum. The hydrogen implantation fluence was \( \sim 0.8 \times 10^{16} \text{ions cm}^{-2} \).

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 \( 1 \) 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 \( \times \) 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 \( (\text{H}_2\text{O} + \text{H}_2) \)-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 1s 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
control. After plasma implantation, the surface Ti undergoes oxidation resulting from water PIII and the Ti 2p peaks shift towards higher energies. The metal Ti peaks become less intense while that of Ti–O (455 eV [24]) increases. The O 1s spectra (Fig. 2b) also confirm that there is very little TiO$_2$ (530.2 eV [30]) on the surface. An asymmetrical peak skewed towards a higher energy can be seen from the O 1s spectra after (H$_2$O+H$_2$) implantation. It can be attributed to the acidic bridged hydroxyl groups associated with oxygen doubly coordinated with titanium (531.6 eV) and the basic terminal hydroxyl groups associated with singly coordinated oxygen (533.3 eV) [29].

FTIR was performed on the samples after H$_2$O PIII as well as (H$_2$O+H$_2$) PIII. The results are shown in Fig. 3. As expected, the presence of surface TiO$_2$ can be detected after H$_2$O PIII. The absorption peaks at 640–700 cm$^{-1}$ are associated with the stretching vibration of Ti–O in TiO$_2$ [32]. The intensities of these peaks diminish after (H$_2$O+H$_2$) PIII. Our results indicate that a smaller amount of surface titanium has been converted to TiO$_2$ after (H$_2$O+H$_2$) PIII but much of the materials remain in the hydroxylation stage. The absorption peaks at about 1048–1220 and 1600–1630 cm$^{-1}$ are believed to derive from the Ti–OH and H–O–H groups [33]. Combining the Ti 2p, O 1s spectra and IR results, it can be deduced that Ti–OH exists on the surface after (H$_2$O+H$_2$) PIII.

Fig. 4 shows the surface morphology of the (H$_2$O+H$_2$) PIII sample after ball-like incubation in simulated body fluids for 14 days. A number of particles can be found on the surface. In contrast, these features are absent on the surfaces of the H$_2$ PIII, H$_2$O PIII, or untreated Ti control even after immersion in SBF for 28
days. The ball-like particles formed on the (H$_2$O+H$_2$) PIII sample surface were studied by thin film XRD and the results are displayed in Fig. 5. The peaks at about 26° and 32° originate from crystalline apatite. With increasing immersion time, the peaks become more intense and sharper, indicating that the crystallinity of the formed apatite increases with incubation time. After 14 days of incubation, the intensity of the titanium peaks decrease to a level that can hardly be detected. Hence, the surface is mainly covered by apatite and this phenomenon is confirmed in our SEM observation.

The sample after incubation in SBF for 28 days was analyzed by FTIR to confirm the composition of the newly formed layer. Fig. 6 shows typical characteristics of the carbonate-containing hydroxyapatite phase. A sharp P–O bending mode doublet at around 600 cm$^{-1}$ is the characteristic band of a crystalline hydroxyapatite phase [34]. The overlapping bands between 900 and 1300 cm$^{-1}$ are associated with phosphate. The peak at 870 cm$^{-1}$ is caused by the carbonate and HPO$_4^{2-}$ ions. An intensive broad band at 2500–3700 cm$^{-1}$ originates from the asymmetrical and symmetrical stretching vibrations of the O–H groups.

Fig. 7 shows the morphologies of the (H$_2$O+H$_2$) PIII sample surface on which OCP-1 cells have been seeded for 4 and 7 days. The cells exhibit good adhesion and spreading on the implanted titanium surface. The dorsal surface ruffles and filapodia can be clearly seen. After 7 days of culture, the surface is completely covered by the human osteoblast cells. This suggests that the surface of the (H$_2$O+H$_2$) PIII sample is favorable to the adhesion and growth of osteoblast cells and good cytocompatibility can be inferred.

Cellular behaviors such as adhesion, morphological change, functional alteration, proliferation, and differentiation are greatly affected by surface properties that include composition, roughness, hydrophilicity, surface texture, and morphology. The surface composition significantly influences the behavior of the osteoblasts [35]. The Ti–OH functional groups on the titanium surface formed in the PIII process are important catalysts for the nucleation of apatite. Takadama et al. [9] have attributed apatite formation on NaOH-treated titanium to Ti–OH groups formed on the bioactive titanium metal surface. The Ti–OH groups combine with calcium ions in the fluid to form calcium titanate and the new surface causes adsorption of phosphate as well as calcium ions to form an apatite nucleation layer. Once this layer is formed, apatite growth becomes spontaneous as more calcium and phosphate ions are consumed from the surrounding body fluid. The layer of
bonelike apatite is believed favorable to the attachment and proliferation of the human osteoblast cells. The dual PIII process obviously increases the Ti–OH groups on titanium surfaces as demonstrated by our XPS and IR results. The good adhesion and proliferation of the OCP-1 cells on the implanted titanium also demonstrate the positive effect of Ti–OH.

In our experiments, we investigated the impact of H2O PIII, H2 PIII, as well as (H2O+H2) PIII on the surface bioactivity of Ti. Our results reveal that Ti–OH is absent on the titanium surface after H2O PIII although more than 95% of the ions in the water plasma are H2O+ and OH+ ions [25]. Consequently, no apatite is observed to precipitate on the H2O PIII after incubating in SBF for 14 and 28 days. The same is true for the H2 PIII sample on which apatite is not observed. On the other hand, our XPS and IR results demonstrate that Ti–OH groups are formed on the titanium surface after (H2O+H2) PIII. In vitro experiments show that carbonate-containing hydroxyapatite is formed on the (H2O+H2) PIII sample surface after 14 days of incubation in SBF. Surface precipitation of carbonate-containing hydroxyapatite can be achieved only by dual (H2O+H2) PIII, but not H2O PIII or H2 PIII individually. It is believed to be a direct consequence of the Ti–OH groups on the sample surface after the proper PIII treatment.

The possibility of embrittlement by hydrogen implantation is also considered. A hydrogen diffusion
barrier could be established by the implantation of oxygen as reported by Ferber et al. [36]. Further study by Soltanni-Farshi et al. [37] found that hydrogen would accumulate in the dislocation or defects layer produced by ion implantation. Our previous experiments on hydrogen and boron co-implantation have also demonstrated that hydrogen can be effectively gettered by implantation-induced damages [38]. In order to alter the structure only in the near-surface region to enhance bioactivity while not allowing hydrogen to penetrate deeply, we have adopted the “H2O PIII first” and “H2 PIII next” approach. First of all, the implanted water species are heavy and significant surface damage is produced in the first implantation step. Secondly, since the projected range of the water species is very shallow, the damage created is close to the surface and so hydrogen implanted in the second step is confined to the near-surface region. The end result is that the surface can be selectively modified to enhance bioconductivity whereas the favorable bulk attributes can be retained.

4. Conclusion

A dual H2O and H2 plasma implantation process is demonstrated to result in good bioactivity on titanium. SBF incubating experiments show that hydroxyapatite can precipitate on the (H2O + H2) PIII titanium surface but not on either H2O PIII or H2 PIII surfaces. It maybe resulted from the Ti–OH functional groups present on the (H2O + H2) PIII titanium surface but they were absent on the H2O PIII or H2 PIII surfaces as our XPS and IR results indicated. The good adhesion, spreading, and growth of human osteoblast cells on the sample surfaces suggest that the (H2O + H2) PIII titanium possess good cytocompatibility. The (H2O + H2) PIII technique which is quite simple and works well for biomedical implants possessing an irregular shape is a viable surface modification method in hard tissue applications.

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