Nano-structured surface modification on Ti alloy by electron cyclotron resonance plasma oxidation

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Introduction:

Metal Ti is used by dentistry and orthopedics as an implant material, since it is excellent in biocompatibility or mechanical property. It is known that the biocompatibility of Ti will change with the condition of the surface oxide (titania: TiO_2) film of implant Ti. However, since the thermal expansion difference of Ti and TiO_2 is large, it is difficult to deposit the good TiO_2 film on Ti at low temperature for a short time. Electron cyclotron resonance (ECR) plasma is high-active plasma and high quality crystalline films can be obtained at low temperature[1]. On the other hand, calcium phosphate, such as hydroxyapatite, β-tricalcium phosphate and octacalcium phosphate [$Ca_8H_2(PO_4)_6 \cdot 5H_2O$, OCP], are utilized as the coating materials for improving the osteoconductive activity. Our previous studies indicated that implantation of OCP efficiently enhanced bone regeneration compared to HAp[2]. In the present study, TiO_2 films were deposited on metal Ti and Ti-alloy by ECR plasma oxidation and the effect of oxidation conditions on structure and precipitation behavior of OCP were investigated.

Experimental:

ECR plasma apparatus was used for oxidation. A magnetic field (8.75×10^{-2} T) was applied to the plasma chamber to satisfy the ECR condition. The microwave power was 900 W. The oxygen gas pressure during ECR oxidation was set to 0.003 -1.5 Pa and the oxidation time was set to 0.3 - 7.2 ks. Metal Ti (10 x 10 x 1.0 mm^3: CP-Ti, JIS Grade 2) and Ti-alloy (Ti - 16mol%Nb - 5.5mol%Sn, 8mm ϕ x 1mm) were used as substrates. An infrared lamp was used for controlling the substrate temperature in the range from room temperature (RT) to 600 °C. Oxidation time was for 15-120 min. OCP was precipitated in phosphate-buffered solution on TiO_2 film deposited Ti substrate[3]. The structure and morphology of the films were characterized by X-ray diffraction analysis (XRD) and optical and scanning electron microscopy (SEM).

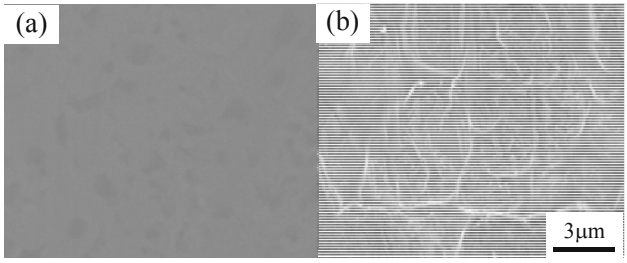

Fig. 1 SEM images of Ti substrate surface before calcification. ((a) before oxidation, (b) after ECR plasma oxidation)

Results:

Ti oxide films were obtained above 300 and 600 °C on Ti and Ti-alloy substrates, respectively. The amount of rutile TiO_2 increased with increasing oxidation temperature on Ti substrate. The ECR plasma was significantly effective to prepare crystallized TiO_2 films at low temperatures.

Fig. 1 shows SEM images of Ti substrate surface before calcification. The substrate surface before oxidation were smooth. Rough morphology was observed in the substrate surface oxidized by ECR plasma. Averages roughness of (a) and (b) were 0.01 and 0.19 μm, respectively. ECR plasma oxidation at low temperature would induce osteoconductive calcium phosphate on implant Ti. Mixtures of OCP and dicalcium phosphate dihydrate (DCPD) peaks were observed after calcification.

Fig. 2 shows the effect of oxidation temperature on precipitates weight ratio. At 600 °C, the amount of precipitates on the Ti and Ti-alloy substrates by ECR plasma oxidation was about 5 and 3 times larger than that before oxidation, respectively. The amount of precipitates increased with increasing ECR plasma oxidation temperature. The TiO_2 films prepared by ECR plasma oxidation has been expected to improve the capability to induce osteoconductive calcium phosphate of implant Ti.

References:

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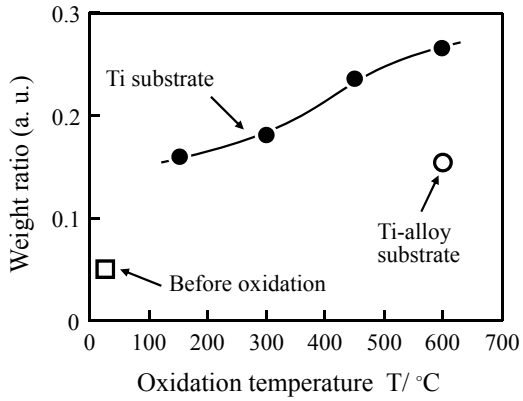

Fig. 2 Effect of oxidation temperature on precipitates weight ratio.