

Effect of surface modification of Ti-6Al-4V alloy by electron cyclotron resonance plasma oxidation

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Ti-6Al-4V alloy is used as biomaterials for dental and orthopedic implants because of their excellent biocompatibilities and mechanical properties. However, it is unclear that electron cyclotron resonance (ECR) plasma oxidation can create the oxide films on Ti-6Al-4V alloy surface, and this technique improves the ability of its osseointegration. The purpose of this study was to investigate the characteristics and calcification ability of the oxide films. X-ray diffraction (XRD) peaks of rutile phase were intensified with increasing the temperature. Scanning electron microscopy (SEM) images showed a crater-like structure, and bonding strengths between the substrate and oxide film reached a maximum at 400°C. Calcium phosphate (CaP) compounds after calcification process were identified as octacalcium phosphate (OCP) and precipitation amount was maximized at 400°C. The results suggested that the altered surface of Ti-6Al-4V alloy by ECR plasma oxidation might have the potential of accelerating the ability of its osseointegration through enhancement of OCP.

Keywords: Ti-6Al-4V alloy, Electron cyclotron resonance (ECR), Plasma oxidation, Octacalcium phosphate (OCP)

INTRODUCTION

Commercially pure titanium (cp-Ti) and titanium alloys are widely used in various types of implants in orthopedic and dental fields because they have high mechanical strength and the most exceptional biocompatibility with bone among the metallic biomaterials¹⁾. For the purpose of early acquisition of the osseointegration, implant surface modifications have been attained with various methods, such as sandblasting²⁾, the acid treatment with sulfuric acid or hydrochloric acid³⁾ and hydroxyapatite (HA) coatings⁴⁾. Further, there is a method of enhancing the biocompatibility by manipulating the surface microstructure and surface properties by forming oxidation film. The anodic oxidation treatment⁵⁾ is difficult for control of film thickness and keeping the ionic composition of the solution, and the sputtering⁶⁾ that can produce the thin film has a disadvantage of low deposition rate.

Electron cyclotron resonance (ECR) plasma is highly active plasma, and therefore, is capable of forming relatively faster well-crystallized oxide films even at low temperature⁷⁻⁹⁾, for example, synthesis of ZrO₂ films at room temperature and low temperature oxidation of SiC. This is because high-density and high-ionization plasmas are generated even under a low oxygen partial pressure. Another advantage to using ECR plasma

oxidation is to minimize the possible contamination of ions other than Ti due to direct oxidation within the reduced chamber. This technique allows the oxide film growth in a condition with lower thermal expansion difference between the substrate and the oxide film in various conditions at low temperatures.

In the previous study, we have succeeded in the preparation of oxide film by ECR plasma oxidation to the disk or porous cp-Ti substrates¹⁰⁻¹²⁾. The study provided evidence that ECR plasma oxidation could be used to improve the osteoconductivity of Ti substrate through enhancement of octacalcium phosphate (OCP) formation on its surface by calcification from supersaturated calcium and phosphate solution. Furthermore, it was confirmed that the OCP deposit formed on an ECR plasma-oxidized Ti surface could progressively be converted to HA within a reasonable experimental period by immersing in simulated body fluid (SBF). OCP has been proposed to be a precursor phase of biological apatite due to its structural similarity with HA¹³⁻¹⁸⁾. The recent intense interest in synthetic OCP could be based on its intrinsic characteristics to stimulate osteoblastic cell differentiation, proliferation, and, in some cases, osteoinductive characteristics^{13,14,19-21)}. However, no reports have been published on the preparation of the oxide film by ECR plasma oxidation to Ti-6Al-4V alloy. The purpose of this study was to modify Ti-6Al-4V alloy surface by ECR plasma oxidation, which is $\alpha+\beta$ type titanium alloy and widely used as an implant material,

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and to evaluate the property of the oxide film, further, to investigate the effects on the calcification ability of calcium phosphate (CaP) including OCP.

MATERIALS AND METHODS

ECR plasma oxidation

The detail on the ECR plasma oxidation apparatus and the optimum conditions have been described in our previously reported paper⁷⁻¹². Briefly, the sources of plasma production were microwave generators at 2.45 GHz frequency and 900 W power, and magnet coil. A rectangular waveguide was connected to the plasma chamber to deliver the generated microwave. The plasma chamber was covered by the magnet coil, and the 8.75×10^{-2} T magnetic field was generated to satisfy the ECR condition of this study. 4.5×10^{-2} T mirror-type magnetic field was applied to gain high plasma density at the substrate stage. The ECR plasma oxidation apparatus was evacuated up to 5.0×10^{-4} Pa using a turbo molecular pump. The condition of oxygen gas pressure was 1.5×10^{-2} Pa during ECR oxidation, and the range of oxidation time was 30 to 90 min. Disk samples made of mirror polishing Ti-6Al-4V alloy with a diameter of 10 mm and a thickness of 1 mm were used as substrates (SHOTOKU, Kanagawa, Japan). The substrate temperature was regulated in the range from room temperature (RT) to 600°C by an infrared lamp and measured by a Pt-13%PtRh thermocouple. The substrate was heated up to about 180°C only by ECR plasma irradiation without intentional heating from the infrared lamp. Macroscopic images of Ti-6Al-4V alloy surfaces oxidized by ECR plasma was taken by the fixed-point camera (D50, NIKON, Tokyo, Japan). The formed oxide films on the substrate were analyzed by X-ray diffraction (XRD). The XRD pattern was recorded using step-scanning at 0.2-degree intervals from 3.5 to 60 degrees with Cu K α X-rays on a diffractometer at 30 kV, 15 mA (Mini Flex, Rigaku Electrical, Tokyo, Japan). The surface morphologies were examined using scanning electron microscope (SEM) (FE-SEM, S-4300, Hitachi, Tokyo, Japan). The thickness of the oxide films was analyzed using an Auger electron spectrometer (JAMP-7100E, JEOL, Tokyo, Japan). The roughness (*Ra*) of films was measured by a three-dimensional non-contact measurement system (NH-3, Mitaka Kohki, Tokyo,

Japan) with 4 mm measuring length and 0.8 mm the cut-off value. The bonding strength between the substrate and oxide film was evaluated by the microtensile test (Romulus, Quad Group, Spokane, WA, USA) (Fig.1). Aluminum test studs with a 2.7 mm diameter head were attached to the oxidized substrate surfaces with an epoxy-adhesive agent, following undergo a thermal curing process (150°C, 1 h). The stud pull test was conducted with a loading rate of 2.0 kg/s.

Calcification experiment

The detail of this synthesis process has been described in our previously paper^{12,22}. Briefly, the calcification process was applied to precipitate OCP on the oxidized substrates after ECR plasma. A phosphate buffer solution was prepared by sodium hydrogen phosphate solutions pH 6.9 and at 25°C. Calcium acetate and sodium hydrogen phosphate solutions were introduced into sodium hydrogen phosphate solution, respectively, to become slightly supersaturated for dicalcium phosphate (DCPD) and supersaturated for both OCP and HA. The degree of super-saturation values calculated by the ratio of the ionic product and the solubility product previously reported were 6.78×10^{15} for HA, 3.4×10^9 for OCP, and 1.23×10^2 for DCPD^{23,24}. After precipitation of CaP, the substrates were washed with pure water to remove the superfluous solution and dried at 50°C for 1 h. The calcified composites on the substrate were analyzed by XRD. The surface morphologies were examined to

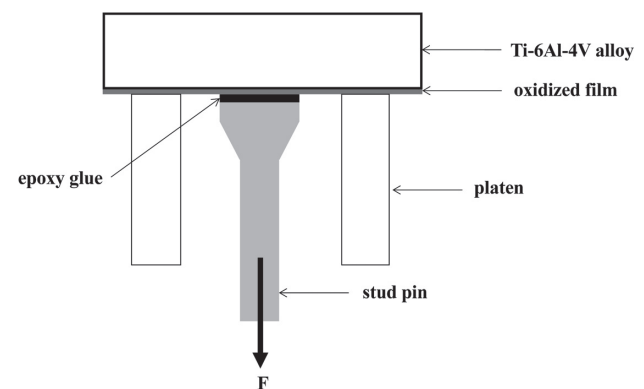


Fig. 1 Schematic representation of the bonding strength test.

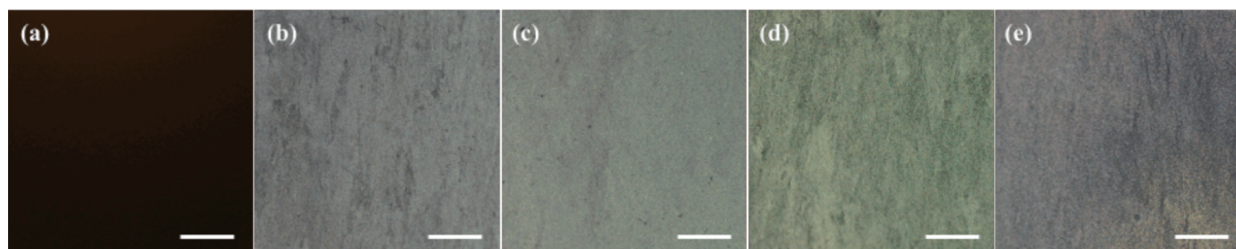


Fig. 2 Macroscopic images of Ti-6Al-4V alloy surfaces oxidized by ECR plasma at different temperatures; (a) RT, (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C; Bar=2 mm.

observe changes before and after the calcification process for the oxidized substrates using SEM. Amount of CaP precipitation in RT and dry conditions was estimated by the weight ratio calculated from the weight differences between before and after the calcification process to examine the effect of oxidation condition through the calcification.

Statistical analysis

Three samples were taken ($n=3$) for the studies. Data were shown as the mean \pm standard deviation. The *Ra* and bonding strength examined the differences in substrate temperatures by one-factor analysis of variance (IBM SPSS statistics 21, Chicago, IL, USA). When necessary, a *post hoc* Kruskal-Wallis test was used; $p<0.05$ was considered significant. The weight ratio before and after the calcification process was analyzed by two-factor analysis of variance. If necessary, a *post hoc* Bonferroni

test was used; $p<0.05$ was considered statistically significant.

RESULTS

Effect of oxidation temperature for the oxide films on Ti-6Al-4V alloy substrate

Figure 2 shows the macroscopic ECR-oxidized Ti-6Al-4V alloys surface at different substrate temperatures in the range from RT to 600°C. All substrates after ECR plasma oxidation were wholly covered with the oxide film.

Figure 3 shows the typical XRD patterns of the substrates that were oxidized by ECR plasma at various temperatures. Over the 400°C, the oxidation produced a TiO₂ rutile phase identified at 2θ of 27.7 degrees. The XRD peaks of rutile phase were intensified with increasing the temperature.

Figure 4 shows scanning electron microscopy (SEM) images of ECR-oxidized Ti-6Al-4V alloy in the range from 300 to 600°C. The substrate surface became rough with increasing the oxidation temperature. A crater-like surface structure about 5 μm in diameter became discernable on the substrate surfaces at 400°C. The diameter of the surface structure grew at 500°C. At 600°C, a crater-like surface structure vanished and granular structure observed.

Figure 5 shows the change of the oxide film thickness under various oxidation temperatures. The thickness of oxide film formed on the substrate surfaces increased

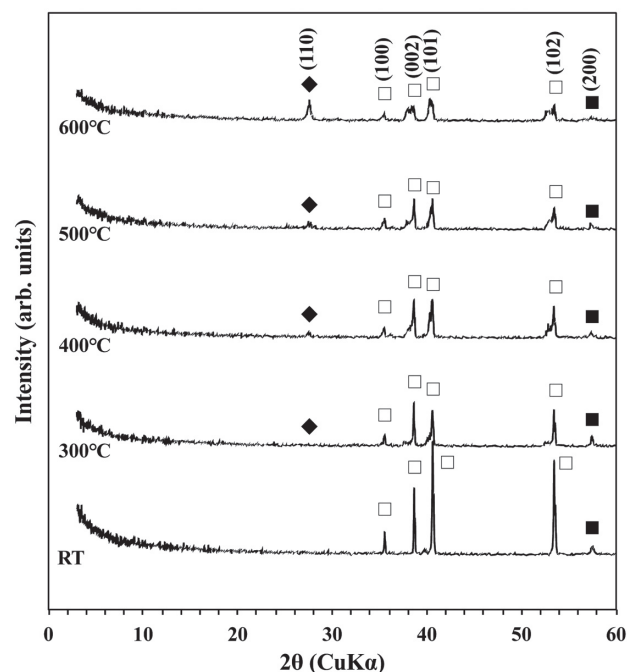


Fig. 3 XRD patterns of surfaces of Ti-6Al-4V alloys oxidized by ECR plasma at various temperatures; diamond, rutile; white square, α titanium; black square, β titanium.

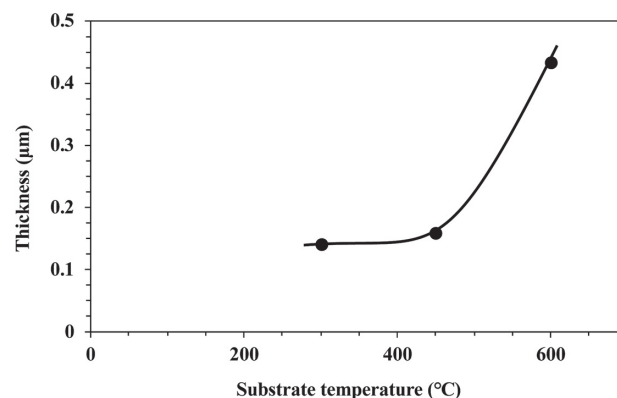


Fig. 5 Thickness of the oxidation films after ECR plasma oxidation estimated by Auger electron spectroscopy.

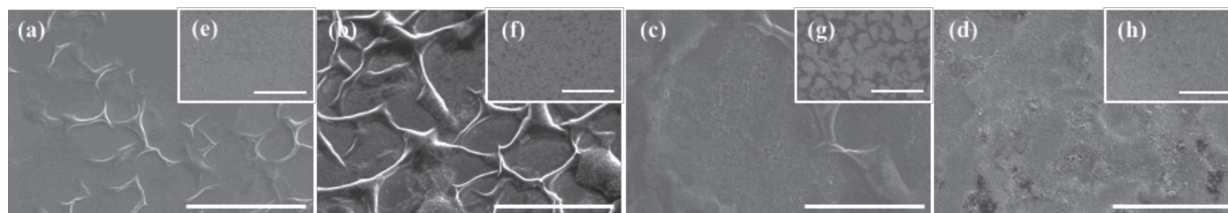


Fig. 4 SEM images of Ti-6Al-4V alloy surfaces oxidized by ECR plasma at different temperatures; (a, e) 300°C, (b, f) 400°C, (c, g) 500°C, (d, h) 600°C; Bars=6 μm (a–d), 50 μm (e–h).

with the oxidation temperature; the thickness increased remarkably over 450°C.

Figure 6 shows Ra of oxide films. Ra tended to increase with increasing the temperature and reached a maximum at 450°C, and slightly decrease at 600°C. However, no significant difference was apparent among

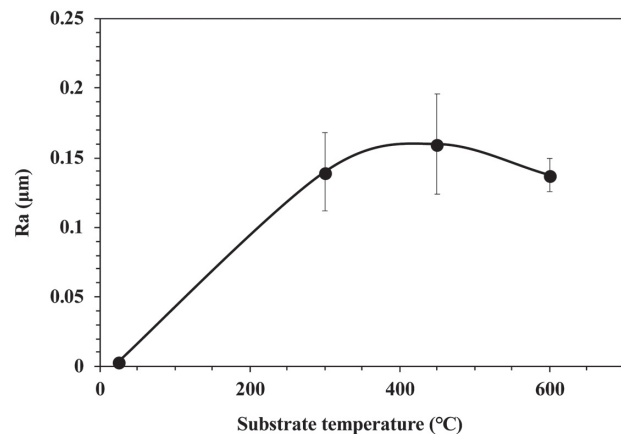


Fig. 6 Roughness of oxide films was measured using a three-dimensional non-contact measurement system.

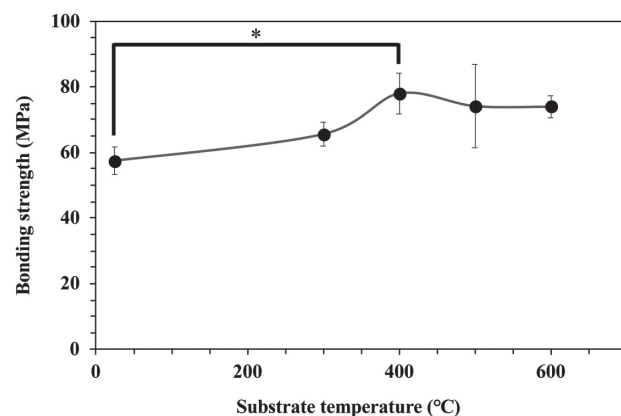


Fig. 7 The bonding strength of the oxide films to surfaces of Ti-6Al-4V alloy.
* $p < 0.05$

the substrate temperatures.

Figure 7 shows the bonding strength of oxide films to surface of the substrate. The peering point predominantly was the interface between epoxy glue and oxide films. The Bonding strengths were intensified with increasing the temperature and reached a maximum at 400°C, and its strength was significantly higher than RT ($p < 0.05$), following decreased over 450°C gradually.

Calcification on the surfaces of substrate after oxidation by ECR-plasma

Figure 8 represents the typical macroscopic images of CaP compounds precipitated on the surface of substrate oxidized by 30 min ECR-plasma after the calcification

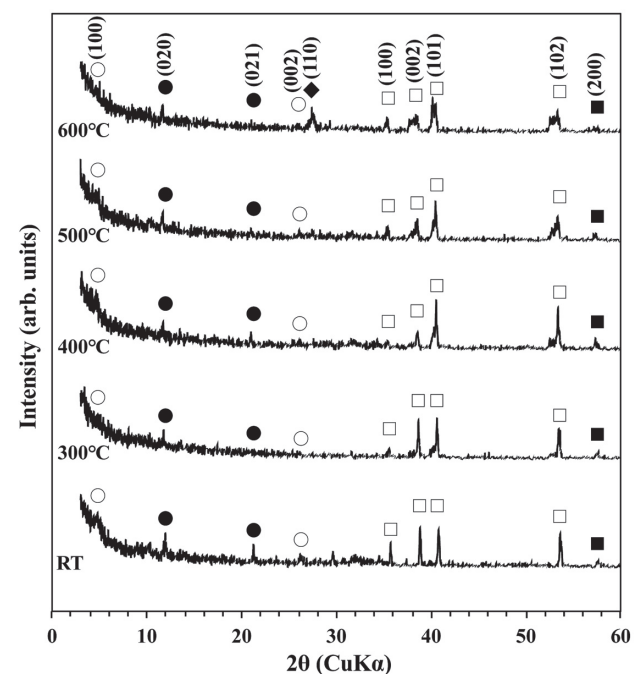


Fig. 9 XRD patterns of the surfaces of Ti-6Al-4V alloys oxidized by ECR plasma after calcification in supersaturated calcium and phosphate solutions, showing the formation of OCP with DCPD; diamond, rutile; white square, α titanium; black square, β titanium; white circle, OCP; black circle, DCPD.

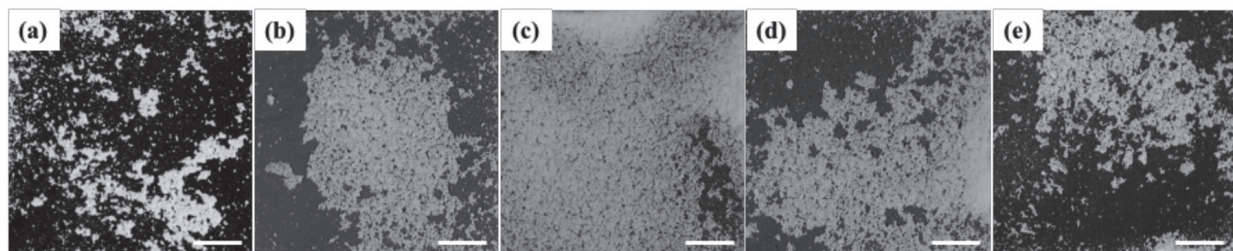


Fig. 8 Macroscopic images of CaP precipitation formed on the Ti-6Al-4V alloy substrate after calcification in supersaturated calcium and phosphate solutions; (a) RT, (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C; Bars=2 mm.

process. The whole surface oxidized at 400°C was covered by CaP deposits. However, others were partially deposited.

Figure 9 shows XRD patterns of substrate with CaP deposits. The results indicate that XRD peaks of OCP (the characteristic peak of OCP around 2θ of 4.8 and 26.0 degrees) and DCPD (the characteristic peak of DCPD around 2θ of 20.5 degrees) were detected.

The characteristic morphological features of the

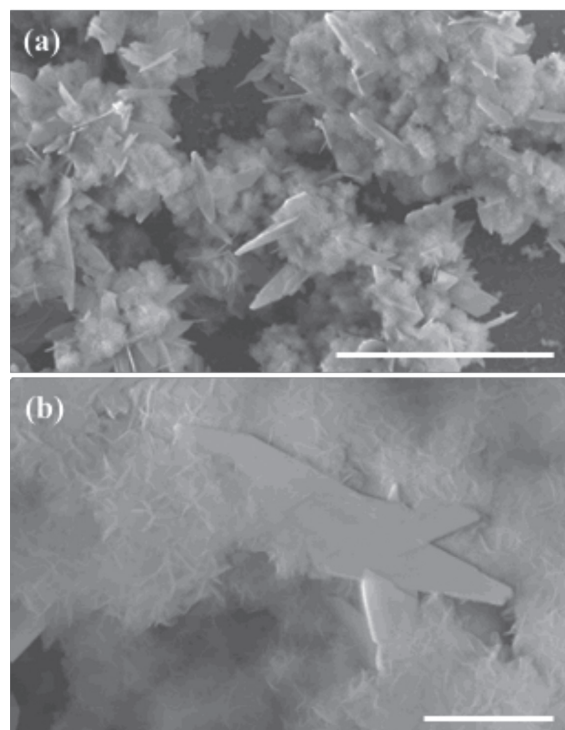


Fig. 10 SEM images of CaP deposits formed on the Ti-6Al-4V alloys after calcification in supersaturated calcium and phosphate solutions, showing the appearance of blade-like OCP deposits; Bars=50 μ m (a), 6 μ m (b).

ECR-plasma oxidized Ti-6Al-4V alloy surface after the calcification process, observed by SEM, are shown in Fig. 10. Its oxidation condition was that the temperature of the substrate was 400°C, and the time was 30 min. Thin plate-like crystals several μ m in length and large plate-like crystals around 20 μ m were co-deposited on the surface. It is generally accepted that the morphology of OCP is plate-like or needle-like structures. On the other hand, DCPD was a large plate-like crystal. Thus, it was assumed that thin plate-like crystals were OCP, and large ones were DCPD.

Figure 11 shows the effect of the oxidation temperature and time on weight ratio of the substrate before and after calcification. The prominent effect on the precipitation was apparent, depending on the oxidation temperature. The amount of CaP precipitation was maximized at 400°C; there were significant differences between the weight ratio for 400°C and others that were apparent in each oxidation time ($p < 0.01$). The weight ratio of 400°C had significant differences among the oxidation times; 30 and 60 min, 30 and 90 min ($p < 0.05$). The 600°C was statistically significant regarding the oxidation time between 60 and 90 min ($p < 0.05$).

DISCUSSION

The present study provided evidence that microstructure was produced on Ti-6Al-4V alloy surface by ECR plasma oxidation, and it was adjustable. Moreover, the ECR plasma oxidation condition might regulate the calcification amount. It was also revealed that ECR plasma oxidation could be used to improve the osteoconductivity of a substrate through enhancement of the OCP formation on its surface in a calcifying supersaturated calcium and phosphate solution.

The previous study reported that optimum condition of ECR plasma oxidation on cp-Ti was total pressure: 1.5×10^{-2} Pa, oxidation time: 30 min, oxidation temperature: 300°C. On this condition, the bonding strength and calcification amount became maximum, and it was revealed that the mechanical properties of

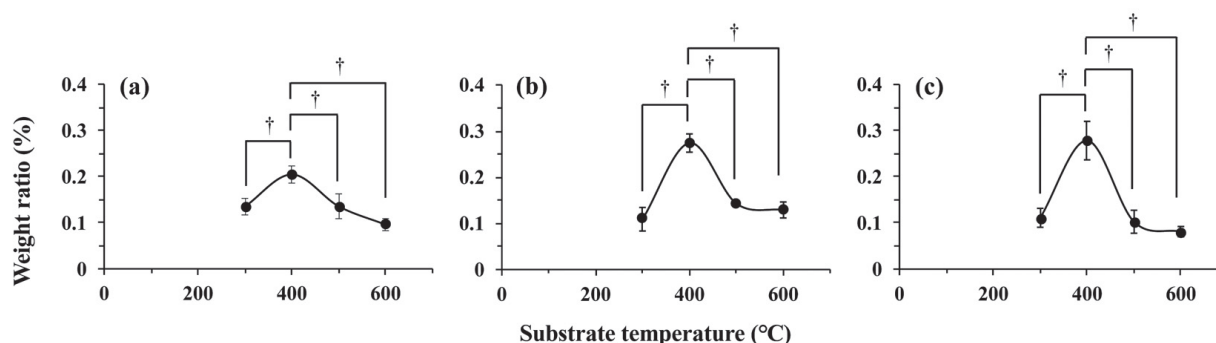


Fig. 11 Amount of CaP precipitation estimated by the weight ratio calculated from the weight differences between before and after the calcification process.

Ti-6Al-4V alloy oxidized at different temperatures and the oxidation time; (a) 30 min, (b) 60 min, (c) 90 min.

† $p < 0.01$

the TiO₂ film might affect the calcification potential¹²⁾. The present study for Ti-6Al-4V alloy indicated similar results under the condition; total pressure: 5.0×10^{-4} Pa, oxidation time: 30 min, oxidation temperature: 400°C.

The oxide films formed on Ti-6Al-4V alloy surface consisted of TiO₂; the XRD pattern identified rutile phase and its peaks were intensified with increasing the temperature (Fig. 3), and anatase phase was not detected in this study. Won *et al.* reported that high temperature by MOCVD on quartz glass transform anatase to rutile phase²⁵⁾. Therefore, it might not induce anatase phase under this condition. Anatase has crystallographically advantage in the photocatalytic chemical reaction over rutile. However, it has been reported that anatase and/or rutile structures on TiO₂ are both active for inducing the apatite formation^{5,26,27)}. (101) and (102) are the peaks for the substrate, 64-Alloy. The peak intensity of the substrate decreased as the thickness of the rutile oxide film (the diamond symbol in the Fig. 3) increased as the oxidation temperature increased.

The SEM images showed that the crater-like surface structure observed at 400°C, however destroyed and the surface was covered with the granular structure at 600°C (Fig. 4d). These phenomena are coincident with the previous reports^{28–30)}.

The thickness of oxide film increased with increasing the oxidized temperature; in particular, it increased remarkably at 600°C (Fig. 5). These characterizations are similar to the properties of the oxide film formed to cp-Ti substrates¹²⁾.

Ra of cp-Ti increased with the oxidation temperature (data not shown), however, that of Ti-6Al-4V alloy reached a maximum at 450°C and slightly decreased at 600°C (Fig. 6). The bonding strength between the oxidation film and the substrate surface reached a maximum at 400°C, and decreased over 450°C gradually (Fig. 7).

Generally, the increase in temperature of titanium alloys causes an increase in the thickness of oxide film, the kinetics of outward growth, finally, the formation of cracks due to the differences in a coefficient of expansion, and the compressive stress^{31,32)}. Therefore, the bonding strength decreases at high temperatures because of above reasons³³⁾. In this study, however, the bonding strength was approximately same levels from 400 to 600°C, but decreased over 450°C gradually (Fig. 7). ECR plasma oxidation has a high oxidation ability at low temperatures^{8–12,34)}. On the other hand, around 500–600°C, the effect of thermal oxidation is more pronounced than that of ECR plasma oxidation. Therefore, we assumed that *Ra* and high bonding strengths at 500 and 600°C were produced by the behavior characterization of thermal oxidized Ti-6Al-4V alloy. It has been reported that when the titanium alloy was thermally oxidized at more than 800°C, an increase in TiO₂ film thickness and an increase in oxygen concentration in the diffusion layer were observed³⁵⁾. Since our experimental conditions were up to 600°C, the thickness of oxide film and the thermal expansion difference with the metal was not large, and there was no significant decrease in the bonding

strength.

In this study, the calcification process was applied to precipitate CaP, expectantly OCP, on the oxidized substrates after ECR plasma^{12,22)} because OCP has been proposed to be a precursor phase of biological apatite due to its structural similarity with HA, and synthesized OCP converted to HA *in vivo*^{13–21)}. Under this condition, the calcified CaP compounds on the Ti-6Al-4V alloy coated with TiO₂ films were identical to OCP and DCPD, and the formation of HA was not utterly detected (Fig. 9). The amount of CaP deposition reached a maximum at 400°C (Fig. 11). This result suggests that ECR plasma on Ti-6Al-4V alloy surface is useful for enhancing OCP precipitation.

CONCLUSION

The present study proposed that ECR plasma with remarkable oxidation ability deposited rutile-dominant TiO₂ on Ti-6Al-4V alloy surface at the low-temperature range. This oxide film had no-cracks structure and high bonding strength at 400 °C, and modified surface after the calcification process could improve the osteoconductivity of the substrate through enhancement of the OCP formation.

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