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Characterization of hydrothermally treated anodic oxides containing Ca and P on titanium

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In this study, the formation of hydroxyapatite (HA) by a series of hydrothermal treatment and properties of the anodic oxide films and HA composite coatings were investigated. Based on the observations using EPMA, SEM, and X-ray diffraction, these needles were suggested to have a HA-like structure and were formed on the anodic oxide surfaces. The formation of these apatite-like needles were either oriented at an angle or formed on porous anodic oxide films. The concentration of Ca and P were enriched in apatite-like needles after hydrothermal treatments, whereas lower concentration of Ca and P were observed on anodic oxide film, particularly around the needles. In conclusion, HA-like needles were formed after hydrothermal treatment at 200 and 300 °C.

1. Introduction

Hydroxyapatite [$Ca_{10}(PO_4)(OH)_2$] (HA), similar to the mineral component of bones and teeth, is widely used as coatings for dental and orthopaedic implants to promote rapid osseointegration [1–3]. Currently, plasma spraying of HA has been the most common method for modifying commercial implant surfaces. Although the mechanisms responsible for the development of interfaces between hard tissues and plasma-sprayed HA coatings are not well understood [4], *in vitro* and *in vivo* investigations have indicated enhanced cellular-mediated events on HA surfaces [5–7]. However, clinical studies demonstrate that failure of the implant system at the coating–substrate interface is often caused by failure within the plasma-sprayed HA coating or with discontinued dissolution of the coating after implantation [8]. Other problems with the plasma-sprayed HA coatings included variation in bond strength between the coatings and the metallic substrates, non uniformity in coating density as a result of the process, poor adhesion between the coatings and metallic substrates, and microcracks on the coating surface [9, 10]. As such, development of coating technology to obtain optimum HA coatings on implants has received considerable attention.

Several techniques such as laser deposition, ion beam dynamic mixing, ion beam deposition, magnetic sputtering, hot isostatic pressing, electrophoretic deposition, sol–gel, ion implantation, NaOH treatment, and electrochemical methods have been employed to deposit HA or calcium phosphate coatings on titanium (Ti) implant surfaces [11–26]. Recently, a combination of anodic oxidation and hydrothermal reaction has been developed as a promising method for producing HA coatings. Coatings produced by a combination of anodic oxidation and hydrothermal reaction were reported to consist of anodic oxides and HA, and these coatings were reported to adhere to titanium substrates [27–29]. Anodic oxide films, as determined by electrolyte composition and electrochemical conditions, play a critical role in the final layer on Ti. Three kinds of electrolytes have been explored to develop anodic oxide films containing Ca and P [27, 29, 30]. The use of a mixture of calcium glycerophosphate (Ca-Gp) and calcium acetate (CA) as an electrolyte was reported to produce porous and adhesive anodic oxide films [29]. No cracks were observed on the anodic oxide films and the Ca/P ratio was reported to be similar to HA (Ca/P 1 : 1.67) [29]. Moreover, anodic oxide films containing Ca and P provide precursors for the further formation of HA through hydrothermal treatment. In this study, the formation of HA by a series of hydrothermal treatment and properties of the anodic oxide films and HA composite coatings were investigated.

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2. Material and methods

Specimens (size 30 × 10 × 1 mm) were cut from cp Ti plate (grade 2). As a pre-treatment procedure, specimens were abraded to SiC sandpaper No. 1500. This was followed by ultrasonic rinsing in acetone for 180 s and subsequently pickled using a mixture of aqueous HF and HNO_3 acids (mole ratio HF/HNO_3 equaled 1 : 3) for 30 s at room temperature. The specimens were then rinsed with distilled water and dried. Anodizing was performed on a regulated DC power supply using a constant current density of $70\,A/m^2$ and a voltage of 350 V. The electrolyte used in this study was prepared by mixing 8.40 g of 0.02 M Ca-GP and 31.64 g of 0.15 M CA in 2 liters of distilled deionized water. The temperature was maintained at 20 °C by water bath during anodizing. After anodization, specimens were rinsed by deionizd water and air-dried.

Hydrothermal treatment was performed by high-pressure steam in an autoclave (volume 1800 ml; Ilshin Engineering, Korea) for either 2 or 4 h. Table I shows the steam pressure and temperature used for this study.

Anodized and hydrothermally treated specimens were uniformly coated with a layer of gold for electric conductivity, and then their morphology was observed in triplicates by scanning electron microscopy (SEM) (Model S-2300, Hitachi, Tokyo, Japan). The structures of composite coatings were analyzed in triplicates using X-ray diffraction with Cu Kα radiation (X'pert-APD, Philips, The Netherlands). The scanning range (2θ) was from 10 to 60 degrees.

Triplicate specimens were also used to measure elemental distribution, depth profile of elements, and thickness of the composite layer using SEM and EPMA (Electron Probe Micro Analyzer, Shimadzu EPMA 1600, Japan), respectively. The composition of the coatings was semi-quantitatively analyzed in triplicates by EPMA. Surface roughness of triplicate specimens was measured by Surftest SV-402 (Mitutoyo Instruments, Tokyo, Japan), and the results of measured roughness were reported as Ra (arithmetic mean deviation of the roughness profile).

3. Results

Fig. 1 shows representative scanning electron micrographs of anodized specimens that were hydrothermally treated at different temperatures for 2 and 4 h. Needle-like crystals were observed to be distributed on all porous anodic oxide films. The needles took two forms. Some of the needles were observed to be formed on the surface, while the rest were formed at some angles to the surface of the anodic oxide with random orientations originating from the pores or low places of anodic oxides.

From the X-ray diffraction analyses, the anodic oxides of all hydrothermal treated samples indicated a mixture of apatite-like structures, rutile titanium oxide and anatase titanium oxide (Fig. 2). An increase in X-ray diffraction peak intensity was observed on the anodic oxide as temperature was increased during hydrothermal treatment. As shown in Figs 2 and 3, the corresponding peaks of needles were observed to have higher peak intensity when the hydrothermal treatment periods were increased from 2 to 4 h, suggesting an increase in the crystallinity of the coatings.

TABLE I Pressure vs. temperature of steam in hydrothermal treatment

Temperature (°C)	Pressure (kPa)
200	2500
300	10 000

As shown in Table II, no significant changes in the surface roughness were observed between the anodized surfaces and hydrothermally treated surfaces at 200 °C. However, a significant difference in surface roughness was observed for specimens that were hydrothermally treated at 200 and 300 °C.

After hydrothermal treatments, line scan of elements on all surfaces revealed the presence of Ca, P and O, with marked richness in Ca and P in the needle (Fig. 4). Furthermore, EPMA semi-quantitative analysis of all hydrothermally treated groups indicates a significantly lower concentration of Ca and P on the anodic oxide and a higher concentration of Ca and P on the needle as compared to the concentration of Ca and P on the anodic oxide before hydrothermal treatment (Table III).

As shown in Fig. 5, the thickness of the anodic oxides of all treated groups was ca. 10 μm. The oxide was also observed to be microporous. In addition, the anodic oxide was observed to bond chemically to the titanium substrate at the Ti-oxide interface. Depth profile analysis also indicated a variation of Ca and P concentrations within the oxide depth, with higher concentrations of Ca and P ions observed at the Ti-oxide interface compared to the surface.

4. Discussion

The reactions between biomaterials and adjacent tissues are directly related to the surfaces of materials. These events were reported to be accompanied by absorption and incorporation of biological molecules and the attachment of surrounding cells [31]. The functional activity of cells in contact with implant surfaces had been reported to be governed by the implant surface [32]. In this study, it was observed that the modification of Ti by anodic oxidation and hydrothermal treatments resulted in the formation of needles and microporous anodic oxides containing Ca and P, with Ra values of less than 1 μm. The presence of calcium ions have been reported to be advantageous to cell growth [33, 34].

X-ray diffraction analyses performed in this study also indicated a higher crystallinity as temperature and pressure during hydrothermal treatment were increased. In addition, presence of apatitic structure after hydrothermal treatments was observed. It has been reported that the crystalline HA dissolves slowly in unsaturated solution [35, 36]. Other studies have also reported that HA of lower crystallinity demonstrated relatively fast dissolution and dissolution–precipitation reactions in the interaction with physiological fluids [31]. As such, the increase of temperature and pressure during the hydrothermal treatment in this study suggested an acceleration of the diffusion and ion exchange process, which included the outward migration of Ca and P ions to

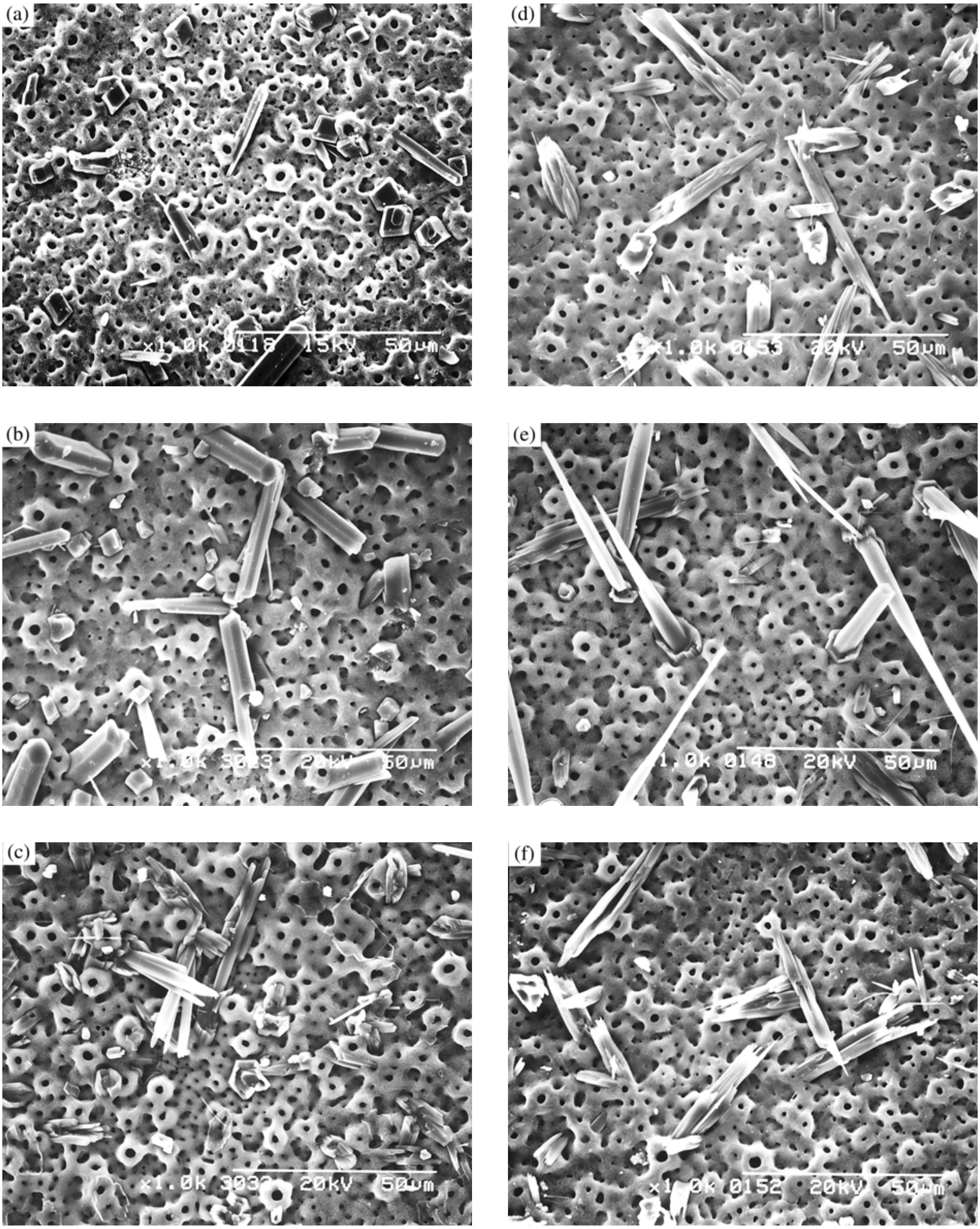

Figure 1 Morphologies of surfaces of titanium by anodic oxidation and hydrothermal treatment under different conditions, (a) 200 °C for 2 h, (b) 300 °C for 2 h, (c) 200 °C for 4 h, (d) 300 °C for 4 h.

the solid–liquid interface, and the HA crystallization during hydrothermal treatments. This is probably ascribed to sufficient time for atom rearrangement during the formation of HA needles. As observed in this study, needles formed after hydrothermal treatments were either on the anodic oxide surface or at some angles to the anodic oxide surface with random orientations originating from the pores.

Another criteria for bone apposition is that thickness of calcium phosphate coatings on implant surfaces has to be at least 10 μm [37]. In this study, the thickness of the present modified layer was observed to be about 10 μm, including needles and anodic oxides containing Ca and P. As such, this thickness met the required minimum of 1 μm for bone apposition. In addition, it was also reported that the adhesive strength of anodic oxides containing Ca and P was relatively high [28]. It was also shown in this study that the concentrations of Ca and P varies with depth of the oxide, suggesting that different charged ions such as Ca and P migrate in different

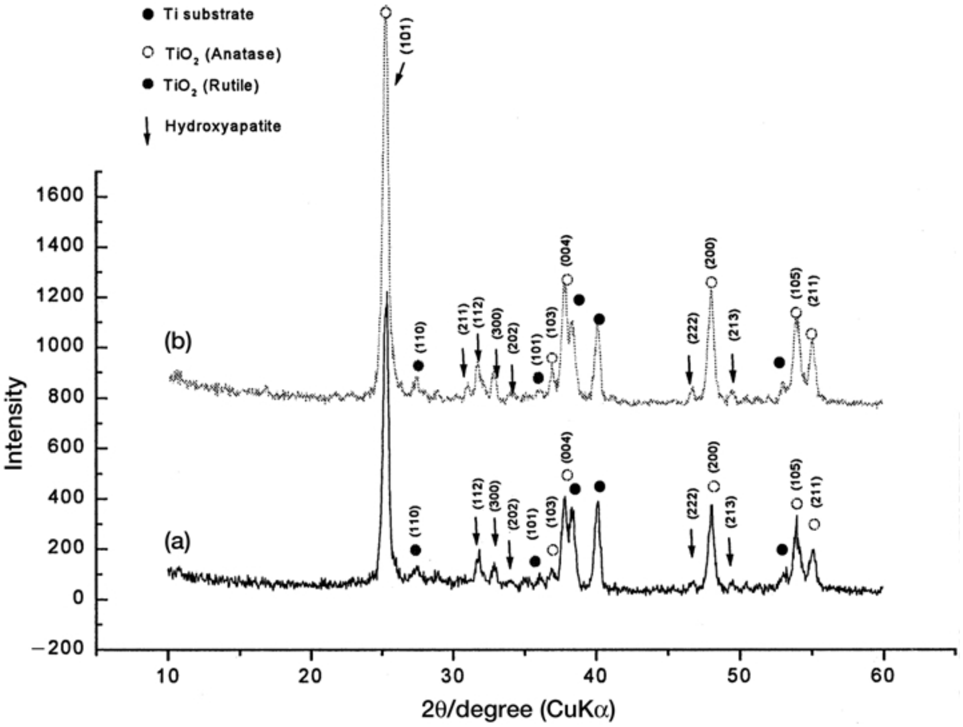

Figure 2 XRD patterns of surfaces of titanium after anodizing and hydrothermal treatment, (a) 200 °C for 2 h, (b) 300 °C for 2 h.

TABLE II Surface roughness of anodized and hydrothermally treated titanium

Sample condition	Hydrothermal duration (h)	Roughness Ra (μm)
Anodized		0.73 ± 0.02
Anodized + hydrothermal treatment at 200 °C	2	0.75 ± 0.01
Anodized + hydrothermal treatment at 300 °C	2	0.79 ± 0.01
Anodized + hydrothermal treatment at 200 °C	4	0.73 ± 0.02
Anodized + hydrothermal treatment at 300 °C	4	0.77 ± 0.01

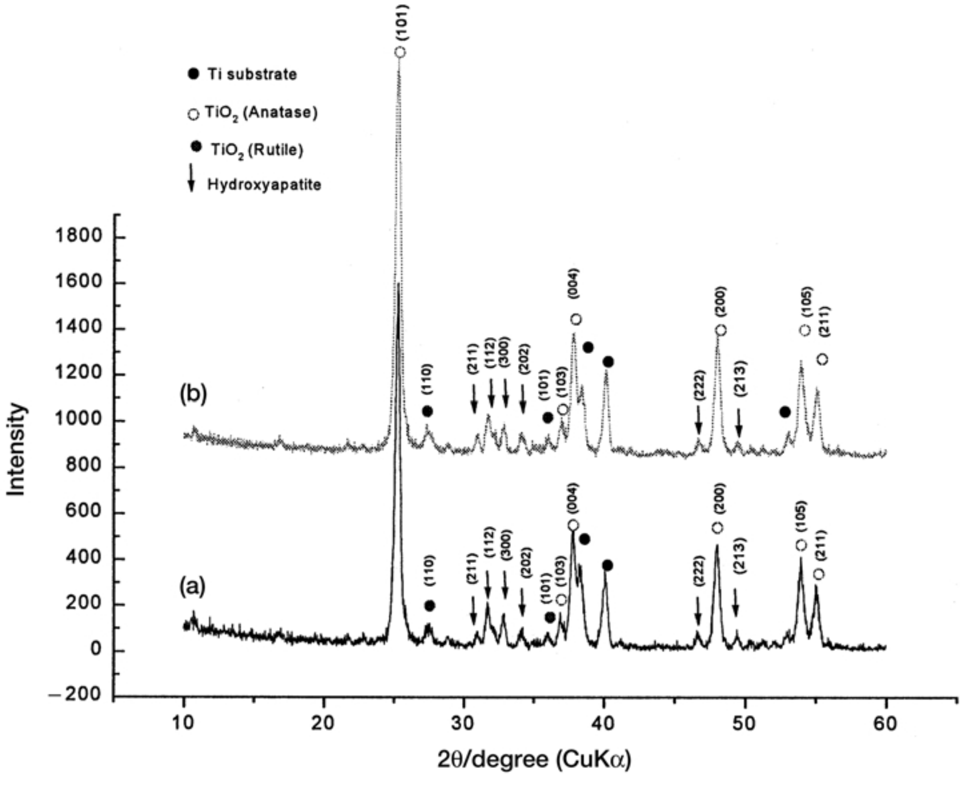

Figure 3 XRD patterns of surfaces of titanium after anodizing and hydrothermal treatment, (a) 200 °C for 4 h, (b) 300 °C for 4 h.

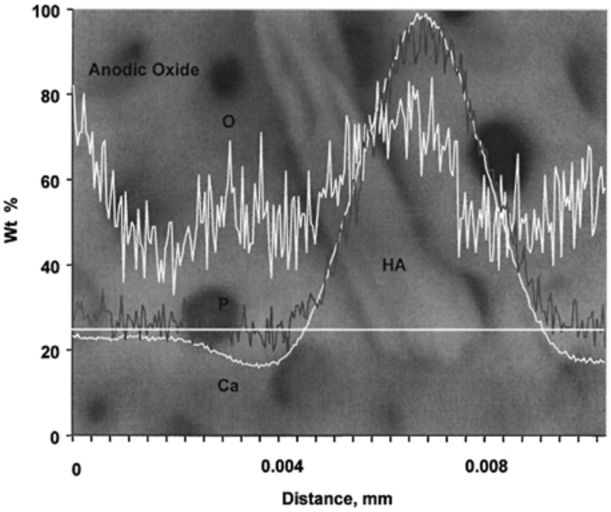

Figure 4 Ca, P and O distribution across HA crystals formed by hydrothermal treatment on anodic oxides on titanium (300 °C for 2 h).

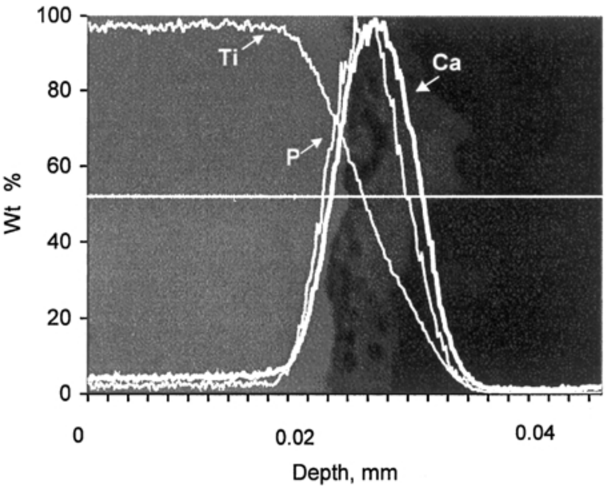

Figure 5 SEM-EPMA analysis of cross section of anodized and hydrothermally treated titanium (300 °C for 2 h).

TABLE III Composition of composite layers on titanium by EPMA analysis

Sample condition	Analysis position	Composition (mol %)			
		Ca	P	O	Ti
Anodized	Anodic oxide	15.30 ± 0.66	9.36 ± 0.13	30.98 ± 1.06	44.31 ± 0.38
Anodized + hydrothermal treatment at 200 °C, 2 h	HA needles	22.89 ± 0.99	15.50 ± 1.61	53.89 ± 1.16	7.72 ± 1.46
	Anodic oxide	4.78 ± 2.23	5.55 ± 1.70	49.50 ± 11.85	40.18 ± 9.34
Anodized + hydrothermal treatment at 300 °C, 2 h	HA needles	21.24 ± 4.62	15.04 ± 2.91	52.87 ± 12.98	10.86 ± 6.68
	Anodic oxide	1.29 ± 0.26	2.67 ± 0.40	48.18 ± 7.52	47.86 ± 7.03
Anodized + hydrothermal treatment at 200 °C, 4 h	HA needles	34.92 ± 4.30	23.98 ± 3.02	39.92 ± 7.54	1.19 ± 0.26
	Anodic oxide	0.97 ± 0.13	1.89 ± 0.37	55.93 ± 4.58	41.21 ± 4.16
Anodized + hydrothermal treatment at 300 °C, 4 h	HA needles	14.09 ± 7.09	11.53 ± 3.66	54.75 ± 7.22	14.78 ± 12.94
	Anodic oxide	2.13 ± 0.88	2.75 ± 1.92	61.29 ± 8.77	38.84 ± 10.87

directions in the electric field during anodization. During hydrothermal treatments, depth profile suggested the diffusion of Ca and P to the surface. The accumulation of localized Ca and P on the surface probably attributes to the formation of the needles during hydrothermal reaction. Also, it can be inferred from all the characterizations performed in this study that the needles formed were HA. These further confirmed the speculation that the nucleation of HA depended on the gradient slope of the composition, and the growth of HA required sufficient supply of Ca and P.

It has been reported that the presence of Ca and P on implant surfaces may influence the nearby cell population, thereby enhancing bone apposition on the implant surface [38, 39]. In addition, Ca and P ions released from the anodic oxides and HA needles may serve as a source of inorganic phosphate to promote bone cell mineralization. However, further studies will have to be performed to confirm their benefits on osseointegration.

5. Conclusions

Using EPMA, SEM, and X-ray diffraction, these needles were suggested to have an HA-like structure and were formed on the anodic oxide surfaces. The formation of these apatite-like needles were either oriented at an angle or formed on porous anodic oxide films. The concentration of Ca and P were enriched in HA-like needles after hydrothermal treatments, whereas lower concentration of Ca and P were observed on anodic oxide film, particularly around the needles. In conclusion, needles exhibiting HA-type structures were formed after hydrothermal treatment at 200 and 300 °C.

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