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Crystallization of hydroxyapatite during hydrothermal treatment on amorphous calcium phosphate layer coated by PEO technique

Mohammad-Ali Faghihi-Sani[a,*], Ali Arbabi[b], Aida Mehdinezhad-Roshan[a,1]

[a] *Materials Science and Engineering Department, Sharif University of Technology, Tehran, Iran*
[b] *METCO srl, Via Galileo Galilei 53, Monteveglio (BO), Italy*

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Abstract

Surface modification of titanium implants is recently considered by several researchers. In this study, PEO was performed over commercially Ti-6Al-4V alloy pellets in an aqueous electrolyte containing calcium acetate (C.A.) and calcium glycerphosphate (Ca–GP) with a Ca/P molar ratio of 6.8, and applying current density of 0.212 A/cm^2, frequency of 100 Hz and duty ratio of 60% for 4 min. In the next step, hydrothermal treatments were carried out for various durations and at different temperatures inside an autoclave chamber containing a NaOH solution with pH of 11.5. XRD and SEM results confirmed formation of needle-shaped HAp after all hydrothermal conditions. Maximum intensity of HAp peaks was observed for the hydrothermally treated sample at 190 °C for 15 h. Moreover, crystallinity degree of HAp was increased by increasing hydrothermal duration and temperature. According to the SEM line scan analysis of cross section of the PEO coated sample after hydrothermal treatment at 190 °C for 15 h, it seems that Ca^{+2} and $[PO_4]^{-3}$ ions from internal layer of amorphous coating diffuse to the coating surface and dissolve into the solution during hydrothermal treatment, and finally precipitate on the outer layer of coating as needle-shaped HAp.
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Keywords: D: Hydroxyapatite; Coating; Hydrothermal; PEO

1. Introduction

Titanium and its alloys such as Ti-6Al-4V are well known as materials that have been used for biomedical applications [1–3]. Despite biocompatibility and excellent mechanical properties, Ti and its alloys does not form a strong bond to the human bones since Ti is not an active metal [4]. In addition, it releases metallic ions like vanadium in physiological environments [5,6]. Therefore, various surface treatments have been applied to modify the structure, chemistry and composition of Ti surface.

One of the best methods to improve the biocompatibility of Ti is to coat it with biocompatible films. Hydroxyapatite (Ca_{10} $(PO_4)_6$ $(OH)_2$; HAp) is an important active biomaterial which chemically bonds to the bone [7]. In this regard, different coating techniques such as sol–gel [8], ion beam assisted deposition [5], sputtering [9], electrophoretic deposition [10], pulsed laser deposition [11] and specially plasma spray [12] have been used to coat HAp on Ti alloys. However, these methods present some drawbacks such as low fatigue strength, high porosity, weak adherence to the metallic substrate and degradation during a long-term implantation [13].

Plasma Electrolytic Oxidation (PEO) is a promising technique for coating ceramic layers on nonferrous metallic substrates. Few researchers have reported formation of amorphous calcium phosphates on Ti substrate by this method [14,15]. Some advantages of this novel method are strict adhere of calcium phosphate layer to the substrate as well as much better bio-compatibility due to the improved morphology of the film. It has been demonstrated that coated Ti implants by HAp have better bioactivity in comparison with the bare one [16]. Unfortunately, because of relatively low crystallinity of the PEO coatings, the coated amorphous calcium phosphate layer is not as stable

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[*] Corresponding author. Tel.: +98 21 66165260; fax: +98 21 66005717.
E-mail address: faghihi@sharif.edu (Faghihi-Sani).

[1] Current address: Materials Science and Engineering Department, University of Texas at Arlington, Texas, USA.

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and bioactive as crystalline HAp. Further hydrothermal process can transform amorphous calcium phosphate phase to the crystalline HAp with high crystallinity and needle-shape structure [7,16–21]. The purpose of the present study is to form HAp coating on Ti-6Al-4V using a hybrid PEO-hydrothermal treatment.

2. Materials and methods

In the first step, PEO performed over commercially Ti-6Al-4V alloy pellets in an aqueous electrolyte containing 0.232 mol/l calcium acetate (C.A., Sigma-Aldrich) and 0.040 mol/l calcium glycerphosphate (Ca–GP, Acros Organics) with Ca/P molar ratio of 6.8 by applying current density of 0.212 A/cm^2, frequency of 100 Hz and duty ratio of 60% for 4 min. The temperature of electrolyte was set between 25 °C and 30 °C by means of a water cooling system.

In the next step, hydrothermal treatment was carried out at various temperatures (160, 190 and 200 °C) for various times (5, 10 and 15 h). The samples were placed at the bottom of 80 ml autoclave containing 16 ml NaOH aqueous solution with pH of 11.5.

Surface morphology and cross section of the treated samples were observed by a scanning electron microscope (SEM) VEGA-TESCAN model coupled by EDS. Phase composition of the coatings was analyzed by X-ray diffraction (XRD, STOE, STADI MT Model X-ray source, using CuK$_\alpha$ = 1.54 Å, 40 kV and 30 mA) with step size of 0.02ο̱ and detecting time of 1 s.

Topography and roughness of the coated samples were inspected by atomic force microscope (AFM) on Nanosurf Easy Scan 2 AFM in Contact Mode.

3. Results and discussion

Fig. 1 shows microstructure of the porous Ca–P layer coated by the PEO technique before hydrothermal treatment. Presence of such kind of porosity is suitable for growing bone tissues [14]. The Ca/P molar ratio of coating, measured by SEM–EDS elemental analysis, was 1.67 which is the same ratio as in stoichiometric HAp. Roughness of the coating, based on AFM result in Fig. 2, was about 2.3 μm. XRD result of the coating in Fig. 3 illustrates presence of amorphous phase as well as anatase, rutile and calcium titanate which all were developed during PEO process.

Fig. 4 shows XRD patterns of the coated samples after hydrothermal treatment at various temperatures and times. Comparing these patterns with the one before hydrothermal treatment (Fig. 3) confirms evolution of crystalline HAp from amorphous phase during hydrothermal treatment. In addition, intensity of the anatase peaks increased, while intensity of the rutile and calcium titanate peaks didn't change sensibly. This evolution of anatase under hydrothermal treatment has been reported before [22,23].

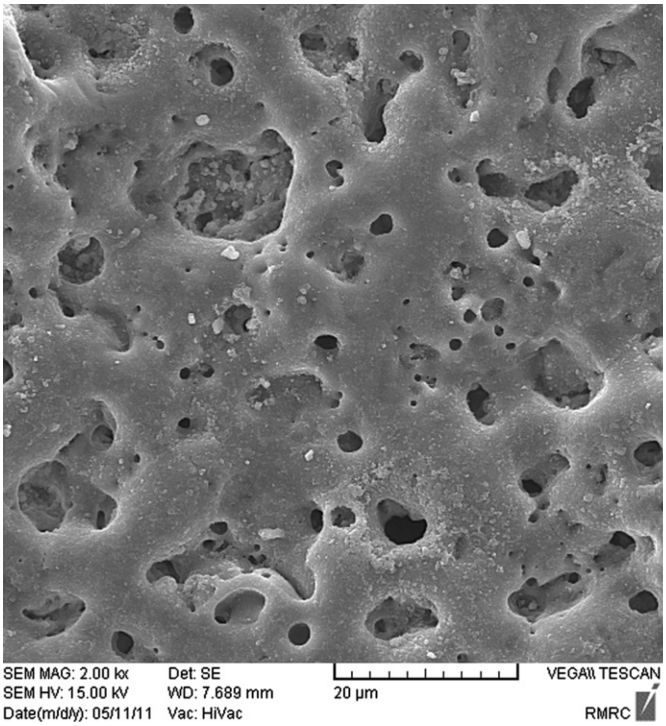

Fig. 1. Microstructure of coating surface after PEO process.

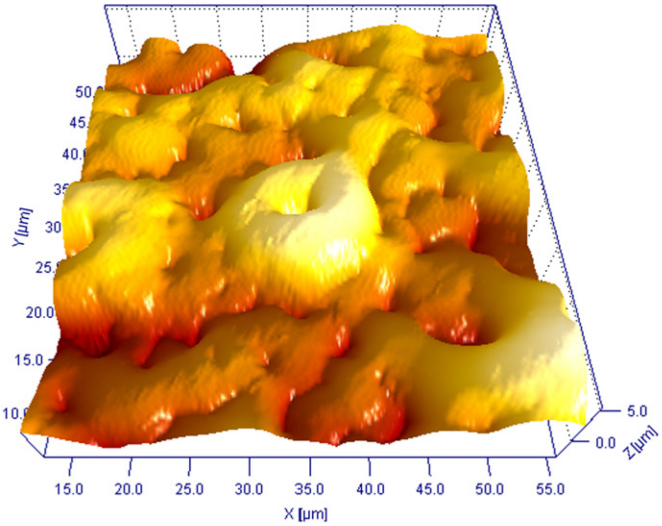

Fig. 2. AFM image of coating surface after PEO process.

Fig. 5 presents diffracted peaks intensity ratio of HAp (211) to Ti (101) planes for hydrothermally treated coats in various conditions. It can be concluded that crystallization of HAp was enhanced by increasing time and temperature. However exceptions were observed for the samples hydrothermally treated at 220 °C for both 10 and 15 h where this ratio was less. In fact at higher temperature (220 °C), crystallization rate of HAp in hydrothermal aqueous solution is lower than its dissolving rate as reported before[24]. In addition, evolution of anatase during hydrothermal treatment at higher temperature (220°) can also justify decrease in ratio of HAp (211) to Ti (101) peaks intensity, as reported by Drnovšek et al. [22]. Maximum

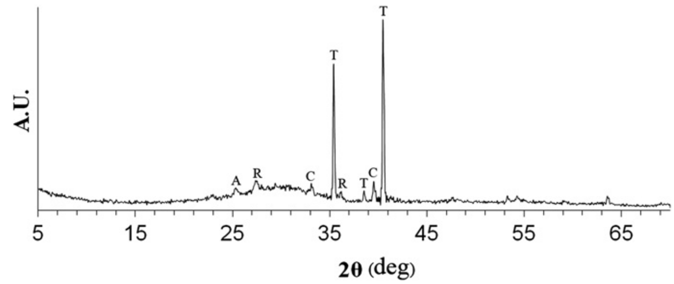

Fig. 3. X-ray diffraction pattern of coated sample by PEO (T:Ti, A: Anatase, R: Rutile and C: Calcium titanate).

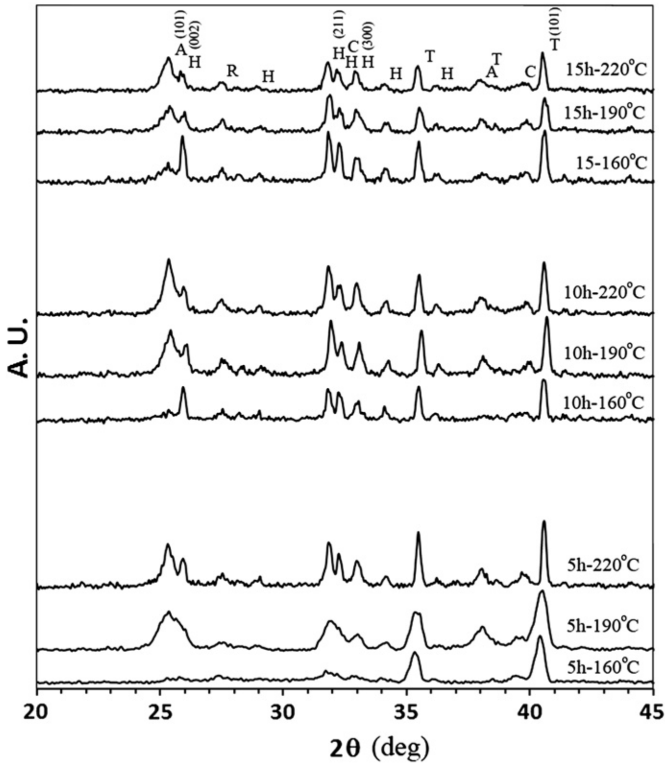

Fig. 4. X-ray diffraction patterns of the coated samples after hydrothermal treatment in various conditions. (T:Ti, H:Hydroxyapatite, A: Anatase, R: Rutile and C: Calcium titanate).

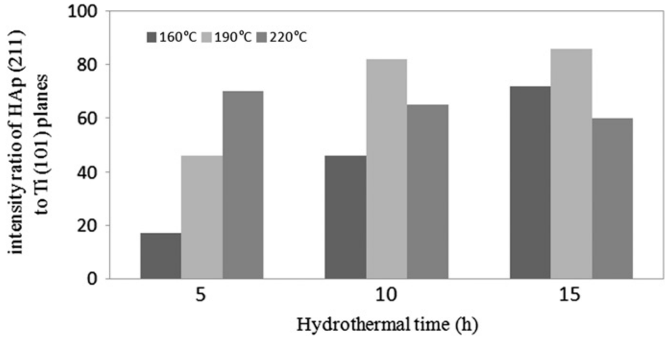

Fig. 5. Diffracted peaks intensity ratio of HAp (211) to Ti (101) planes for hydrothermally treated coats in various conditions.

ratio was observed for the sample hydrothermally treated at 190 °C for 15 h. Figs. 6 and 7 present SEM and three dimensional AFM view of this coated sample, respectively. Due to the growth of HAp crystals inside open pores, surface roughness of the hydrothermally treated sample (1.5 μm) was lower than that of the PEO coated sample (2.3 μm). Crystallinity of HAp in all samples (except those hydrothermally treated for 5 h at 160 and 190 °C) was around 70%, according to the equation of landi [25]. It seems that 5 hours was not enough for growing HAp crystals.

The cross-section SEM image and the related line-scan of hydrothermally treated sample at 190 °C for 15 h in Fig. 8 indicate a thickness of 15 μm for the coating. Moreover, the layer of HAp crystals with 200–300 nm length can be clearly seen at the outer surface, perpendicular to the coating.

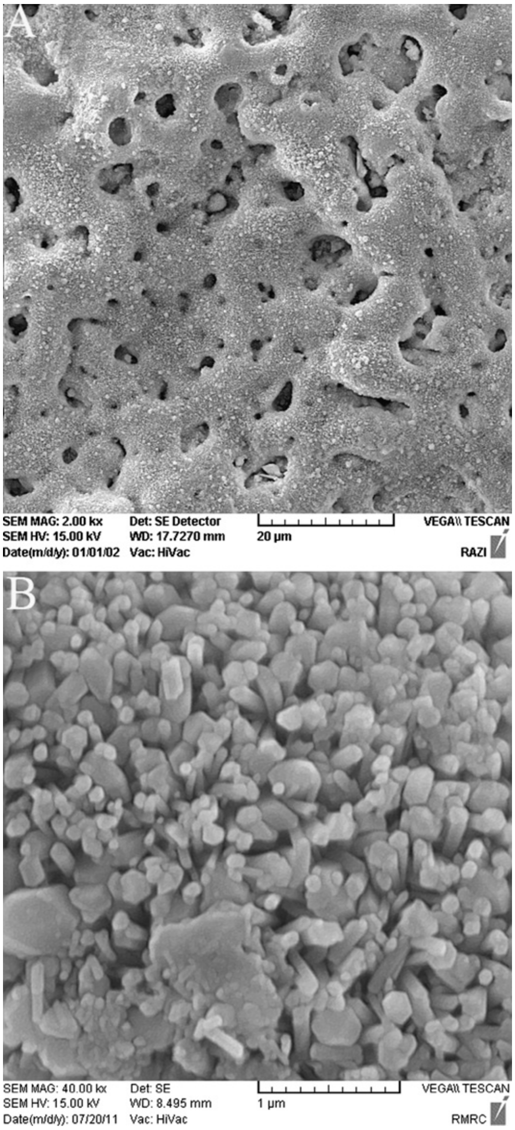

Fig. 6. Microstructure of hydrothermally treated coats at 190 °C for 15 h. (A) 2000x and (B) 40000x.

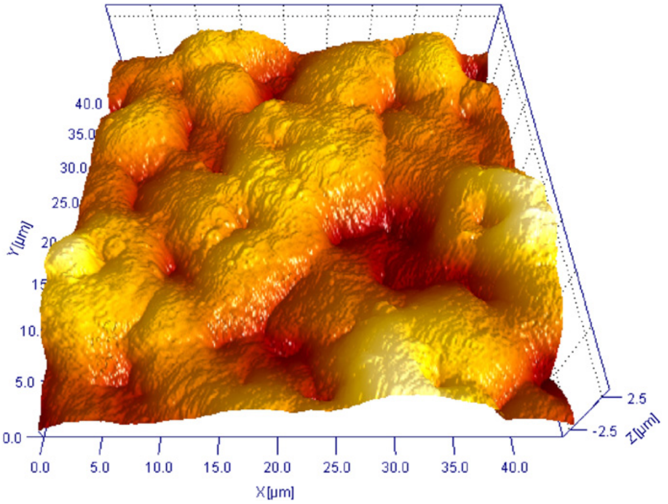

Fig. 7. AFM three-dimensional image of coating surface after hydrothermal treatment at 190 °C for 15 h.

As line scan result in Fig. 8 shows, there is a depletion of Ca and P concentration just behind the surface, where HAp crystals grow on the coating. This depletion is due to diffusion of Ca and P from the bulk towards the surface, dissolving in the hydrothermal aqueous solution and nucleation of HAp on the surface by the following reaction:

$$10Ca^{+2}+6(PO_4)^{-3}+2(OH)^{-}\leftrightarrow Ca_{10}(PO_4)_6(OH)_2$$

According to the above mentioned reaction, high concentration of OH^{-} (high pH) is necessary for precipitation of HAp crystals.

Consumption of Ca^{+2} and $[PO_4]^{-3}$ on the surface of coating for formation of HAp, is compensated by diffusion of these ions from the inner layer towards the surface of film.

As Kokubo et al. have explained before, HAp nucleation is induced by Ti–OH groups [26]. When the TiO_2 coating is exposed to an aqueous solution with a pH of more than 11 inside an autoclave, Ti–OH group is formed on the surface. This group is responsible for nucleation of HAp crystals on the surface of coating. The porous structure of TiO_2 coating (by PEO) with a high surface area is also important for inducing nucleation of HAp, as reported before [27].

Diffracted peaks intensity ratio of (002) to (300) planes for the precipitated hydroxyapatite film after various hydrothermal treatments is presented in Fig. 9. As these results show, although the mentioned ratio increases with time at low temperature (160 °C), it decreases with time at higher temperatures.

Since $I_{(002)}/I_{(300)}$ ratio for the standard HAp is 0.67 (JCPDS No.9-432), higher value of this ratio implies preferentially growth of needle like HAp crystals along the *c*-axis [28]. This ratio for the hydrothermally treated sample at 160 °C for 15 h was maximum (2.1) as shown in Fig. 10. Increase in hydrothermal treating temperature promotes growing rate of HAp crystals along *a*-axis and therefore decreases the $I_{(002)}/I_{(300)}$ ratio.

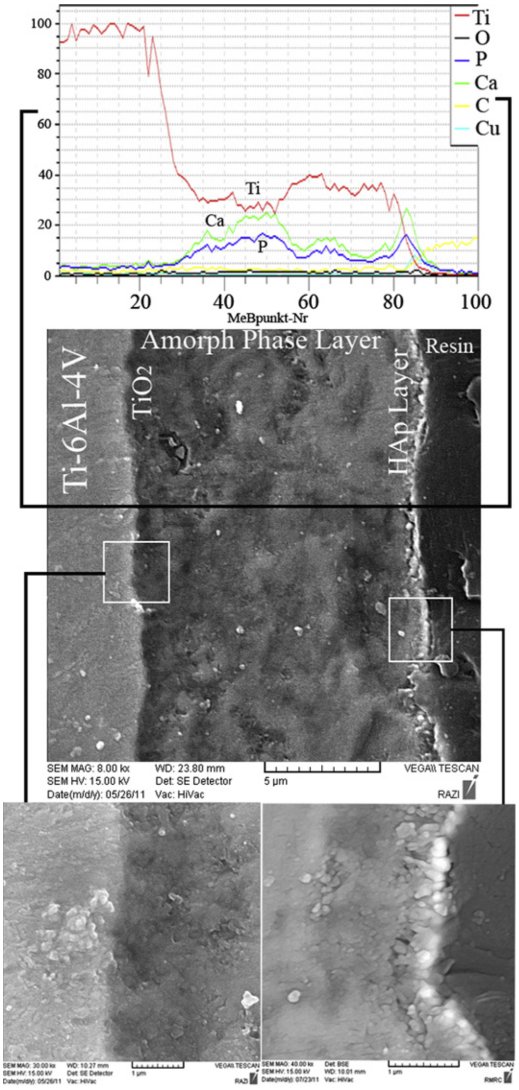

Fig. 8. Cross-section image of hydrothermally treated sample at 190 °C for 15 h and related line-scan.

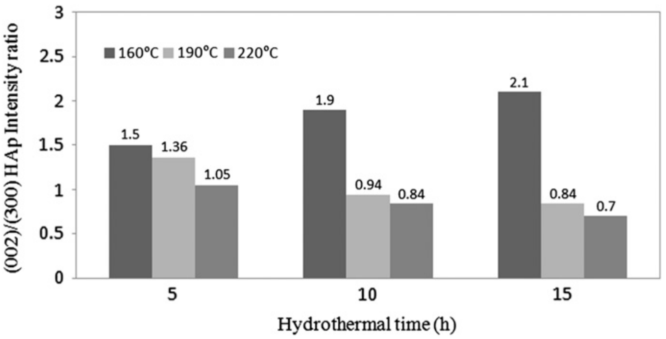

Fig. 9. Diffracted peaks intensity ratio of (002) to (300) planes for precipitated hydroxyapatite after various hydrothermal treatments.

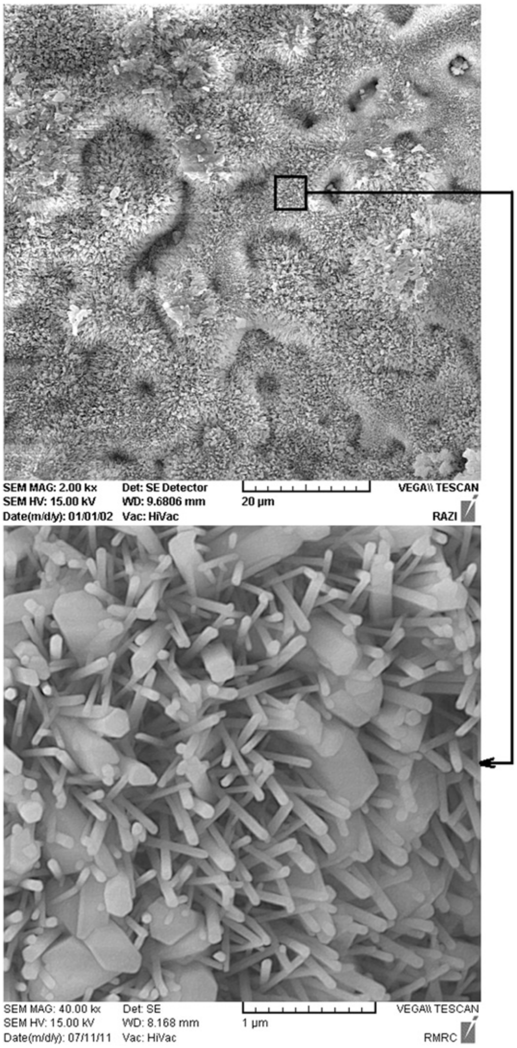

Fig. 10. Preferentially growth of needle-like HAp in the sample hydrothermally treated at 160 °C for 15 h.

4. Conclusion

In the first step of this research, an amorphous calcium phosphate layer, with Ca/P molar ratio of 1.67 (similar to stoichiometric HAp) was coated on Ti-6Al-4V substrate by PEO technique. This amorphous phase was transformed to crystalline hydroxyapatite through hydrothermal treatment inside a basic aqueous solution with a pH of 11.5. Detecting a depletion of Ca and P concentration just behind the surface confirmed diffusion of Ca and P from the bulk towards the surface of the film to form HAp crystals during the hydrothermal treatment. Diffracted peaks intensity ratio of (002) to (300) planes for the precipitated hydroxyapatite was increased with increasing time at low temperature, implying preferred growth of needle-like HAp crystals on outer surface of coating. Increasing duration and temperature of hydrothermal treatment enhanced crystallization of HAp. Maximum peak intensity of HAp was observed in the sample hydrothermally treated at 190 °C for 15 h.

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