

Preparation and characterization of bio-ceramic coatings on the surface of pure titanium by plasma electrolytic oxidation-alkali and heat treatment

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A type of TiO₂-based bioactive ceramic coatings containing Ca and P with the capability of inducing hydroxyapatite (HA) was obtained on the surface of pure titanium samples by plasma electrolytic oxidation(PEO)-alkali and heat (PEOAH) treatment. The morphologies, elemental compositions and phase components of the coatings at different stages were characterized by SEM, EDX and XRD. The results show that TiO₂-based ceramic coatings were obtained on pure titanium by PEO within an electrolyte containing calcium salt and phosphate. Alkali and heat treatment helped calcium titanate and calcium phosphate form in the coatings. Having been immersed in simulated body fluid for 7 days, the PEOAH samples lost their original porous structures. Instead, the coatings were completely covered with a dense layer of spherical apatite. After 14 days' immersion, the apatite layer became denser and stick-shaped apatite crystals with higher crystallinity began to form. The apatite layers are composed of mesh structures, and the diameters of the mesh pores are less than 100 nm.

Key words: Titanium, Plasma electrolyte oxidation (PEO), Alkali and heat treatment, Hydroxyapatite (HA).

Introduction

Ti and Ti-based alloys are promising substitutes for hard tissues of the human body because their elastic constants are similar to human bones. However, Ti and Ti-based alloys are bio-inert materials. If they were directly implanted into human bodies, there would be a number of problems, such as poor bioactivity, low bond-strength, and a long time needed to heal etc [1]. Therefore, focus has been directed on how to improve the bioactivity and bio-compatibility of Ti and Ti-based alloys by surface modifications.

Nowadays, plasma spraying, roasting, and laser-deposition are the main methods to modify surfaces of Ti and Ti-based alloys in clinical applications. These methods have similar routines: the first thing is to prepare bio-ceramic powders (such as hydroxyapatite (HA), calcium titanate (CaTiO₃) and calcium phosphate (TCP)); and the second is to coat these powders onto substrates by the methods listed above. The coatings prepared by these methods have a low bond-strength between themselves and substrate. In addition, their fatigue strengths are low and they are easy to decompose or crack. All of these flaws affect their use badly [2].

Plasma electrolytic oxidation (PEO) could be used to prepare TiO₂-based ceramic coatings with a porous structure on the surfaces of Ti and Ti-based alloys, combining the substrate and coatings in a metallurgical way [3]. Within

an electrolyte containing calcium salt and phosphate, Ca ions and P ions would enter the TiO₂-based ceramic coatings during the process of plasma discharging, existing in the form of an amorphous calcium salt and amorphous phosphate [4], which could be transformed into calcium titanate crystals and calcium phosphate crystals by an alkali and heat treatment, respectively [5]. After an alkali and heat treatment, it could induce a type of HA coating on the surfaces of samples by immersing the treated samples in simulated body fluid (SBF).

Previous work focused mainly on titanium alloys such as Ti6Al4V, however, the more complicated the elements the involved in the films, the more complexities for biologists to determine the biological safety of an alloy. By this means, we choose pure titanium to carry out our research on in order to avoid some irrelevant element entering the film such as V.

In this study, a type of bioactive ceramic coatings with TiO₂/CaTiO₃/HA was first fabricated on the surface of pure titanium by a novel process involving PEO, alkali and heat treatment and SBF immersion in a Ca (CH₃COO)₂·H₂O-Ca (H₂PO₄)₂·H₂O electrolyte system. The morphologies, elemental compositions and phase components of the coatings at different stages were analyzed by SEM, EDX and XRD.

Experimental Procedure

Sample preparation

Materials used in this experiment were pure titanium for industrial use. Samples were cut into pieces 30 mm × 13 mm × 2 mm and abraded by 600# and 1200# waterproof

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abrasive papers. The samples were then washed by acetone and de-ionized water, and later were dried by hot air. This “wash and dry” treatment is abbreviated as WD below. The major ingredients of the electrolyte were: 5 g/l Ca $(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 10 g/l Ca $(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, 10 g/l $(\text{NaPO}_3)_6$, 15 g/l NaOH and 10 g/l EDTA-2Na. This experiment adopted a PEO system with a bidirectional-pulse electrical supply whose wave is square to make the PEO treatment. The positive voltage, negative voltage, frequency, duty cycle and oxidizing time were 300 V, 30 V, 600 Hz, 20% and 5 minutes, respectively. The temperature of the electrolyte was kept in the range of 25 °C–40 °C with the aid of a cooling system. The coatings obtained after PEO were noted as PEO.

After WD, the PEO samples were immersed in 7 M NaOH solution for 24 h at a temperature of 90 °C. After being immersed in an alkali solution, they were again treated by WD. Then they were heat treated for 3 h at a temperature of 700 °C. The PEO samples after alkali-and-heat treatment were noted as PEOAH. Again, the PEOAH samples were also treated by WD.

SBF immersion of the samples

The PEOAH samples were immersed in SBF for 3, 7 and 14 days. Simulated body fluid (SBF) was prepared according to the recipe in Table 1 [6], buffering at pH 7.4 with 1 mol/l HCl and $(\text{CH}_2\text{OH})_3\text{CNH}_2$ at 36.5 °C. In order to keep it fresh during the whole process, SBF should be refreshed every day.

Characterization of the compositions and structures of the coatings

The phases of the PEO, PEOAH and SBF-immersed PEOAH samples were analyzed by X-ray diffraction (XRD, Philips X'Pert, Holland) using $\text{Cu K}\alpha$ radiation with a glancing angle of 1°. The measurements were performed with a continuous scanning mode at a rate of 2°/minute. The surface morphologies were observed using scanning electron microscopy (FEI/PHILIPS Quanta 200, Holland). The elemental compositions were examined with an energy-dispersive X-ray spectrometer (EDX).

Results and Discussion

Morphologies and components of PEO coatings

The morphologies of PEO coatings are shown in Fig. 1.

Table 1. Composition and concentration of SBF

Reagent	Concentration/g·l ⁻¹
NaCl	7.996
NaHCO ₃	0.350
KCl	0.224
CaCl ₂	0.278
Na ₂ SO ₄	0.071
MgCl ₂ ·6H ₂ O	0.305
K ₂ HPO ₄ ·3H ₂ O	0.228

The PEO coatings show a type of porous structure. The volcanic vent like micro-pores formed during the plasma discharge process, are distributed at regular intervals (Fig. 1(a)). In the higher magnified image (Fig. 1(b)), the diameters of the pores are < 5 μm. Porous structures are beneficial for cell attachment, propagation and bone-growth.

The cross-sectional morphology of a PEO coating is shown in Fig. 2(a). In Fig. 2(a), the thickness of the PEO coating is about 65 μm, and there is a serrated shape between the coating and the substrate, which shows that the PEO coatings combine with the substrate in a metallurgical way. There is no obvious transition layer between the coating and the substrate, and the part of coating near the interior substrate is denser than that near the exterior.

In order to detect the distributions of components in the PEO coating, points 1, 2 and 3 were chosen on the cross-section to do electron spectroscopy characterization (Fig. 2(a)). It is shown from the statistics in Fig. 2 and Table 2 that distributions of the components on one fracture plane are not quite similar: distributions of Ca and P in the coatings change by a gradient and decrease gradually from the exterior to the interior along the coating fracture; by contrast, the distribution of Ti decreases gradually from the interior to the exterior; the distribution of O is the

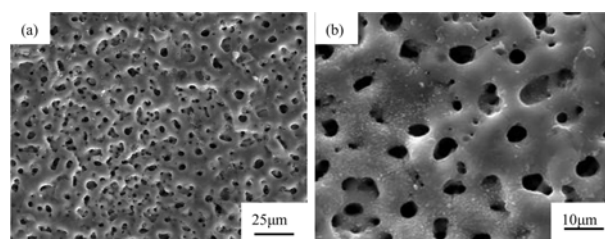


Fig. 1. Surface morphology of PEO films on pure titanium (a) low magnification and (b) high magnification.

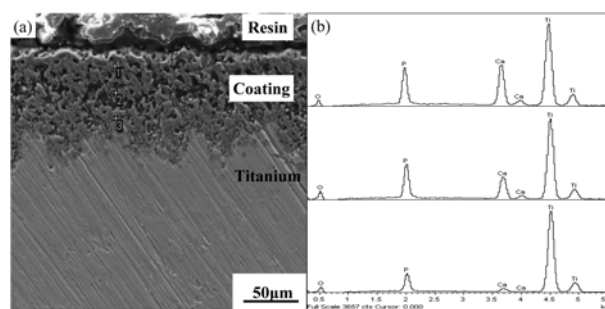


Fig. 2. Cross-sectional SEM view of a PEO coating and EDX analysis (a) Cross-sectional SEM view of PEO coating; (b)EDX spectra of points 1, 2, 3 in (a).

Table 2. Composition and content of PEO films

Points	Composition and content of PEO films(a.t.%)				Ca/ P
	Ti	O	Ca	P	
A	20.57	65.13	7.41	6.89	1.08
B	22.15	66.44	4.71	6.70	0.70
C	27.22	67.21	0.78	4.79	0.16

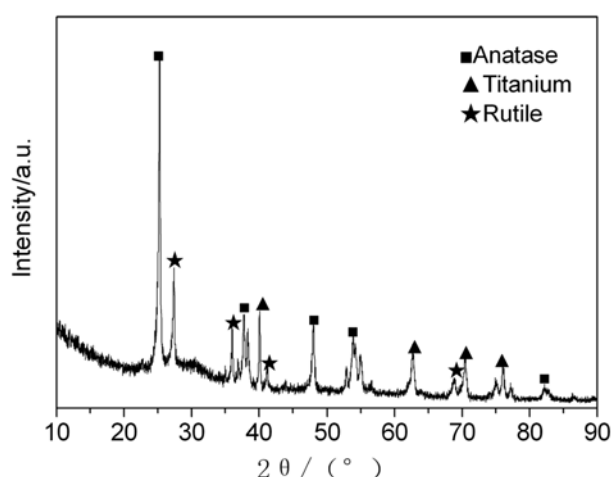


Fig. 3. XRD pattern of a film after plasma electrolyte oxidation.

biggest portion among all the components, but it does not change obviously in the coating, with a little greater in the interior portion than in the exterior.

An X-ray diffraction pattern of a PEO coating is shown in Fig. 3. According to Fig. 3, PEO coatings are mainly composed of two types of phase modifications of titanium dioxide, i.e., metastable anatase at low temperature and stable rutile at high temperature. The anatase form is the predominant phase in the coatings. It can be observed from Fig. 3 that the diffraction peaks of titanium are very strong. This should come from the substrate due to the fact that the coatings formed in so short a period of oxidation are too thin. In PEO coatings, no phase containing Ca, P was found from XRD, while Ca, P could be seen from the EDX spectra (Fig. 2(b)), which indicates that Ca, P should exist in coatings in an amorphous way. Some previous research also show that PEO coatings, prepared in an electrolyte containing calcium salt and phosphate, contain amorphous phases made up of Ca, P etc [4]. During the process of PEO, there are some complicated physical and chemical reactions related to the plasma on the surface of the electrode. Ionization and concentration of the plasma are such reactions. Within the processes of ionization and plasma concentration on the surface of the electrodes, there were a great amount of heating effects and chilling effects, which caused PEO coatings to have a special surface structure, e.g. amorphous phases.

In this experiment, an electrolyte containing Ca (CH_3COO)₂·H₂O, Ca (H_2PO_4)₂·H₂O, (NaPO_3)₆ was used for preparing the PEO coatings with Ca, P on the surface of pure titanium samples. The result shows that group components (such as Ca^{2+} , PO_4^{3-}) in the electrolyte have been involved in PEO. Huang *et al* [7]. have reported that electrophoresis and diffusion are the main mechanisms for group components to enter thin coatings. According to the above analysis, distributions of Ca and P in the coatings change in a gradient, which indicates diffusion is one of the main means for Ca, P to enter into a PEO coating. Plasma discharge channels provided a passage

for Ca^{2+} and PO_4^{3-} to rapidly diffuse. As the thickness of coatings increases, P changes gently and O distributes uniformly. This indicates that electrophoresis is another mechanism for P to enter PEO coatings. During the early stage of plasma discharging, Ca^{2+} and PO_4^{3-} rapidly reached the surface of the metal through discharging channels. During the later stages they entered PEO coatings as newly formed TiO_2 melted and solidified. As time and the thickness of coatings increased, the discharging channels were gradually blocked by a great deal of molten TiO_2 . At this time PO_4^{3-} ions entered coatings by way of electrophoresis. Thus, the ratio of Ca to P in PEO coatings could be controlled to meet the need of bio-coatings by manipulating the components and concentration of electrolyte.

Morphologies and components of PEOAH coatings

Morphologies of PEOAH coatings are shown in Fig. 4.

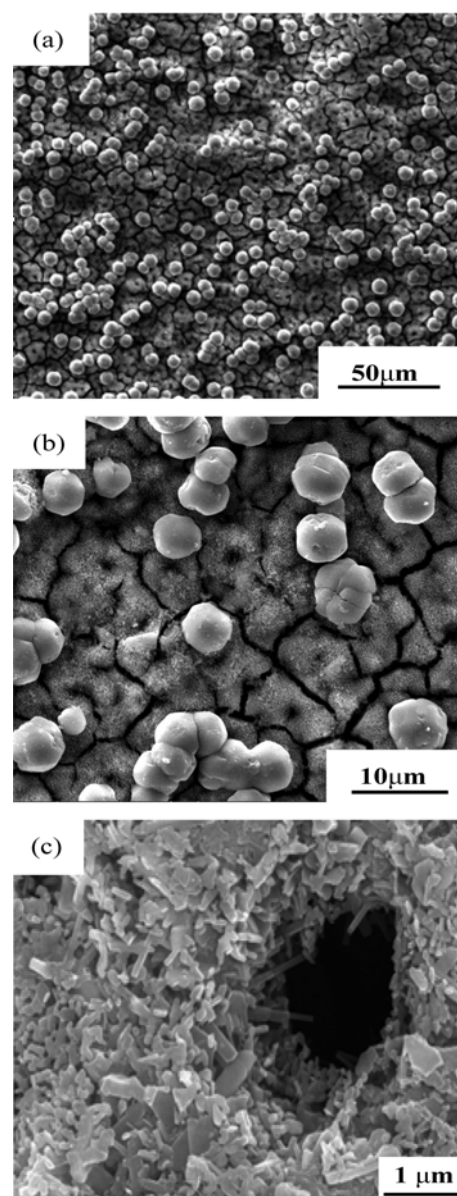
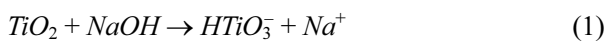


Fig. 4. Surface morphology of coatings after alkali and heat treatment.

Compared with SEM images of PEO coatings in Fig. 1, the PEOAH coatings have smaller pore sizes and a lower porosity density. Moreover, the surfaces of PEOAH coatings have become coarser. In the higher magnified SEM image, it is obvious that the coarse coatings are made up of many nano-flake structures and some nano-granules. All of these nano-flakes have a crystalline shape, with a uniform dimension at about 30 nm in the thickness direction.

An XRD pattern of PEOAH coating is shown in Fig. 5. According to Fig. 5, new phases of CaTiO_3 and $\text{Ca}_2\text{P}_2\text{O}_7$ have been found, and CaTiO_3 has become the predominant phase in the PEOAH coatings. Anatase and rutile still exist, but the content of anatase has decreased and that of rutile has increased in the PEOAH coatings, compared with those in PEO coatings (Fig. 3). Titanium dioxide phases are known to differ not only in their structures, but also in their properties. Generally, rutile exhibits much better protective properties than anatase because of better corrosion resistance and higher hardness. The Gibbs energy of the anatase-to-rutile transition is negative, i.e., the anatase phase is thermodynamically unstable at all temperatures. It is known that the anatase-to-rutile transition begins at temperatures above 610 °C, and a complete transition can be made up to 915 °C [4]. During the alkali and heat treatment, the temperature reached 700 °C, which facilitates the transition of anatase to rutile. Furthermore, the low thermal conductivity of titanium dioxide causes the underlying layer of the coatings to become heated and also promotes the further transition of the initially formed metastable anatase into the stable rutile. Thereby, the proportion of anatase in the PEOAH coatings decreases as the heating time increases.

According to ref [8], in the process of the alkali and heat treatment, due to the attack of the hydroxyl group, a part of the TiO_2 in the PEO coatings becomes dissolved in alkali solution:



The above reaction occurs at the same time as hydration;

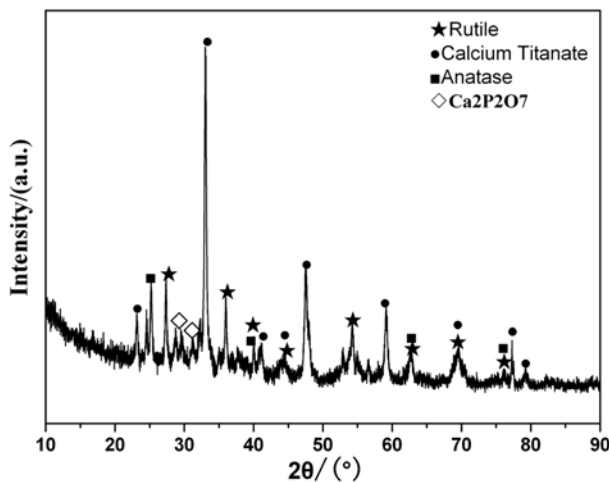
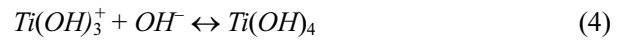
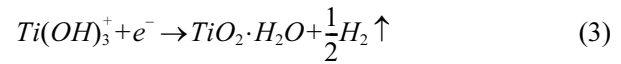
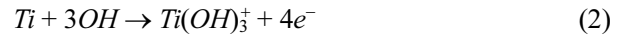
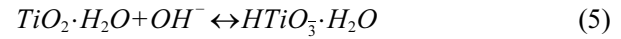


Fig. 5. XRD pattern of a film after alkali and heat treatment.



The hydrated TiO_2 would form negatively charged hydrated ions when it is further attacked by a hydroxyl group, and the reaction is:



These electronegative materials and alkali ions in the electrolyte combine together to form a layer of alkaline TiO_2 hydro gel, which could be changed into calcium titanate by dehydration after the alkali-and-heat treatment [5].

Morphologies and compositions of PEOAH coatings after immersion in SBF

The surface morphologies of the PEOAH coatings after being immersed in the SBF for 3, 7 and 14 days are shown in Fig. 6. After 3 days' immersion, the surfaces of the samples exhibited a reduction of pore size and pore density, and started to be covered with the mineralized apatite (Fig. 6(a)). After being immersed for 7 days, PEOAH samples lost their original porous structures. Instead, their surfaces were completely covered with a dense layer of spherical apatite (Fig. 6(b)). After 14 days' immersion, the apatite layer became denser and stick-shaped apatite crystals with higher crystallinity began to form (Fig. 6(c)). When observed at high magnification, the apatite layers are in fact seen to be composed of mesh structures, and the diameters of the net pores are less than 100 nm (Fig. 6(d)). The morphology of the apatite layer is very similar to that of bone-like apatite mineralized on NaOH-treated titanium in a SBF solution as reported by Kokubo et al and Kim et al [9, 10].

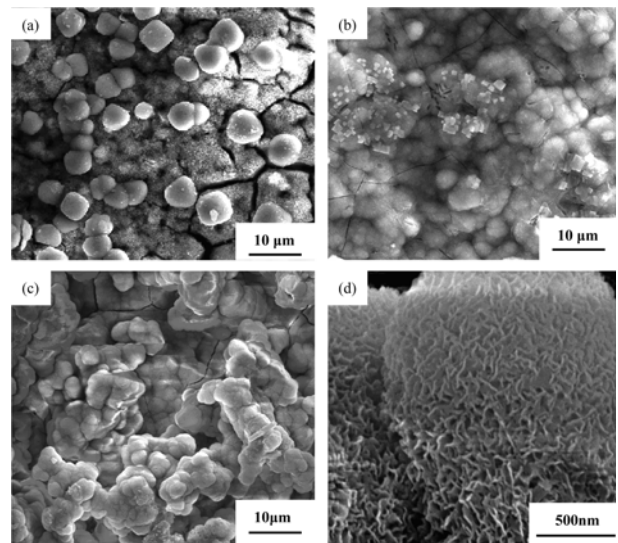


Fig. 6. Surface morphologies of films after SBF immersion (a) low magnification for 3 days (b) low magnification for 7 days (c) low magnification for 14 days (d) high magnification for 14 days.

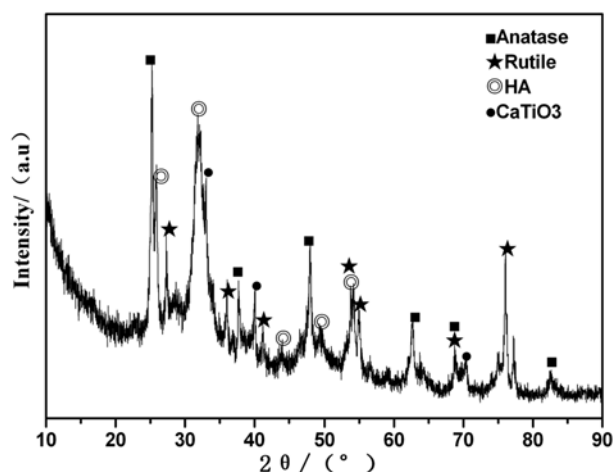
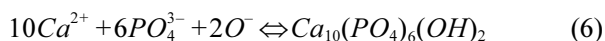


Fig. 7. XRD pattern of a coating after SBF immersion for 7 days.

An XRD pattern of a PEOAH coating after being immersed in SBF for 7 days is shown in Fig. 7. According to Fig. 7, HA has been found as a new phase, which is coherent with the phenomenon and explanation above; anatase and rutile still exist in the coatings. After a series of treatments discussed above, a layer of bio-ceramic coating containing $\text{TiO}_2/\text{CaTiO}_3/\text{HA}$ was formed on surface of pure titanium.

As reference [11] describes, there are two key reasons for HA to form in SBF. Firstly, it is related to the surface and components of the material itself. In this experiment, the PEO coatings have many pores and contain Ca, P. These factors have provided more nucleation points for HA's deposition. Secondly, in the solution at the temperature of the human body, only two types of phosphate are stable. When the value of $\text{pH} < 4.2$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is the most stable form; while that when the $\text{pH} > 4.2$, HA is the most stable form, and when the $\text{pH} > 5.3$, HA would take priority to precipitate from solution [1]. Therefore, it could be inferred that HA is the most stable form among all the calcium salts in the SBF whose $\text{pH} > 7$. The SBF used in this experiment was a supersaturated solution, which has a strong trend for deposition thermodynamically. Therefore, as soon as HA nucleation formed, it would grow spontaneously by consuming Ca^{2+} and PO_4^{3-} around itself in the SBF, which could be described as [11]:



Therefore, the formation mechanism of HA could be described like this: after the alkali and heat treatment, the surfaces of samples would be attached by many $\text{HTiO}_3 \cdot \text{H}_2\text{O}$ groups. When the samples were immersed in SBF, due to electrostatic attraction, Ca^{2+} with a high electrovalence was first absorbed on the surface, followed by PO_4^{3-} . When their density was up to some degree, they would also nucleate; after nucleation started, Ca^{2+} and PO_4^{3-} would diffuse to nucleate due to the concentration gradient, making nuclei spontaneously absorb new Ca^{2+} and PO_4^{3-} and grow.

When the nucleus reached a certain size, it would grow spontaneously with an adequate supply of ions. Nucleation and growth compete with each other; and the more rapid the nucleation is, the smaller the final crystals are; by contrast, there would be spherical HA crystals with a high degree of crystallinity in SBF [6]. The morphologies formed in the early period were related to the surfaces of the coatings, but in the later period, when the surfaces of the coatings were completely covered by HA, the growth of HA has little relationship with the surfaces of samples. At this time, the growth of HA would obey a common law for crystals to grow: as long as the density of Ca ions and P ions and the temperature of the electrolyte were kept stable, growth would continue. These crystals in the shape of clusters could be later transformed into spherical crystals or club-shaped crystals with a higher degree of crystallinity after a solid-phase transformation [8].

Conclusions

TiO_2 -based coatings containing Ca and P on titanium were obtained by PEO in an electrolyte composed of a chelate complex of EDTA-2Na, $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and phosphate salts, etc.; distributions of Ca and P in the coatings change by a gradient and decrease gradually from the exterior to the interior. After an alkali and heat treatment, the size and the density of the pores on the surface of the coatings both decreased. Meanwhile, calcium titanate and calcium phosphate phases with bioactivity were formed in the coatings. After being immersed in simulated body fluid for 7 days, HA layers with nano-sized mesh structures were induced on the surface of the samples. After a series of treatments discussed above, a layer of bio-ceramic coating containing $\text{TiO}_2/\text{CaTiO}_3/\text{HA}$ was formed on the surface of pure titanium.

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