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Deposition of hydroxyl-apatite on titanium subjected to electrochemical plasma coating

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ABSTRACT

This work investigated the direct deposition of hydroxyl-apatite (HA) on pure titanium via an electrochemical plasma (EP) coating. For this purpose, the EP coatings were deposited at 200 mA/cm^2 for 900 s in HA-containing electrolytes with and without tripotassium phosphate (K_3PO_4). At the onset of the ignition phenomenon during the EP coatings, the HA particles began to nucleate on the titanium sample due to the electrophoresis of the negatively charged HA particles in both electrolytes. The amounts of Ca and P in the coating layer produced in the electrolyte without K_3PO_4 was higher than that in the electrolyte with K_3PO_4 since the HA coating layer grew without a transformation in case of the electrolyte without K_3PO_4. In contrast, most HA particles in the coating layer of the electrolyte with K_3PO_4 decomposed readily to α-, β-tricalcium phosphate ($Ca_3(PO_4)_2$) and calcium titanate ($CaTiO_3$) compounds with the aid of the plasma-assisted electrochemical reactions found between the HA particles and phosphate ions or titanium oxide. Immersion tests in a simulated body fluid solution showed that the titanium samples coated with the biochemically stable HA particles, which were formed in the electrolyte without K_3PO_4, exhibited the accelerated growth of biomimetic apatite.

1. Introduction

Pure titanium and its alloys have been used widely in biomedical applications owing to their high specific strength, high corrosion resistance, and biocompatibility in biological environments [1–3]. Nevertheless, biological integration between the bone and titanium implant was delayed after surgical implantation because the natural passivation layer of titanium was bio-inert [4]. To enhance the osseointegration response, the development of bioactive hydroxyl-apatite (HA) formed on titanium has been studied using surface modification techniques, such as plasma spaying and sol–gel [5–7]. Although HA coating via these techniques has been commercialized, the coating layer contains a range of chemical compounds that might deteriorate the bioactive properties of titanium [8].

An electrochemical plasma (EP) coating was a promising method to produce adhesive ceramic layers whose constituent compounds depended strongly on the composition of the electrolyte [9,10]. Therefore, EP coatings have recently been employed to introduce HA layers by choosing suitable electrolytes with chemical additives, such as calcium acetate monohydrate [11], sodium dihydrogen phosphate [12] and β-glycerophosphate disodium pentahydrate [13], because these chemical additives played an important role as precursors in accelerating the formation of HA. Nie et al. [14] first reported the formation of HA layer on duplex titanium alloys by micro-arc oxidation with two steps, where the sample was coated in the conventional electrolyte for 600 s to produce a TiO_2 layer, and it was treated again in a phosphate electrolyte containing HA powders. Bai et al. [15] fabricated HA coating layer on titanium by micro-arc oxidation in a NaOH electrolyte with HA powders. Although several studies have addressed the processing of pure HA layer, the issues, including the decomposition of HA by electrochemical reactions and the transformation from crystalline to amorphous phases due to the chemical additives, remained unsolved yet. Unless the electrolyte contained chemical additives that might react with the HA agglomerates incorporated, pure HA layer formed successfully on titanium. Therefore, the aim of the study is to fabricate the pure HA layer via EP coating in the KOH-electrolyte containing HA particles. This is compared to that in the KOH + K_3PO_4 electrolyte with HA particles in order to understand the effect of phosphate ions on the growth of the HA layer. In addition, the mechanism underlying the growth of pure HA layer is

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discussed in relation to the microstructures with increasing coating time.

2. Experimental procedures

Commercially pure titanium (Grade II) plates, $20\,\text{mm}^3 \times 30\,\text{mm}^3 \times 2\,\text{mm}^3$ in size, were used as a substrate. Before the EP coating, the titanium plates were ground with # 200-1000 abrasive papers and cleaned in pure acetone. The two electrolytes with the addition of 20 g/l HA powder with a mean size of ~0.1 μm were prepared; bath A contained an electrolyte consisting of 0.05 M KOH and 0.02 M K_3PO_4, whereas the electrolyte in bath B contained 0.05 M KOH. The pH values of both electrolytes were ~14, but the electrical conductivities of baths A and B were quite different, 19.5 and 8.7 mS/cm, respectively. Using an AC power supply attached to an electrolyte cell consisting of titanium anode and stainless steel cathode, a series of EP coatings were prepared for 900 s at a current density of $200\,\text{mA/cm}^2$. The temperature of the electrolyte was kept at 293 K to stabilize the electrochemical conditions during the EP coatings.

The surface and cross section morphologies of each sample were observed by field-emission scanning electron microscope (FE-SEM, HITACHI S-4800) equipped with energy dispersive spectroscopy (EDS). Electron probe microanalysis (EPMA, CAMECA SX-100) was used for compositional mapping of Ti, Ca, and P on the cross sectional samples. The phase components of the samples were measured by X-ray diffraction (XRD, RIGAKU D/MAX 2500). To examine the capability for the growth of biomimetic apatite at 37 °C, the EP-coated samples were immersed for 3 days in a simulated body fluid (SBF) solution whose ion concentrations were similar to the human blood plasma condition [16]. The SBF solution was refreshed every day to maintain the ionic concentrations. After immersion tests, the weight changes of each sample were recorded.

3. Results

Fig. 1 shows the voltage–time curves of the titanium samples during the EP coatings in baths A and B along with the dotted curve (marked 'A') obtained from the KOH-electrolyte without K_3PO_4 and HA. In case of the dotted curve with a plateau in voltage, no significant growth of the titanium oxide was observed. The voltage of the two samples increased steeply according to Ohm's law. This increasing rate of the voltage response became lower when the responding voltage exceeded the ignition voltage at which the plasma-arcs were initiated. The ignition voltage of the sample coated in bath B was ~27 V higher than that in bath A, because the ignition voltage was inversely proportional to the electric conductivity of the electrolyte, as reported earlier [17]. The whole curve of the sample coated in bath A exhibited the type typical for voltage–time relation of the EP-coated metals. On the other hand, the coating voltage of the sample coated in bath B was locally saturated at the onset of the ignition phenomenon until it was observed to increase rapidly. In addition, such curve saturated locally was overlapped with line A, as shown in Fig. 1. In

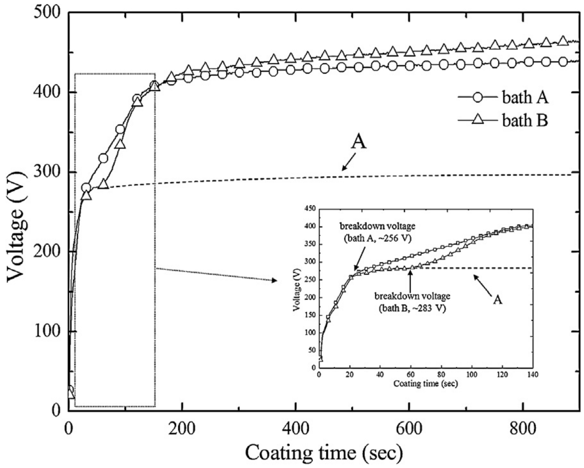

Fig. 1. Voltage–time curves of the titanium samples during the EP coatings in baths A and B; the dotted curve (marked 'A') indicates the voltage–time curve from the KOH-electrolyte without K_3PO_4 and HA powder.

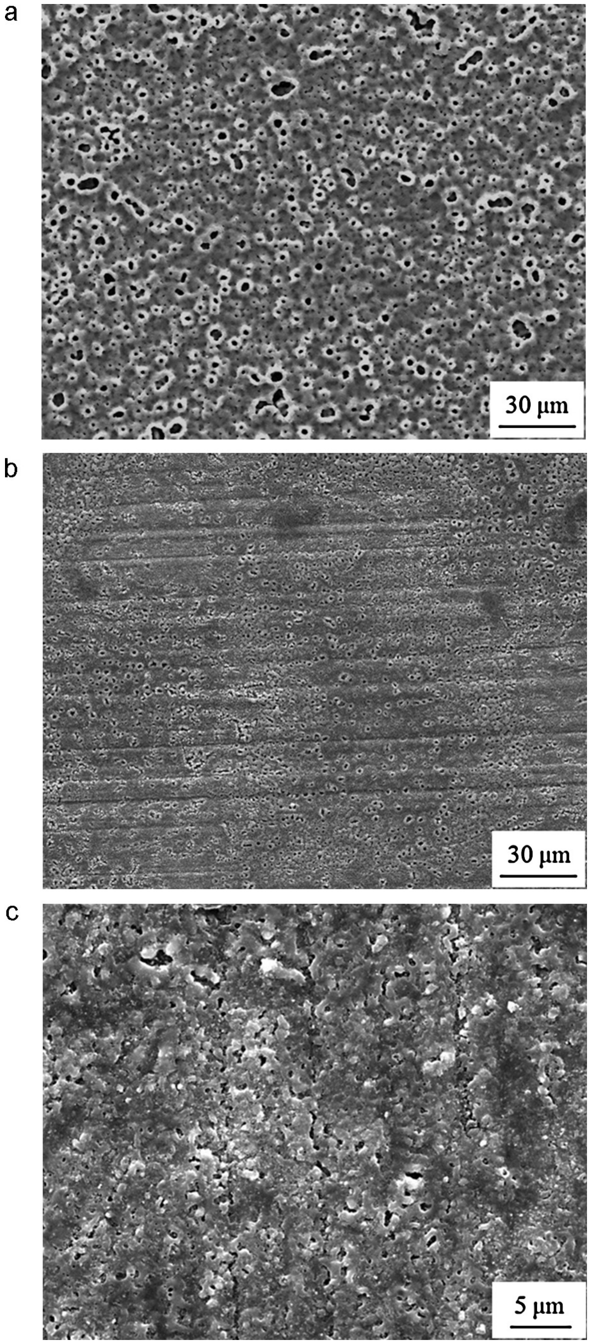

Fig. 2. Surface morphologies of the samples after EP coating for 30 s in (a) bath A and (b) bath B, and (c) for 60 s in bath B.