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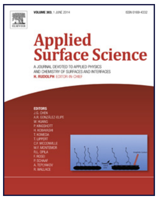

Effect of hydrothermal treatment model on stability and bioactivity of microarc oxidized titania coatings

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ABSTRACT

Different types of Sr-doped hydroxyapatite (Sr-HA) nanorod arrays were prepared on microarc oxidized (MAOed) TiO_2 coatings after hydrothermal treatment (HT) for 24 h in the case of different HT models, namely the MAOed TiO_2 coatings to be hanged up in the autoclave without touching the HT solution (termed as H-HT) and immersed in the HT solution (termed as I-HT). The MAO+H-HT (HT in the case of H-HT model) and MAO+I-HT (HT in the case of I-HT model) coatings are multilayered by nanorod-shaped Sr-HA as outer layer, $Ca_{0.5}Sr_{0.5}TiO_3$ as middle layer and TiO_2 as inner layer adjacent to Ti substrate. The Sr-HA nanorods on the coatings are randomly oriented, homogeneous and a similar mean diameter of 70 nm. However, the lateral spacing between the Sr-HA nanorods on MAO+H-HT coating is much smaller compared with those on MAO+I-HT coating. The effects of the HT models on the roughness, in vitro structure and bond strength stability and apatite inducing ability of the coatings were examined. AFM evaluation reveals that the coatings have a similar microscale roughness. The as-MAOed, MAO+H-HT and MAO+I-HT coatings exhibit long-term structure and adhesive strength stability as indicated by immersion tests in physiological saline solutions for 0–48 weeks, although their adhesive strengths decrease a little after immersion in physiological saline solutions, for example, to about 10.2%, 7.8% and 6.9% at 48 weeks, respectively. Furthermore, the MAO+H-HT coating can induce apatite formation after 12 h of SBF immersion due to the compacted Sr-HA nanorods layer, and the induced apatite prefers to nucleate on the basal-faceted surfaces of Sr-HA nanorods.

1. Introduction

It has been demonstrated that hydroxyapatite (HA) coatings on metal substrates significantly enhance osteoblast functions and bone formation because of their excellent biocompatibility, bioactivity and osteoconductivity properties, compared with uncoated ones [1–5]. As a result, many processing techniques, such as plasma spraying [6], laser deposition [7,8], ion beam dynamic mixing [9], ion beam deposition [10], magnetic sputtering [11], sol–gel precipitation [12], ion implantation [13], NaOH treatment and electrochemical methods [14,15], have been developed to fabricate HA coatings on the surfaces of metallic substrates. Among the different processes described, plasma spraying has been the most common method for modifying metal implant surfaces. However, numerous problems with the plasma-sprayed coatings have also been cited, including low fatigue strength, degradation, a weak adherence to metallic substrates, delamination during a long-term implantation and microcracks on the coating surface [16–19]. Furthermore, the rest of techniques all present some drawbacks, as described elsewhere in detail [20,21].

Different from the above-mentioned methods, microarc oxidation (MAO) has been developed as an alternative means of modifying metal surfaces. Through MAO, a porous, uniform and tightly bound oxide ceramic layer formed on metal surfaces, such as Al [22,23], Ti [24–26], Mg [27], Zr [28] Ta [29] and their alloys. The composition of ceramic layer formed has been reported to be dependent on the composition of the electrolyte, the use of electrolyte containing a mixture of calcium glycerophosphate and calcium acetate resulted in the formation of a porous oxide ceramic layer whose composition includes Ca and P. Furthermore, these amorphous Ca–P compounds can migrate from the ceramic layer and transform to HA during hydrothermal treatment (HT) [30–34]. So the hybrid approach of MAO and HT has received considerable attention and been proved to be an effective method to form HA coating on Ti and its alloys [30–34]. Unfortunately, up till now, there has been no significant progress in morphology and size control of

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the HA crystals although great efforts have been made, the HA crystals formed via the hybrid approach of MAO and HT not only have been submicrometer-sized short rod-like but have also only inhomogeneous covered approximately 40–60% of the MAOed titania surface. It is difficult to fabricate a high density of HA nanorods and control the arrays of the HA nanorod on the MAOed titania coating. In our recent work [35], Sr-doped hydroxyapatite (Sr_1-HA) nanorod layer were prepared by the hybrid approach of MAO and HT on Ti, furthermore, the effects of HT models, namely the MAOed TiO_2 coatings to be hanged up in the autoclave without touching the HT solution (termed as H-HT) and immersed in the HT solution (termed as I-HT), on the growth of Sr_1-HA nanorod arrays were investigated. It was found that the Sr_1-HA nanorods were compacted, randomly oriented and homogeneous after HT for 24 h in the case of H-HT model, while the Sr_1-HA nanorods were randomly oriented and homogeneous but sparse after HT for 24 h in the case of I-HT model. In this study, the effects of the HT models on the microscale roughness, in vitro structure and bond strength stability and apatite inducing ability of the MAOed TiO_2 coating were examined.

2. Materials and methods

2.1. Microarc oxidation of Ti disk and hydrothermal treatment of the MAOed TiO_2 coatings

Microarc oxidation of Ti disk and hydrothermal treatment of the MAOed TiO_2 coatings were described in our previous works [26,35–37]. Briefly, the Ti disks with size of ϕ 15 mm × 2 mm were used as anodes and treated in an aqueous electrolyte containing 0.167 M calcium acetate, 0.033 M strontium acetate and 0.02 M β-glycerophosphate disodium at an applied positive pulse voltage of 380 V, a negative pulse voltage of 100 V, a pulse frequency of 100 Hz and a duty ratio of 26% for 5 min. After adding 6 ml of distilled water with an initial pH value of 6.4 into the Teflon-lined autoclave with a volume of 40 ml, the MAOed TiO_2 coatings were be hanged up in the autoclave without touching the distilled water or immersed in the distilled water, then received HT at 140 °C for 24 h.

2.2. Structural analysis of the MAOed and HTed coatings

The morphologies of the MAOed TiO_2 coatings before and after HT were examined by a field emission scanning electron microscope (FESEM; JEOL JSM-6700F, Japan). The roughness of the coatings was examined by atomic force microscopy (AFM; SPM-9500J3, Japan).

2.3. Evaluation of in vitro structure and adhesion strength stability of the coatings

In vitro structure and adhesion strength stability of the coatings were evaluated by means of immersing them in physiological saline solutions (PS solutions, e.g., 0.9 wt.% NaCl aqueous solutions) at 36.5 °C for 0–48 weeks, then examining the changes in ion concentrations of the obtained PS solutions, surface morphologies and bond strengths of the immersed coatings. Each coating was immersed in 50 ml solution in a plastic vial without refreshing the solution during immersion. Five specimens were employed for each coating at each immersion time. Concentrations of the Ca, P and Sr ions in each coating immersed solution were measured by an inductively coupled plasma emission spectroscopy (ICP-AES; Perkin Elmer, Optima 3000DV, USA). Scratch tests of the samples immersed for different times were performed using an auto scratch coating tester to evaluate their adhesive strengths. The critical load, L_c, was defined as the smallest load at which a recognizable failure occurred, and was determined from the load versus acoustic output characteristics. The critical load of each coating was averaged by tests of three samples.

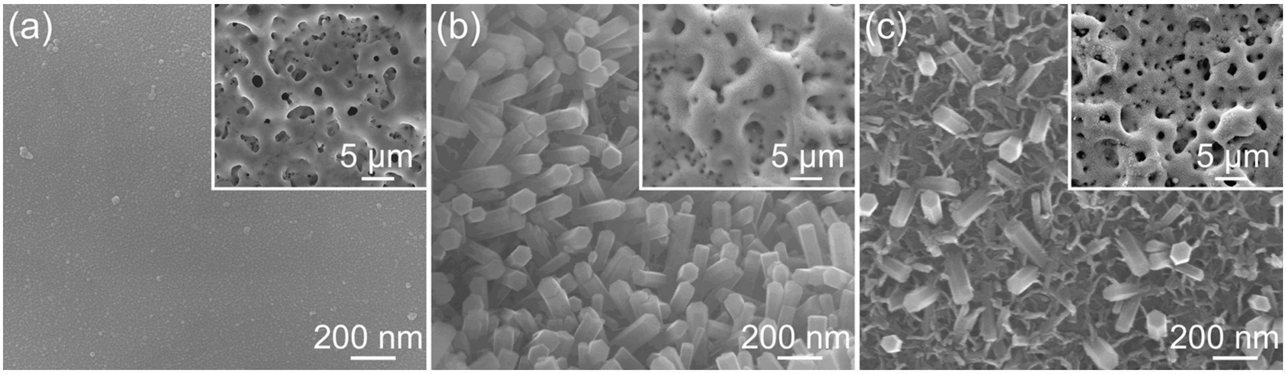

Fig. 1. SEM images of the coatings: (a) as-MAOed, (b) MAO+H-HT and (c) MAO+I-HT; the top insets are the corresponding low-magnification images.

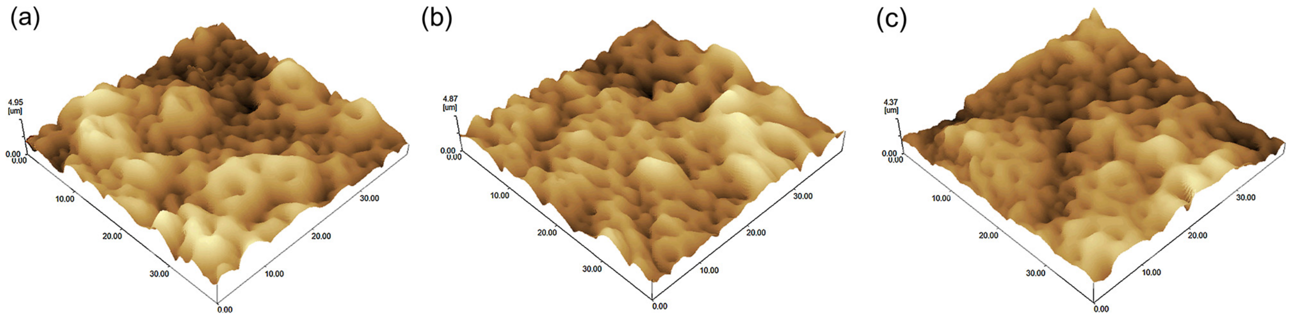

Fig. 2. AFM images of the coatings: (a) as-MAOed, (b) MAO+H-HT and (c) MAO+I-HT.