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Rapid deposition of spherical apatite on alkali–heat treated titanium in modified simulated body fluid at high temperature

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ABSTRACT

Biomimetic deposition in simulated body fluid (SBF) has been widely used to evaluate the bioactivity of implants and to prepare bioactive coatings. In this research, deposition of hydroxyapatite (HA) was studied during immersion in modified simulated body fluid (3 × SBF) at 57 °C of titanium samples heat-treated in alkaline solution (alkali–heat treatment, AH). SEM results show uniform large spherical agglomerates formed by soaking for only 1 day. In addition, the results of XRD and FTIR indicate that the coating consists of hydroxyapatite (HA) and brushite ($CaHPO_4 \cdot 2H_2O$). The large spherical apatite agglomerates were embedded into the whole deposited layer. High temperature and high concentration of SBF can greatly accelerate the deposition and increase the size of HA, even affect the morphology of deposited HA. In addition, the mechanical adhesive strength between the deposited coating and the substrate is relatively high, and slightly enhances with increasing immersion time.

1. Introduction

Due to the intrinsic inertness of titanium, researchers study various methods to improve the bioactivity of titanium implants [1–3]. Biomimetic deposition of apatite in simulated body fluid (SBF) has been widely used to evaluate the in vitro bioactivity of titanium. In addition, the deposition process is used to deposit a functional coating on metallic substrate with specific characteristics [4]. Alkali–heat treatment (AH) can form an amorphous sodium titanate layer with nanosponge morphology on the surface of titanium, which can improve its bioactivity markedly [5–7]. In addition, several researchers have also reported that nanoscale morphologies can increase the nucleation and growth of the HA particles soaked in SBF [8–10]. The time required for deposition of a fully covering apatite layer by immersion in SBF was usually in excess of 4 weeks [3,11,12]. Some researchers studied the deposition behavior of apatite on titanium (or titanium alloys) soaked in modified SBF at high temperature and/or high concentration [4,13,14], and rapid formation of apatite was achieved. However, the morphological and structural evolution of deposited apatite under these conditions is not very clear. In this study, titanium samples were treated by AH and then soaked at 57 °C, in 3 × SBF for several days. Large-sized apatite spheres were formed on the surface of AH treated substrates, and their surface and inner structure as well as formation process were analyzed.

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2. Materials and methods

2.1. Specimen preparation

Commercially pure Ti (TA2) disks of 10 mm diameter and 3 mm height were successively abraded with #240, #400 and #600 SiC papers, then washed with acetone, ethanol and deionized water in an ultrasonic cleaner. Subsequently, AH was performed by soaking the disks in 30 ml of 5 M NaOH aqueous solution at 60 °C for 24 h. After alkali treatment, the disks were washed with distilled water and dried at 40 °C for 24 h in air. Then, the disks were heated to 600 °C for 1 h in an electric furnace and cooled to room temperature in the furnace [6].

2.2. Soaking in vitro

Modified simulated body fluid (3 × SBF) was prepared by dissolving appropriate amounts of reagent-grade chemicals of NaCl, $NaHCO_3$, KCl, K_2HPO_4, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, and Na_2SO_4 in distilled water, buffered at pH 6.8 with $(HOCH_2)_3CNH_2$ (Tris) and 1 M HCl at 37 °C [15]. The mass of every agent was tripled, except for Tris and 1 M HCl. The ionic concentrations in the modified simulated body fluid and human blood plasma are shown in Table 1. Ti specimens pretreated by AH were vertically placed in plastic containers with about 35 ml 3 × SBF. These containers were immersed in an oscillating water bath at 57 °C (20 °C higher than the body temperature). After immersion in SBF for 1, 2 and 4 days, the samples were cleaned and dried. The SBF was refreshed once a day.

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Table 1
Comparison of ion concentrations of SBF, m-SBF (3 × SBF) solutions and human blood plasma (HBP).

	Ion concentrations							
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
Human blood plasma (HBP)	142.0	5.0	1.5	2.5	103.0	27.0	27.0	0.5
SBF	142.0	5.0	1.5	2.5	147.8	4.2	4.2	0.5
m-SBF (3 × SBF)	426.0	15.0	4.5	7.5	443.4	12.6	12.6	1.5

2.3. Characterization

The phase composition of deposited coating was examined by X-ray diffractometry (XRD, Rigaku, Tokyo, Japan) using Cu Kα radiation with a wavelength of 0.15406 nm. The X-rays were generated from a copper source operating at 40 kV and 100 mA. The goniometer was set at a scan rate of 4° min^{-1} with 2θ range of 10–60°. The surface morphology of samples was observed by field emission scanning electron microscopy (FE-SEM, HATA-CHI SU-70) equipped with an energy dispersive X-spectroscope (EDS). A Fourier transformed infrared spectrometer (FTIR, BRUKER TENSOR 37) with resolution of 8 cm^{-1} was used to characterize functional groups of the coatings, and revealed all major peaks in a range of 400–4000 cm^{-1}. Besides, adhesive strength between the deposited layer and substrate was investigated by a scratch test using an automatic scratch tester (WS-2005, Lanzhou Institute of Chemical Physics, CAS, China) with a progressive load increasing from 0.2 to 50 N, loading velocity of 50 N/min and scratch length of 4 mm. The load at which the coating was totally peeled off from the Ti substrate was designated as the critical load. Three single scratches were performed for each sample in order to ensure result stability.

3. Results and discussion

3.1. Characterization of deposited layer

The morphology of the deposited layer is shown in Fig. 1. A characteristic fine and porous structure is formed on the surface of the titanium treated by AH (Fig. 1a, e). Fig. 1b–d shows the surface morphologies of AH pretreated samples soaked in SBF for 1, 2 and 4 days, respectively. A large number of uniform spherical agglomerates formed on the surface of Ti samples soaked for only 1 day (Fig. 1b, f). In addition, the sphericity of the agglomerates improved and their size increased with increasing immersion time. The growth rate slowed down during immersion for 2 to 4 days. The diameters of spherical agglomerates formed after soaking for 1, 2 and 4 days were found to be about 38–42, 90–95 and 115–120 μm, respectively. This is in contrast to previous research that showed the diameter of deposited HA particles by soaking various substrates in SBF to be generally around 10 μm (Table 2) [3,5,13,15–18]. These spherical agglomerates show surficial petal-like structure that densified with increasing immersion time.

In local areas of the substrates, spherical agglomerates collected into a continuous coating with incomplete coverage (Fig. 1). Although high temperature and high concentration of SBF enlarged the size of spherical apatite, they did not improve the uniformity of the deposition layer. According to previous reports, the deposition layer is often not uniform, which may be affected by many factors, e.g. chemical composition and grain size of substrate, phase and chemical composition of surface, surface roughness, as well as soaking time [3,16,17,19,20].

Fig. 2 shows sections of deposited layers and spherical agglomerates. The thickness of deposited layers increases with the increase of immersion time (Fig. 2a–c). Fig. 2d indicates that the densities of several annular areas of spherical agglomerates are different, which is considered to be caused by the daily refreshed SBF. Fig. 3 is the EDS analysis that indicates atomic Ca/P ratios of deposited layers to be 1.07, 1.17 and 1.28 after 1, 2 and 4 days of immersion, much less than those of stoichiometric HA (1.67). Fig. 4 shows typical loading-scratch curves and morphologies of the deposited coating formed on the surface of AH treated Ti substrate. Initially, the slope of friction force versus load is linear until it suddenly changes as the load reaches a certain degree (as shown by vertical arrows). This indicates that the adhesion strength of the deposited layer transforms during the test (Fig. 4a–c). The transformation of the force curve indirectly illustrates the adhesive strength of coating and substrate. In addition, Fig. 4(d), (e) and (f) shows the SEM micrographs of the scratch tracks on HA coated Ti substrates soaked in 3 × SBF for 1, 2 and 4 days, respectively. With the load increasing, the depth of scratch tracks increases suddenly, which indicates that the layer is broken under the certain force (critical load). The critical loads of the deposited layer formed after soaking in 3 × SBF for 1, 2 and 4 days are about 18.6, 19.4 and 21.5 N, respectively, which shows that the adhesive strength of the layer increases slightly with increasing immersion time. However, other researchers have reported that the critical loads of the HA and HA/TiO_2 manufactured by different technologies are no more than 10 N [8,21]. The enhancement of adhesive strength results from the increase in thickness and density of the deposited layer after long soaking time.

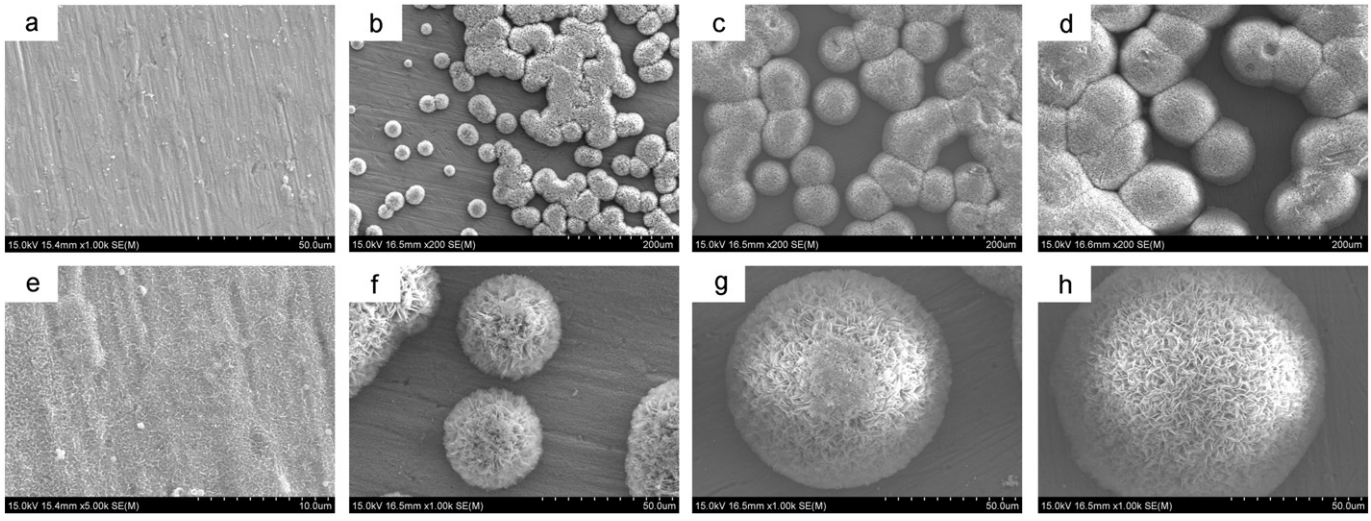

Fig. 1. SEM images of (a) Ti samples treated by AH, and subsequently soaked in 57 °C, 3 × SBF for (b) 1 day, (c) 2 days and (d) 4 days. Panels (e), (f), (g) and (h) are their high magnification images, respectively.