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Bioactivity of hydroxyapatite/wollastonite composite films deposited by pulsed laser

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ABSTRACT

Hydroxyapatite/wollastonite (HA/WS) composite films on titanium alloy were prepared by pulsed laser deposition, and their bioactivity was studied. The dissolution and precipitation behaviors of the films were evaluated by soaking in simulated body fluid (SBF), and the osseointegration ability was evaluated by in vivo test. In the early soaking stage, the dissolution action will dominate, thus resulting in the gradual disappearance of the smooth spherical feature of the particles. After 7 days of soaking, new precipitates were observed which indicates that reprecipitation reaction dominates, and the surface was almost completely covered by new precipitates after the film was soaked for 28 days. The in vivo test showed that the composite films have excellent osseointegration ability. When the sample was embedded in the shin bone of rabbit for 3 weeks, a good combination of bone tissue and implant was achieved, and after embedding for 6 weeks, osteoblasts were observed between the bone tissue and implant.

1. Introduction

In recent years, a series of bioceramics have attracted significant attention and interest for biomaterial application because of their excellent biocompatibility and bioactivity [1,2]. Among these, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) is one of the most attractive biomaterials and widely used as a bone substitute due to its chemical similarity to the inorganic component of hard tissues [3,4]. HA can promote tissue growth and can bond structurally and functionally with hard tissue inducing the osteogenesis without immune response from human tissues, thus make it as an ideal material in orthopedic and dental applications [5].

Nevertheless, the extensive use of HA is still limited in load bearing applications by their brittle nature. To overcome this drawback, bioceramic films on titanium or titanium alloy have been developed, thus combining the good mechanical properties of the metal or alloy with the excellent bioactivity conferred by the bioceramics [6]. However, HA film exhibits minimal dissolubility in physiological environment which is not benefit for the rapid formation of bone apatite [7]. In order to improve this property, it is a feasible way to fabricate HA composite films by doping some additives with high dissolution rate.

Beta-wollastonite (β-$CaSiO_3$) and alpha-wollastonite (α-$CaSiO_3$), which are the low and high temperature forms of wollastonite (WS) respectively, are the most common calcium silicate bioactive ceramics proposed for bone tissue regeneration with the same or better possibilities than classic ceramic particles such as HA [8,9]. The presence of silicon in WS plays an essential role for the growth and development of the skeletal system [10]. WS bioceramic has relatively faster dissolution rate than HA, and it is suitable to be used as a modifier to fabricate HA composites with improved mechanical and biological properties [11].

At present, HA composite films have been prepared by many techniques including plasma spraying, microarc oxidation, magnetron sputtering, sol-gel method, pulsed laser deposition (PLD) and so on [12–16]. In the field of thin film growth, PLD has been proven to be among the most versatile and effective methods characterized by fast processing, reliability and low production cost [17]. The detailed mechanisms of PLD include the ablation process of the target material by the laser irradiation, the development of a plasma plume consisting of high energetic ions, electrons as well as neutrals and the crystalline growth of the film itself on the substrate. PLD technique ensures the stoichiometric transfer of the material from target to film, and has been widely used to fabricate HA composite thin films [18].

HA/WS composite films on titanium alloy were fabricated by pulsed laser deposition technique in this paper. The dissolution and precipitation behaviors of the films were evaluated by soaking in simulated body fluid (SBF), and the osseointegration ability was evaluated by in

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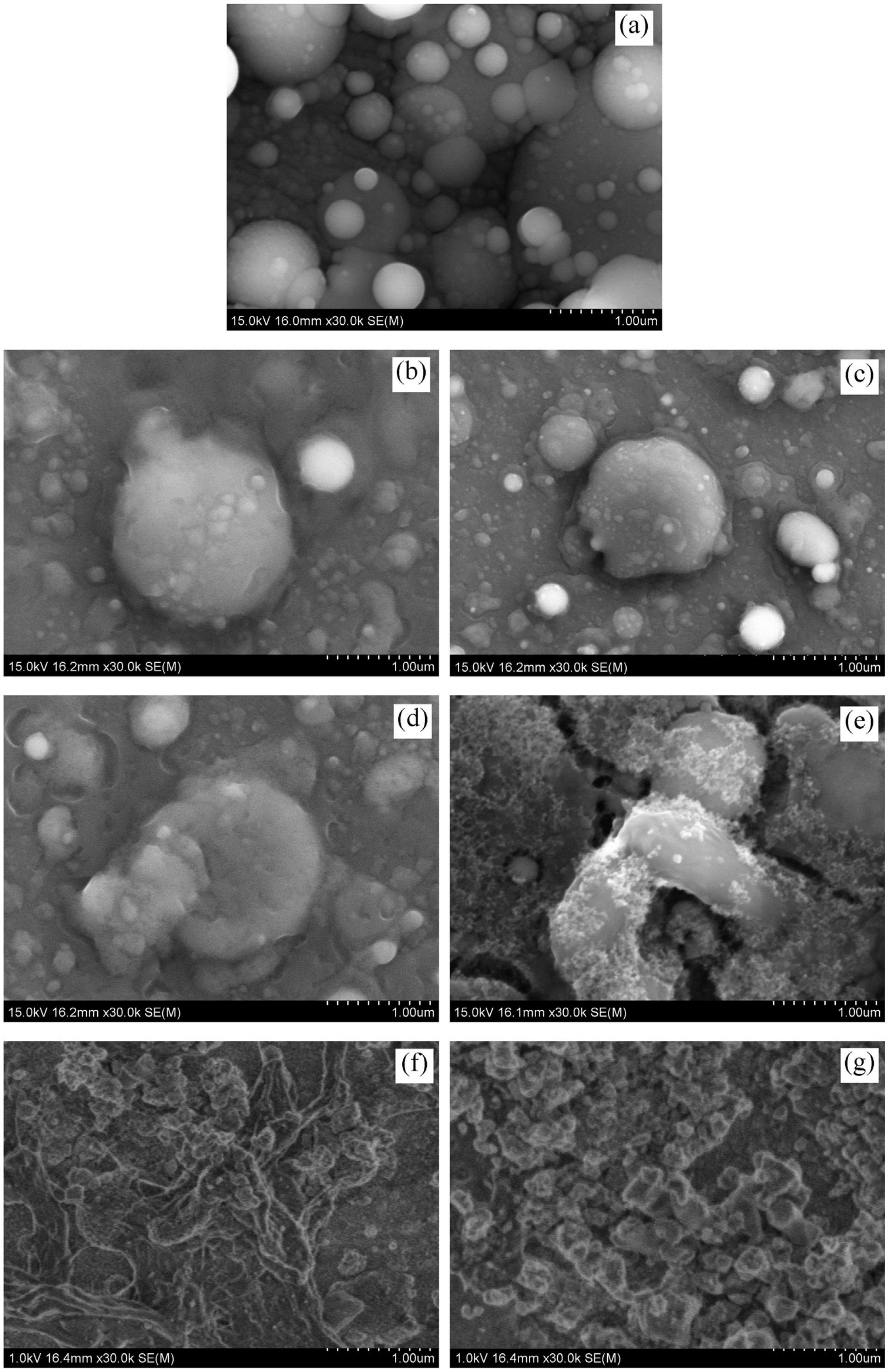

Fig. 1. Morphologies of HA composite films before and after soaking in SBF with different time: (a) as-deposited film; (b) half a day; (c) 1 day; (d) 3 days; (e) 7 days; (f) 14 days; (g) 28 days.

vivo test.

2. Materials and methods

Commercially available Ti6Al4V plates with size of Φ25 mm × 1 mm (99.7% purity, Baoji Bangnuo Ltd) were adopted as substrates, and the chemical composition of titanium alloy is as follows: 5.5–6.8 wt% Al, and 3.5–4.5 wt% V, and balance of Ti. The substrates were polished with different grades of SiC powders, and cleaned ultrasonically in acetone and methanol for 10 min. Trimethyl phosphate ($(CH_3O)_3PO$, Kermel Chemical Industry) and calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Guangcheng Co., Ltd) were employed to prepare HA powders by a sol-gel method. $Ca(NO_3)_2 \cdot 4H_2O$ and $(CH_3O)_3PO$ were dissolved in ethanol respectively, and then they were mixed together to form sol according to the Ca/P atomic ratio of 1.67. After ageing at 65 °C under stirring for about 12 h, the sol was dried at 350 °C for 10 min to form a gel and calcined at 800 °C for 15 min to obtain crystalline HA. After grinding and ball milling, HA powders with