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HA/BG composite films deposited by pulse laser under O_2 atmosphere

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A B S T R A C T

HA/BG composite films have been deposited on Ti-6Al-4V by pulse laser under O_2 atmosphere, and EPMA-EDS, SEM, XRD, FTIR measurements have been performed. Under O_2 atmosphere, the crystallinity of the deposited films increases and Ca/P atomic ratio slightly decreases with increasing the substrate temperature. When the film was deposited at 600 °C, the film was compact and crystalline HA was observed. Comparing with Ar atmosphere, O_2 atmosphere is benefical for decreasing Ca/P atomic ratio of the films, and the in vivo test indicates that the film obtained under O_2 atmosphere has excellent osteoinductivity. So O_2 atmosphere is a promise alternative atmosphere to fabricate HA/BG composite films by pulsed laser deposition.

1. Introduction

Due to their high strength, low toxicity, excellent corrosion resistance and endurance, many metallic biomaterials like titanium (Ti) and its alloys have been widely used in clinic to assist and replace human bones. However, the lack of osteoconductivity and osteoinductivity of metallic biomaterials will result in poor fixation or failure of the implant [1,2]. Surface modification of the metallic biomaterials has been essential to establish a direct chemical bonding between the implant and the host bone tissue. Fabricating bioactive thin film on metallic implant surface using various routes is an effective approach to enhance the bioactivity and improve the bone response to implant surface [3].

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), the main inorganic composition of the bone tissue, is a particularly attractive material to fabricate films on Ti and its alloys because HA has good bioactivity and biocompatibility [4]. However the mismatch of thermal expansion coefficients between HA and Ti alloys can induce a tensile thermal stress in the films which leads to the failure of the implant. The relatively slow biological interaction rate of HA also limits its further application in biomedical fields [5]. For further improvement of the bioactivity and adhesive strength of the HA.

films, some additions have been introduced into the HA film. The bioactive glass (BG) containing less than 60 wt% SiO_2 is a promising additive material because of its better bioactivity and lower coefficient of thermal expansion [6,7].

Pulsed laser deposition (PLD) technique, which has the capability to restore complex stoichiometry and to produce crystalline and highly adherent films, has been used successfully to fabricate HA-based bioactive films [8,9]. However, re-evaporation of volatile species such as P during deposition process may cause the Ca/P atomic ratio increasing, consequently, the bioactivity of the deposited films decreases [10–12].

Thus, in order to decrease or inhibit P depletion, O_2 atmosphere with low pressure was introduced to deposit HA/BG composite films in this research. As a comparison, the traditional Ar atmosphere was also selected to fabricate the HA/BG film.

2. Materials and methods

45S5 bioglass and high crystallized HA powders were selected as the target materials. The composition of 45S5 bioglass includes SiO_2 (45 wt%), Na_2O (24.5 wt%), CaO (24.5 wt%) and P_2O_5 (6 wt%). Bioglass and HA powders were mixed with the weight ratio of 1:1, after forming disks (Φ25mm×3 mm) by uniaxial and cold isostatic pressing at 240 MPa, the targets were sintered at 600 °C for 2 h.

The films were deposited on titanium alloy Ti-6Al-4V by TOL-200 KrF excimer laser with a wavelength of 248 nm and a pulsed duration of 20 ns. The laser pulse energy is ~200 mJ, and the energy density is ~5 J/cm^{-1} with a repetition rate of 5 Hz. At a starting vacuum of 3×10^{-5} Pa, Ar or O_2 gas was introduced into the chamber, and the final pressure was controlled at 5 Pa for Ar atmosphere and 5×10^{-3} Pa for O_2 atmosphere. The laser beam hit the target at an angle of 45° and the substrates were heated at 200 °C, 400 °C or 600 °C. In order to avoid drilling during the laser ablation, the targets have been rotated at a frequency of 6 rpm.

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The deposited samples with the size of 1 mm×1 mm×2 mm were implanted in the shin bones of adult New Zealand rabbits. The rabbit was anaesthetized before surgery, the skin and muscle of the rabbit leg were in turn cut, and the shin bone was exposed. After a hole with a diameter of 1 mm in the shin bone was drilled, the implant was inserted, then suture process was followed. The specimens were harvested after 1 month. After the specimens were fixed in 10% formalin solution over 48 h, dehydrating process by ethanol and acetone was carried out before observation.

Film morphologies and element analysis were examined using JXA-8800 R electron probe microanalyser (EPMA) and the accessory of LinkSIS300 energy spectrum analyser (EDS), the phase constitutions were studied by X′Pert X-ray diffractometer (XRD) using Cu radiation (λ=1.5406 nm). Fourier transform infrared spectroscopy (FTIR) analyses were conducted on NICOLET Avatar370 Fourier transform infrared spectrometer (FTIR), and the morphologies of the implants after embedding in shin bones were observed by XU-70 scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 is the morphologies of the composite films deposited with different substrate temperatures and atmosphere. The films are compact without obvious cracks existence, and all the surface morphologies have the typical characteristics of PLD grown films, exhibiting droplets with different size on uniform thin film [13]. When the films were deposited under O_2 atmosphere, it seems that the number of the droplets increases with the substrate temperature increasing. However, when the films were deposited at 600 °C with different atmosphere, there is no obvious difference of the morphologies. When energetic laser pulses hit the target, it can evaporate materials from the surface to form ablation plume which consists of several types of species: ions, neutral atoms, electrons and so on. When the emitted species condense on the substrate surface, a PLD film can be formed [14]. During expansion of the plume, the inter-collision of the species consumes some kinetic energies, which reduces their probability to deposit on the substrate [15]. High substrate temperature can compensate part of the energy loss, so it is benefit for the growth of the deposited films..

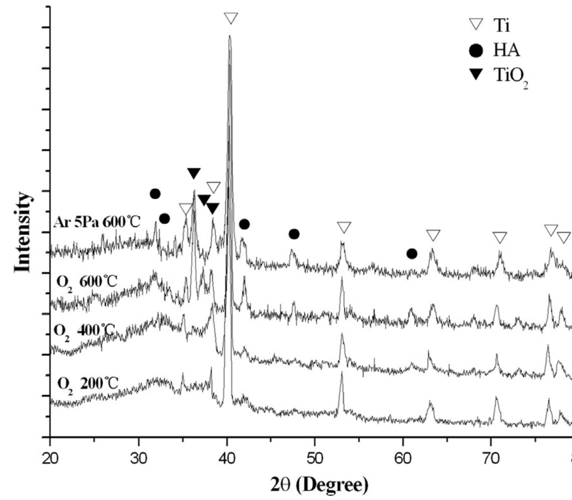

Fig. 2. XRD patterns of the films deposited with different substrate temperature and atmosphere.

The composition analysis by EDS shows that the Ca/P atomic ratio

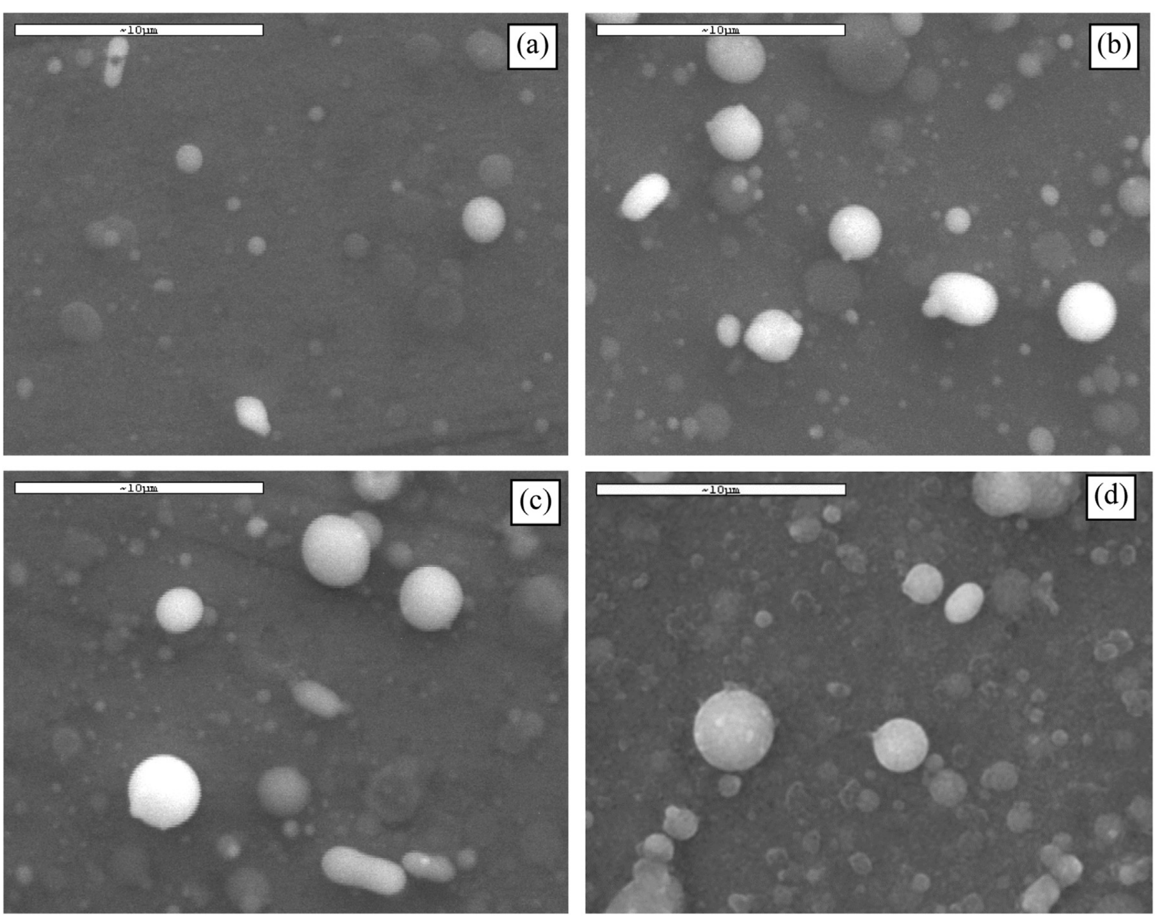

Fig. 1. Morphologies of the films deposited with different substrate temperature and atmosphere. (a) 200 °C, O_2 atmosphere; (b) 400 °C, O_2 atmosphere; (c) 600 °C, O_2 atmosphere; (d) 600 °C, Ar atmosphere.