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Influence of annealing on the phase transformation of pulsed laser deposited HA/45S5 films

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ABSTRACT

HA/45S5 composite films were deposited by a KrF excimer laser on Ti-6Al-4 V, and a post annealing was carried out. HA/45S5 composite film deposited at 200 °C is amorphous, and the post annealing can't promote the crystallization of 45S5 bioglass but can increase the crystallinity of HA greatly. The composition of the composite films and the annealing process play an important role on the formation of the oriented HA. Slight a-axis preferred orientation of HA structure was observed in the films treated at 700 °C for 2 h, and c-axis preferred orientation of HA structure was observed at 800 °C for 2 h or 4 h.

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) films on metallic substrates such as titanium alloys have attracted more and more attention in the field of medical implants, as they combine good mechanical properties of the metal with excellent biocompatibility of the HA films [1,2]. It was also found that implants with HA films could lead to fast bony adaptation, firm implant-bone attachment and inhibition of ion release from metallic bulk materials [3,4]. However, the difference of thermal conductive coefficient between HA and metal substrate induces the cracks formation which decreases the service life of the implants [5,6].

In 1971, Hench and co-workers discovered bioactive glass that contain SiO_2, Na_2O, CaO and P_2O_5, which unveiled the prelude the bioglass research [7,8]. Generally, bioglass has low thermal conductive coefficient and even better bioactivity than HA, so it may serve as a good candidate to fabricate bioactive films on titanium alloys. Nevertheless the dissolution rate of bioglass in simulated body fluid is rapid, consequently the bioglass film may disappear completely before the new bone tissue forms on the implant surface [9,10]. In recent years, composite materials comprised of HA and bioglass have been deposited on metal substrate, and this kind of HA/bioglass composite films have higher bioactivity and bonding strength between film and substrate than HA films [11–13].

Currently, pulsed laser deposition (PLD), has emerged as one of the most popular and intrinsically simple techniques for depositing a wide range of the most exciting materials [14]. The principle attractive features of PLD include the stoichiometric transfer, simplicity in initial setup and deposition of the films with high bonding strength. So it is promising to fabricate HA composite films by PLD, and the related studies have been carried out by many researchers [15,16].

The bone of human beings is composed of inorganic hydroxyapatite nanocrystals with c-axis orientation and organic collagen, and the oriented HA is preferentially aligned parallel to the longitudinal direction of collagen fibrils [17,18]. And c-axis oriented HA films possess better mechanical properties and bioactivities compared with randomly oriented films [19]. In this paper, HA/bioglass composite films with c-axis oriented HA crystals were attempted to fabricate by PLD method and post annealing, and the influence of annealing on the phase transformation was studied.

2. Materials and methods

Titanium alloy Ti-6Al-4 V was selected as the substrate which was machined with a diameter of 20 mm and a thick of 1 mm. 45S5 bioglass and high crystallized HA powders were mixed with

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the weight ratio of 1:1 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%). After ball-milling, the mixture was made into disks (Φ25 mm × 3 mm) by uniaxial and cold isostatical pressing at 240 MPa. Then the targets were sintered in air at 600 °C for 2 h.

A TOL-200 KrF excimer laser with a wavelength of 248 nm and a pulsed duration of 20 ns was focused on the target surface with 45° beam incident angle from the normal to the target surface. 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 strarting vacuum of 3×10^{-5}Pa, Ar gas was introduced into the chamber and the final pressure was controlled at 45 Pa. During deposition, the target was rotated at a speed of 6 rpm and the substrate was heated to 200 °C.

After deposition, a post annealling treatment in air was carried out in an oven with a constant heating rate of 5 °C/min. Generally, the lowest temperature T_s for atomic diffusion is about 0.3 of the melting temperature T_m of the material. In the case of HA, T_s is about 530 °C [20]. So the annealing temperatures were set to 600 °C, 700 °C or 800 °C, and holding time were set for 1 h, 2 h or 4 h. After annealing, the furnace was allowed to cool naturally to room temperature. The phase constitutions of the films were studied using the X'Pert X-ray diffractometer (XRD), and the film morphologies were examined using XU-70 scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 is the XRD patterns of the as-deposited HA/45S5 film and the annealed films treated at different temperature for 2 h. It is clear to see that all the sharp diffraction peaks of the as-deposited film are corresponding to the Ti which is derived of the substrate, which means that the as-deposited film is amorphous. Particularly, the XRD patterns exhibit a broad diffuse peak near the diffraction angle of 30°, indicating the amorphous state of HA. When the as-deposited films were annealed for 2 h, the crystallinity of the films increases with the increase of the annealing temperature. When the film was treated at 700 °C, more diffraction peaks of HA crystal appear, and simultaneously the peaks of TiO_2 appear because of the oxidation of Ti. However, X-ray peak corresponding to HA (3 0 0) diffraction appeared markedly higher than other HA peaks, which means the formation of a-axis preferred orientated HA [21]. A more attractive phenomenon was observed when the annealing temperature reached to 800 °C, that is, the c-axis preferred orientation of HA crystal was observed which can be confirmed by the intensity of (0 0 2) diffraction [3]. No peaks corresponding to the composition in 45S5 bioglass were detected in the four samples, which means the bioglass can't be crystallized under the conditions mentioned in this experiment. The existence of amorphous bioglass can increase the bioactivity of the films and promote the formation of new bone tissues near the surface [11,22].

Fig. 2 shows the XRD patterns of the films treated at 600 °C for different time. With the holding time prolonging, the crystallinity of films increases and the peak intensity corresponding to TiO_2 phase strengthens. All the XRD patterns revealed that the diffraction intensity of HA (2 1 1) diffraction surpasses that of other HA diffractions, which means that HA in the films annealed at 600 °C has random orientation.

When the as-deposited films were annealed at 800 °C for different time, Fig. 3 shows that HA has a high crystallinity, and the crystallinity of HA changes little with the prolongation of holding time. However, the holding time influences the preferred orientation of HA crystal. Random orientation of the HA grains were obtained after treatment for 1 h, but c-axis texture of HA grains in the film treated for 2 h appears and the degree of c-axis texture change little after 4 h treatment. High temperature and long holding time are more likely to promote c-axis preferentially oriented growth.

Generally, the HA crystal has two major crystal faces, and HA fibres can develop along a or c-axis. However, c-axis preferred orientation is easier to be obtained than a-axis orientation since the area of a(b)-plane is wider than that of c-plane [23–25]. In the HA cell, OH^- groups are aligned in columns which are isolated from PO_4^{3-} tetrahedra by the Ca^{2+} atoms, and these columns has the [0 0 1] direction presenting a preferential orientation for OH channeling [26]. In the presence of a sufficiently strong driving force, this atomic arrangement allows efficient transport of OH^- along [0 0 1] direction, which favors the crystallization of HA grains with the c-axis aligned in the direction of OH^- transport [6]. On the other hand, OH^- groups are often deficient in the as-deposited film which results in the formation of "cavity" channeling with [0 0 1] orientation. During annealing process, atomic arrangement allows the foreign groups from 45S5 bioglass enter the HA texture to occupy the cavities along the cavity channeling, which induces the arrangement of Ca^{2+} and PO_4^{3-} groups along the same direction, consequently the c-axis oriented HA forms. The

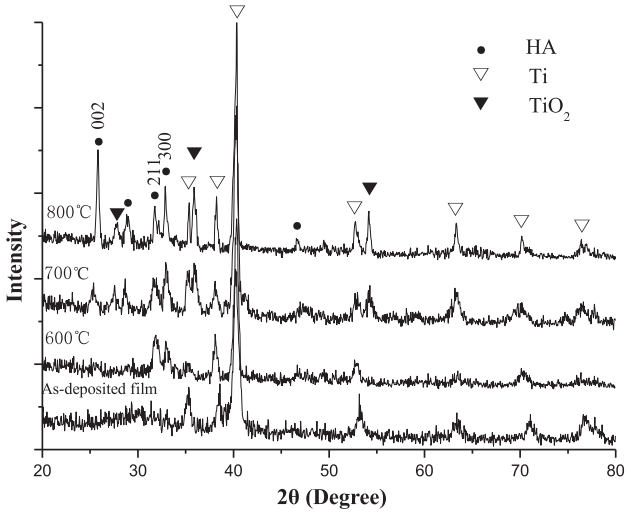

Fig. 1. XRD patterns of the PLD films treated at different temperature for 2 h.

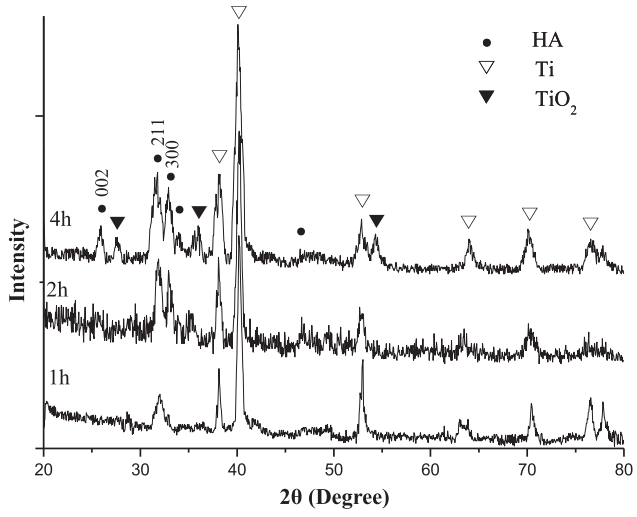

Fig. 2. XRD patterns of the PLD films treated at 600 °C for different time.