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Chemical solution derived hydroxyapatite films on Si substrates

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화학 용액법으로 Si 기판 위에 제조한 하이드록시아파타이트 박막에 관한 연구

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Abstract Hydroxyapatite films were prepared on Si(100) substrates by using a sol-gel method with calcium nitrate and phosphoric acid as starting materials. Precursor sols were spin-coated onto the substrates and prefired at 500℃ for 10 min in air. Formation of the hydroxyapatite structure was confirmed in the sample annealed at 500℃ by the X-ray diffraction θ - 2θ scans and a tricalcium phosphate phase was observed in the samples annealed at both temperature regions of 500°C~700°C and 900°C. From the results of Fourier transform infrared spectroscopy, the change of a carbon content and improvement of crystallinity have been discussed as a function of increase of annealing temperature.

요 약 Ca nitrate와 인산을 혼합한 용액을 졸-겔법을 이용하여 Si(100) 기판 위에 스핀 코팅하여 열처리 함으로써 의치공재료에 응용되는 하이드록시아파타이트 박막을 제조하였다. Si 기판 위에 하이드록시아파타이트막을 코팅하여 건조시킨 다음, 500°C에서 10분간 초벌구이 열처리를 하였다. X-선 회절 분석을 이용하여 500°C에서 하이드록시아파타이트 상의 생성을 확인하였고, 500°C~700°C 및 900°C에서 각각 tricalcium phosphate상의 생성을 확인하였다. FTIR(Fourier transform infrared spectroscopy)의 결과를 바탕으로 열처리 온도 증가에 따른 탄소량의 변화와 결정화도의 증가를 확인하려 한다.

1. Introduction

Inorganic bioceramic hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] (HAP) [1, 2] has attracted widespread interest from both the orthopaedic and dental fields due to its excellent biocompatibility and tissue bioactivity properties. This material belongs to an intermediate group between the inert materials and resorbable materials, which are progressively dissolved by the human body.

However, the mechanical properties of HAP are not good enough to be used as an implant subjected to be a load. Therefore, most of all bone and tooth implants are made from metal alloys, which have a higher durability than bulk HAP. If HAP is produced in the form of films, its advantages can be properly taken. The concept of coating of HAP films on metal implant surfaces provides the mechanical benefits of metal alloys as well as the biocompatibility of HAP.

There are various methods to prepare HAP films: plasma spraying, pulsed laser deposition and RF sputtering [3-5] to prepare HAP films. At present, plasma spraying is the widely used technique. This method includes the presence of calcium phosphate crystalline phases other than HAP and amorphous material resulting from the extremely high temperature used in the plasma spray process. Chemical solution process such as a sol-gel method [6, 7] needs no high vacuum and no high temperature, and is easily applicable to substrate with any shape and size; therefore, this is considered to be one of the most flexible and commercially promising technique for preparation of high quality HAP thin films on metal substrates.

In this paper, HAP films were prepared on Si(100) substrates by using a sol-gel method. The effect of annealing temperature on their crystallinity and surface morphology will be discussed.

2. Experimental

HAP sols (concentration: 24.72 mg metal/ml coating solution) which were derived from calcium nitrate [$Ca(NO_3)_2 \cdot 4H_2O$] and phosphoric acid (H_3PO_4) dissolved in 2-methoxyethanol were used as precursors. The sol was diluted with 2-methoxyethanol to adjust the concentration and viscosity for depositing smooth films. Si(100) cleaned in H_2O_2 solution and rinsed in acetone were used as substrates. The substrates were spin-coated with a dipping solution at 3500 rpm for 5 sec and dried at 150°C for 15 min on hot plate. The dried films were preannealed at 500°C for 10 min and then these processes were repeated 10 times in order to increase the thickness of the film. The coated Film were crystallized at final annealing temperatures region of 500°C~900°C for 30 min in air ambient by directly inserting the samples into a furnace and controlled to be slowly cooled down at the rate of 5°C/min to keep from cracking by during rapid cooling.

Films produced were characterized by X-ray diffraction (XRD) θ - 2θ scans (Rigaku Co. D-Max-1200). The XRD patterns were recorded using CuKα radiation (λ = 1.5418 Å generated at 40 kV and 30 mA, in the 25°<2θ<45° range. Fourier transform infrared (FTIR) spectroscopy (BIO-RAD Digilab Co. FTS-60 FTIR) in absorption mode with 4 cm^{-1} resolution was chosen to monitor the spectral evolution of chemical bonding. Morphological observation of the films were done in a scanning electron microscope (SEM, JEOL Co. JSM-5400).

3. Results and discussion

Figure 1 shows the XRD patterns of the annealed films for each annealing temperatures. At 500°C several XRD peaks show the HAP structure and the corresponding orientations are related to (002), (210), (211), (112), (300), (202) and (310). Further more, the corresponding HAP peaks are shown with similar intensities in the temperature range of 500°C~800°C. However, the HAP peaks are shown with relatively larger intensities from the sample annealed at 900°C than those of films annealed at the region of 500°C~800°C. The tricalcium phosphate [TCP, $Ca_3(PO_4)_2$]phase is also appeared with minor peaks in all annealed samples.

In the sol-gel method, precursor films generally contain a larger amount of carbon originated from organic sol. At 500°C~800°C the carbonated HAP is crystallized to both type A- and B-carbonated HAP and TCP [8]. The A- and B-carbonated HAP related to TCP in atmospheric water vapor to form stoichiometric and well-crystallized HAP, in the temperature range of 600°C~850°C [8]. This indicates that the carbonated HAP films contained non-stoichiometric TCP phases may be converted to well-crystallized HAP films with

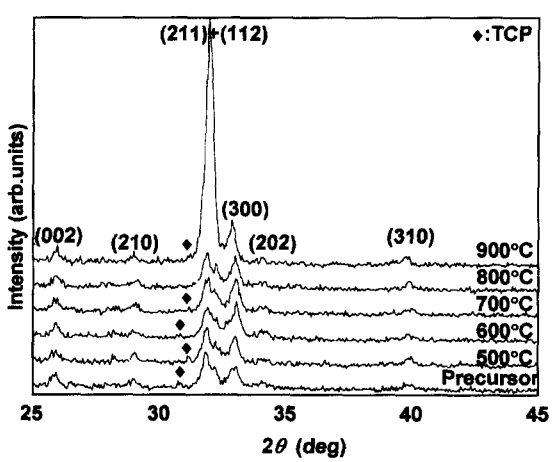

Fig. 1. XRD patterns of the precursor film and the films annealed at 500°C, 600°C, 700°C, 800°C and 900°C.

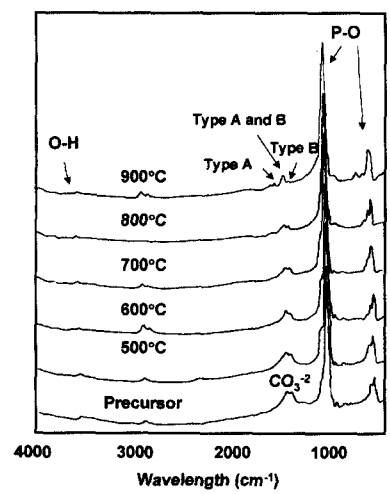

Fig. 2. FTIR spectra of the precursor film and the films annealed at 500°C, 600°C, 700°C, 800°C and 900°C.

a reaction of atmospheric water vapor during final annealing at 900°C.

In order to confirm the change of the carbon content, we performed a FTIR analysis for the HAP films on Si substrates annealed at various temperatures. As shown in Fig. 2, FTIR measurement provides for all the films two peaks from 1100 and from 570 cm^{-1}, which can be attributed to the major absorption modes associated with the presence of phosphate [9]. These two peaks became more intense and narrower as the annealing temperature was increased. Film annealed at 500°C showed a band at 3575 cm^{-1} related to OH group, and a band at 1400~1500 cm^{-1}, which correspond to CO_3^{-2} [9]. For all the films, the appearance of three distinct peaks at 1100, 570 and 3575 cm^{-1} has been observed as a signature of HAP. With increase of annealing temperature, there is no significant difference in the peak at 3575 cm^{-1}, while the peak related to CO_3^{-2} was gradually reduced. At 800° and 900°C, the peak related to CO_3^{-2} was split into three peaks related to AB carbonated HAP as revealed by the v_3 carbonated bands at 1550 and 1460 cm^{-1}, which correspond to type A carbonate, and those at 1460 and 1420 cm^{-1}, which correspond to type B carbonate [9]. Some authors discussed that the carbonate in the A site for low carbonate contents (<4 wt%) could be formed by high-temperature reaction of HAP, yielding a highly crystalline phase, whereas at higher carbonate contents (>4 wt%) type B carbonated HAP has been found to reduce crystallinity [10].

In our work, FTIR and XRD analysis suggesting that a great number of carbon from the organics may primarily exist in the type B carbonate after annealing at lower temperatures (500°C, 600°C and 700°C). Thus, crystal growth may be suppressed by residual carbon during annealing, resulting in lower crystallinity (see Fig. 1). However, at higher annealing temperature (900°C), the carbonate ions substituted at two sites in the HAP structure, namely the hydroxyl and the phosphate ion positions, giving type A- and B-carbonated HAP, respectively. It is noted that non-stoichiometric TCP peak on the XRD spectra was recognized in the HAP film after annealing at 900°C, while at 800°C the TCP-free structure was obtained. Presumably reformation of non-stoichiometric TCP phase at 900°C may be due to the decomposition of HAP during annealing at high temperatures[3].

The SEM micrograph of the film annealed at 800°C [Fig. 3 (a)] shows that the grains are difficult to be identified. On the other hand, when the film was annealed at 900°C, as shown in Fig. 3. (b), the HAP grain size is found to be about 0.6 μm and the grains have a good connection. In the chemical solution process, residual organic components such as carbon play an important role to the formation of the surface morphology of the films.

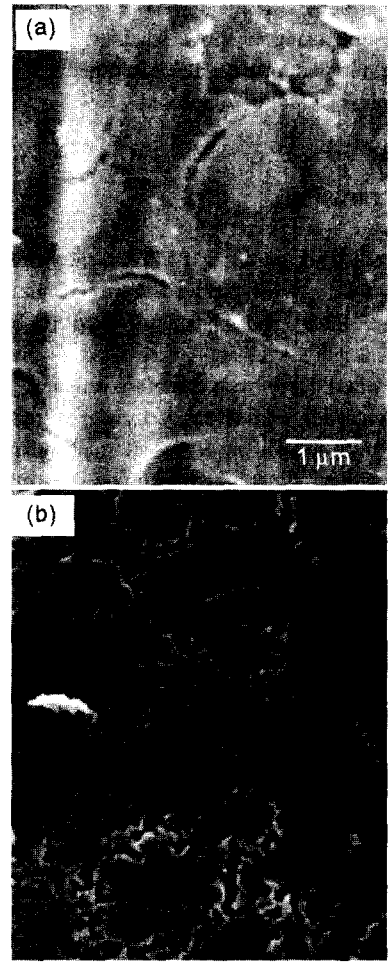

Fig. 3. SEM micrographs of the surfaces of the films annealed at (a) 800°C and (b) 900°C.

Further work is required to carry out in vitro evaluation of the film.

4. Conclusions

We were prepared hydroxyapatite films using a sol-gel method with calcium nitrate and phosphoric acid as starting materials. The films annealed at temperatures range of 500°C~700°C showed mainly type B-carbon-

ated (high carbonate contents >4 wt%) HAP, while after annealing at 800°C type A- and B-carbonated HAP were obtained. At higher annealing temperature (900°C) the crystallinity was improved and surface texture was porous.

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