



BIOMINERALIZATION BEHAVIOR OF HAp/CNTs/Ti6Al4V INTO THE SIMULATED BODY FLUID SOLUTION

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Abstract. Hydroxyapatite doped carbon nanotubes (HAp/CNTs) was synthesized successfully as a coating on the surface of titanium alloy (Ti6Al4V) by a scanning potential method. The biomineralization of the materials soaked into a simulated body fluid (SBF) solution was investigated. The SEM images observed indicated that the formation of new hydroxyapatite crystals on the surface of Ti6Al4V with HAp or HAp/CNTs coating is better than that of Ti6Al4V. The formed hydroxyapatite crystals are confirmed by XRD patterns of Ti6Al4V after 21 days soaked in SBF solution. These results indicated that the coatings of HAp or HAp/CNTs have a good biomineralization.

Keywords: HAp/CNTs/Ti6Al4V, simulated body fluid solution, biomineralization, hydroxyapatite crystal.

Classification numbers: 2.4.3, 2.5.3.

1. INTRODUCTION

Titanium and titanium alloys such as Ti6Al4V have excellent mechanical and biomineralization with the human body fluids. They have attracted scientists for a purpose of application in biomedical implant. In particular, they are used to replace load bearing bone [1, 2]. However, these materials lack biomimetic surface properties leading to the osseointegration can require 3–4 months. In order to enhance their biomineralization as well as to shorten the healing time, the scientists modified surface properties of these materials by pure HAp coating or doped HAp coating. The results were reported that the presence of HAp or doped HAp coatings on the substrate surface can promote the formation of new hydroxyapatite crystals [3, 4].

Recently, carbon nanotubes (CNTs) are used as a reinforcement for the HAp coatings [5-14]. The researches [7 - 14] showed that the presence of CNTs in HAp/CNTs nanocomposite

improved mechanical properties as well as the biomineralization of the materials. The formation of hydroxyapatite crystals on the surface of HAp/CNTs/substrates immersed in a physiological environment was reported. In our previous report, the coating of HAp/CNTs was realized successfully on the surface of 316L SS [15]. The results confirmed the role of CNTs in improving the mechanical and biological properties of the material. Nowadays, Ti6Al4V substrate receives the attention of scientists because of its excellent mechanical properties. Therefore, the biomineralization testing of this material is necessary.

In this study, the biomineralization of Ti6Al4V with and without HAp or HAp/CNTs coating in the SBF solution is investigated. The characteristics of these materials after an immersion period in the SBF solution were analyzed by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD).

2. MATERIALS AND METHODS

The chemicals such as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99 %), $\text{NH}_4\text{H}_2\text{PO}_4$ (99 %), NaNO_3 (99 %) were imported from China. Multi-walled carbon nanotubes (CNTs) (90 % pure, diameter of $20 \div 100$ nm, length of $1 \div 10$ μm) was synthesized by chemical vapour deposition (CVD) from Institute of Materials Science, Viet Nam.

Ti6Al4V substrate was used as a working electrode (size of $12 \times 10 \times 2$ mm) with elemental content including Ti (89.63 %), Al (6.04 %), V (4.11 %), C (0.05 %) and Fe (balance). The working surface area was limited to 1 cm^2 using epoxy. The surface of Ti6Al4V substrate was treated similarly as in our previous report [16]. An electrolyte solution containing $3 \times 10^{-2} \text{ M}$ $\text{Ca}(\text{NO}_3)_2$, $1.8 \times 10^{-2} \text{ M}$ $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.15 M NaNO_3 was used to synthesize coating HAp. To synthesize nanocomposite HAp/CNTs, 5 g/L of modified carbon nanotubes was dispersed into the above electrolyte solution using a microwave for 10 minutes [16]. The coating of HAp or HAp/CNTs was performed on the surface of Ti6Al4V by the scanning potential method with synthesis conditions as the following: a potential range of $0 \div -2.0 \text{ V/SCE}$, scanning rate of 5 mV/s , 5 scans at 45°C in a cell of three electrodes, i.e. working electrode (Ti6Al4V), counter electrode (Pt) and reference electrode (SCE).

Three materials of Ti6Al4V, HAp/Ti6Al4V and HAp/CNTs/Ti6Al4V were investigated of the biomineralization in SBF solution. A liter of the SBF solution was prepared by dissolution of chemicals in distilled water (8.00 gL^{-1} NaCl; 0.40 gL^{-1} KCl; 0.18 gL^{-1} CaCl_2 ; 0.35 gL^{-1} NaHCO_3 ; 0.48 gL^{-1} $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$; 0.10 gL^{-1} $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; 0.06 gL^{-1} KH_2PO_4 ; 0.10 gL^{-1} $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 1.00 gL^{-1} glucose). These chemicals have purity of 99% and were purchased from China. The pH of this solution was adjusted to 7.4 using a solution of 1 M HCl. The experiments were performed at a temperature of $37^\circ\text{C} \pm 1^\circ\text{C}$ by a thermostat.

The variation of the solution pH and material weight were determined using pH3110 Meter and Precisa XR 205 SM-DR analysis balance, respectively. The surface morphology and phase composition of these materials before and after 21 days soaked in the SBF solution were determined correspondingly by SEM (S4800 of Hitachi, Japan) and XRD (SIEMENS D5005 Bruker-Germany).

3. RESULTS AND DISCUSSION

3.1. The variation of solution pH

The bioactivity and biomineralization of Ti6Al4V, HAp/Ti6Al4V and HAp/CNTs/Ti6Al4V were investigated in the SBF solution at 37 ± 1 °C. Figure 1 shows the variation of the pH of solutions containing the above materials with different immersion times. The pH of the initial solution is 7.4. After 1 soaked day, the pH of all three SBF solutions containing the materials rises.

With the SBF solution containing Ti6Al4V, the pH has a slight variation throughout the immersion period. The value tends to decrease with a long immersion time. After 21 days of immersion, the pH value of the solution containing Ti6Al4V material is 7.22.

The variation is the same for both of solutions containing HAp/Ti6Al4V and HAp/CNTs/Ti6Al4V. The pH solution rises with a short immersion time (1, 3 or 5 days) and tends to decrease strongly at the long immersion time. The pH value of the SBF solution containing HAp/Ti6Al4V rises strongly and reaches 7.75 after 5 soaked days. The value tends to decrease at the next immersion time. After 21 soaked days, the pH value of the SBF solution is 6.86.

For the SBF solution containing HAp/CNTs/Ti6Al4V, the pH value of the solution increases slightly at time of 1 and 3 immersion days, then tends to decrease at the next immersion times. The pH value decreases slightly after 5 days of immersion then decreases strongly at 7, 14 and 21 days. The pH of the solution reaches 6.28 after 21 soaked days.

The variation of the solution pH can be explained as the following: When these materials were immersed in SBF, Ca^{2+} ions in SBF were increased by the dissolving of materials; and then OH^- was accumulated gradually because of the exchange of Ca^{2+} and H^+ , which resulted in the increase of pH value. The accumulation of OH^- on the surface is believed necessary for hydroxyapatite nucleation. The results are in agreement with other reports [9, 17].

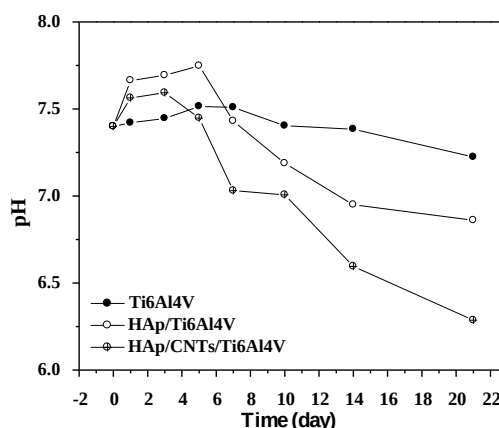


Figure 1. The time variation of pH value of SBF solution containing Ti6Al4V, HAp/Ti6Al4V, and HAp/CNTs/Ti6Al4V.

Figure 1 is clearly that the pH values of the SBF solution containing HAp/CNTs/Ti6Al4V are always lower than that of the solution containing HAp/Ti6Al4V. The results show that the dissolution of HAp/CNTs coating is lower than that of HAp coating. In addition, the HAp/CNTs coating has ability to promote the formation of hydroxyapatite crystals faster than the HAp coating.

3.2. The variation of material weight

Figure 2 shows the weight variation of HAp and HAp/CNTs coatings on the surface of Ti6Al4V substrate following soaked time in the SBF solution.

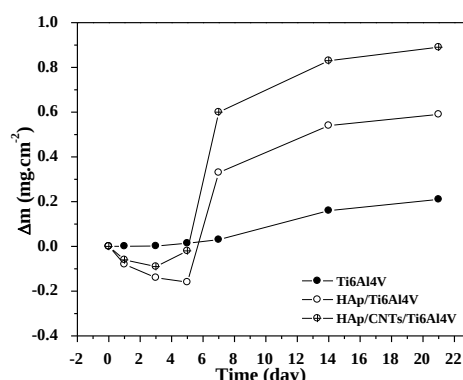


Figure 2. The variation of material weight with immersion time.

For Ti6Al4V substrate, the material weight is nearly unchanged at beginning times of immersion period and tends to increase slightly with long immersed times. The weight of Ti6Al4V increases by 0.21 mg.cm⁻² after 21 soaked days.

With the material of HAp/Ti6Al4V, the weight decreases slightly at 1, 3 and 5 soaked days and reaches $\Delta m = -0.16$ mg.cm⁻² after 5 days. The value rises strongly after 14 soaked days and continues to rise at 21 soaked days ($\Delta m = +0.59$ mg.cm⁻²).

The weight variation of the material coated with HAp/CNTs can be described as following: the weight decreases after 1 and 3 soaked days and then increases strongly with the long soaked times. After 21 days soaked in SBF solution, the weight variation of HAp/CNTs/Ti6Al4V is $\Delta m = +0.89$ mg.cm⁻².

The variation of weight is explained as the following: When the materials based on hydroxyapatite immersed in the SBF solution, there are two processes occurring simultaneously: the dissolution of HAp or HAp/CNT coating and the formation of new hydroxyapatite crystals. These processes affect to the weight of materials during immersion time. If the formation of hydroxyapatite occurs faster than the coating dissolution, this leads to the increase of material weight. On the contrary, the material weight decreases in the case of the coating dissolution process domination. In this study, the material weight decreased at early stage (after 1 or 3 immersed days) because of the dissolution of the coating. The result is the formation of OH⁻ ions around of the working electrode. The combination of OH⁻ ions and Ca²⁺, PO₄³⁻ in SBF solution forms new hydroxyapatite crystals on the surface of the material. It is cause of the strong increase of the material weight at long immersion time. The experimental results are clear that the weight of HAp/CNTs/Ti6Al4V increases more than that of HAp/Ti6Al4V or Ti6Al4V. Thus, HAp/CNTs or HAp coatings act as nucleus to promote the formation of hydroxyapatite crystals on the surface of the material.

3.3. The surface morphology

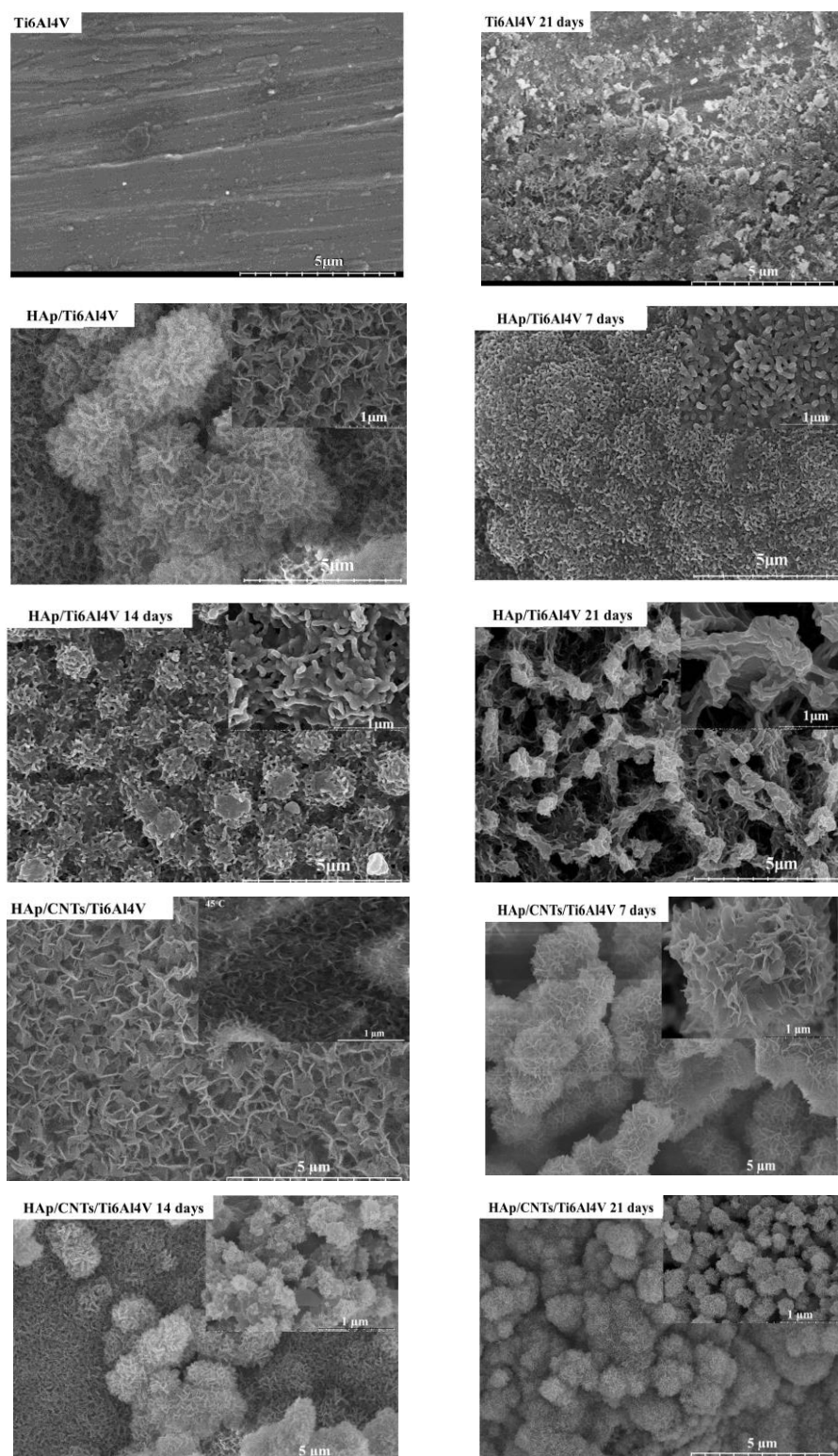


Figure 3. SEM images of Ti6Al4V, HAp/Ti6Al4V and HAp/CNTs/Ti6Al4V before and after soaked in SBF solution with different times.

The SEM images of Ti6Al4V, HAp/Ti6Al4V and HAp/CNTs/Ti6Al4V before and after being soaked in SBF solution are presented in Figure 3.

It can be seen that the formation of hydroxyapatite crystals on the surface of Ti6Al4V occurs after 21 days of soaking in SBF solution. However, hydroxyapatite crystals still are not fully covered the substrate.

HAp/Ti6Al4V has scaly-like shapes and arranges to form big particles. After being soaked in SBF solution, their morphology changes clearly. It indicates a formation of hydroxyapatite crystals on the material surface. The observed hydroxyapatite crystals are of cylinder-like shapes which cluster to form cactus-like shapes. In particular, after 21 days soaked in SBF solution, the new hydroxyapatite crystals formed to a thick layer on the surface of the material.

The morphology of HAp/CNTs/Ti6Al4V before soaked in SBF solution has scaly-like shapes. After being soaked in SBF solution, the morphology changes considerably. It confirms the formation of new hydroxyapatite crystals like corals on the surface of HAp/CNTs/Ti6Al4V. Especially, after 14 and 21 days of immersion, hydroxyapatite crystals formed with high density. The formation of hydroxyapatite crystals shows a biom mineralization of these materials when they are soaked into SBF solution.

3.4. Phase composition

To confirm the formation of the new hydroxyapatite crystals, the phase composition of Ti6Al4V, HAp/Ti6Al4V and HAp/CNTs/Ti6Al4V before and after 21 days soaked in SBF solution was analyzed by XRD (Figure 4). We can see the characteristic peaks for HAp at $2\theta \approx 25.8^\circ$ and 32° in the XRD patterns of Ti6Al4V after 21 days soaked in the SBF solution. In the X-Ray diffraction patterns of HAp/Ti6Al4V and HAp/CNTs/Ti6Al4V after an immersion period, there is no new peak observed. The result confirms the formation of hydroxyapatite crystals on the material surface and the soaking process does not change the phase composition of the materials.

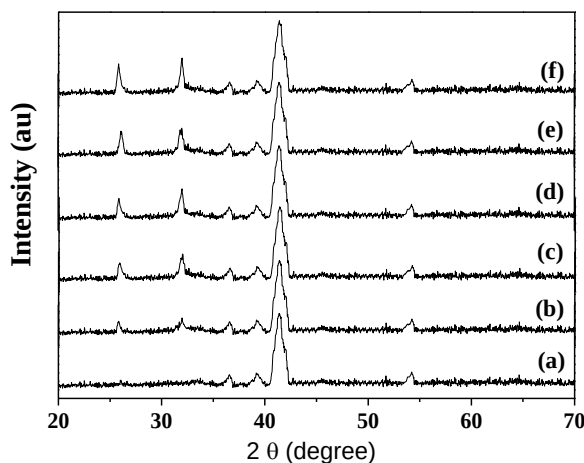


Figure 4. XRD patterns of (a) Ti6Al4V, (b) Ti6Al4V-21 soaked days, (c) HAp/Ti6Al4V, (d) HAp/Ti6Al4V-21 soaked days, (e) HAp/CNTs/Ti6Al4V and (f) HAp/CNTs/Ti6Al4V-21 soaked days.

4. CONCLUSION

The results of the variation of solution pH, material weight and structural characteristics after an immersion period confirm the biomineralization of these materials in the SBF solution. They confirm the formation of new hydroxyapatite crystals on the surface of the materials. Specially, after 21 days soaked in the SBF, the hydroxyapatite crystals formed thick blocks as observed by SEM images. Thus, the HAp/Ti6Al4V and HAp/CNTs/Ti6Al4V are promising to become potential materials for bone implant.

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