

# Preparation and characterization of hydroxyapatite coating on $Ti_6Al_4V$ cylinders by combination of alkali-heat treatments and biomimetic method

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## Abstract

Biomimetic method was used to apply hydroxyapatite (HA) coating onto  $Ti_6Al_4V$  cylinders. This process is a physicochemical method in which a substrate is soaked in a solution simulating the physiological conditions, for a period of time enough to form a desirable layer of the calcium phosphate on the substrate. In the present study, specimens were soaked in 5, 10 M solutions of NaOH at temperatures of 60 or 80°C for 24 and 72 h. Surface of samples were characterized using scanning electron microscopy (SEM) and thin film X-ray diffraction (TF-XRD). The optimum condition was found to be 72 h of soaking in 5 M NaOH at 80°C. Specimens treated under these optimum conditions were subsequently heat-treated at 500, 600, and 700°C for 1h in order to consolidate the sodium titanate hydrogel layer. Under the heat treatment condition of 600°C for 1h and subsequent soaking in simulated body fluid (SBF), apatite formed within 3 days. It was observed that, apatite formation increased significantly, which is an indication of the materials ability for use as a load bearing implant.

**Keywords:** Apatite; Biomimetic; Simulated body fluid; Coating; Alkaline treatment.

## INTRODUCTION

Titanium and its alloys have been widely used as artificial implant materials in dental, maxillofacial, and orthopedic surgery because of their good mechanical

and chemical properties, lightness, excellent corrosion resistance and biocompatibility (Lee *et al.*, 2002). However, since titanium and its alloys have no ability to bond to living bone directly, they are generally encapsulated after implantation into the living body by fibrous tissue that isolates them from the surrounding bone (Barrere *et al.*, 1998; Kim *et al.*, 1999).

It is well known that bioactive materials such as sintered hydroxyapatite (HA) and glass-ceramic apatite-wollastonite (A-W) form bioactive bonding with the living bone without formation of fibrous tissue, by forming an apatite layer on their surfaces after they are implanted in the bone-site. However their fracture resistance is not enough to replace bones at load-bearing sites (Bigi *et al.*, 2005; Lee *et al.*, 2002; Kim *et al.*, 1999; Yan *et al.*, 1997).

In order to create an implant with both superior mechanical properties and excellent bioactivity, several physical and chemical methods have been employed. Ceramic coating on the metal implant is one of the most widely investigated methods (Bigi *et al.*, 2005; Lee *et al.*, 2002; Kim *et al.*, 1999; Yan *et al.*, 1997). Many coating methods such as plasma spray, dip-coating, sputtering, electrophoretic deposition, and electrochemical deposition have been used. HA plasma spraying is one of the most widely investigated methods for coating titanium (Yan *et al.*, 1997). By using this method, HA powder is heated at extremely high temperatures and deposited at very high velocity on the metal surface. But the structure, phase composition and crystallinity of plasma sprayed coatings are different from those of natural bone and are difficult to be controlled at high temperatures. In addition, the

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cost of this method is rather high (Yan *et al.*, 1997; Wen *et al.*, 1998).

Alternatives to the plasma spraying method have been developed to obtain films of calcium phosphate, like the biomimetic method. The biomimetic process is a physicochemical method in which a substrate is soaked in a solution that simulates the physiological conditions (SBF), with ion concentrations nearly equal to those of the inorganic part of human blood plasma, for a period of time enough to form a desirable layer of calcium phosphate on the substrate (Bigi *et al.*, 2005; Lu *et al.*, 2005; Wen *et al.*, 1998). Many investigations have been focused on optimizing the characteristics of coatings and acceleration of its formation. Prior to immersion into the simulated body fluid (SBF) solution, the substrate is usually treated with an alkaline solution to generate a modified surface that induces the formation of a calcium phosphate layer. In case of titanium substrate a titanate hydrogel  $\text{HTiO}_3^+$  forms by NaOH treatment. Subsequent heat treatment dehydrates this hydrogel layer and stabilizes it by formation of an amorphous sodium titanate layer ( $\text{HTiO}_3\text{Na}$ ) (Takadama *et al.*, 2001; Kim *et al.*, 1999; Wen *et al.*, 1998). Advantages of this method are its simplicity and low costs in comparison to the plasma spray process. Besides, it can be used to coat porous substrates or those with complex geometry and because of the graded structure between apatite and metal, the bonding strength of coatings and substrate is high (Takadama *et al.*, 2001; Kim *et al.*, 1999). Therefore, the aim of this study is to form an apatite layer on  $\text{Ti}_6\text{Al}_4\text{V}$  by the biomimetic method. Also, the effects of pre-treatment (alkaline, heat treatment) on formation of the apatite layer were investigated in order to accelerate apatite formation.

## MATERIALS AND METHODS

Titanium alloy  $\text{Ti}_6\text{Al}_4\text{V}$  ASTM F620 (Ti) discs with a diameter of 25 mm and a thickness of 2 mm were prepared. They were metallographically gritted until 1000 # using a SiC (Silicium Carbide) emery paper. The discs were ultrasonically cleaned in water and acetone, then dried in an oven at 40°C. The samples were divided into 3 groups: control, alkali treated and alkali-heat treated group. For the alkali treated group, discs were soaked in 5 and 10 M NaOH aqueous solution at 60 and 80°C for 24 h and 72 h, then washed gently with acetone and distilled water, and dried at 40°C for 24 h in an air atmosphere. For the alkali-heat treated group,

the discs were heated after alkaline treatment to 500, 600 and 700°C at a rate of 5°C/min in an electric furnace, kept at the given temperatures for 1 h, and cooled to room temperature in the furnace. These discs were then soaked in 30 ml of SBF solution at 36.5°C for 1 and 3 days. The SBF solution was prepared by dissolving reagent-grade NaCl, KCl,  $\text{NaHCO}_3$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2$  and  $\text{KH}_2\text{PO}_4$  into distilled water and buffered at pH 7.25 with tris(hydroxymethyl) aminomethane (TRIS) and HCl (1 N), at 37°C. Its composition is given in Table 1 and is compared with human blood plasma. (Lu *et al.*, 2005; Kim *et al.*, 2003; Wang *et al.*, 2003; Wen *et al.*, 1998).

Morphology of specimens were examined by scanning electron microscopy (SEM) before and after alkali and heat treatment and soaking in SBF. The effects of alkaline treatment on the substrate surface and the titanium substrate structure, gel layer and bone-like apatite coatings were evaluated using thin film X-ray diffraction (TF-XRD).

**Table 1.** Composition of SBF and the inorganic part of human blood plasma (mmol/l) Jonasova *et al.*

	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{+2}$	$\text{Ca}^{+2}$	$\text{Cl}^-$	$\text{HCO}_3^-$	$\text{HPO}_4^{-2}$	$\text{SO}_4^{-2}$
Plasma	142	5.0	1.5	2.5	103	27	1.0	0.5
SBF	142	5.0	1.5	2.5	148	4.2	1.0	0.5

## RESULTS

$\text{Ti}_6\text{Al}_4\text{V}$  specimens, except for the control group, were subjected to 5 and 10 M NaOH treatment at either 60 or 80°C for 24 and 72 h. The SEM images of the control group and  $\text{Ti}_6\text{Al}_4\text{V}$  specimens subjected to 5 and 10 M NaOH treatment at 60°C for 24 h are shown in Figure 1. As it is shown the control titanium has a smooth surface texture with abrasive marks, however, a porous structure was achieved for the specimens treated with 5, and 10 M NaOH solutions.

The effects of alkali-treatment time and temperature on morphology of the  $\text{Ti}_6\text{Al}_4\text{V}$  surface were also investigated (Figure 2). At the same alkaline treatment temperature, more porous structure was observed with increasing treatment time. At a constant alkaline concentration, more homogeneously distributed porous surface structures were observed for the specimens treated at 80°C in comparison to those treated at 60°C.

Figures 3 and 4 indicate that after alkali treatment, broad peaks at 23-30° and 47-49° in 2 $\theta$  were created on the XRD pattern. These can be due to an amorphous or

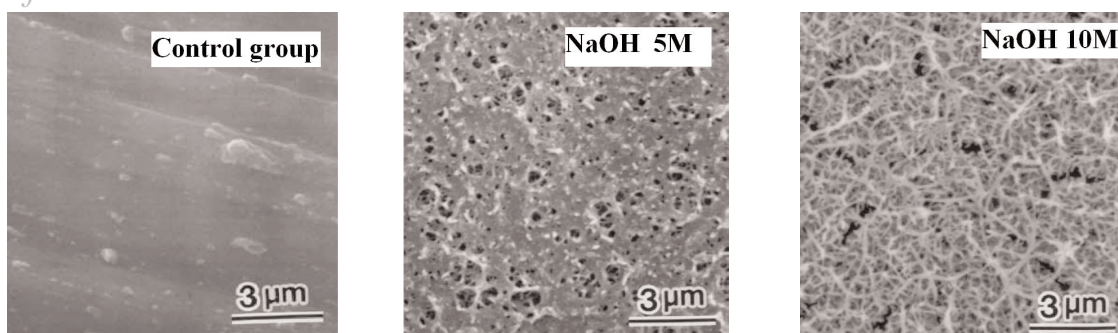


Figure 1. Surface morphologies (by SEM) of the specimens subjected to 0.5 and 10 NaOH treatment at 60°C for 24 h.

a microcrystalline phase. At the same treating temperature and period, the sodium titanate peaks increased with increasing concentrations of NaOH solution. In raising the treatment concentration from 5 to 10 M, the increase in the intensity of sodium titanate peaks was minor. At the same NaOH-treating concentration and -treating temperature, the temperature increase was only 20°C (from 60 to 80°C); however, the intensity of the sodium titanate peaks was greatly increased.

Figure 5 shows the TF-XRD patterns of  $Ti_6Al_4V$  alloys treated with 5 M NaOH solution at 80°C for 72 h, those without heat treatment or samples heat-treated at 500, 600 or 700°C for 1 h, and soaked in SBF for 1 and 3 days. Amorphous sodium titanate was detected on the specimens prior to heat treatment or following heat treatment at 500°C. However, when the specimens were heat-treated at 600 or 700°C, the rutile phase appeared, and its intensity increased with increasing heat treatment temperatures. After 3 days of soaking in SBF, apatite was formed on the surface of the specimens without heat treatment or those heat-treated at 500 or 600°C, but it was not detected on those which were heat-treated at 700°C.

Figure 6 and 7 show SEM images of corresponding  $Ti_6Al_4V$  alloys. Examination of specimens before soaking in SBF revealed a porous network structure on all the specimens except those heat-treated at 700°C, which showed a needlelike porous structure. Also, it

was observed that apatite formed on the surface of all specimens after soaking in SBF for only 1 day except for the specimens heat-treated at 700°C, which showed no apatite deposition even after 3 days of soaking in SBF. It was also observed that relatively bigger apatite crystals, approximately 5 μm, formed on the surface of the specimens not heat-treated, while smaller apatite, with a size of approximately 2.5 μm, formed on those heat-treated at either 500 or 600°C.

## DISCUSSION

As mentioned in the literature, the requirement for titanium to bond with living bone is the formation of biologically active bone-like apatite on its surface (Lee *et al.*, 2002; Wen *et al.*, 1998). Titanium treated in NaOH can form apatite after being exposed to simulated body fluid (SBF) (Lu *et al.*, 2005; Wen *et al.*, 1998).  $Ti_6Al_4V$  is normally covered with a passive titanium oxide layer. When this layer reacts with NaOH solution,  $HTiO_3^-$  is formed. The negatively charged  $HTiO_3^-$  interacts with positively charged  $Na^+$  ions. By increasing the concentration of NaOH solution, treatment time or treatment temperature, the rate of reaction increases and more  $Na^+$  ions are incorporated onto the metal surface. As a result, the thickness of gel layer increases with increasing concentrations

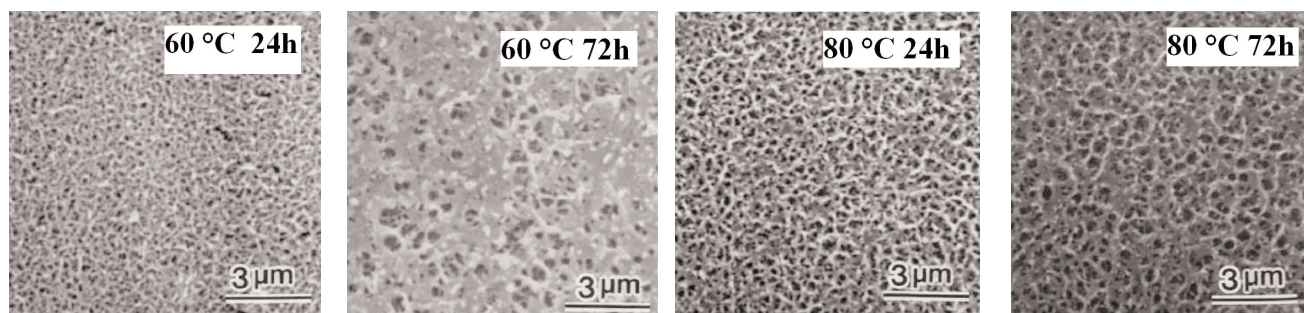
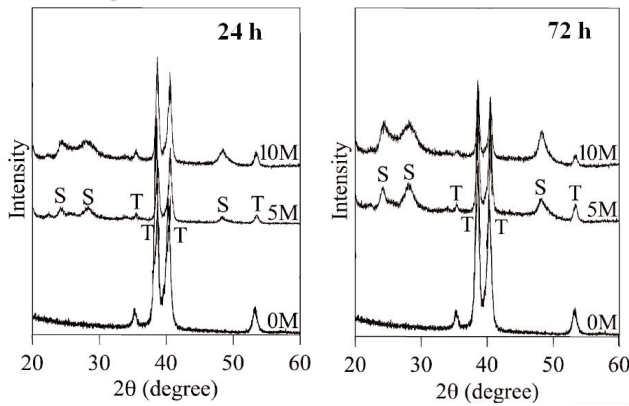
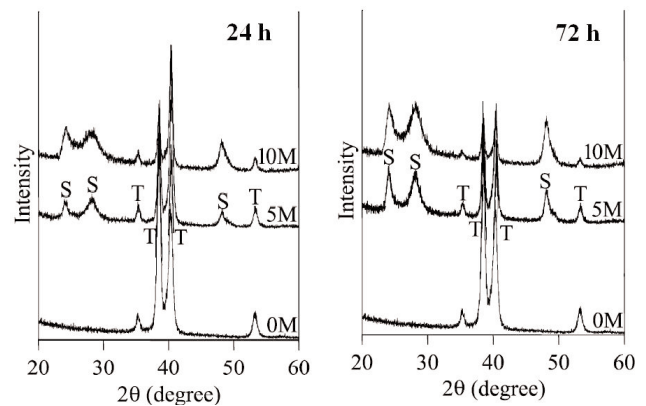


Figure 2. Surface morphologies (by SEM) of the specimens subjected to 5 M NaOH treatment at 60 and 80°C for 24 and 72 h.



**Figure 3.** TF-XRD patterns of the specimens subjected to 0, 5 and 10 M NaOH treatment at 60°C for 24 and 72 h T: titanium and S: sodium titanate.



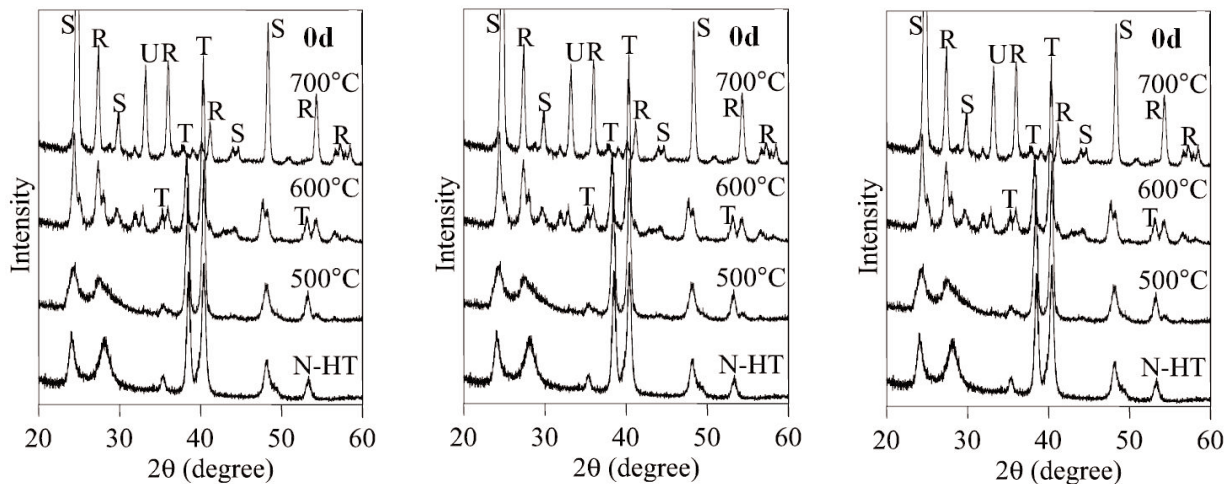
**Figure 4.** TF-XRD patterns of the specimens subjected to 0, 5, and 10 M NaOH treatment at 80°C for 24 and 72 h. T: titanium and S: sodium titanate.

of NaOH solution, alkaline-treatment time, and alkaline-treatment temperature (Lu *et al.*, 2005; Teixeira *et al.*, 2004).

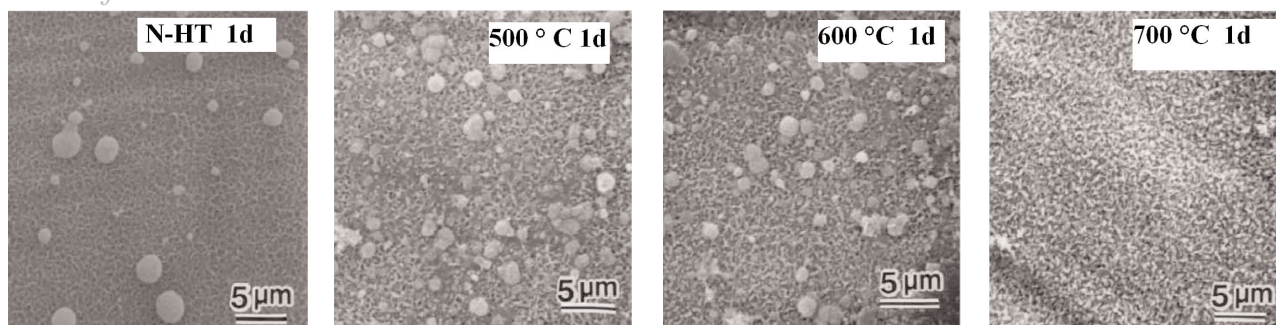
Similar intensities of sodium titanate peaks were detected for all specimens treated with 5 or 10 M NaOH at 80°C for 24 or 72 h. Thus, it seems that the least aggressive treatment resulting in the thickest layer of sodium titanate is to soak in 5 M NaOH solution at 80°C for 72 h.

It was clearly observed by SEM that apatite was formed on the surface of the specimens treated with 5 M NaOH at 80°C for 72 h, soaked in SBF for 1 day, either with or without heat treatment at 500 or 600°C for 1 h. However, apatite did not form on the surface of the specimens heat-treated at 700°C. The lack of apatite formation on these specimens may be due to the surface structural changes produced by the heat treatment. During SBF soaking, sodium ions released

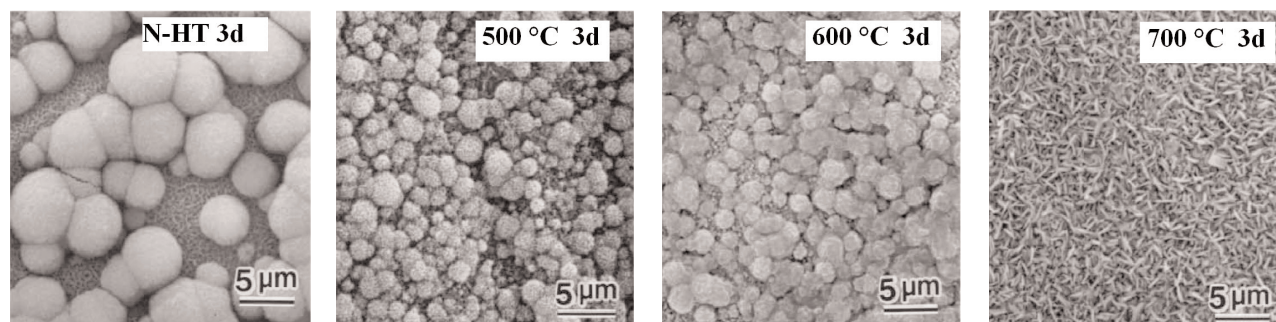
from the substrate via exchange with the  $H_3O^+$  ions in the SBF lead to the formation of Ti-OH groups on their surfaces. These Ti-OH groups induce apatite nucleation (Lu *et al.*, 2005; Kim *et al.*, 2003; Jonsova *et al.*, 2002). The thicker the sodium titanate layer, the more sodium ions are released. The release of sodium ions also accelerates apatite nucleation by increasing the  $OH^-$  concentration. Since, at the relatively high sintering temperature (700°C), the surface structure became more stable and less sodium ions were released from the substrate and thus, less Ti-OH groups were formed. At 25°C, there were many TiOH groups on the surface of the specimens, so large-sized apatites were easily formed. Because, the sodium titanate film formed at this temperature was weakly bonded to the titanium alloy substrate, post-sintering was carried out after alkaline treatment. At 500°C, apatite was detected by TF-XRD after 3 days of soaking in SBF; however, the



**Figure 5.** TF-XRD patterns of the specimens subjected to 5 M NaOH treatment at 80°C for 72 h without heat treatment (N-HT) or heat-treated at 500, 600 and 700°C for 1 h, and soaked in SBF for 1 and 3 days, R: rutile, T: titanium, S: sodium titanate, O: apatite, and U: unknown.



**Figure 6.** Surface morphologies (by SEM) of the specimens subjected to 5 M NaOH treatment, without heat treatment (N-HT) or heat-treated at 500, 600 and 700°C for 1 h, and soaked in SBF for 1 day.



**Figure 7.** Surface morphologies (by SEM) of the specimens subjected to 5 M NaOH treatment, without heat treatment (N-HT) or heat-treated at 500, 600 and 700°C for 1 h, and soaked in SBF for 3 days.

bonding between the sodium titanate and the substrate was poor (Fatehi *et al.*, 2007). Relatively small apatite crystals were formed on the heat-treated specimens at both 500 and 600°C, which could be result of reduction in TiOH groups on the surface of the heat-treated specimens.

It was found that the best treatment conditions for  $Ti_6Al_4V$  specimens were immersion in 5 M NaOH solution at 80°C for 72 h followed by heat treatment at 600°C for 1 h. Apatite was observed by TF-XRD on the surface of  $Ti_6Al_4V$  specimens treated under these conditions after only 3 days of soaking in SBF. This induction period for apatite formation on  $Ti_6Al_4V$  is much shorter than the 7 days previously reported by Kim *et al.* (1996).

## CONCLUSION

The NaOH and heat treatment of the  $Ti_6Al_4V$  alloy produce an amorphous sodium titanate hydrogel layer which after immersion in SBF can form an apatite layer on the surface. We have tried to determine the parameters of alkaline and subsequent heat treatment which lead to the most rapid formation of apatite. It was found that the optimum alkaline treatment for the

$Ti_6Al_4V$  alloy was a 72 h soak in 5 M NaOH solution at 80°C and the optimum heat treatment for these specimens was at 600°C for 1 h. On soaking in SBF, apatite formed within 3 days, as compared to the 7 day formation, which was the best rate previously reported (Kim *et al.*, 1996). The significant increase in rate of apatite formation is an indication of the potential of the  $Ti_6Al_4V$ -treated specimen for use as a load bearing implant.

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