

Effect of Alkali and Heat Treatment on Biomimetic HA Coating on Ti6Al4V

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ABSTRACT

In this study, time of calcium phosphate formation on Ti6Al4V alloy with or without alkali and heat treatments was investigated. Specimens were soaked in 0, 5, 10 M solutions of NaOH at temperatures of 60 or 80 °C for 24, 72 h. Their surfaces were characterized using scanning electron microscopy and thin film X-ray diffraction. It was found that optimum condition is 72h soaking in 5 M NaOH in 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. With heat treatment at 600 °C for 1h and then soaking in simulated body fluid (SBF), apatite formed within 3 days. But there were no signs of apatite formation in control samples (without alkali and heat treatment) up to 7 days soaking in SBF. So, it was concluded that alkali-heat treatment is an effective way for accelerating apatite formation and the optimum condition is 72 h soaking in 5 M NaOH solution at 80°C and then heat treatment at 600 °C resulted for 1 h.

KEYWORDS

Biomimetic coating, hydroxyapatite, alkali- heat treatment

1. INTRODUCTION

Excellent biocompatibility is needed for biomaterials because when the implant is introduced into the human body, it causes an immunizing and foreign reaction within the body and emits toxicity on the cells and organization. Also, excellent mechanical property is needed to endure heavy load, wear, and fatigue along with excellent corrosion resistance to minimize the elution of toxic metal ions.

Titanium and its alloys are used widely in orthopedic implants because of their high toughness and excellent biocompatibility. However, bone does not bond directly to these metals. Bioceramic coatings on metallic substrates have been widely used in medicine and dentistry to combine the excellent mechanical properties of metal alloys with the bioactive properties of bioceramics [1,2].

Titanium alloys (Ti6Al4V) coated with plasma-sprayed hydroxylapatite (HA) are currently used for orthopedic applications. Despite excellent clinical results, plasma-sprayed HA coatings have specific drawbacks related to the extremely high processing temperatures and lines of sight application[3,4].

Recently, several groups have focused their attention on low temperature methods such as electrophoretic [5],

electrochemical [6] and biomimetic deposition. The biomimetic process is a physicochemical method in which a substrate is soaked in a solution that simulates the physiologic conditions (SBF), with ion concentration nearly equal to those of inorganic part of human blood plasma, for a period of time enough to form a desirable layer of calcium phosphate on the substrate. In contrast to plasma spraying, biomimetic methods offer the possibility to cover complex shaped implants and to elaborate films of different Ca-P phases [7,8]. In recent years, different metal pretreatments such as, alkaline treatment [9], acid treatment [10], have been used for accelerating and enhancing of biomimetic coating method. In this study, time of calcium phosphate formation on Ti6Al4V alloy with or without alkali and heat treatments was investigated.

2. MATERIALS AND METHOD

Thirty-six Ti6Al4V (ASTM-F620) discs (5mm thickness and 20 mm diameter) were polished with 200, 400, and 600 silicon carbide paper, then ultrasonically cleaned successively in acetone, ethanol (70%), and finally demineralized water and air dried. The discs were divided into three groups (12 discs per group) and subjected to the following treatments: 1) control group

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without any treatment. 2) alkali treated that were soaked in 50 ml of 5, 10 M in NaOH aqueous solution at 60 and 80°C for 24 h and 72 h. 3) alkali and heat treated that were heated at 500, 600 or 700 °C for 1 h in a Ni–Cr electrical furnace in air and cooled to room temperature in the furnace.

The SBF solution was prepared by dissolving reagent-grade NaCl (Merck Art.1.06400) , KCl (Merck Art. 1.04936), NaHCO₃ (Merck Art. 1.06329), MgCl₂.6H₂O (Merck Art.1.05833), CaCl₂ (Merck Art.2388) and KH₂PO₄ (Merck Art.5099) into distilled water and buffered at pH=7.25 with TRIS (trishydroxymethyl aminomethane) (Merck Art.1.08387) and HCl (Merck Art.1.00314.2500) 1N at 37 °C. Its composition is given in Table 1 and is compared with that of human blood plasma. The discs were then soaked in 30 ml SBF solution at 36.5 °C for 3days and 7 days. The morphologies of the specimens before and after alkali and heat treatment and soaking in SBF were examined by scanning electron microscopy (SEM). The effects of alkaline treatment on the surface of the substrate and the structure of the titanium substrate, gel layer and bone-like apatite coatings obtained 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)[10].

	Plasma(mmol/l)	SBF(mmol/l)
Na ⁺	142.0	142.0
K ⁺	5.0	5.0
Mg ⁺²	1.5	1.5
Ca ⁺²	2.5	2.5
Cl ⁻	103.0	148.0
HCO ₃ ⁻	27.0	4.2
HPO ₄ ⁻²	1.0	1.0
SO ₄ ⁻²	0.5	0.5

3. RESULT AND DISCUSSION

Figs. 1 and 2 indicate that after the alkaline treatment, there are broad peaks at 23–30° and 47–49° in 2h on XRD patterns. These can be ascribed to an amorphous or a microcrystalline phase. Also, it has been reported that it is the sodium titanate hydrogel layer formed by alkaline treatment which is responsible for apatite formation [11]. At the same treating temperature and period, the sodium titanate peaks increased with increasing concentration of NaOH treatment solution. Because more Na⁺ ions are incorporated into the metal surface, and the thickness of the gel layer increases with increasing concentration of the NaOH solution, alkaline-treating time, and alkaline-treating temperature but it has found that in higher concentration than 10 M NaOH, the thick sodium titanate film peeled off either during the alkaline treatment itself

or later during water rinsing. Similar intensities of sodium titanate peaks were detected for all specimens treated with 5 or 10 M NaOH at 80 °C for 3 days. Thus, the least aggressive treatment resulting in the thickest layer of sodium titanate is to soak in 5 M NaOH solution at 80 °C for 3 days.

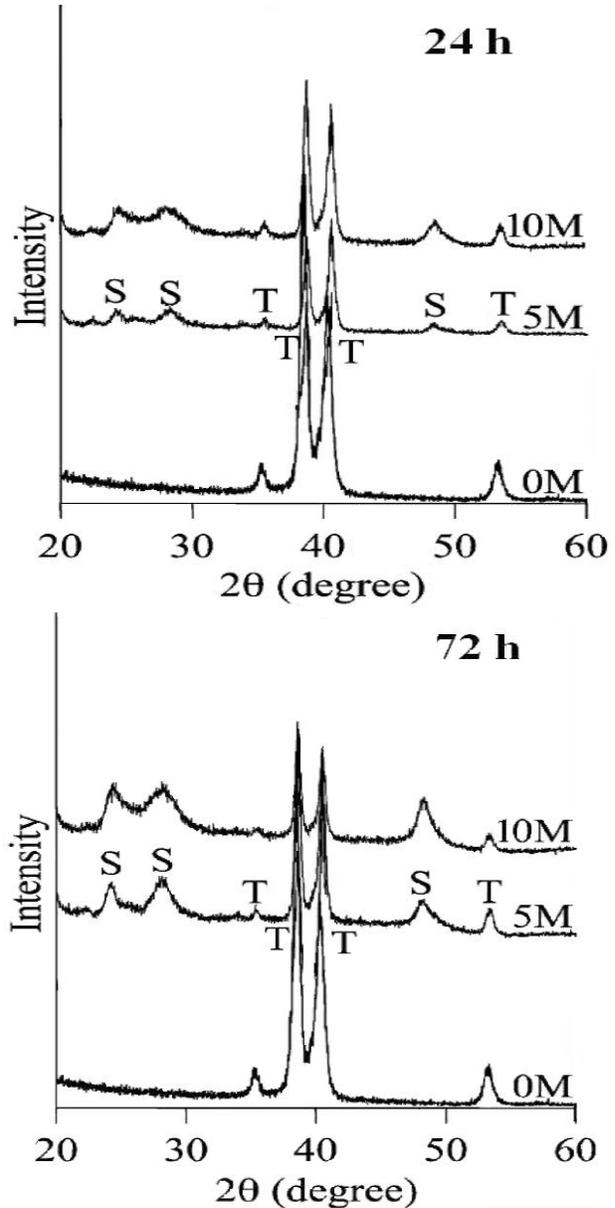


Figure 1: TF-XRD patterns of the specimens subjected to 0, 5, 10 M NaOH treatment at 60 °C for 24h, 72h. T: titanium and S: sodium titanate.

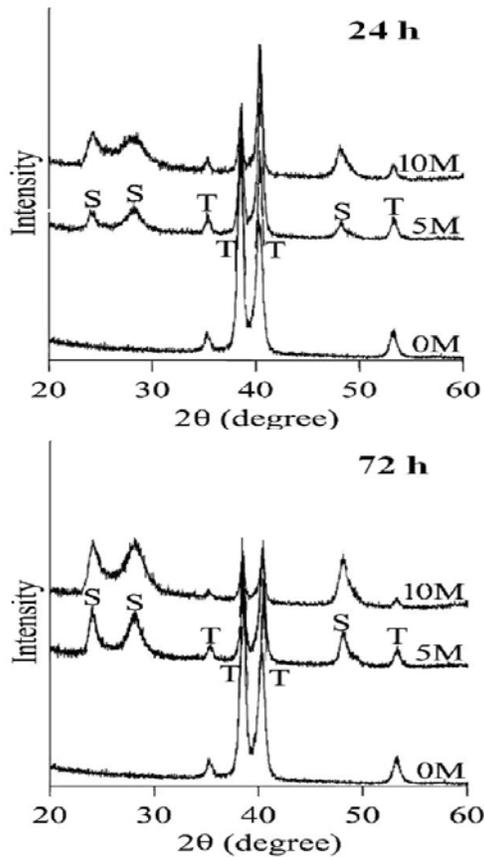


Figure 2: TF-XRD patterns of the specimens subjected to 0, 5, 10 M NaOH treatment at 80 °C for 24h, 72h. T: titanium and S: sodium titanate.

Scanning electron microscopy (SEM) revealed that the control titanium had a smooth surface texture with abrasive marks (Fig. 3a). In contrast, the alkali-treated and alkali- and heat-treated titanium had porous surfaces. At the same alkaline-treating temperature, a much porous structure was observed with increasing treatment time (Fig. 4). At a constant alkaline concentration, more homogeneously distributed porous surface structure was observed for the specimens treated at 80 °C than for those treated at 60°C.

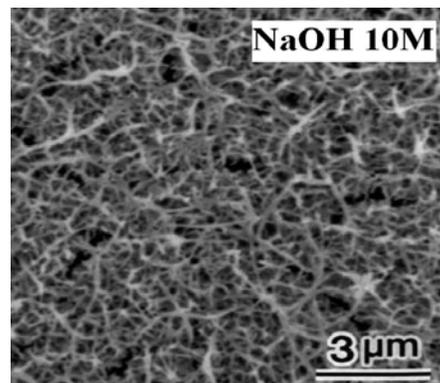
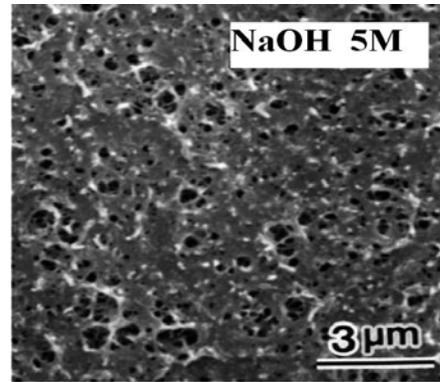
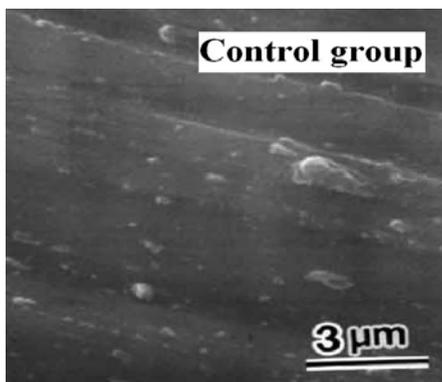
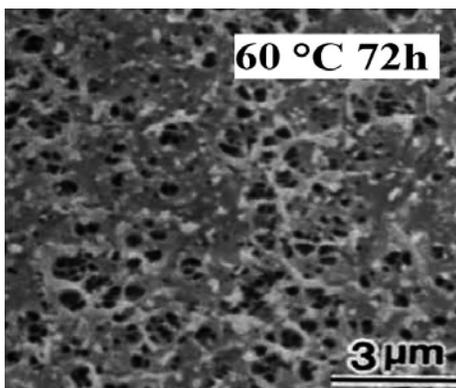
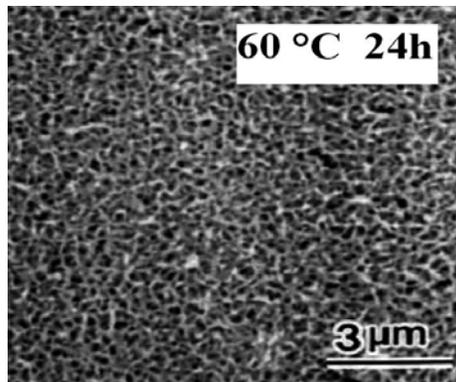


Figure 3: Surface morphologies (by SEM) of the specimens subjected to 0, 5, 10 M NaOH treatment at 60 °C for 72h.



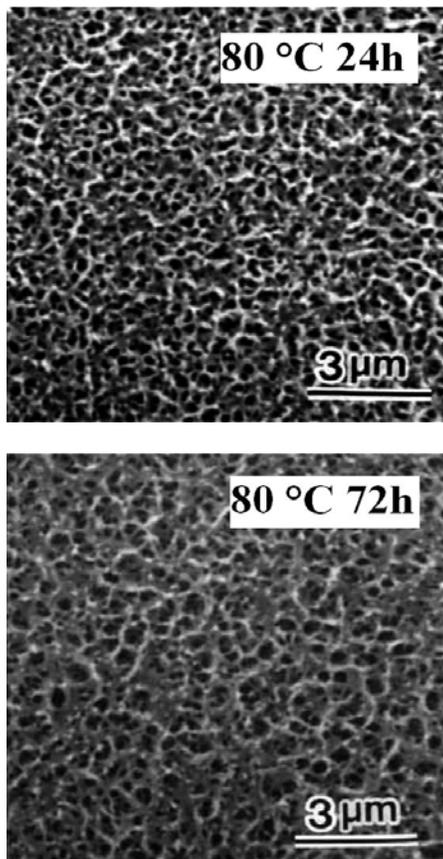


Figure 4: Surface morphologies (by SEM) of the specimens subjected to 5 M NaOH treatment at either 60 or 80 °C for 24, 72 h.

After soaking in SBF, it was clearly observed in XRD patterns (Fig. 5) that apatite was formed on the surface of the specimens treated with 5 M NaOH at 80 °C for 72h when soaked in SBF for 1 day, either with or without heat treatment at 500 or 600 °C for 1 h. However, apatite was not formed 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 structure changes produced by the heat treatment. During the SBF soaking, sodium ions released from the substrate via exchange with the H_3O^+ ions in the SBF form the Ti-OH groups on their surfaces [12-14]. These Ti-OH groups induce the apatite nucleation. The thicker the sodium titanate layer, the more sodium ions can be released. The release of sodium ions also accelerates apatite nucleation by increasing the OH concentration. However, at the relatively high sintering temperature (700 °C), the surface structure became more stable and less sodium ions were released from the substrate, so less TiOH groups were formed [14].

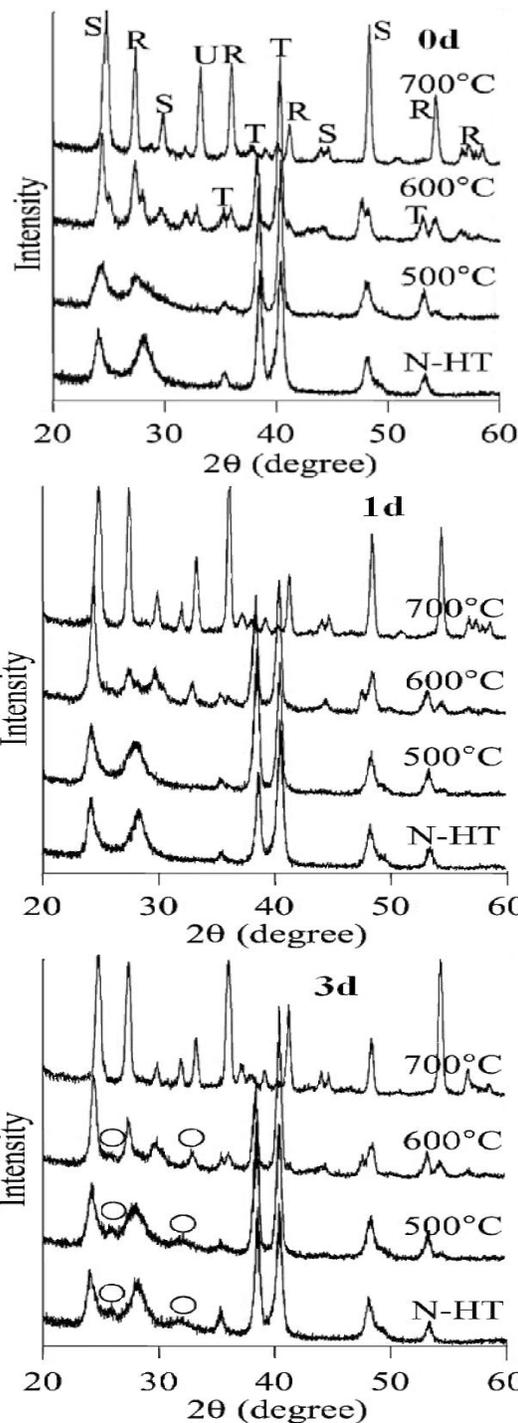


Figure 5: TF-XRD patterns of the specimens subjected to 5 M NaOH treatment at 80 °C for 72 h without heat treatment (N-HT) or heat-treated at 500, 600 or 700 °C for 1 h, and soaked in SBF for 0, 1, 2 or 3 days, R: rutile, T: titanium, S: so sodium titanate, O: apatite, and U: unknown.

At 25 °C, there were many TiOH groups on the surface of the specimens, so apatite was easily formed with large size particles; however, it seems they were weakly bonded to the substrate. Relatively small apatite crystals were

formed on the specimens heat-treated at both 500 and 600 °C, and this might be due to the reduction of the number of TiOH groups on the surface of the heat-treated specimens. However, apatite coverage of the heat treated specimens at 600°C is more than 500 °C. It was determined that the best treating conditions for Ti6Al4V specimens were immersion in 5 M NaOH solution at 80 °C for 3 days followed by heat treatment at 600 °C for 1 h.

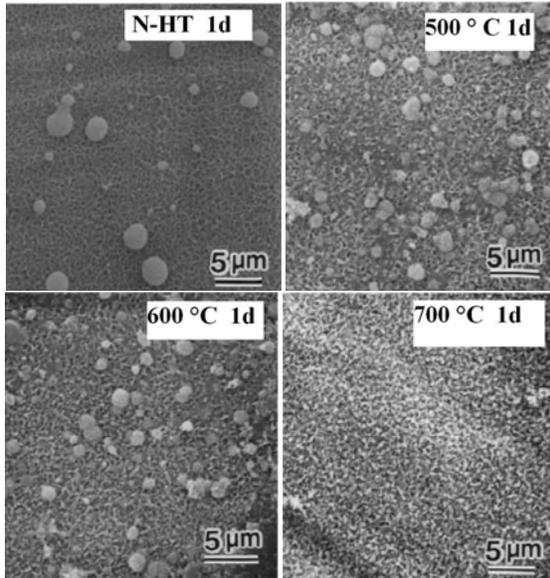


Figure 6: Surface morphologies (by SEM) of the specimens subjected to 5 M NaOH treatment, without heat treatment (N-HT) or heat-treated at 500, 600 or 700 °C for 1 h, and soaked in SBF for 1 days.

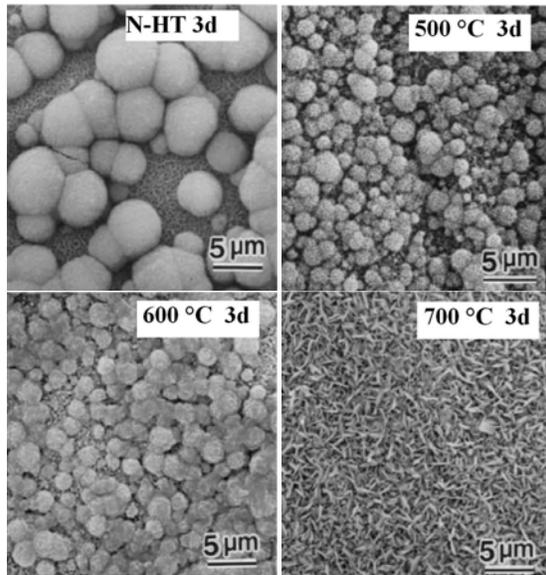


Figure 7: Surface morphologies (by SEM) of the specimens subjected to 5 M NaOH treatment, without heat treatment (N-HT) or heat-treated at 500, 600 or 700 °C for 1 h, and soaked in SBF for 3 days.

4. CONCLUSIONS

The NaOH and heat treatment of the Ti6Al4V alloy produce an amorphous sodium titanate surface layer on the surface. On immersion in the SBF, the alloy forms Ti-OH groups on its surface by exchanging Na⁺ ions from the surface sodium titanate layer with H₃O⁺ ions in the fluid. The Ti-OH groups on the alloy thereafter induce the apatite formation indirectly, by forming a calcium titanate and an amorphous calcium phosphate. So, alkali and heat treatment is an effective pre-treatment for apatite formation on Ti6Al4V surface and optimum condition is a 3-day soak in 5 M NaOH solution at 80°C and then heat treatment at 600 °C resulted for 1 h.

5. REFERENCES

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