J Mater Sci: Mater Med (2011) 22:273–278
DOI 10.1007/s10856-010-4218-y

Effect of heat treatments on apatite-forming ability of NaOH- and HCl-treated titanium metal

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Received: 6 October 2010 / Accepted: 11 December 2010 / Published online: 29 December 2010

Abstract Titanium (Ti) metal was soaked in HCl solution after NaOH treatment and then subjected to heat treatments at different temperatures. Their apatite-forming abilities in a simulated body fluid (SBF) were discussed in terms of their surface structures and properties. The nanometer scale roughness formed on Ti metal after NaOH treatment remained after the HCl treatment and a subsequent heat treatment below 700°C. Hydrogen titanate was formed on Ti metal from an HCl treatment after NaOH treatment, and this was converted into titanium oxide of anatase and rutile phases by a subsequent heat treatment above 500°C. The scratch resistance of the surface layer increased with the formation of the titanium oxide after a heat treatment up to 700°C, and then decreased with increasing temperature. The Ti metal with a titanium oxide layer formed on its surface showed a high apatite-forming ability in SBF when the heat treatment temperature was in the range 500–700°C. The high apatite-forming ability was attributed to the positive surface charge in an SBF. These positive surface charges were ascribed to the presence of chloride ions, which were adsorbed on the surfaces and dissociated in the SBF to give an acid environment.

1 Introduction

Titanium (Ti) metal and its alloys are widely used as various implants in orthopedic and dental fields because of their high mechanical strength and good biocompatibility [1]. However, they do not bond to living bone [2]. Early on, it was shown that Ti metal forms a bone-like apatite layer on its surface in the living body, and bonds to living bone through this apatite layer, if it is subjected to NaOH and heat treatment to form sodium titanate on its surface [3–6]. These treatments have been applied to the porous layer of an artificial hip joint and the resulting implant has been used clinically in Japan since 2007 [7].

Later it was also found that Ti metal forms the bone-like apatite on its surface in a simulated body fluid (SBF), even if it is soaked in water or HCl solution after the NaOH treatment and then heat-treated at 600°C to form titanium oxide on its surface [8]. Its apatite-forming ability increased with increasing concentration of the HCl solution, and assumed to be attributed to positive surface charge of the Ti metal increased with increasing concentration of the HCl solution [8].

In this study, Ti metal was soaked in 50 mM HCl solution after the NaOH treatment and then subjected to heat treatment at different temperatures. Their apatite-forming abilities in SBF were discussed in terms of their surface structures and properties. Much attention has been paid on bioactive Ti metal prepared by HCl and heat treatments after the NaOH treatment, because a porous Ti metal subjected to these treatments was found to exhibit osteoconductivity [9] as well as osteoinductivity [10]. It is already being subjected to clinical trial for application to spinal fusion devices [11].

2 Materials and methods

2.1 Preparation of specimens

Commercially pure Ti metal (Kobe Steel, Ltd., Japan) was cut into rectangular samples (dimensions = 10 × 10 × 1 mm^3),

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abraded with a #400 diamond plate, washed with acetone, 2-propanol, and ultrapure water for 30 min each in an ultrasonic cleaner, and then dried overnight in an oven at 40°C. The samples were then soaked in 5 ml of a 5 M NaOH solution at 60°C in an oil bath while being shaken at 120 strokes/min for a period of 24 h, and then gently washed with ultrapure water. Subsequently, the samples were soaked in 10 ml of a 50 mM HCl solution at 40°C in an oil bath while being shaken at 120 strokes/min for a period of 24 h. The samples were then gently washed with ultrapure water and dried overnight in an oven at 40°C. The samples were heated to several temperatures in the range 400–800°C at a rate of 5°C/min in Fe–Cr electric furnace in air, maintained at the desired temperature for a period of 1 h, and then allowed to cool at the natural rate of the furnace to room temperature. For the present study, ten samples were prepared in each heat treatment condition.

2.2 Examination of the apatite-forming ability in an SBF

The samples subjected to NaOH, HCl, and heat treatments were soaked at 36.5°C in 30 ml of an acellular SBF with ion concentrations nearly equal to those of human blood plasma (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, and SO_4^{2-} 0.5 mM). The SBF was prepared by dissolving reagent grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 (Nacalai Tesque, Inc., Japan) in ultrapure water, and the solution was buffered at pH = 7.40 using tris (hydroxymethyl) aminomethane [$(CH_2OH)_3CNH_2$] and 1 M HCl (Nacalai Tesque, Inc.) [12]. The samples were removed from the SBF after 1 day, gently washed with ultrapure water, and dried in an oven at 40°C. The formation of apatite on the surface of the samples was examined using scanning electron microscopy (SEM) and thin film X-ray diffraction (TF-XRD) using the methods described in the next section.

2.3 Surface analysis of treated Ti metals

The surface of the Ti metals subjected to NaOH, HCl, and heat treatments, and those subsequently soaked in an SBF for several periods were analyzed using TF-XRD (TF-XRD; RINT-2500, Rigaku Co., Japan) and X-ray photoelectron spectroscopy (XPS; ESCA-3300KM, Shimadzu Co., Japan). In the TF-XRD experiments, CuKα radiation was used as the X-ray source, and the angle of the incident beam was 1° against the sample surface. In the XPS experiments, MgKα radiation was used as the X-ray source ($\lambda = 9.8903$ Å). The XPS takeoff angle was set at 45°, which enabled the system to detect photoelectrons to a depth of 5–10 nm from the surface of the substrate. The binding energy of the measured spectra was calibrated by reference to the C_{1s} peak of the surfactant's CH_2 group on the substrate occurring at 284.6 eV.

The sample surfaces were coated with a Pt/Pd film and observed under a field emission scanning electron microscope (FE-SEM; Hitachi S-4300, Hitachi Co., Japan) using an acceleration voltage of 15 kV.

The scratch resistance of the surfaces of the treated Ti metals was measured using a scratch tester (CSR-2000; Rhesca Co., Ltd., Japan). In this measurement, a stylus with diamond tip was moved on the sample surface at a speed of 10 mm/s under an applied load of 100 mN/min. The critical scratch load was estimated from an abrupt change in the signal of the sensor output, which indicated a complete peeling of the surface layer.

The zeta potential of the treated Ti metals was measured using plate samples (dimensions = $13 \times 33 \times 1$ mm^3). In the preparation of these plate samples, 20 ml of the NaOH solution and 30 ml of the HCl solution were used. The Ti metal samples were first grounded to allow for leakage of any stray charge, and were then immediately set in a zeta potential and particle size analyzer (ELS-Z1, Otsuka Electronics Co., Japan) using a glass cell for the plate sample. The zeta potential was measured under an applied voltage of 40 V in a 10 mM NaCl solution with dispersed monitor particles composed of polystyrene latex particles (diameter = 500 nm) coated with hydroxyl propyl cellulose. Five samples were measured for each experimental condition, and the average values were used in the analysis.

3 Results

3.1 Surface structure of the treated Ti metal

Figure 1 shows FE-SEM photographs of the surface of Ti metal subjected to heat treatments at various temperatures after NaOH and HCl treatments. A fine network structure on the nanometer scale formed on the surface of the Ti metal after the initial NaOH treatment, and this remained essentially unchanged after the subsequent HCl and heat treatments up to 700°C, but began to fade for a heat treatment of 800°C.

Figure 2 shows the TF-XRD patterns of surface of Ti metal subjected to heat treatment at various temperatures after NaOH and HCl treatments. From Fig. 2, it can be seen that hydrogen titanate ($H_2Ti_3O_7$) had formed on the Ti metal surface after the NaOH and HCl treatments [8, 13, 14], and that this phase had converted to anatase and rutile after subsequent heat treatments above 500°C. The ratio of rutile to anatase increased with increasing heat treatment temperature, and only rutile was detected for a heat treatment temperature of 800°C.

Figure 3 shows the scratch resistance of the surface of Ti metal subjected to heat treatments at various

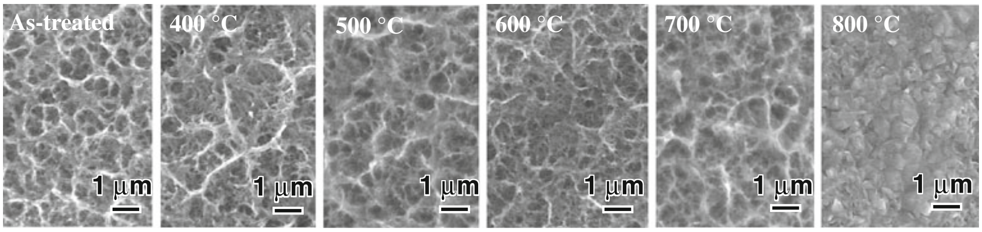

Fig. 1 FE-SEM photographs of surface of Ti metals subjected to heat treatments after NaOH and HCl treatments at various temperatures

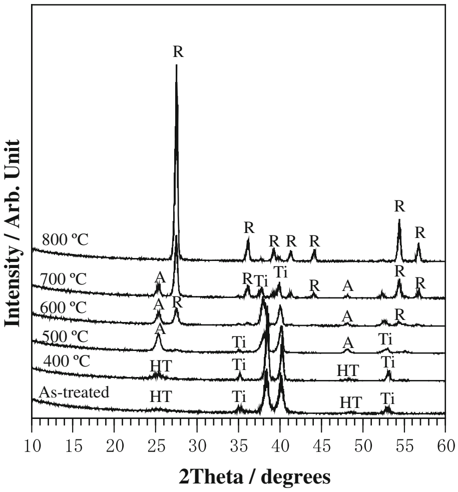

Fig. 2 TF-XRD patterns of surfaces of Ti metals subjected to heat treatments at various temperatures after NaOH and HCl treatments. *Ti* α Titanium, *HT* Hydrogen titanate, *A* anatase, *R* Rutile

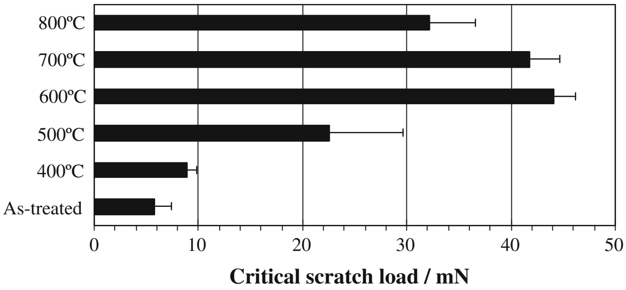

Fig. 3 Scratch resistances of surfaces of Ti metals subjected to heat treatments at various temperatures after NaOH and HCl treatments

temperatures after NaOH and HCl treatments. From Fig. 3, it can be seen that the scratch resistance of the surface of the Ti metal was as low as 5 mN after the NaOH and HCl treatments, and this increased to 45 mN with increasing heat treatment temperature up to 600°C, and that the scratch resistance decreased for heat treatment temperatures above 700°C.

3.2 Apatite-forming ability of treated Ti metal in an SBF

Figure 4 shows FE-SEM photographs of the surface of Ti metal soaked in an SBF for 1 day after heat treatment at various temperatures following NaOH and HCl treatments. A small number of spherical particles was observed on the surface of the Ti metal treated with NaOH and HCl solutions, and the number of these particles increased with increasing heat treatment temperature up to 700°C, and then decreased for a heat treatment temperature of 800°C.

Figure 5 shows the TF-XRD patterns of Ti metal soaked in an SBF for 1 day after heat treatment at various temperatures following NaOH and HCl treatments. From Fig. 5, it can be seen that apatite had precipitated on the Ti metal heat-treated at temperatures in the range 500–700°C. These results indicate that the spherical particles observed on the surface of the Ti metal samples in Fig. 4 were composed of apatite.

3.3 Zeta potential of treated Ti metal

Figure 6 shows the zeta potential of the surface of Ti metal subjected to heat treatment at various temperatures

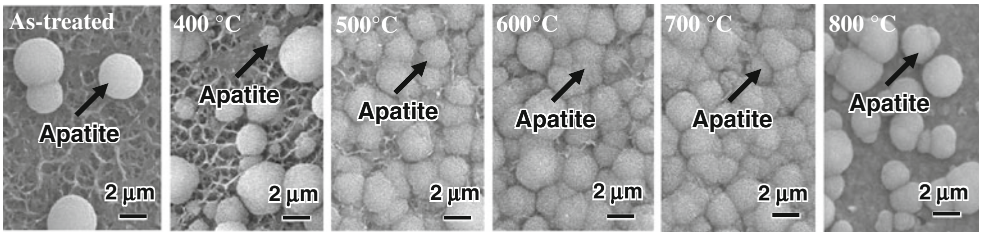

Fig. 4 FE-SEM photographs of surfaces of Ti metals soaked in SBF for 1 day, after heat treatments at various temperatures following the NaOH and HCl treatments

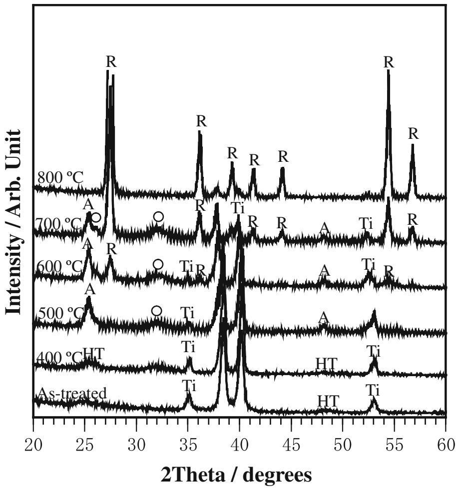

Fig. 5 TF-XRD patterns of the surfaces of Ti metals soaked in SBF for 1 day after heat treatments at various temperatures following the NaOH and HCl treatments. *Ti* α Titanium, *HT* Hydrogen titanate, *A* anatase, *R* Rutile, *O* Apatite

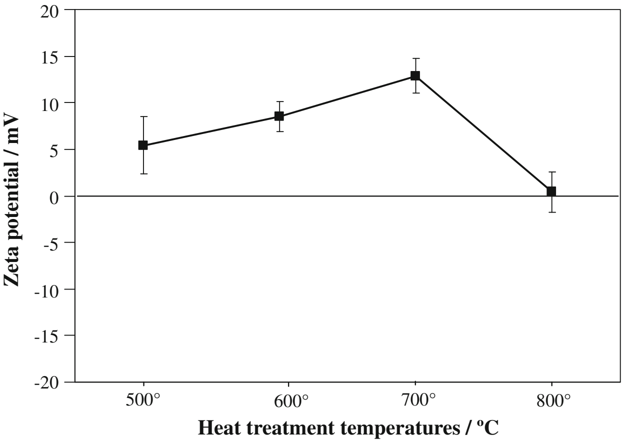

Fig. 6 Zeta potentials of surfaces of Ti metals subjected to heat treatments at various temperatures after NaOH and HCl treatments

following NaOH and HCl treatments. The zeta potential of the samples that had been heat-treated at temperatures below 400°C was not able to be measured, because no, or only a thin, insulating titanium oxide layer had formed on the surface. The Ti metal heat-treated at temperatures in the range 500–700°C exhibited a positive zeta potential that increased with increasing heat treatment temperature up to 700°C, while the Ti metal samples heat-treated at 800°C exhibited a zeta potential of zero.

3.4 XPS spectra of treated Ti metal

Figure 7 shows the XPS spectra of the Ca and P ions on the surface of the Ti metal samples subjected to heat treatment at 400, 600, and 800°C as a function of the soaking time in an SBF after NaOH and HCl treatments. From Fig. 7, it can be seen that Ti metal treated with NaOH and HCl solutions that was subsequently heat-treated at 400°C adsorbed both calcium and phosphate ions almost simultaneously on its surface from the initial stages of soaking in the SBF, whereas Ti metal samples heat-treated at 600 and 800°C only adsorbed phosphate ions during the early stages of soaking in the SBF.

Figure 8 shows the XPS spectra of Cl ions of the surface of Ti metal subjected to heat treatment at 600 and 800°C after NaOH and HCl treatments. From Fig. 8, it can be seen that Cl ions were adsorbed on the surface of the Ti metal after the NaOH and HCl treatments, and that these ions remained on the surface even after the subsequent heat treatment at 600°C, but the samples showed a slight decrease in the number of Cl ions after a heat treatment at 800°C.

4 Discussion

It is apparent from the experimental results described above that the nanometer scale roughness formed on the surface of Ti metal after the NaOH treatment remained after the HCl treatment, and even after a subsequent heat treatment at temperatures below 700°C (see Fig. 1). The decrease in roughness at a heat treatment temperature of 800°C is because of sintering and thickening of the surface oxide layer. The NaOH- and HCl-treated Ti metal formed titanium oxide of anatase and rutile phases when heat-treated at temperatures above 500°C (see Fig. 2).

The scratch resistance of the surface of NaOH- and HCl-treated Ti metal increased with the formation of a titanium oxide layer for heat treatment temperatures above 500°C, but decreased for a heat treatment temperature of 800°C. This decrease may be attributed to the difference in thermal expansion coefficients between the Ti metal substrate and the thick titanium oxide layer.

The titanium oxide formed on the NaOH- and HCl-treated Ti metal samples showed a high apatite-forming ability in an SBF when the temperature of the heat treatment was in the range 500–700°C. This high apatite-forming ability was not attributable to the surface roughness, since the surface roughness of Ti metal samples heat-treated in this temperature range was not different from that of samples heat-treated at lower temperature. Nor was it attributable to a specific crystalline phase, as the ratio of rutile to anatase on the surface of the Ti metal samples was largely changed in this temperature range (see Fig. 2). Therefore, the high apatite-forming ability was attributed to the positive surface charge, as the Ti metal samples only showed a positive zeta potential when the samples were heat-treated in the temperature range of 500–700°C (see Fig. 6). When the Ti metal samples had a positively charged surface,

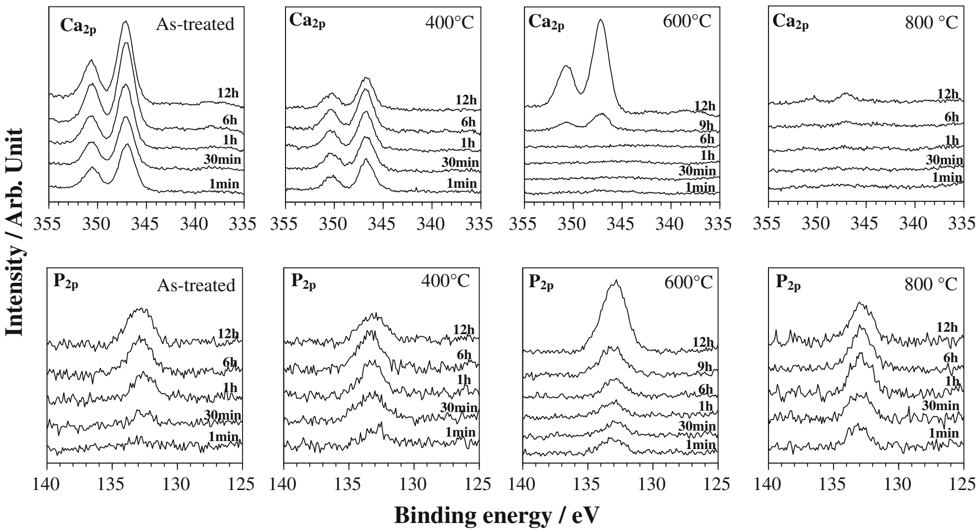

Fig. 7 XPS spectra of Ca and P of the surface of Ti metals as a function of soaking period in SBF subjected to heat treatments at 400, 600 and 800°C after NaOH and HCl treatments

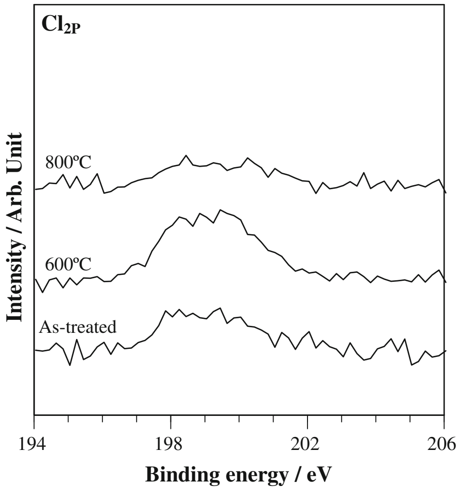

Fig. 8 XPS spectra of Cl ion on the surface of Ti metals as a function of soaking period in SBF subjected to heat treatments at 600 and 800°C after NaOH and HCl treatments

negatively charged phosphate ions were selectively adsorbed on the surface in the SBF. As the phosphate ions begin to accumulate, the surface becomes negatively charged, and, therefore, positively charged calcium ions are adsorbed on the surface to form an apatite layer. This sequential adsorption of phosphate and calcium ions on the Ti metal samples was confirmed by the XPS spectra of Ti metal samples heat-treated at 600°C after NaOH and HCl treatments (see Fig. 7). According to the data in Fig. 7, Ti metal samples heat-treated at 800°C also showed an initial selective adsorption of phosphate ions. However, this tendency was weak. Both Ti metal samples treated with NaOH and HCl solutions and those subsequently heat-treated at 400°C did not show any selective adsorption of phosphate ions, but showed the simultaneous adsorption of calcium and phosphate ions (see Fig. 7). When the calcium and phosphate ions were adsorbed simultaneously on the surface, then its charge was soon neutralized and the calcium phosphate formed could not grow to form an apatite layer.

The reason for the positive surface charge of Ti metal samples heat-treated in the temperature range 500–700°C was attributed to the presence of chloride ions that were adsorbed on the hydrogen titanate layer formed on the Ti metal after the HCl treatment. These remained on the surface, even after the conversion of the hydrogen titanate into titanium oxide by a heat treatment below 700°C. The adsorbed chloride ions dissociate from the surface of the titanium oxide in an SBF to create an acidic environment on the Ti metal. Titanium oxide has been reported to have a positively charged surface in an acidic environment [1]. Above a temperature of 800°C, the chloride ions on the surface of the titanium oxide decompose (see Fig. 8), and so do not form a strong acidic environment and a positive surface charge in an SBF.

Recently, it was reported that Ti metal subjected to a mixed acid treatment shows high apatite-forming ability when it was heat-treated at temperatures ranged from 500 to 650°C, and that their high apatite-forming abilities are also attributed to their positive surface charge [15]. This is consistent with the present results.

It has been reported that osteoconduction and osteoinduction are closely related to an apatite-forming ability [16]. Our present results could establish the fundamental conditions required for chemical and heat treatments to obtain porous titanium metal that could induce high osteoconductivity and osteoinductivity.

5 Conclusions

1. A nanometer scale roughness formed on Ti metal samples after an NaOH treatment remains after an HCl

treatment and a subsequent heat treatment below 700°C.

2. NaOH- and HCl-treated Ti metal forms titanium oxide of anatase and rutile phases on its surface after a heat treatment above 500°C.
3. The scratch resistance of the surface of Ti metal increases with the formation of titanium oxide up to 700°C, and then decreases with increasing temperature.
4. The apatite-forming ability in an SBF of Ti metal is remarkably high when the Ti metal is heat-treated in the temperature range 500–700°C after NaOH and HCl treatments.
5. The high apatite-forming ability of Ti metal subjected to the above treatments is attributed to positive surface charges.
6. These positive surface charges arise from the presence of chloride ions adsorbed on the titanium oxide layer, which dissociate in an SBF to give an acidic environment.
7. Our present results could establish the conditions required for the chemical and heat treatments to obtain porous Ti metal oxide that could induce high osteoconductivity and osteoinductivity.

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