Bioactive ability of alkali treated titanium alloy

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ABSTRACT: *Studies have demonstrated that the bone bonding ability of a titanium alloy material could be evaluated by testing the titanium material in a simulated body fluid. The capability of forming hydroxyapatite on the surface of alkali treated titanium in simulated body fluid has been considered to indicate its bone bonding potential. To the extent that titanium may be capable of inducing apatite formation in a simulated body fluid, any modification of the titanium surface to speed up apatite formation can lead to enhanced Osseo integration. It was the objective of this study, as the first phase of our program addressing the subject of bone bonding alkali treated titanium implants; to investigate the potential of alkali treated titanium for inducing apatite formation in a simulated body fluid. And also, the influence of simulated body fluid corrosion upon the mechanical properties and changes in microstructure of alkali treated titanium alloy was investigated*.

INTRODUCTION

Calcium hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$), is the mineral component of bone which has attracted wide interest from both the dental and orthopedic fields. Because of the frequent failure of the cemented implants, cement less implants coated with calcium hydroxyapatite has been suggested. A hydroxyapatite coating with ability to enhance the bone ingrowths over a gap that divides the implant surface from the tissue and improves fixation to the natural bone tissue improves the fixation and lifetime of the osteoconductive process.

Hydroxyapatite coating have been prepared by a variety to techniques, including sol-gel [1], plasma spray [2], sputtering [3], laser ablation method [4] and hydrothermal methods [5, 6]. The problems associated with coatings prepared by sputtering are phosphorus deficiency and amorphous nature of the material. The latter causes fast resorption of the material by body fluids. The ion beam sputtering methods as well as a hot isostatic pressing methods have a problem with ability to coat odd-shaped objects. The electrophoresis methods have problems with poor adhesion and formation of other phases. Plasma spray has been the commercial method

for preparation of the calcium hydroxyapatite coatings. However this method suffers from formation of other phases like tricalcium phosphate, characterized with lack of crystalline and poor adhesion to the substrate.

Implant materials to be used as substitutes for high bearing bone such as femoral bone and tibia bone need to possess not only bone bonding ability but also high fracture toughness. However, neither the currently available bioactive ceramics nor biocompatible metals fulfill both these requirements, the fracture toughness of the ceramics is lower than that of human cortical bone and none of the metals directly bonds to living bone [7,8]. Coating bioactive ceramics onto tough metals is therefore a popular method to provide the metals with bone bonding ability [9, 10]. As exemplified by a plasma-sprayed hydroxyapatite coated bioactive ceramics typically contain resorbable molten phase and thus degrade in a short period after implantation, decreasing their adhesion to the surrounding bone, as well as to the metal substrate. [11,12]

Recently, we revealed that titanium alloy spontaneously from bonelike apatite layer on their surface in the body environment and bond to living bone through this apatite layer when they have been previously subjected to NaOH and subsequent heat treatments to from an amorphous sodium titanate layer on their surfaces [13,14,15]. Bioactive metals obtained in this way are believed to be useful as bone substitutes even under bearing conditions, because they are not only intrinsically tough but are also able to tightly bond to living bone. A characteristic of this type of bioactive metals is to form the bonded to the substrates. It is speculated that this tight bond might be attributed to a graded interface structure between the apatite layer and the substrates (Figure 1).

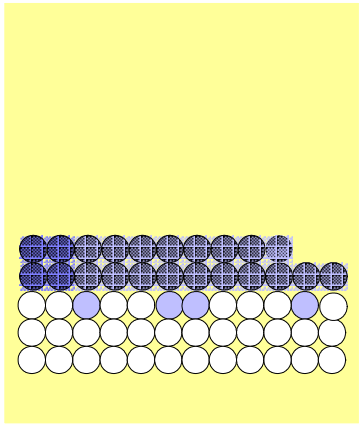


Figure 1 Schematic of graded interface structure

The purpose of the present study is to investigate structural variations near

the surface of titanium alloy metals treated with an alkali treated solution that are subsequently subjected to heat treatments and then soaked in simulated body fluid (SBF). And also, its materials of mechanical properties were investigated.

MATERIALS AND METHODS

Alkali treatments of Ti-6Al-4V alloys metal

Ti-6Al-4V alloys specimen plates $35\times36\times4mm^3$ in size were abraded with 360 diamond plates, and washed with pure acetone and distilled water in an ultrasonic cleaner. They were treated with 5.0mol/l NaOH aqueous solution at 60°C for 24hrs, washed gently with distilled water and dried at 37°C for 24hrs (Alkali treatment method). Then, the Ti-6Al-4V alloys metal plates were heated to temperature 600°C at a rate of 10°C/min, kept at the desired temperature for 1hrs and allowed to cool in the furnace

Soaking of Ti-6Al-4V alloys metal in SBF

The Ti-6Al-4V alloys specimen subjected to the NaOH and subsequent heat treatments were soaked in an a cellular simulated body fluid (SBF) with pH and ion concentrations nearly equal to those of human blood plasma, as given in Table 1. 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 into distilled water, and buffered at pH 7.40 with tris (hydroxymethyl) amminomethane ($(CH_2OH)_3CNH_3$) and hydrochloric acid a 37°C. Each specimen was soaked in 30ml of SBF at 37°C for various periods, and then removed from the fluid and washed with pure acetone.

Table 1 Ion concentrations and pH of simulated body fluid (SBF) and those of human blood plasma.

(mEq/L)

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}	other
Sodium chloride	154.0			154.0					
Ringer fluid	130.4	4.0	2.7	109.4					27.7(Lact.)
Simulated body fluid	142.0	5.0	2.5	1.5	147.8	4.2	1.0	0.5	100(Tris)
Blood plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5	

Tris: Tri-hydroxymethyl amminomethane

Analysis of specimen surface and SBF

Surface structural changes of the Ti-6Al-4V alloys specimens due to the NaOH and heat treatment and the subsequent soaking in SBF were analysis by thin film X-ray diffraction (TF-XRD: Model 2100, Rigaku, Japan), Auger electron spectrometer (AES: Model JAMP-7810, JEOL) and scanning electron microscope (SEM: Model SSX550, Shimadzu Japan). Changes in pH and element concentrations of SBF due to the soaking of the Ti-6Al-4V alloys specimen were analyzed by pH mater (Model HM60G, TOA Japan) and inductively coupled plasma atomic emission spectroscopy (ICP: Model ISPS7000, Shimadzu Japan), receptivity.

Mechanical Test Methods

Fracture resistance measurements were performed at room temperature, the standard shaped compact specimen is a single edge-notched and fatigue crack disk segment loaded in tension. The general proportions of this specimen configuration are shown Figure 2 and Figure 3.

$$Kq = (Pq/BW^{1/2}) \cdot f(a/w) \qquad (1)$$

The fracture resistance (*Kc*) was determining by employing tension testing method (ASTM E399). *Kq* values were calculated by using the following equation, where *Kc* is fracture resistance [MPa·m$^{1/2}$], *Pq* is fracture load [kN], *B* is thickness [cm], *a* is crack length [cm] and w is width [cm] generated in the material tested.

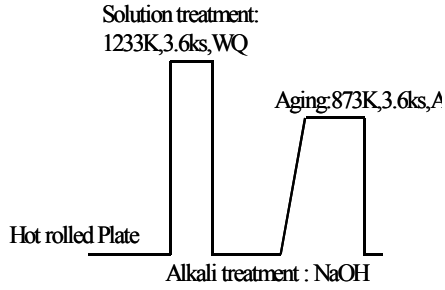


Figure 2 Schematic drawings of conventional thermo mechanical processing.

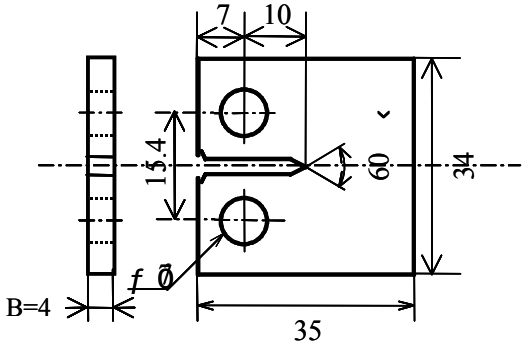


Figure 3 CT specimen configurations

RESULTS AND DISSCUTION

Figure 4 shows the SEM photographs of the surface of Ti-6Al-4V alloys soaked in SBF, after being treated with NaOH alkali solutions. Acicular structural of Figure 4 is the apatite. It is confirmed from Figure 4 that the

amount of the apatite formed on the Ti-6Al-4V alloys increase with increasing period of the SBF soaking.

Figure 5 shows TF-XRD patterns of the surface of Ti-6Al-4V alloys that were soaked in SBF for 3weeks after 5.0mol/l NaOH alkali aqueous solution at 60°C for 24hrs and subsequent heat treatments at 600°C for 1hrs. The new XRD peaks appearing after soaking in SBF are all ascribed to crystalline apatite. Figure 3 and 4 show that the island likes substances

(a) 3wweks (b) 6weeks (c) 9weeks

Figure 4 SEM photograph of alkali treatment with HA surface of Ti-6Al-4V alloys that were soaking in SBF for 3, 6, 9weeks

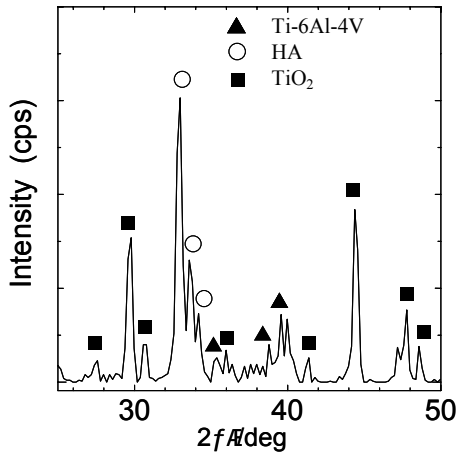


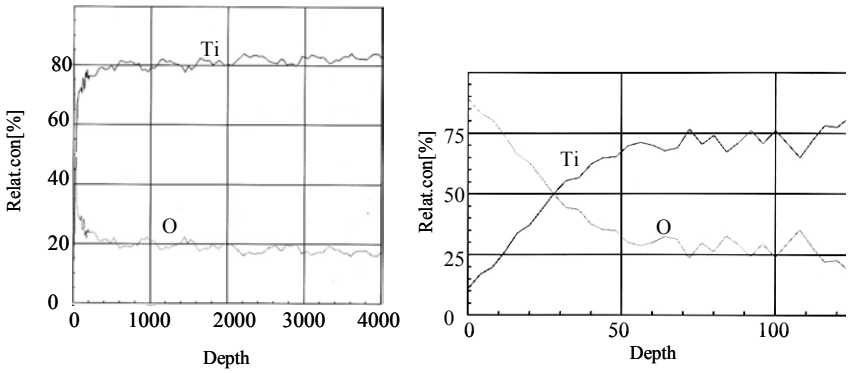
Figure 5 TF-XRD analysis of alkali treatment with HA surface of Ti-6Al-4V alloys, soaking in SBF for 3weeks

alloy, soaking in SBF for 3weeks formed on the apatite formation is considerably increased by the period of the SBF soaking.

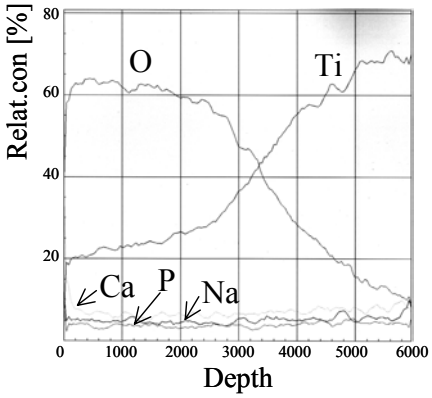
Figure 6 shows AES depth profile near the surfaces that were soaked in SBF after 5.0mol/l NaOH alkali aqueous solution at 60°C for 24hrs and subsequent heat treatments at 600°C for 1hrs. The soaking periods in SBF were the same as those for SEM observation. It can be seen from Figure 5 that the Na is completely released from all the substrates into the SBF, and

instead the Ca and P penetrate into the substrates to from the apatite. Their concentrations gradually decreased with increasing depth from the top surfaces to about 500nm in depth. Distributions of the Ti and O were little changed by the soaking in SBF. This indicated that the apatite formed on the substrates gradually changed into Ti-6Al-4V alloys through the titanium oxide and the thickness of the titanium oxide increased with increased heat treatments temperature.

When expose to SBF, the Alkali NaOH treated Ti-6Al-4V alloys released the Na^+ ion from its surface sodium titanate hydro gel layer into SBF via exchanges for H_3O^+ ion in the fluid. As a result, pH of the fluid increase, and almost simultaneously, a hydrated titanina is formed on the surface of Ti-6Al-4V alloys. The hydrated titanina induced the apatite nucleation, as proved for sol-gel derived TiO_2 hydro gel [16,17], and the pH increase accelerates the apatite nucleation by increasing the ionic activity product of



(a) Ti-6Al-4V alloys (b) heat treatments 600℃ for 1hrs



(c) With HA coating surface

Figure 6 Augur electron depth profile of alkali treatment with HA surface of Ti-6Al-4V alloys, soaking in SBF for 3weeks

apatite in SBF [18]. A large number of apatite nuclei are thus formed on the surface of the Ti-6Al-4V alloys. Once the apatite nuclei are formed, they spontaneously grow by consuming the calcium and phosphate ions from the surrounding fluid, since SBF is already highly supersaturated with respect to the apatite even before the soaking of the Ti-6Al-4V alloys [19]. When NaOH alkali treated Ti-6Al-4V alloys is subjected to a heat treatment, its surface sodium titanate hydro gel layer is dehydrated and transformed into an amorphous sodium titanate at 600°C. The rate of the Na^+ ion release from the surface layer decreases with the structural changes from the gel to amorphous phase and then crystalline phases. Therefore, the rates of formation of the hydrated titania on the surface of Ti-6Al-4V alloys and the increase in pH of the surrounding fluid degrease. As a result, the induction period for the apatite formation decrease. The decrease in the Na+ ion release rate with the transformation from the amorphous phase to crystalline phases is remarkable, and hence the increase in the induction period for the apatite formation is also remarkable [19].

The standard compact specimen is a single edge-notched and fatigue crack plate loading in tension. The fracture resistance of Ti-6Al-4V alloys, with apatite coating and without apatite coating is shown in figure 7. In test results of with apatite coating specimens extremely higher fracture strength, compared with monolithic Ti-6Al-4V alloys whose fracture strength was $60MPa{\cdot}m^{1/2}$. For apatite coating Ti-6Al-4V alloys the general tendencies in the fracture strength depending upon apatite coating were understood as follows. With apatite coating Ti-6Al-4V alloys it is recognized that speculated that this tight bond might be attributed to a graded interface structure between the apatite layer and the substrates.

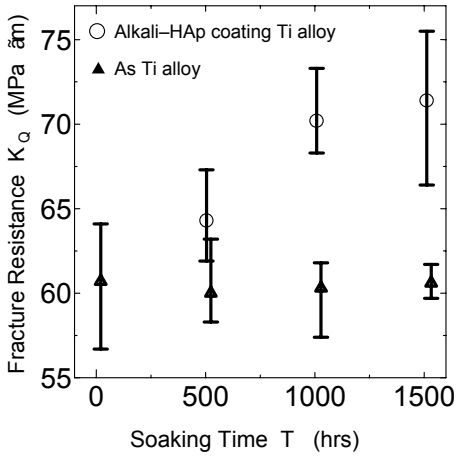


Figure.7 Effects of immersing time upon fracture resistance of Ti-6Al-4V alloys in SBF environment for 3weeks

CONCLUTION

The Ti-6Al-4V alloys shows a fairly apatite forming ability in a simulated body fluid environment, and hence bonding ability, as well as mechanical stability of its surface when it is subjected to a Alkali NaOH treatment and a subsequent heat treatment to form an amorphous sodium titanium layer on its surface. Thus a treated Ti-6Al-4V alloy is believed to be useful as a substitute even under highly conditions.

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