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Surface characteristics and in-vitro behavior of chemically treated bulk Ti6Al7Nb alloys

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ABSTRACT

The effect of various treatments on surface chemical composition and structure, and bioactivity of Ti6Al7Nb bulk alloys has been investigated. The alloys were treated employing aqueous solutions of NaOH and $CaCl_2$ separately, and also by subsequent $CaCl_2$ treatment after NaOH treatment (NaOH-$CaCl_2$ treatment) which were followed by heat treatment. NaOH treatment was observed to be effective in enrichment of surface layer with Na. On the other hand, Na^+ ions were mostly replaced by Ca^{2+} ions as a result of NaOH-$CaCl_2$ treatment, while single step $CaCl_2$ treatment was less effective in Ca incorporation. Additionally, porous network surface structure seen in NaOH and NaOH-$CaCl_2$ treated samples was completely different than globular morphology detected in $CaCl_2$-treated samples in single step. Subsequent heat treatments caused coarsening of surface structure and loss of some Na^+ and Ca^{2+} ions. NaOH and NaOH-heat treated samples did not exhibit apatite formation within 15 days immersion in simulated body fluid (SBF). On the other hand, NaOH-$CaCl_2$ samples had the highest apatite formation; however, NaOH-$CaCl_2$-heat treated samples did not display any mineralization. Conversely, $CaCl_2$ treated samples allowed apatite formation after heat treatment.

1. Introduction

High biocompatibility and osseointegration as well as high corrosion and wear resistance are the primary requirements for artificial biomaterials to fulfill the desired function properly. Implants used in joint replacements such as elbow, knee and hip are also needed to possess mechanical properties similar to that of bone. High fatigue strength is another service requirement to withstand cyclic loads which makes metallic materials indispensable in load bearing applications. However, the metallic implant should also preserve its mechanical stability to perform desired mechanical function properly during service [1]. The breakdown of a material through some chemical reactions with body fluid, proteins and various cells in the biological environment [2–6] is the main concern as material loss change the mechanical stability of the implant. Unlike the bioactive materials like hydroxyapatite (HAP) and some biodegradable metals such as iron-alloys [7] and Mg-alloys [8], most of the load bearing metallic materials are classified as biotolerant materials and expected to remain as permanent fixtures during the service.

The rate of attack of corrosion or breakdown in some of metallic materials such as Co-Cr alloys, stainless steels and titanium alloys is usually low and they are self-protected as they contain inherent passive oxide films [1]. In fact, the type, structure, thickness and spontaneous regeneration in milliseconds even after damage determine the protectiveness and the rate of ion transfer through the passive film. The oxide film in Co-Cr based alloys and stainless-steels is rich in Cr_2O_3 [9–13]. Therefore, Cr is responsible for high passivation and it increases the resistance against localized breakdown of passivity. However, stainless steels containing nickel may cause a negative reaction and induce harmful effects when nickel ions are released [14–16]. In addition, mechanical mismatch related "stress-shielding" problem may appear due to comparatively higher elastic moduli of stainless steels like those of Co-Cr alloys. Accordingly, titanium and titanium alloys are more frequently used as they mechanically more compatible to bone and more passive due to 3–7 nm thick [17] amorphous [18] or crystalline native titanium oxide (TiO_2) [3–5]. $\alpha + \beta$ titanium alloys like Ti6Al4V and Ti6Al7Nb, also contain surface oxides of the alloying elements such as Al_2O_3, V_2O_5 and Nb_2O_5 [19–22]. As alloying elements like vanadium are considered as potential toxic elements, which may cause allergic and adverse reactions in human body, they are replaced with more inert elements like Nb as in the case of Ti6Al7Nb. Nb_2O_5 is considered to be more stable, less soluble and more biocompatible oxide compared to V_2O_5 [1]. Ti6Al7Nb alloys, therefore, are produced as alternative $\alpha + \beta$

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alloys exhibiting higher biocompatibility, but similar mechanical properties to those of Ti6Al4V alloys.

Osseointegration, which is defined as the direct integration of living bone to artificial implant surface, is crucial as well as the biocompatibility to not to repeat the surgery operation and for using the implants safely for long period. For stable implant fixation, the bone tissues are expected to attach and bond to implant surface to ensure an interface matrix, equivalent to bone structure [23,24]. For example, in load bearing implants used in knee and hip joints, the surface portion of the implant anchored into bone is desired to exhibit high osseointegration for inducing sufficient bone growth during the healing stage. Two methods, namely, cement fixation and cementless implantation, are used for titanium implant fixation in bones. Bone cements based on polymethylmethacrylate (PMMA) are prepared and employed during surgery [25]. Although durability and bond strength of the cement affect its lifetime, the micro-movements across the metal-cement interface may induce failure and/or end up with metal ion release into body fluid [26]. Therefore, implantation with direct cementless technique through osseointegration is more promising in terms of obtaining safer fixation [27]. However, cementless implanted bioinert materials like titanium are generally encapsulated with fibrous tissue in the body thereby, eliminating direct contact with the surrounding bone. Accordingly, the surface modification technologies with the aim of enhancing osseointegration have become inevitable to increase bonding between implant surface and the bone, and to form new bones tissues at the early stages after surgery [1,28]. Mechanical methods such as machining, grinding or blasting are usually used to roughen the surface and produce high surface area [22]. On the other hand, most of the physical and chemical methods form a new layer which is compositionally different from the base and biologically more active that it induces bone like apatite formation when implanted in the living body [17]. Among these techniques, sol-gel technique is widely used to deposit thin ceramic coatings such as titanium oxide (TiO_2) [29], calcium phosphate [30,31] especially hydroxyapatite (HA) coatings, [32] and TiO_2–CaP composite [33]. Some silica-based coatings have also been produced using the sol–gel technique [34]. On the other hand, anodic oxidation is used to form porous titania of the anatase and/or rutile [35], titania nanotube [36] and for Ca incorporation [37]. Spray methods like thermal and plasma spraying are used to obtain HA [38,39] and calcium silicate [40] and titanium coatings [41] with porous structure on various implants, respectively. Sputtering, a physical deposition technique, is mainly utilized to produce bioactive glass–ceramic coatings on titanium based on MgO–CaO–P_2O_5–SiO_2 [42] and calcium phosphate [30,31]. The incorporation of Ca ions by ion implantation [43] is known to increase bone conductivity as well. Successive implantation of calcium and phosphorus with subsequent annealing results formation of apatite layer [44]. Apart from the traditional coating methods, biochemical methods aim to obtain an ultrathin layer consisting of bioactive molecules [45]. A variety of techniques, such as silanized titania [46], self-assembled monolayers [47] and protein immobilization [48] have been used to obtain bioactive surface on titanium and titanium alloys.

Possibility of processing at lower temperatures, applicability to complex geometries and use of simple equipments make chemical treatments advantageous over the physical deposition techniques. Enrichment of the surface layers with elements of Na [49,50], Ca [51], Mg [52] and Sr [53] using aqueous solutions and formation titanate phases of corresponding elements by subsequent heat treatment have been shown to allow growth of bone. For example, chemical treatment in aqueous solution of NaOH at 60 °C and subsequent heat treatment at 600 °C result in bioactive sodium titanate layer which forms bone-like apatite when soaked in SBF [49,54,55]. However, it has been shown that all subsequent heat treatments negatively affect the in vitro bioactivity by causing thermal decomposition of the dense sodium titanate leaving less exchangeable sodium ions [56]. Bioactivity of the sodium titanate layer is also deteriorated when kept in a humid environment for a long period of time. In contrast to sodium titanate, calcium titanate obtained as a result of aqueous Ca solution treatment exhibits stable apatite formation even after storage in a humid environment [53]. Obtaining Ca-rich or calcium titanate layers simply by using aqueous solutions of calcium necessitates relatively higher temperatures and prolonged time. $CaCl_2$ aqueous solution treatment after the NaOH treatment is shown to be a simpler and effective way of obtaining Ca-rich coating layer as it allows incorporation of Ca^{2+} ions into surface through exchange of Na^+ ions. The combined chemical treatment including NaOH and $CaCl_2$ have been used previously for surface modification of titanium [51] and titanium alloys like Ti–15Zr–4Nb–4Ta [57] and Ti–36Nb–2Ta–3Zr–0.3O [58].

Authors have also previously shown that the method can be successfully used for surface modification of porous Ti6Al7Nb alloy foams containing porosity as high as 70% [59]. However, the response of bulk or non-porous Ti6Al7Nb alloy, an orthopedics load bearing material [60], towards various solutions is not as same as their porous counterparts due to less active and relatively smaller surface area. Therefore, in the current study, the response of bulk Ti6Al7Nb alloys to combined NaOH and $CaCl_2$ treatment was examined in detail by considering the surface chemical composition and structure of the alloy before and after the treatment. Moreover, the effectiveness of combined chemical treatment in terms of Ca incorporation to the surface, which was not clarified before, was also checked by comparing the combined treated samples with those $CaCl_2$ treated in single step. The samples were modified chemically using aqueous solutions of NaOH, $CaCl_2$ and combined treatment of NaOH and $CaCl_2$ solutions, which were followed by heat treatment in air. Response to in vitro environment and apatite formation abilities were compared using SBF by immersing the samples for different periods.

Microstructural and structural changes observed before and after various surface treatments, including SBF tests, were examined using Scanning Electron Microscope (SEM) and Thin-film X-Ray Diffraction (TF-XRD). Energy Dispersion X-ray Spectroscopy (EDX) and X-Ray Photoelectron Spectroscopy (XPS) were utilized to reveal the surface chemical compositions of the samples. Atomic Force Microscope (AFM) was also used to characterize the surface morphology and roughness of the starting sample.

2. Material and methods

2.1. Raw materials and sample preparation

Ti6Al7Nb alloy bars (∅ 18 mm, supplied from Acnis International, France) with chemical composition presented in Table 1, was used throughout the surface treatment studies.

Alloy samples were initially heat treated to ensure homogenous and similar microstructures in all test samples. Heat treatment was carried out by heating the samples under high purity argon gas atmosphere up to 1100 °C at which they were hold for 30 min followed by cooling naturally in furnace. Next, the samples (10 mm × 10 mm × 4 mm) cut from heat treated alloy bars were ground with emery papers and grinding operation was finalized using #2000 grit SiC paper. Finally, all of the ground samples were ultrasonically washed with pure acetone, ethanol and deionized water, and dried in the hot oven at 40 °C for 2 h under vacuum.

2.2. Surface treatment

Basically six groups of surface treated specimens were prepared by soaking the alloy in NaOH and $CaCl_2$ aqueous solutions, and by applying subsequent heat treatment in air, Table 2. The first group of specimens were alkali treated only in 5.0 M NaOH aqueous solutions at 60 °C for 24 h. Some of the NaOH-treated samples were then soaked in 0.1 M aqueous $CaCl_2$ solution at 40 °C for 24 h for production of group 3 samples. After each solution treatment operation conducted using either NaOH or combined NaOH-$CaCl_2$, the samples were washed with

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