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Bioactivity of hybrid micro/nano-textured Ti-5Si surface by acid etching and heat treatment

Hsueh-Chuan Hsu [a], Shih-Ching Wu [a], Shih-Kuang Hsu [a], Yi-Hang Liao [b], Wen-Fu Ho [c,*]

[a] Department of Dental Technology and Materials Science, Central Taiwan University of Science and Technology, Taiwan, ROC
[b] Department of Materials Science and Engineering, Da-Yeh University, Taiwan, ROC
[c] Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 81148, Taiwan, ROC

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ABSTRACT

The surfaces of the Ti-5Si specimens tested in this study displayed micro-pores and a nano-textured structure after being etched with a H_2SO_4 solution. After immersion in a simulated body fluid (SBF) solution for 7 days, numerous apatite nucleation spheres were found on the outer and inner surfaces of the micro-pores after acid-etching and acid-heat treatments. Apatite precipitation was clearly observed on the surfaces of the Ti-5Si specimens without heat treatment, suggesting that heat treatment is not necessary for apatite precipitation on the surface of Ti-5Si that has undergone the acid etching process. Additionally, there was apatite formation on the surface of the as-cast Ti-5Si specimens that were soaked in SBF solution for 14 days, although the ability of as-cast Ti-5Si alloy to form apatite was slightly lower than that of its acid-etched or acid-heat-treated counterparts. This acid treatment has the potential to enhance the bioactivity of Ti-5Si and is expected to be able to strengthen the fixation of the implant with bone through a hybrid micro/nano-textured surface. Therefore, it can be concluded that etching in sulfuric acid is an effective and simple surface treatment for Ti-5Si alloy destined for biological applications.

1. Introduction

Titanium (Ti) and its alloys are widely used for implant applications in dentistry and orthopedics due to their appropriate mechanical properties, high corrosion resistance, and superior biocompatibility [1]. However, they cannot bond chemically to the surrounding bone in the early post-implantation stage, which can result in bone resorption around the implant, thus raising the potential risk of loosening when the implant is used long-term [2]. To form a chemical bond with living bone, various surface modifications have been developed over the past few decades. Among these methods, one of the most popular and commercialized is plasma spraying of hydroxyapatite (HA) on Ti. However, there are several problems with the poor characteristics of plasma-sprayed HA coatings, which can lead to the deterioration of the long-term durability and stability of the implant [3]. Alternative treatments have been proposed to induce a bioactive layer directly on the metal surface without the deposition of a coating.

Among the methods of preparing bioactive surfaces on Ti, NaOH and/or heat treatment, which produces a sodium titanate layer on the Ti surface, has been recognized as an effective technique and accordingly, has been studied widely during the past few years [4–9]. Another commonly used chemical method is H_2O_2 treatment, which results in the formation of a relatively thick porous oxide layer on the Ti surface [10]. The stable oxide that forms on the Ti surface has been attributed to its biocompatibility [11]. Recently, anodic oxidation technique has been used to create controllable nanostructures on the Ti surface [12]. Self-organized and highly ordered TiO_2 nanotubular structures on Ti, created using anodization, have been shown to increase the osseointegration of an implant material [13]. Additionally, thermal oxidation treatment is an effective and simple method that can be used to form a compact oxide layer on the Ti surface that enhances its surface characteristics and bioactivity [14].

Recently, the surface topography of an implant for biomedical applications has provoked considerable interest. Researchers have produced micro- and nano-scaled structures through different methods, revealing that these structures promote a variety of selective cellular functions, such as enhancing the attachment, spreading, adhesion, proliferation, and differentiation of osteoblasts [15–19]. Zhao et al. [20] produced a hierarchical micro/nano-textured surface topography, which may result in better osseointegration in vivo. Wan et al. [21] stated that cell adhesion strength was enhanced because of nano/micro-scale roughness (compared with a controlled smooth surface). Ferraris et al. [22] proposed an innovative patented treatment integrated with an industrial sandblasting-acid etching process, resulting in a multi scale surface

* Corresponding author at: Department of Chemical and Materials Engineering, National University of Kaohsiung, 700 Kaohsiung University Rd., Nanzih District, Kaohsiung 81148, Taiwan, ROC.
E-mail addresses: fujii@nuk.edu.tw, titi0918@yahoo.com.tw (W.-F. Ho).

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topography (micro-and nano-roughness). In another interesting study, using a unique micro-nano-hierarchical topography of TiO_2, Hori et al. [23] revealed that the addition of 200-nm nanonodules to micropits increased osteoblast proliferation while enhancing their functional differentiation. Another study by Gittens et al. [24] suggested that the introduction of nanoscale structures in combination with micro-/submicro-scale roughness improves osteoblast differentiation and local factor production.

Ti-6Al-4V ELI alloys have been widely used in the biomedical field for many years. However, the Al and V ions released from metal implants severely affect the long-term biocompatibility of these alloys. For example, V ions are cytotoxic, and Al ions are neurotoxic and inhibit bone mineralization [25,26]. Therefore, several new Ti-based alloys have been developed for biomedical applications. Recently, in the authors' research group, the microstructure and mechanical properties of Ti-5Si alloy were investigated for implant applications [27]. Si element has been reported to be non-toxic and non-allergic [28], and it may be clinically beneficial for the growth and development of bone and connective tissue [29]. The main goal of this study was to create a bioactive surface on a Ti-5Si alloy and evaluate the apatite-forming capabilities through immersion in simulated body fluid (SBF). The surface treatment of Ti-5Si alloy was processed using a H_2SO_4 solution in order to create a hybrid micro/nano-textured topography. The results were compared with as-cast Ti-5Si without acid pre-treatment and all samples were soaked in SBF to confirm their bioactivities.

2. Experimental procedures

Ti-5Si alloy (in wt.%) was fabricated from grade 2 Ti (99.7% in purity) and sheet Si (99.999% in purity) in the appropriate proportions. Melting was carried out under a high-purity argon atmosphere using a commercial arc-melting vacuum-pressure-type casting system. The ingots of approximately 15 g were flipped between two melting processes and melted 5 times to further promote chemical homogeneity. Prior to casting, the ingots were melted again. The detailed casting procedure has been described previously [30].

The as-cast Ti-5Si specimens were cut to make plates with the dimension of $1 \times 10 \times 10$ mm^3, which were used as substrate materials. The Ti-5Si plates were ground to a final level of 600-grit paper, and then ultrasonically cleaned with distilled water and ethanol for 10 min. They were rinsed with distilled water and dried. The cleaned specimens then went through an acid treatment, which was performed by immersing the specimens in 0.05 M H_2SO_4 aqueous solutions at 40 °C for 24 h, which was decided by the results of preliminary tests. The temperature was maintained using a water bath. The specimens were washed with distilled water. Afterwards, some parts of the acid-etched samples were heated to 650 °C at a rate of 5 °C min^{-1} in an electric furnace, maintained at this temperature for 3 h, and then cooled naturally to room temperature in the furnace. Surface roughness was measured using a profilometer (Surfcorder SE 1700, Kosaka, Tokyo, Japan) with a 2 μm radius tip, which contacted the surface at a constant speed of 0.05 mm/s with a force of 75 μN. Two samples from each of the specimens with three different surface conditions (untreated, H_2SO_4-etched, and H_2SO_4 + heat-treated Ti-5Si alloys) were measured. Three readings were performed on each sample and an average surface roughness (Ra) was determined. The cut-off value was set at 0.08 mm to characterize surface roughness.

After the acid and/or heat treatment, the specimens were immediately soaked in 30 ml of SBF to test the capability of Ti-5Si to spontaneously form a bone-like apatite layer in vitro. The same immersion test was conducted on as-cast Ti-5Si without acid-heat treatment for the purpose of comparison. The in vitro bioactivity of all the samples was evaluated in terms of their apatite-forming ability by soaking the samples in SBF for 3, 7, and 14 days. The temperature was maintained at 37 °C using a water bath. 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 in distilled water [31]. After being soaked for selected durations, the specimens were removed from the fluid, washed with distilled water, and air dried. The SBF was refreshed every 2 days to preserve its ion concentrations. After the acid treatment and/or subsequent heat treatment, the surfaces of the Ti-5Si specimens were examined by field-emission scanning electron microscopy (FE-SEM; JSM-7401F, JEOL, Japan) and X-ray diffractometry (XRD; D8-Discover, BRUKER, Germany). The formation of apatite on the surfaces of the Ti-5Si specimens was examined using SEM (S-3000N, Hitachi, Japan) and XRD. The phases of pre-treated and SBF-immersed samples were analyzed by XRD using Cu Kα radiation (λ = 0.154 nm) at 40 kV and 35 mA between 2θ values of 20° and 50° with a step size of 0.02° and a scanning rate of 2°/min. The surface chemical analysis was implemented by energy-dispersive X-ray spectroscopy (EDS) attached to the SEM. The surface of the specimen was examined by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR; FTS-40, Bio-Rad, USA). The measurements were carried out within the range of 400–4000 cm^{-1} in the % transmittance mode at a resolution of 8 cm^{-1} in order to confirm the presence of functional groups in SBF-immersed samples.

3. Results and discussion

3.1. Surface morphologies after acid and heat treatment

Fig. 1 shows the XRD patterns of the as-cast, acid-etched, and acid-heat-treated Ti-5Si alloys. In the diffraction pattern of the as-cast sample, only α-Ti and Ti_5Si_3 phases could be found. After etching in 0.05 M H_2SO_4, a TiH_2 peak was observed in addition to the diffraction peaks of the α-Ti and Ti_5Si_3 phases. After heat treatment at 650 °C for 3 h, diffraction peaks corresponding to anatase and rutile TiO_2 appeared. The diffraction peak of the rutile phase has a greater intensity than that of the anatase phase, because the rutile TiO_2 structure is more stable than the anatase structure after heat treatment above 500 °C in air [32]. From a chemical thermodynamic standpoint, the formation of rutile TiO_2 is a favorable process, since the Gibbs function of formation of rutile is lower than that of anatase [33]. For the etched sample, the oxide layer could not be detected by XRD, although a new oxide layer may have formed on the TiH_2 layer owing to contact with moisture in the air. Another report [34] also showed similar outcome, where a new oxide layer can form on the TiH_2 intermediate layer with air moisture after acid-etching treatment in HCl. Jonášová et al. proposed that the titanium oxide layer is thinner than the initial one that forms

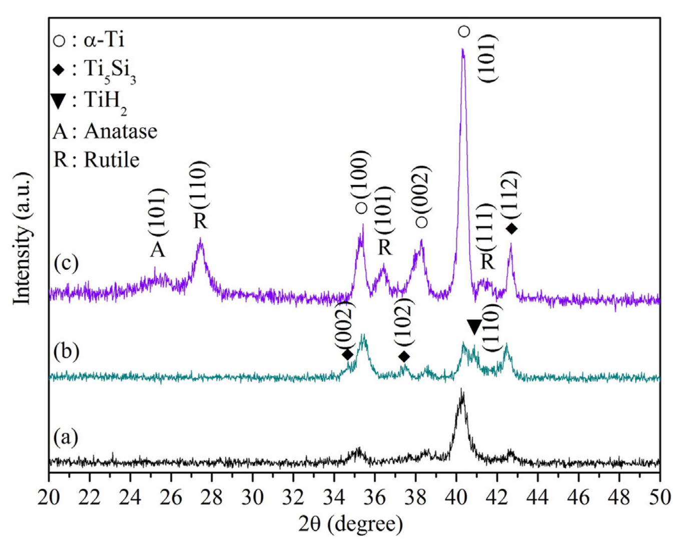

Fig. 1. XRD patterns of the surfaces of as-cast (a), H_2SO_4-etched (b), and subsequently heat-treated (c) Ti-5Si alloy.