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Surface modification of Ti–Nb–Zr–Sn alloy by thermal and hydrothermal treatments

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ABSTRACT

Surface modifications by thermal and hydrothermal treatments in solution with calcium ions were investigated with the aim of improving bioactivity and wear resistance of a Ti–Nb–Zr–Sn alloy. The results showed that the first step of thermal treatment at 600 °C significantly increases the surface hardness and energy by forming oxides of Ti and Nb. The second step of hydrothermal treatment in a boiled supersaturated $Ca(OH)_2$ solution induces a bioactive layer containing $CaTiO_3$, $CaCO_3$, $Ca(OH)_2$ and TiO_2. Using this treatment, a complete Ca–P layer can be formed within 3 days of soaking in simulated body fluid (SBF). The origin of such fast apatite formation was analyzed by comparison with single step thermal or hydrothermal treatment and with thermal plus hydrothermal treatment without calcium ions. The results suggest that the increase of surface energy by thermal treatment and the incorporation of calcium ions by the hydrothermal treatment in calcium ion solution play important roles in the formation of bioactive apatite.
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1. Introduction

Titanium and its alloys are widely used for load-bearing dental and orthopedic implants because of their superior mechanical properties, good biocompatibility and high corrosion resistance [1,2]. Since the natural passive films with thickness of only a few nanometers have poor ability to form direct bonding with surrounding bone tissue, several typical surface modification techniques have been developed so far. For example, the titania layer fabricated by the chemical methods such as alkali, acid and hydrogen peroxide treatments as well as thermal and anodic oxidations promotes the formation of bioactive apatite layer after implantations [3–14].

In spite of the enhancements of the single step treatments on apatite formation, their contributions are generally weaker than the duplex surface modification techniques such as the acid plus alkali treatments, the alkali/acid plus thermal treatments, the thermal plus alkali treatments as well as the anodic oxidation plus hydrothermal treatment [10–14]. To overcome the weak wear resistance of titanium and its alloys, the rutile and/or anatase oxides with higher hardness are always fabricated by the surface oxidation techniques such as the thermal and anodic treatments [11]. Since the oxidation would cause damage to the bioactive hydroxyl groups obtained by previous chemical treatments [15], it would be preferred as the first step treatment in duplex surface modification techniques.

The hydrothermal treatment, a kind of chemical treatment technique, has been used widely to induce the formation of bioactive surface layers on titanium and its alloys. As a single step treatment, the apatite forming ability can be enhanced by changing surface morphologies and compositions of titanium surfaces, for example of porous surface structure in NaOH solution [16], rearrangement of Ti–OH when aged in hot water [17] and introduction of calcium ions in calcium hydroxide solution [18–21]. Combined with the pre-micro-oxidation, it is helpful to precipitate the bioactive calcium phosphate [22–25]. Apart from the

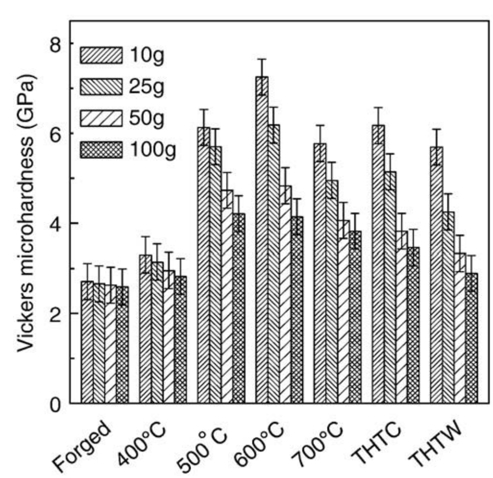

Fig. 1. Microhardness of the samples with treatments listed in Table 1.

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Table 1
Scheme of surface modification of TNZS with the thermal treatment (TT) and the hydrothermal treatment (HT).

Sample	TT	HT in supersaturated $Ca(OH)_2$ solution	HT in distilled water
TT	600 °C for 1 h		
HTW			Boiled for 1 h
THTW	600 °C for 1 h		Boiled for 1 h
HTC		Boiled for 0.5 h	
THTC	600 °C for 1 h	Boiled for 0.5 h	

surface modification, the hydrothermal treatment has also been used to synthesize hydroxyapatite [26,27] and TiO_2 particles as well as to enhance apatite-forming ability of calcium pyrophosphate glasses [28].

Ti–24Nb–4Zr–7.9Sn is a new β-type alloy which possesses elastic modulus close to that of human bone and has improved balance of high strength and low modulus as compared with other titanium alloys having low elastic modulus [29–31]. Similar to other biomedical titanium alloys, it still belongs to bio-inert materials [32]. In the present study, duplex surface modifications combining both the thermal and the hydrothermal treatments have been investigated, in the hope of achieving a kind of bioactive and wear resistant surface layer.

2. Materials and methods

2.1. Surface modification

Ingot with nominal chemical composition Ti–24Nb–4Zr–7.9Sn (wt.%, abbreviated as TNZS below) was fabricated by vacuum arc remelting using a Ti–Sn master alloy and pure Ti, Nb and Zr as raw materials. The ingot with a diameter of 180 mm was hot forged at 1000 and 850 °C to round bars with diameter of 25 mm. Rectangular strips with typical dimensions of $10\times10\times2$ mm^3 were cut by electrical spark, ground with 100 grit SiC paper, cleaned ultrasonically in acetone for 10 min, in ethanol for 10 min and in distilled water for 10 min in turn, and then dried at 40 °C in a dryer.

Some of the cleaned samples were heated to 400, 500, 600 and 700 °C at a heating rate of 5 °C/min, then kept for 1 h and cooled in furnace. Vickers hardness measurements showed that the oxidation treatments have significant contributions to hardness and the maximum was achieved at 600 °C (Fig. 1). To improve wear resistance of the alloy, the oxidation at 600 °C was selected as the thermal treatment in the study. The following hydrothermal treatment was conducted in supersaturated $Ca(OH)_2$ solutions and in distilled water at their boiling temperatures. To compare the bioactivity, the samples were divided into several groups. The single step treatments include the thermal treatment at 600 °C for 1 h (TT), the hydrothermal treatment in supersaturated $Ca(OH)_2$ solutions (HTC) or in distilled water (HTW), while the duplex treatments are the thermal plus hydrothermal treatment in supersaturated $Ca(OH)_2$ solutions (THTC) or in distilled water (THTW). The details are listed in Table 1.

2.2. Evaluation of the performance of the modified sample surface

The bioactivity of the modified TNZS alloy was evaluated by soaking in simulated body fluid (SBF) proposed by Kokubo [33] without organic species at 37 °C. The ion concentrations are as follows: Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, HCO_3^- 4.2, Cl^- 147.8, HPO_4^{2-} 1.0, SO_4^{2-} 0.5 mM, which is nearly equal to those of human blood plasma except HCO_3^- being 27.0 mM. The surface modified TNZS samples were placed in SBF

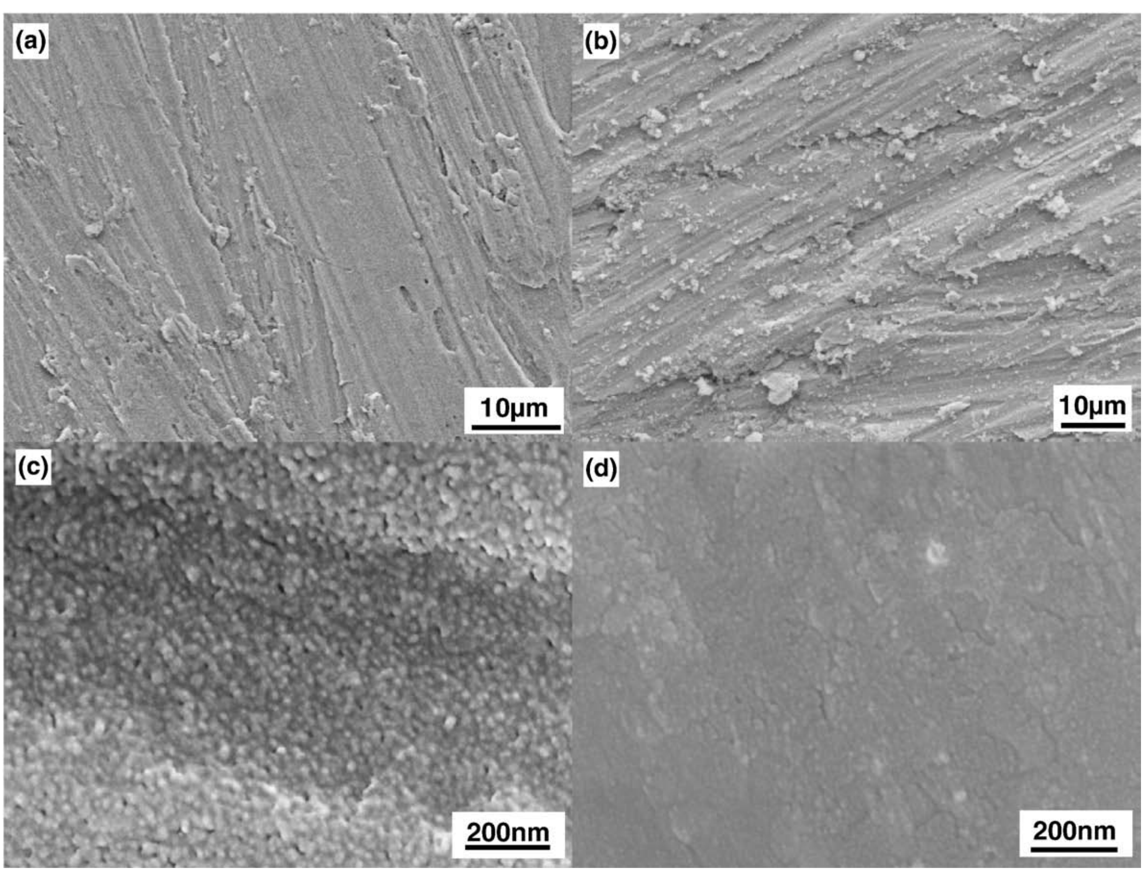

Fig. 2. SEM surface morphologies of the as-forged (a) and THTC treated (b) samples at low magnification as well as high magnification of samples treated by THTC (c) and HTC (d).

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