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Enhancement of wear and corrosion resistance of low modulus β-type Zr-20Nb-xTi (x = 0, 3) dental alloys through thermal oxidation treatment

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ABSTRACT

In order to obtain material with low elastic modulus, good abrasion resistance and high corrosion stability as screw for dental implant, the biomedical Zr-20Nb and Zr-20Nb-3Ti alloy with low elastic modulus were thermal oxidized respectively at 700 °C for 1 h and 600 °C for 1.25 h to obtain the compact oxidized layer to improve its wear resistance and corrosion resistance. The results show that smooth compact oxidized layer (composed of monoclinic ZrO_2, tetragonal ZrO_2 and $6ZrO_2$-Nb_2O_5) with 22.6 μm–43.5 μm thickness and 1252–1306 HV hardness can be in-situ formed on the surface of the Zr-20Nb-xTi (x = 0, 3). The adhesion of oxidized layers to the substrates is determined to be 58.35–66.25 N. The oxidized Zr-20Nb-xTi alloys reveal great improvement of the pitting corrosion resistance in comparison with the un-oxidized alloys. In addition, the oxidized Zr-20Nb-3Ti exhibits sharply reduction of the corrosion rates and the oxidized Zr-20Nb shows higher corrosion rates than un-oxidized alloys, which is relevant with the content of the t-ZrO_2. Wear test in artificial saliva demonstrates that the wear losses of the oxidized Zr-20Nb-xTi (x = 0, 3) are superior to pure Ti. All of the un-oxidized Zr-20Nb-xTi (x = 0, 3) alloys suffer from serious adhesive wear due to its high plasticity. Because of the protection from compact oxide layer with high adhesion and high hardness, the coefficients of friction and wear losses of the oxidized Zr-20Nb-xTi (x = 0, 3) alloys decrease 50% and 95%, respectively. The defects on the oxidized Zr-20Nb have a negative effect on the friction and wear properties. In addition, after the thermal oxidation, compression test show that elastic modulus and strength of Zr-20Nb-xTi (x = 0, 3) increase slightly with plastic deformation after 40% of transformation. Furthermore, stripping of the oxidized layer from the alloy matrix did not occur during the whole experiments. As the surface oxidized Zr-20Nb-3Ti alloy has a combination of excellent performance such as high chemical stability, good wear resistance performance and low elastic modulus, moderate strength, it is considered an alternative material as dental implant.

1. Introduction

In the field of biomedical applications, pure Ti it has been widely used as the abutment and screw of dental implant in clinical, due to its special physical properties and corrosion resistance. However, its disadvantages are also obvious. Firstly, due to the poor resistance of pure Ti, the loss of the materials from implant would embed into the body tissues, people would suffer from the inflections caused by the bacteria and loss materials in saliva. Moreover, it would accelerate friction and wear processes between the implant and the organ because the organ, abrasive particles and implant itself would form three-body wear in saliva. Secondly, it is likely to form new corrosive wear because the naturally formed layer on Ti would be destroyed. Thus, surface of the implant would turn rough due to the new corrosion and wear behaviors. Finally, the suitable elasticity modulus is vital for the implant. It is reported that elastic modulus of human bone and teeth is about 15–30 GPa, while that of pure Ti is about 102.7–104.1 GPa [1,2]. Stress shielding phenomenon may be caused by this obvious difference of elastic modulus, which shortens the life of both implants and organs. As an implant material, Zr and its alloys have high mechanical strength, excellent fracture toughness and good corrosion resistance [3–5]. Zr element is non-toxic to human body. A newly designed Zr-20Nb-xTi (x = 0, 3, in atomic fraction) alloys with low elastic modulus, high plasticity and moderate strength have been recently developed by the authors [6]. Further

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Table 1
Compositions of the artificial saliva.

NaCl	KCl	$CaCl_2 \cdot H_2O$	$NaH_2PO_4 \cdot 2H_2O$	$Na_2S \cdot H_2O$	Urea	Distilled-water
0.4 g	0.4 g	0.795 g	0.78 g	0.005 g	1 g	1000 ml

researches were then carried out to improve the combination properties and promote the clinical application.

It is well known that surface treatment, such as nitriding, carburizing and oxidation can improve the wear resistance by forming a hardness surface layer [7]. There are many approaches, such as laser nitridation [8], microarc oxidation [9], and magnetron sputtering [10], preparing oxide or nitride layer to improve the wear resistance and corrosive resistance of Ti and its alloys. Among several technologies of the surface treatment, the oxidation method is economic and simple processing. However, there are few articles well resolving simultaneously about the surface finish, uniformity, density, adhesion strength of the layer and its effects of to the substrates. Besides, its expensive equipment, high energy consumption and complex process increase the cost of the layer.

Recently, heat oxidation has been used to enhance the wear and corrosion resistance of the Ti-based alloys and Zr-based alloys in the field of medical science [11–13]. Most importantly, it does not rely on the shape of the implant. Cells can grow normally on its oxide layer [14]. Lately, the oxidized Zr was designed to use as the man-made ball head in total knee and hip replacement [15,16]. Currently, Zr-20Nb-xTi ($x = 0, 3$) alloys have become one of the important candidate materials to be used in permanent prosthesis of dental or orthopedic treatments due to its superior properties. However, other research about the friction and wear properties of the other Zr alloys discovers that, compared with steel, Zr and its alloys possess poor friction and wear properties because of the adhesive properties and high coefficient of friction [17].

The purpose of this work is to obtain a kind of oxide layer on the Zr-20Nb-xTi ($x = 0, 3$) alloys to improve its corrosion and wear resistance without changing the properties of the substrate by thermal oxidation treatment under certain temperature. The phase constitutes, surface finish, adhesive strength of the oxide layer are examined. In addition, the wear resistance, corrosion resistance and compress properties of the un-oxidized and oxidized Zr-20Nb-xTi ($x = 0, 3$) alloys are carried out.

2. Experimental procedure

Zr-20Nb-xTi ($x = 0, 3$ in atomic fraction) were melted by using the WK-II type non-consumable vacuum arc melting furnace. The starting materials used in the experiment were pure niobium, pure zirconium and pure titanium, with purities all higher than 99.8 wt%. By controlling the current intensity of the non-consumable vacuum arc melting furnace, the melting temperature of the alloys was adjusted to be about 3000 °C. In order to obtain uniform composition of samples, the melting time duration lasted about 120 s. After each melting, the samples were cooled in a water-cooled copper crucible (by running water in room temperature) to room temperature. The cooling time took about 500 s. The samples were melted for 8 times. The resultant samples were weighed to ensure that each melting loss was less than 1% by mass.

Specimens for oxidation with dimension of 10 mm × 10 mm × 1.5 mm, specimens for compression with dimension of 5 mm × 5 mm × 10 mm, specimens for coating adhesion test with dimension of 14 mm × 14 mm × 2 mm, specimens for electrochemical corrosion test with dimension of 10 mm × 10 mm × 2 mm, pins with the dimension of Φ4.6 mm × 11.2 mm and disks with dimension of Φ60 mm × 4 mm for friction and wear experiment, were all machined by electrical discharge machining (EDM). All specimens were ground by the 2000 grit silicon carbide (SiC) paper with water. And the specimens for surface morphology observation and electrochemical corrosion test were polished by Al_2O_3 particles with water. Then they were washed in acetone and alcohol for 30 min successively in an ultrasonic bath and then dried with hair dryer drum.

The polished Zr-20Nb-3Ti was oxidized at 600 °C for 1.25 h and Zr-20Nb was oxidized at 700 °C for 1 h in the resistance furnace calibrated by K-thermocouple to obtain the oxide layer. Then the oxidized

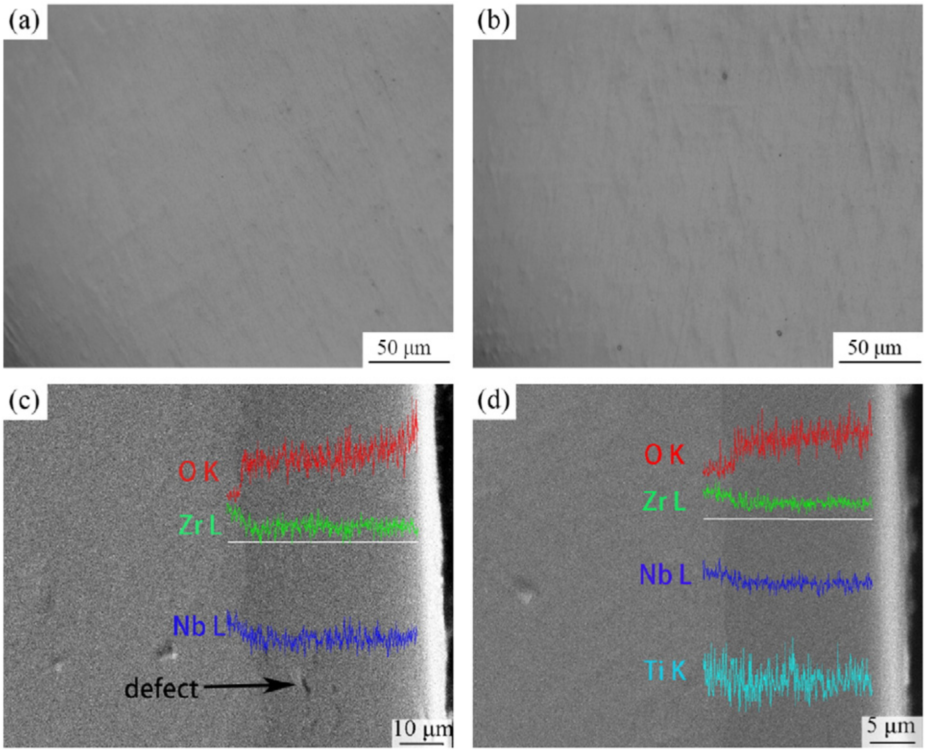

Fig. 1. Optical microscopic images of the oxidized alloys: (a) Zr-20Nb and (b) Zr-20Nb-3Ti, cross-section SEM images with EDS of the oxidized alloys: (c) Zr-20Nb and (d) Zr-20Nb-3Ti.