Surface & Coatings Technology 283 (2015) 101–107

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

The improved corrosion resistance and anti-wear performance of Zr–*x*Ti alloys by thermal oxidation treatment

W.F. Cui [a,*], C.J. Shao [b]

[a] Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), Northeastern University, Shenyang 110004, China
[b] Liaoning Equipment Manufacture College of Vocational Technology, Shenyang 110161, China

ARTICLE INFO

Article history:
Received 31 July 2015
Revised 20 October 2015
Accepted in revised form 22 October 2015
Available online 24 October 2015

Keywords:
Zr–*x*Ti alloy
Oxide coating
Bonding force
Corrosion
Wear

ABSTRACT

By thermal oxidation treatment at 500 °C in air, the monoclinic ZrO_2 and orthorhombic $ZrTiO_4$ oxide coatings were *in-situ* formed on the surfaces of biomedical Zr–20Ti and Zr–40Ti alloys, respectively. The hardness and adhesion strength of the oxide coatings were measured by indentation and scratching tests. The electrochemical corrosion of the Zr–*x*Ti alloys before and after thermal oxidation treatment was performed in the acidified artificial saliva containing 0.1% NaF at 37 °C. The friction and wear performances of the un-oxidized and oxidized Zr–*x*Ti alloys were evaluated by reciprocating ball-on-disc wear tests under the load of 10 N. The results show that the oxide coatings have the hardness of 1420–1480 HV and the adhesion forces of 51 N to the substrates. The oxidized Zr–*x*Ti alloys exhibit the reduced corrosion rates and improved pitting corrosion resistance in comparison with the un-oxidized Zr–*x*Ti alloys. The wear tests demonstrate that the un-oxidized Zr–*x*Ti alloys show the serious adhesive wear and abrasive wear due to the high plasticity and chemical activity. The coefficients of friction and wear rates of the oxidized Zr–*x*Ti alloys decrease 30% and 90%, respectively, which are attributed to the hard oxide coatings with enhanced toughness. Nevertheless, the scabies defects in the oxide coating of Zr–20Ti alloy have a negative effect on the friction and wear property. The oxidized Zr–40Ti alloy has the excellent chemical stability and anti-abrasion performance. It has a great application prospect as dental implant material.

1. Introduction

Commercially pure titanium (cp Ti) has been used as the abutment and screw of dental implants due to its excellent corrosion resistance, good biocompatibility and low modulus. However, the low strength of cp Ti increases the risk of small diameter screw fracture (≤3.5 mm). It has been reported that at least 5% fracture in dental implants arises from fatigue over the last decades [1]. Increasing the strength of the materials is an effective approach to prolong the service life of the metal implants. Zirconium is an ideal alloying element for titanium in biomedical applications. Zr–Ti (or Ti–Zr) binary alloys exhibit high strength and good osseointegration in animal and clinical studies [2–6]. Zr–Ti alloys also present other advantages such as lower melting point, lower magnetic susceptibility, lower linear expansion coefficient and less hydrogen absorption than cp Ti and other Ti alloys [7]. Currently, Zr–Ti alloys have become one of the important candidate materials to be used in permanent prosthesis of dental or orthopedic treatments [8].

In oral environment, wear and corrosion frequently occur at interface between metal implant and zirconia abutment [9]. The fine debris particles produced by the poor wear resistance of Ti alloys result in the aseptic loosening of the implant. At the same time, the dental implants are frequently eroded by fluoride ions from toothpastes, orthodontic gels, dietary supplements, *etc.* Acidic foods or inflammation in the oral cavity accelerates the damage of fluoride ions to the passive film of titanium metal. The released metal ions stimulate the growth of the macrophage. The rough surfaces caused by corrosion and wear are favorable to the adhesion of various bacteria and the formation of plaque. Therefore, high corrosion resistance and anti-wear performance of dental material are vital for the safe use of the dental implants.

The modern surface engineering technologies, such as laser nitridation [10], microarc oxidation [11] and magnetron sputtering [12], provide many approaches preparing oxide or nitride coatings to improve the corrosive wear resistance of titanium and titanium alloys. However, some issues in the use of these technologies, such as the surface finish, uniformity, density and adhesion strength of the coating, are not well resolved simultaneously. Moreover, the expensive equipments, complex process and high energy consumption also increase the cost of the coatings.

Recently, a simple thermal oxidation method was suggested to modify the surface properties of biomedical metal materials. It has been reported that the thermally oxidized Ti–6Al–4V and Zr–2.5Nb alloys reduced the adhesive wear tendency and improved the corrosion resistance in simulated body fluid [13–17]. However, the hardness and

* Corresponding author.
E-mail address: cuiwf@atm.neu.edu.cn (W.F. Cui).

http://dx.doi.org/10.1016/j.surfcoat.2015.10.051
0257-8972/

adhesion strength of these oxide coatings formed on Ti alloy or Zr alloy are not high enough. The exfoliation of the oxide layer will increase coefficient of friction and decrease anti-wear performance.

Since Ti and Zr metals are easily oxidized by heat treatment in air, the zirconia–titania oxide coatings can rapidly form on the surfaces of the thermally oxidized Zr–Ti alloys. The composite oxides possess higher hardness and toughness than single zirconia or titania oxide [18]. Thus, the thermally oxidized Zr–Ti alloys are expected to have greatly improved corrosive wear resistance. In the present study, the thermal oxidation treatment was performed on Zr–20Ti and Zr–40Ti alloys at 500 °C in air. The phase constitutes, surface morphologies and adhesion strength of the thermally oxidized coatings were examined. The effects of titanium content on the electrochemical corrosion and the wear performance of the un-oxidized and oxidized Zr–*x*Ti alloys were clarified.

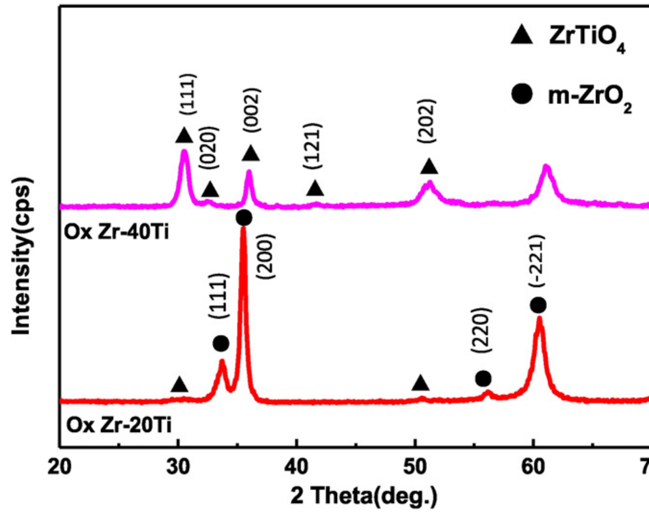

Fig. 2. XRD profiles of the thermally oxidized Zr–20Ti and Zr–40Ti alloys.

2. Experimental

Zr–20Ti and Zr–40Ti alloys (wt.%) were prepared using arc melting in argon atmosphere for six times. The ingots were hot forged at 800 °C into the rectangular slabs. After the surface oxide layers were removed, the slabs were heat-treated at 750 °C followed by water cooling. Specimens were machined by electric spark cutting with the dimension of $20 \times 10 \times 5$ (mm^3) for wear tests and $10 \times 10 \times 2$ (mm^3) for electrochemical tests. All specimens were ground with a SiC abrasive paper up to 3000 grit, and then ultrasonically cleaned in acetone for 10 min. Some of the specimens were thermally oxidized at 500 °C for 2 h in air.

The surfaces and cross section morphologies of the thermally oxidized specimens were observed by an optical microscope and a scanning electron microscope (SSX-550, Japan). The phase compositions of the oxide coatings were identified by X-ray diffraction (Smart Lab, Japan) using Cu Kα radiation with the scan rate of 3°/min. The bonding forces of the oxide coatings to the substrates were measured by a micro-scratch tester (WS-2005, China) with a diamond stylus of 0.2 mm radius. The load increased from 0 to 200 N with a loading rate of 100 N/min. The critical loads at which the oxide started to crack were measured. The Vickers microhardness of the oxidized and un-oxidized specimens were measured by a hardness tester (401 MVDTM, China) with a load of 25 g and a loading time of 30 s. The final hardness was obtained from the average values of the ten testing results.

The electrochemical experiments were carried out in the naturally aerated artificial saliva containing 0.1% NaF at 37 °C (pH = 4). The components of the artificial saliva were as follows: NaCl (0.4 g/l), KCl (0.4 g/1), $NaH_2PO_4 \cdot 2H_2O$ (0.78 g/l), $CaCl_2 \cdot 2H_2O$ (0.795 g/l), $Na_2S \cdot 2H_2O$ (0.005 g/l), urea (1.0 g/l) and 1000 ml distilled water. All the chemicals were provided by Guoyao Group Chemical Reagent Co. Ltd. (Shenyang). Three-electrode electrochemical working station (Zennium, Germany) was used with saturated calomel electrode as reference electrode, platinum plate as counter electrode and the specimens as working electrode (1 cm^2 exposure area to the solution). Potentiodynamic polarization curves (PPC) were recorded over the potential range of −1.5 V to +1.5 V at a scanning rate of 1 mV/s. The electrochemical impedance spectra (EIS) were measured by applying a sinusoidal potential perturbation of 5 mV with a frequency from 10^{-2} Hz to 10^5 Hz in logarithmic increment at the open circuit potential. Before the tests, the specimens were immersed in the electrolyte for 1 h in order to attain stable open

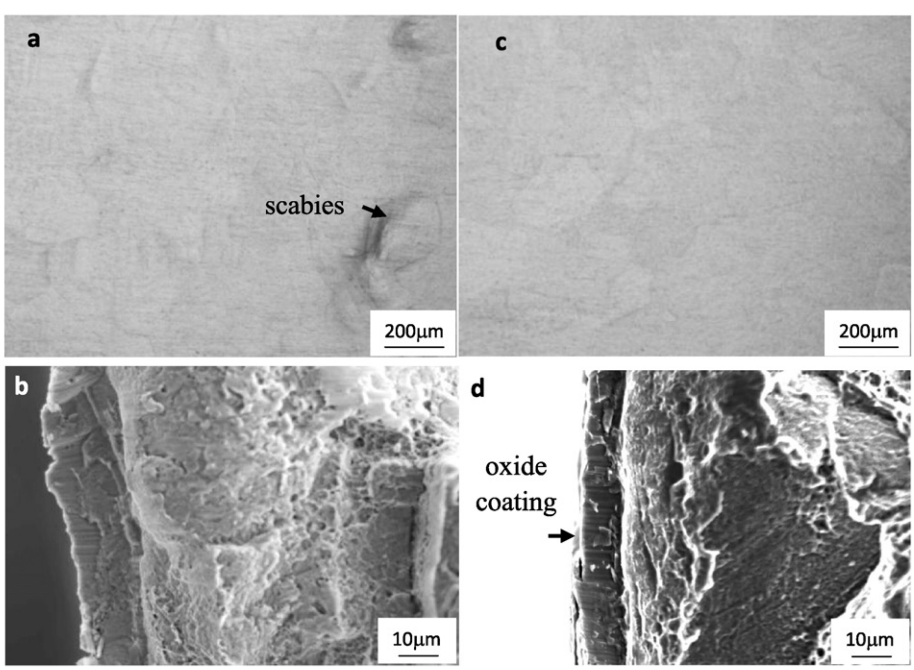

Fig. 1. Oxide coating morphologies of the Zr–20Ti and Zr–40Ti alloys thermally oxidized at 500 °C for 2 h. (a),(b) surface and fracture cross-section images of the oxidized Zr–20Ti alloy showing the scabies defects and uneven top surface, (c),(d) surface and fracture cross-section images of the oxidized Zr–40Ti alloy showing the smooth surface and columnar structure.