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A comparative study of the mechanical behaviour of thermally oxidised commercially pure titanium and zirconium

A. Alansari, Y. Sun*

School of Engineering and Sustainable Development, Faculty of Technology, De Montfort University, Leicester LE1 9BH, UK

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ABSTRACT

The objective of this study is to compare the mechanical behaviour of thermally oxidised commercially pure titanium (CP-Ti) and commercially pure zirconium (CP-Zr). For this purpose, these two bio-metals were thermally oxidised under the same condition (650 °C for 6 h) and the oxidised specimens were characterised using various analytical and experimental techniques, including oxygen uptake analysis, layer thickness and hardness measurements, scratch tests, dry sliding friction and wear tests and tribocorrosion tests in Ringer's solution. The results show that under the present thermal oxidation condition, 4 times more oxygen is introduced into CP-Zr than into CP-Ti and the oxide layer produced on CP-Zr is nearly 6 times thicker than that on CP-Ti. Thermally oxidised CP-Zr possesses a higher hardness, a deeper hardening depth and better scratch resistance than thermally oxidised CP-Ti. Under dry sliding and tribocorrosion conditions, thermally oxidised CP-Zr also possesses much better resistance to material removal and a higher load bearing capacity than thermally oxidised CP-Ti. Thus, thermally oxidised Zr possesses much better mechanical behaviour than thermally oxidised Ti.

1. Introduction

Titanium (Ti) and zirconium (Zr) are bio-metals that are used in the biomedical sector to make medical devices and implants (Byeli et al., 2012; Chevalier, 2006; Gepreel and Niinomi, 2013). They possess a good combination of strength, corrosion resistance and biocompatibility, which are desirable as biomaterials (Niinomi, 2002). Both metals have a hexagonal close packed (HCP) crystal structure at room temperature and derive their corrosion resistance and passivity by the naturally occurring oxide film at the surface. Both Ti and Zr are also known to possess poor tribological properties. When in contact motion with themselves or other materials, they suffer from severe metallic wear with the tendency towards galling and seizure (Haygarth and Fenwick, 1984; Bloyce, 1998; Byeli et al., 2012). Thus, the uses of Ti and Zr have been restricted to mostly non-tribological applications. However, with proper surface modification to alter the surface chemical, physical and mechanical properties, Ti and Zr and their alloys can be used to make bearing components such as in artificial hip and knee joints (Dong and Bell, 1999; Hunter et al., 2002).

Thermal oxidation offers a simple and cost-effective way to modify the surfaces of Ti and Zr and their alloys to achieve much enhanced tribological and bio-tribological properties (Bloyce et al., 1998; Guleryuz and Cimenoglu, 2004; Haygarth and Fenwick, 1984; Pawar et al., 2011; Ji et al., 2010; Kumar et al., 2010;). Indeed, thermally oxidised Ti alloys have been reported to have the potential use in artificial hip joints (Yamamoto et al., 2009; Wang et al., 2014b; Lieblich et al., 2016), and thermally oxidised Zr has recently been introduced as an alternative bearing in total joint arthroplasty for artificial knee and hip joints (Patel and Spector, 1997; Good et al., 2005; Galetz et al., 2010; Innocenti et al., 2014). Thermally oxidised Ti and Zr possess the desirable combination of a ceramic bearing surface to resist wear and a tough metallic core to resist fracture (Bell et al., 1998; Pawar et al., 2011; Alansari and Sun, 2017).

Both Ti and Zr are reactive metals with a high affinity with oxygen to form an oxide film easily. They can also dissolve a large amount of oxygen in the HCP lattice to form a solid solution with a significant hardening effect. Thermal oxidation is normally carried out at temperatures between 500 °C and 700 °C in ambient atmosphere or in controlled atmospheres. During thermal oxidation, oxygen diffuses into the CP materials to form an oxygen diffusion zone (ODZ) with interstitial solid solution hardening, and once the surface is saturated with oxygen, an oxide layer (OL) develops at the surface. Thus thermally oxidised CP-Ti and CP-Zr comprise an OL at the surface and a hardened ODZ in the subsurface (Dong and Bell, 1999; Alansari and Sun, 2017; Ji et al., 2010; Bailey and Sun, 2013). The OL can improve frictional characteristics and offer wear resistance, while the ODZ can offer load bearing capacity. However, the quality of the OL depends on thermal oxidation conditions, such as temperature and time. High temperature

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* Corresponding author.
E-mail address: ysun01@dmu.ac.uk (Y. Sun).

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and/or long time oxidation would produce a none-adherent, fragile and crumbly OL on Ti, which has a tendency to delaminate from the substrate (Bailey and Sun, 2013; Biswas and Majumdar, 2009; Sun et al., 2016). Similarly, oxidation breakaway would occur to Zr during high temperature or long time oxidation, characterised by the formation of pore and cracks in the OL (Wallwork et al. 1965; Ploc, 1980; Maekawa and Ishii, 1962). It has been observed that an oxidation temperature between 600 °C and 700 °C offers the best compromise between generating a sufficiently thick oxide layer and maintaining good adhesion between the OL and the substrate for both Ti and Zr (Krishna et al. 2007; Wang et al. 2014a; Pawar et al., 2011).

Despite the extensive research in recent years on thermal oxidation of Ti and Zr for enhanced tribological properties and biomedical applications, no studies have been reported to directly compare their oxidation behaviour and their mechanical performances after thermal oxidation. Due to the importance of these two bio-metals and their ability to be hardened by oxidation, it is necessary to compare the thermal oxidation behaviour of these two bio-metals and their response to mechanical and combined mechanical and chemical actions. In this investigation, commercially pure Ti and Zr were thermally oxidised under the same condition. Using the same oxidation condition provides a direct comparison of the oxidation behaviour and the resultant mechanical properties of the two biometals. The oxidised specimens were compared in terms of layer thickness, hardness, scratch resistance, and tribological behaviour under dry unlubricated conditions and tribocorrosion behaviour under simulated physiological conditions.

2. Material and methods

2.1. Materials and thermal oxidation

Commercially pure titanium (CP-Ti) grade 2 (99.4% purity) and commercially pure zirconium (CP-Zr) grade 2 (99.2% purity) were used in this work. The original metallurgical structure of these CP materials comprised HCP α-phase. Specimens of 20 mm × 15 mm × 1 mm were prepared by machining the as-received plates. The specimens were wet ground using metallographic SiC grinding papers down to the P1200 grade, then polished in 6 µm diamond suspensions for 5 min, and finally finished by polishing in silica suspensions for 40 min to achieve a mirror-like surface finish of 0.03 µm (R_a).

Before thermal oxidation (TO), the specimens were ultrasonically cleaned in methanol for 10 min, thoroughly dried in a stream of hot air, and weighed using an analytical balance accurate to 0.1 mg. After TO, the specimens were weighed again to obtain the total mass gain by each type of specimens. The total mass gain was divided by the total surface area of the specimens to obtain the mass gain per unit surface area (mg cm^{-2}). This provides information regarding oxygen uptake by the CP-Ti and CP-Zr specimens during the TO process.

Thermal oxidation was conducted in an air furnace at a constant temperature of 650 °C for a constant time of 6 h. After 6 h at 650 °C, the specimens were allowed to cool slowly in the furnace down to room temperature. This TO condition was chosen based on many preliminary experiments and previous work, which can produce an adherent oxide layer at the surface and an oxygen diffusion zone in the subsurface of CP-Ti and Ti alloys (Sun et al., 2016; Aniolek et al., 2016; Bailey and Sun, 2013) and in CP-Zr and Zr alloys (Pawar et al., 2011; Alansari and Sun, 2017). This condition also ensured that no phase transformation took place in the core of the CP materials because the oxidation temperature was below the α-β transformation temperatures.

2.2. Characterisation of TO specimens

After TO, the specimens were characterised by (1) surface roughness measurements using a contact mode profilometer (Mitutoyo SJ-400); (2) surface hardness measurements using a micro Vickers hardness tester (Indentc ZHV) at various loads from 0.025 to 1.0 kg; (3) X-ray diffraction (XRD) analysis using Cu-K_α radiation to identify the phases of thermally oxidised specimens; (4) microscopic examination of the cross sectional morphology and measurement of the thicknesses of the oxidised layers; (5) micro Vickers hardness profile measurements across the oxidised layers in the cross section using an indentation load of 0.025 kg; and (6) scratch testing of the oxidised surface using a Rockwell diamond tip with a radius of 200 µm under various constant loads from 1 N to 30 N. After scratch testing, the width of each resultant scratch mark was measured and the morphology of the scratch was examined microscopically to assess the failure modes and the critical failure load of the oxide layer. A ball crater of about 1 mm diameter was also made on the scratch by rotating a bearing steel ball of 25.4 mm diameter at the same spot at a speed of 60 revolutions per minute to provide an inclined and enlarged view of the deformation behaviour beneath the scratch. Fig. 1 shows a typical scratch on the TO-Zr surface and a ball crater made on the scratch which provides a clear view of the scratch depth and the deformation of the OL towards the substrate. By zooming in the highlighted rectangular zone, the deformation and crack penetration behaviour could be more clearly observed.

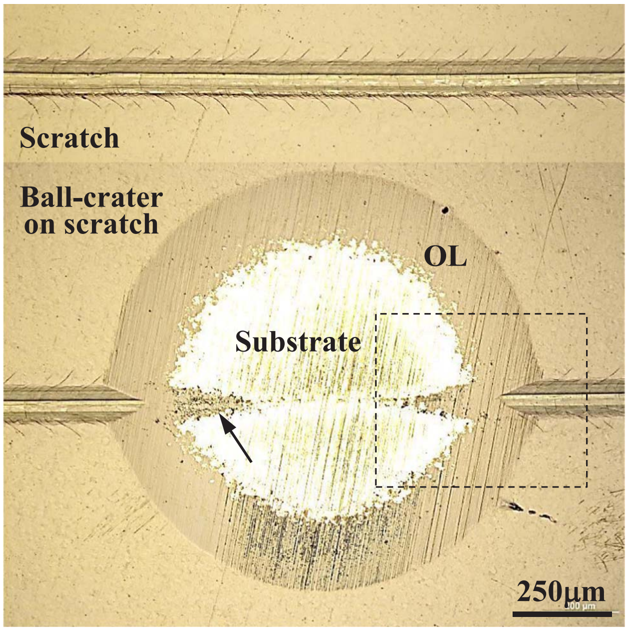

Fig. 1. A typical scratch on the TO-Zr surface and a ball crater made on the scratch to provide an enlarged view of the OL and the material deformation behaviour beneath the scratch (arrowed).

2.3. Dry sliding wear and tribocorrosion tests

Dry sliding friction and wear tests were conducted using a laboratory-scale reciprocating wear tester. During the test, the specimen reciprocated linearly at a frequency of 1 Hz and amplitude of 8 mm. The contacting counterface was an 8 mm diameter alumina ball (Grade 25 Al_2O_3 supplied by Trafalgar Bearings Ltd) due to its inertness and high hardness. The tests were carried out at room temperature (22 °C), in ambient environment for duration of 3600 s. During the test, the coefficient of friction (COF) was recorded by a computer data acquisition system. The contact loads ranged from 1 N to 20 N. Hertzian contact stress calculation showed that these contact loads resulted in initial maximum contact pressures ranging from 468 MPa to 1272 MPa for the Ti specimens and from 412 MPa to 1119 MPa for the Zr specimens. All tests were duplicated and the mean results are presented.

Tribocorrosion tests were conducted using the same reciprocating wear tester at a reciprocating frequency of 1 Hz and amplitude of 8 mm. The tests were carried out by immersing the test specimen in 1 M Ringer's solution maintained at 37 °C, contained in a tribo-