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Research Paper

Wear and friction properties of experimental Ti–Si–Zr alloys for biomedical applications

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ABSTRACT

Titanium alloys are widely used in biomedical applications due to their higher biocompatibility in comparison to other metallic biomaterials. However, they commonly contain aluminum and vanadium, whose ions may be detrimental to the nervous system. Furthermore, they suffer from poor wear resistance, which limits their applications. The aim of this study was to evaluate the tribological performance of experimental Ti–1.25Si–5Zr, Ti–2.5Si–5Zr, Ti–6Si–5Zr and Ti–2.5Si–5Zr–0.2Pd alloys as compared to that of control Ti–6Al–4V, CoCr F75 and CoCr F799 alloys. Friction and wear tests were performed using a standard ball-on-disc rig in serum solution at ambient temperature with Si_3N_4-balls as counterparts. The alloys microstructure and hardness were investigated using optical microscopy, XRD, scanning electron microscopy (SEM) and Vickers indentation.

The coefficients of friction of the experimental Ti–Si–Zr alloys were generally lower than the commercial ones with Ti–6Si–5Zr presenting the lowest value (approx. 0.1). Their wear rates were found to be 2–7 times lower than that of the commercial Ti–6Al–4V alloy, but still higher than those of the CoCr alloys. SEM analysis of worn surfaces showed that abrasion was the predominant wear mechanism for all studied materials. Wear and friction were influenced by the formation and stability of transfer layers, and while commercial Ti–6Al–4V as well as the experimental Ti–Si–Zr alloys demonstrated extensive material transfer to the ceramic counterparts, the CoCr alloys did not show such material transfer.

1. Introduction

Titanium alloys are widely used in medicine, as hard tissue replacement materials as well as for fracture fixation and in dental applications, due to their remarkable combination of high strength-to-weight ratio, good fatigue resistance, relatively low Young's modulus, good biocompatibility and high corrosion resistance (Geetha et al., 2009; Takao, 2012). However, their broader use is somewhat limited by their low wear resistance, high friction coefficients and disposition to galling

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in comparison with other metals or surface treated titanium alloys (Miyoshi and Buckley, 1982; Budinski, 1991; Hiratsuka et al., 1992; Takadoum, 1993; Dong and Bell, 1999; Dong and Bell, 2000; Qu et al., 2005; Yildiz et al., 2009). Poor tribological properties may lead to an unacceptable wear of the implant surfaces, release and accumulation of metal wear debris in surrounding tissues and hence a reduction of the implant service life due to adverse tissue reactions (Rogers, Howie et al., 1997; Duisabeau, Combrade et al., 2004; Virtanen, Milošev et al., 2008). The main reasons for the poor tribological properties of titanium alloys in biomedical applications include the high chemical reactivity of titanium, low shear strength and work hardening, and insufficient stability of the surface oxide film (Yerramareddy and Bahadur, 1991). Moreover, despite its renowned biocompatibility, the most commonly used titanium alloy for biomedical purposes, Ti–6Al–4V, contains aluminum and vanadium, and there have been concerns that ions from these metals could have detrimental effects on the central nervous system (Li, Zhou et al., 2013; Shaw and Tomljenovic, 2013). The substitution of these metals for other alloying elements is therefore desired and Zr, Si, Ta, Nb and Pd have been proposed as more biocompatible alternatives (Niinomi, 2002; Eisenbarth et al., 2004).

Previous studies on titanium-silicon based alloys in combination with thermal treatment (Flower et al., 1972; Alhammad et al., 2008; Firstov et al., 2009; Tkachenko et al., 2009) have shown the possibility of improving the material's hardness, strength and wear resistance by producing a fine martensitic microstructure, in the same way as the harder martensitic microstructure in Ti–6Al–4V alloy provides a better wear resistance than equiaxed grains (Cvijović-Alagić et al., 2011). Also, eutectic transformation in the Ti–Si–Zr system gives the possibility to obtain eutectic-reinforced composites (Bulanova et al., 2004), containing hard silicide particles. However, so far no studies of wear and friction of titanium alloys containing silicon and zirconium have been performed.

Therefore, the present work was undertaken to explore wear and frictional properties of a series of experimental Ti–xSi–5Zr alloys (where $x=1.25$; 2.5; 6.0 wt%) and to assess whether Ti–Si–Zr alloys could be a valid alternative to standard titanium Ti–6Al–4V and CoCr alloys in certain biomedical applications. The effects of chemical composition, microstructural features and hardness on the tribological properties and wear mechanisms of these alloys were studied though X-ray diffraction analysis, optical microscopy, SEM, Vickers indentation and ball-on-disc wear testing. Finally, additional alloying with Pd was utilized for a Ti–2.5Si–5Zr alloy. Small amounts of Pd have been shown to significantly increase the corrosion resistance of titanium in various solutions (Brossia and Cragnolino, 2004), and Pd may contribute to a reduction of the tribocorrosive degradation of the material in biofluids.

2. Materials and methods

2.1. Materials

The following titanium alloys were studied: Ti–1.25Si–5Zr, Ti–2.5Si–5Zr, Ti–6Si–5Zr and Ti–2.5Si–5Zr–0.2Pd (henceforth alloy compositions are denoted by their approximate composition in wt%). Ingots of alloys of approximately 900 g weight were produced through melting in a vacuum-arc furnace (designed and constructed in the Frantsevich Institute for Problems of Materials Science) with a non-consumable tungsten electrode and water-cooled copper hearth under a protective argon atmosphere. The initial materials were 99.95% titanium, 99.95% zirconium, 99.9% pure silicon and 99.95% palladium. Weight changes resulting from melting were small (approx. 0.05%), so the alloy compositions were taken to be those calculated from the component weights. Ingots were remelted six times to ensure compositional homogeneity. The ingots, with the exception of alloy Ti–6Si–5Zr, were then deformed at 900 °C through upset forging with a total deformation degree of 60%, followed by heat treatment at 800 °C for 3 h and cooling to room temperature within the furnace. Plates for wear testing of dimensions $20\times45\times5\ mm^3$ were then cut from the ingots. Plates of Ti–1.25Si–5Zr, Ti–2.5Si–5Zr and Ti–2.5Si–5Zr–0.2Pd alloys were placed in silica tubes under argon atmosphere, heated up to 1300 °C, homogenized for 30 min and subsequently quenched in a 10%–NaCl water solution. Plates of Ti–6Si–5Zr alloy were used in the experiments in as-cast condition. Plates of similar size were also cut from cast CoCr F75 alloy (Sandvik AB, Sweden), forged CoCr F799 alloy (Stainless, France) and commercially available Ti–6Al–4V alloy (Edstraco, Sweden), for use as reference materials. All plates were ground with SiC paper of 120, 320, 500, 800 and 1200 grit and polished with 6; 3; 1 μm diamond suspension to achieve minimal surface roughness (R_a).

2.2. Microstructural characterization

Microstructural analysis was conducted using an optical microscope (Olympus AX70, Olympus Optical Co., Ltd., Tokyo, Japan) and scanning electron microscopes (SEM) (LEO 440, Carl Zeiss SMT Inc., Peabody, MA and table top SEM microscope TM-1000, Hitachi high technologies, Tokyo, Japan). To reveal the microstructure of the titanium alloys, the samples were etched with Kroll's reagent consisting of 92 vol% H_2O, 5 vol% HNO_3 and 3 vol % HF. Cast CoCr F75 was etched with a mixture of 90 vol% of H_2SO_4 and 10 vol% of 30%–H_2O_2. Forged CoCr F799 was etched with an electrolyte containing 92vol% HCl, 5 vol% H_2SO_4 and 3 vol% HNO_3 at a voltage of 2.4 V and a current of 1.2 A/cm^2 during 30 s. Analysis of grain sizes and phase volume fractions were done using the MVision software (LK, India).

Crystal structure analysis and phase identification were made using an X-ray diffractometer (Siemens, D5000, Germany) with monochromated Co Kα radiation over $10\le 2\Theta \le 90^\circ$.

Roughness of the samples was measured with a vertical scanning interferometer (Wyko NT-110, Veeco Instruments Inc., USA).

2.3. Hardness, friction and wear testing

The hardness of the samples was measured with a Vickers hardness tester MXT50 (Matsuzawa Seiki Co. Ltd., Tokyo, Japan) under a load of 500 g.

Friction and wear tests were performed with a standard ball-on-disc apparatus, where a stationary ball was pressed against a rotating disc (Czichos et al., 1989). Although the ball-on-disc test does not emulate real contact conditions of implant bearings, it is commonly used as a simple and