TRIBOLOGICAL PROPERTIES OF Ti-Si-Zr ALLOYS

Sergey TKACHENKO\textsuperscript{a}, Oleg DATSKEVICH\textsuperscript{b}, Leonid KULAK\textsuperscript{b}, Håkan ENGQVIST\textsuperscript{c}, Cecilia PERSSON\textsuperscript{c}

\textsuperscript{a} Brno University of Technology, Brno, Czech Republic, EU
\textsuperscript{b} Frantsevich Institute for Problems of Materials Science, Kyiv, Ukraine
\textsuperscript{c} Uppsala University, Uppsala, Sweden, EU

Abstract

Nowadays titanium alloys are extensively used for aerospace and biomedical applications. However, despite good mechanical properties and excellent corrosion resistance they possess poor wear resistance and a tendency to galling and seizure. In this study the tribological properties of experimental Ti-Si-Zr based alloys were studied using a standard ball-on-disc wear testing system. The wear and friction tests were conducted in bovine serum solution under room temperature using silicon nitride balls as counter-bodies. Measurements of friction coefficients and volumetric wear rate were made and microscopic investigations of the wear tracks were performed along with examination of structure and properties using light microscopy, XRD, SEM and hardness testing.

Keywords: Ti-Si-Zr alloys; Ball-on-disc rig; Friction and wear; Titanium alloys

1. INTRODUCTION

Titanium alloys are widely used for aerospace and biomedical applications due to their remarkable combination of high specific strength, good fatigue resistance, relatively low Young modulus, good biocompatibility and excellent corrosion resistance. However, they possess a low wear resistance, high friction coefficients when worn against metallic and ceramic counter bodies and disposition to galling and seizure [1-4]. A multitude of surface-engineering techniques have been used to increase the wear and friction properties of titanium alloys, including ion implantation, plasma spray coating, nitriding, oxygen diffusion hardening, carburization or boriding [5-7]. These methods permit to obtain a high surface hardness and significantly reduce the wear intensity and coefficient of friction of the titanium substrate; however, there are several drawbacks, such as poor adhesion of coatings to the substrate and presence of high inner stresses. Thus, the development of new titanium-based materials with enhanced tribological properties is of great importance.

Silicon has traditionally been used as an alloying element to increase the high-temperature strength and heat resistance in some titanium alloys for aerospace applications. However, the silicon content in commercial titanium alloys has not exceeded its solubility range in α-titanium (up to 0.4 wt. %) due to the risk of a decrease in ductility [8]. Earlier studies showed that the complex alloying of titanium with silicon (~2.5 wt.%) and some other elements (zirconium, aluminum, niobium, molybdenum) in combination with strengthening heat treatment offer a promising way to significantly increase the hardness and strength [9, 10]. According to Archard's law [11], materials with high hardness potentially possess a better wear resistance compared to softer materials. Thus, it was hypothesized that water-quenched Ti-Si-based alloys with high hardness and martensitic structure may offer enhanced tribological properties. The purpose of this study was to evaluate the friction and wear properties of some experimental Ti-Si-Zr alloys and compare with those of a commercial Ti-6Al-4V alloy and Co-Cr alloys, which are traditionally used as biomaterials.
2. MATERIALS AND METHODS

For this study several experimental titanium alloys composed of non-toxic elements like silicon and zirconium were designed [12]. Also an alloying with palladium was used for one of the alloys, since palladium is known to significantly increase the resistance of titanium to crevice corrosion [13], being a possible advantage in a biologically active environment. The following titanium alloys were studied: Ti–1.25Si–5Zr, Ti–2.5Si–5Zr, Ti–6.0Si–5Zr and Ti–2.5Si–5Zr–0.2Pd (alloy compositions are denoted in wt. %). Ingots of alloys of approximately 900 g weight and 55 mm in diameter and 65 mm high were melted using an argon arc furnace with a non-consumable tungsten electrode in water-cooled copper hearth. The initial materials were iodine titanium, iodine zirconium and pure silicon and palladium. Weight changes resulting from melting were small (±0.05%), so the compositions of alloys were taken as those calculated from the weights of the components. Ingots were remelted six times to ensure compositional homogeneity.

Ingots of Ti–1.25Si–5Zr, Ti–2.5Si–5Zr and Ti–2.5Si–5Zr–0.2Pd alloys were then deformed at 900 °C through upset forging with a deformation degree of 60%. Then ingots of all alloys were heated at 800 °C for 3 hours and cooled to room temperature within the furnace.

Plates for wear testing of dimensions 20×45×5 mm were cut from the ingots. The 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 and homogenized for 0.5 h and subsequently quenched in a 10 %-NaCl water solution. 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 (Ra).

Microstructural analysis was conducted using light microscopy (Olympus AX70), scanning electron microscopy (LEO 440 SEM, Carl Zeiss) and X-ray diffractometry (D5000, Siemens). Light and SEM micrographs were analysed using MVision software (LK, India). The roughness of the samples was measured with a vertical scanning interferometer (Wyko NT-110, Veeco Instruments Inc). The hardness of the samples was measured with a Vickers indenter under a load of 100 g.

Friction and wear tests were performed using a ball-on-disc system in a 25% fetal serum solution with additions of sodium azide and ethylenediaminetetraacetic acid in accordance with standard ASTM, F732-00 [14]. The metal plates were run against 6 mm balls of silicon nitride (Specuma, Sweden, Ra ~ 45±8 nm), which was chosen as counter-body material due to its recent evaluation as bearing surface in hip joints [15], having a high hardness and strength, excellent corrosion and wear resistance. Wear tracks of 5 mm diameter were used and 2-4 tracks were made on each sample. Sliding speed was 0.04 m/s and the total sliding distance was up to 1.024×10^5 cycles. A constant normal load of 0.5 N was applied to each specimen to achieve a maximum Hertzian contact pressure of 0.63 MPa according to Johnson’s theory [16]. The coefficient of friction μ was calculated as the relation of the tangential friction force (F_t) to the normal load (F_n). The wear of the materials was quantified in terms of the specific wear rate, determined as the wear volume normalized by the applied load and the sliding distance of the pin. The wear volumes were calculated from the worn cross-sectional areas of the wear tracks measured with the optical profiler.

3. RESULTS AND DISCUSSION

The water-quenched Ti–1.25Si–5Zr, Ti–2.5Si–5Zr and Ti–2.5Si–5Zr–0.2Pd alloys revealed a microstructure of a plate-like martensite (Fig. 1 a-c) of large grains with average sizes of ~1030±220, 230±140 and 660±290 μm respectively. The Ti–2.5Si–5Zr alloy also contained silicide particles, located at grain boundaries as well as inside grains (Fig. 1 b). The phase composition of the Ti–1.25Si–5Zr alloy was represented by a martensitic α’-phase with HCP lattice, while alloys Ti–2.5Si–5Zr and Ti–2.5Si–5Zr–0.2Pd had a α”-martensitic structure with orthorhombic lattice. The Ti–6.0Si–5Zr alloy demonstrated a typical hypo-eutectic
microstructure of α-titanium matrix and interdendritic eutectic silicide phase of Ti₅Si₃-type (Fig. 1 d). No retained β-phase was detected.

CoCr F75 alloy had a microstructure of large grains of about 110±30 μm size with intergranular carbide phase, while the structure of CoCr F799 alloy consisted of small grains of 4 μm average size and fine carbide particles on grain boundaries. Microstructure of the Ti-6Al-4V alloy was two-phase of fine α-phase grains of 5 μm average size with β-phase interlayers. The microstructure appearances and phase compositions were typical for these commercially available alloys [1, 15].

![Fig. 1 Microstructure of (a) Ti–1.25Si–5Zr, (c) Ti–2.5Si–5Zr, (e) Ti–2.5Si–5Zr–0.2Pd and (g) Ti–6.0Si–5Zr alloys (SEM)](image)

Water-quenched Ti–Si–Zr alloys had a higher hardness compared to Ti-6Al-4V and CoCr alloys due to the fine martensitic structure and solid solution strengthening with silicon and zirconium. The hypo-eutectic Ti–6.0Si–5Zr alloy had the lowest hardness among all materials due to the soft α-titanium matrix. Polished samples of CoCr F799 and Ti-6Al-4V alloys had the smoothest surfaces due to their fine grain size. Samples of CoCr F75, Ti–1.25Si–5Zr, Ti–2.5Si–5Zr, Ti–2.5Si–5Zr–0.2Pd alloys had a higher roughness due to differences in polishing properties between matrix and intergranular carbides for CoCr F75 and between adjacent grains for titanium alloys. The Ti–6.0Si–5Zr alloy had the roughest surface due to differences in polishing properties between the soft matrix and the eutectic phase.

Friction tests showed that coefficients of friction depended more on structural peculiarities of materials than on surface roughness. All friction curves had two distinguishable periods: a wear-in period, where the coefficient of friction monotonously increased (for both CoCr alloys) or decreased (for all titanium alloys) and a plateau phase, where friction was nearly stable. Friction curves of all titanium alloys except Ti–6.0Si–5.0Zr alloy had a multitude of peaks indicating a possible materials transfer and interaction between mating surfaces. This was confirmed by the SEM investigations of wear tracks on metal plates and wear marks on silicon-nitride balls. The Ti–6.0Si–5.0Zr alloy had the lowest coefficient of friction, despite the presence of material transfer between silicon nitride balls and the sample, confirmed by SEM.

Table 1 Hardness and roughness parameters of the alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Hardness</th>
<th>Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCr F75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCr F799</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti–1.25Si–5Zr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti–2.5Si–5Zr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti–2.5Si–5Zr–0.2Pd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti–6.0Si–5Zr</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Hardness, GPa</th>
<th>Mean roughness R&lt;sub&gt;a&lt;/sub&gt;, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–1.25Si–5Zr</td>
<td>3.5±0.1</td>
<td>28±5</td>
</tr>
<tr>
<td>Ti–2.5Si–5Zr</td>
<td>5.6±0.2</td>
<td>33±10</td>
</tr>
<tr>
<td>Ti–6.0Si–5Zr</td>
<td>2.4±0.1</td>
<td>122±29</td>
</tr>
<tr>
<td>Ti–2.5Si–5Zr-0.2Pd</td>
<td>4.1±0.1</td>
<td>22±13</td>
</tr>
<tr>
<td>CoCr ASTM F75</td>
<td>3.3±0.1</td>
<td>19±2</td>
</tr>
<tr>
<td>CoCr ASTM F799</td>
<td>3.5±0.1</td>
<td>5±1</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>3.3±0.1</td>
<td>12±3</td>
</tr>
</tbody>
</table>

**Fig. 2** Coefficient of friction as a function of the number of revolutions in the ball-on-disc test for (a) Co-Cr F75, Co-Cr F799, Ti-6Al-4V and Ti-2.5Si-5Zr-0.2Pd alloys and (b) Ti-1.25Si-5Zr, Ti-2.5Si-5Zr and Ti-6Si-5Zr alloys.

The wear tracks on CoCr F75 and CoCr F799 had the smallest depth and width and the wear was accomplished mostly by mechanical wear (Fig. 3 a). On the contrary, the wear tracks on the Ti–6Al–4V and the Ti–Si–Zr alloys were non-uniform and had continuous sliding marks with plastically deformed scratches and grooves, with a lot of pits and sections of smeared material (Fig. 3 b). Analysis of silicon nitride balls slid against CoCr alloys did not show any visible sign of material transfer from the plates to the balls, while balls slid against all titanium alloys showed signs of extensive material transfer and wear spots were of oval shape and significantly larger than that for CoCr alloys. Such a behavior along with appearances and topography of the wear tracks and the results for the coefficients of friction indicated that the predominant mechanism of wear for all titanium alloys was adhesive, while for CoCr alloys it was abrasive.

Analysis of the wear loss showed that the Ti-Si-Zr alloys with higher hardness did not show any advantages in wear performance in comparison to the softer materials. Ti–Si–Zr alloys had 2-7 times smaller weight loss compared to those of commercial titanium Ti-6Al-4V alloy, however, both CoCr F75 and CoCr F799 presented the least amount of wear among all studied materials. The Ti–6.0Si–5Zr alloy had the least wear among the titanium alloys. Obviously, higher wear loss of titanium materials was determined by adhesive interaction between the investigated materials and the silicon nitride balls.
Fig. 3 Typical SEM appearances of the wear-tracks on the (a) CoCr alloys (CoCr F799) and (b) titanium alloys (alloy Ti-1.25Si-5.0Zr with 67° sample tilt)

Fig. 4 Optical profile images of worn discs and the calculated specific wear rates. The z-scale is magnified 10 times compared to the x and y scales

CONCLUSIONS

- Ti-Si-Zr alloys with higher hardness did not show any advantages in better wear resistance than softer CoCr F75 and CoCr F799 alloys, but they demonstrated 2-5 times lower wear than commercial titanium Ti-6Al-4V;
The weight losses and coefficients of friction of the experimental Ti-Si-Zr alloys slid against silicon nitride balls were 2-7 times lower compared to that of commercial Ti-6Al-4V alloy;

The alloy Ti–6.0Si–5Zr had the lowest coefficient of friction among all materials and the lowest wear intensity among titanium alloys;

The predominant mechanism of wear was adhesive for all titanium alloys, while for CoCr alloys it was abrasive.

ACKNOWLEDGEMENTS
The authors are grateful for the financial support from the Swedish Institute as well as to Sandvik AB and Stainless for supplying CoCr material.

LITERATURE