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Low-friction carbon-based tribofilm from poly-alpha-olefin oil on thermally oxidized Ti6Al4V

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ABSTRACT

Titanium alloy shows a poor tribological performance even under lubrication. In this paper, we report the formation of carbon-based tribofilms from poly-alpha-olefin (PAO) base oil molecules on Ti6Al4V (Ti64) samples after thermal oxidization treatment, where PAO enabling base oils to provide not only the fluid but also the solid tribofilm. Ball-on-disk tests at contact pressures of 2.0 GPa reveal that these carbon-based tribofilms on thermally oxidized Ti64 samples decrease the friction coefficient by about 3 times and wear rate by up to 2 orders magnitude as comparing to untreated one.

1. Introduction

It is estimated that about 19% of the world's energy per year is consumed in the transportation vehicles, which emit 23% of greenhouse gas and other pollutants every year [1–3]. The problem would become more and more serious with the increasing car population. The enforcement of new emission standards imposed on vehicles have driven the need to explore different possibilities to achieve lower friction and wear with reduced lubrication. So far, most efforts have been involved in developing cleaner and more fuel-efficient lubricants, including lowering the viscosity of base oils, and replacing zinc dialkyldithiophosphate (ZDDP) and other additives that contain sulfated ash, phosphorous and sulphur (SAPS) with more environmentally friendly alternatives, including inorganic nanoparticles, ionic liquids and other environmentally friendly additives [4–6]. A variety of surface engineering, surface treatments, coatings, texture are applied on critical components in order to improve the wear resistance and lower the friction of tribological systems [7,8]. The other effective approach decreasing energy consumption and improving machine efficiency is to reduce the dead weight of engines. Titanium and its alloy, a kind of common material in aeronautical manufacturing fields, are gradually introduced into automobile manufacturing fields, due to their excellent mechanical properties and relatively low density [9,10]. However, titanium alloy has a poor tribological performance even in the case of lubrication [11]. This may result from the present additives, such as ZDDP, which are specially designed for ferrous materials [12,13], are not effective to reduce the friction and wear of titanium alloy. The main reason may lay on that titanium alloy cannot enable anti-wear boundary film formation on sliding surfaces in presence of ZDDP-containing lubricants [14]. Surface treatments are being investigated as effective solutions to improve the wear and corrosion resistance of titanium alloy. Many surface modification processes such as thermal oxidation [15–18], ion implantation [19], physical vapor deposition (PVD) [20,21], chemical vapor deposition (CVD) [22], plasma nitriding [23,24], and plasma oxidizing [25], have been proposed in the past. Among them, the surface modified by the relatively simple thermal oxidation technique shows better properties than the others since thick, highly crystalline oxide film is produced. Dong and Bell found that the thermal oxidization treatment can significantly enhance the wear resistance of titanium alloy under lubrication of a fully formulated oil [26]. Qu and co-workers investigated the tribochemical reaction of oxygen diffusion-treated titanium surface with a ZDDP-containing oil [14]. Their results demonstrated that oxygen diffusion treatment can significantly improve the wear resistance of Ti6Al4V (Ti64) by enabling the formation of an effective ZDDP-based boundary film. Our study reveals that excellent tribological performance can be achieved on thermally oxidized Ti64 surface under lubrication of poly-alpha-olefin (PAO) oil without any additives. The results are important to reduce the use of environmentally harmful additives, i.e. ZDDP, in lubricating oil without compromising on performance in terms of protection against

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Table 1
the chemical composition of Ti64.

Elements (%)	Ti	Al	V	Zr	Mo	Fe	Ni
	89.740	6.188	4.067	< 0.100	< 0.100	< 0.100	0.005

friction and wear. The action mechanism of PAO oil for reducing friction and wear of Ti64 is investigated in this paper.

2. Experimental

2.1. Materials and sample preparation

In this study, commercially obtained Ti64 specimen (Boti International Metal Co. Ltd., China) with the thickness of about 1.5 mm was cut into the coupons with 31 mm × 31 mm surface area. The chemical composition of Ti64 specimens, which is provided by the manufacturer, is shown in Table 1. The specimens were successively polished by 400, 800, 1200 grade sandpaper, then ultrasonically cleaned in absolute ethyl alcohol and deionized water, each for 10 min. In the end, they were dried in N_2 atmosphere. The average roughness of the Ti64 samples after pretreatment showed Ra < 0.1 μm, measured by a stylus profilometer.

Thermal oxidation treatment of titanium was carried out using a muffle at the temperatures of 700 °C for 5 h in air. The heating rate was about 5 °C/min. These specimens were cooled to room temperature (about 25 °C) in the furnace.

2.2. Surface characterization

X-ray diffraction (XRD; D/MAX-RB, Rigaku, Japan) using Cu-Kα radiation was undertaken to identify phases and chemical composition present in the thermally oxidized samples surface. The scanning angle ranged from 20° to 60° at a scanning speed of 1°/min with a 0.02° step size. Scanning electron microscope (SEM; S-3500 N, Hitachi, Japan) was used to characterize the micro-structural features of the unworn and worn surfaces and to perform the cross-section analysis of thermally oxidized specimens. The elements concentration profile measured across the oxidized layer by glow discharge spectrometry (GDA 750HP, Spectruma Analytik GmbH, German). The hardness was performed by a nanoindenter (G200, MTS, America) with a Berkovich diamond indenter and using the continuous stiffness measurement (CSM) mode with a displacement penetration depth limit of 2000 nm. The hardness of the layers was chosen in a depth of around 1/10 of the layers thickness, which was not affected by the substrate and 6 indentation tests were performed to obtain the mean value. As a contrast, the hardness of Ti64 substrate was measured by the same mode. The roughness was gathered by profilometer (SJ-200, Mitutoyo, Japan). These measurements were repeated five times for each sample, and the average values were regarded as the effective data. Wear depth and width from each sample were then analyzed using a stylus profilometer (SJ-200, Mitutoyo, Japan) to measure the surface profiles across the wear track at 4 different locations. Wear track morphology was investigated using optical microscope (U3CMOS, Hangzhou ToupTek Photonics Co., Ltd., China).

2.3. Tribological experiments

The tribological tests were carried out by a the ball-on-disk tribometer (UMT-3, Bruker, America), in which a stationary 9.525 mm diameter GCr15 steel ball (the hardness is about 7.3 GPa) was pressing against a disk (untreated and thermally oxidized Ti64 samples) under lubrication by a PAO base oil (dynamic viscosity = 57.1 mPa.s@20 °C) at room temperature (about 20 °C). A commercial fully formulated 5W30 oil (dynamic viscosity = 144.2 mPa.s@20 °C) is also used as the reference. The sliding pair was immersed in the lubricant to be tested. For each test 5 ml of lubricant was used.

Two types of experiments are used to investigate the tribological performance of untreated and thermally treated Ti64 samples. Firstly, tribological tests were performed in a reciprocating sliding mode at a normal load of 1, 10 and 80 N, corresponding to 0.5, 1 and 2 GPa of initial Hertzian contact pressure, respectively. In each test cycles were made with a stroke of 6 mm. A wide range of average contact velocities, from 0.0012 to 0.12 m/s, were applied to obtain the Stribeck curves. Then, the experiments are conducted when a steel ball is rotating against Ti64 samples at the sliding velocity of 0.2 m/s and total sliding time of 1 h, which corresponds to a total sliding distance of 720 m. The normal force was 80 N. The lambda ratio (λ) was calculated as a ratio of minimum lubricant film thickness and starting composite root mean square surface roughness (σ_{rms}) and on the minimum film thickness based on Hamrock and Dowson equation in [27]. As λ was only 0.10 using PAO viscosity, suggesting that the lubrication is in the boundary lubrication regime. The total material loss in volume is the product of the area of cross section of wear track and the stroke length.

The surface chemistry of tribofilms on both untreated and treated Ti64 samples was investigated by using Bruker SENTERRA micro Raman spectrometer with a 532-nm laser.

3. Result and discussion

3.1. Characterization of thermally oxidized samples

The XRD patterns of untreated and thermally oxidized samples at 700 °C for 5 h are shown in Fig. 1. Only hexagonal α-Ti (denoted as α-Ti in Fig. 1, PDF-65-6231) phase appears for the untreated sample. The thermally oxidized sample exhibits different XRD patterns. The peaks from oxygen diffused Ti (denoted as Ti(O) in Fig. 1) except for α-Ti phase is present in the XRD pattern and the peaks from rutile phase TiO_2 (denoted as R in Fig. 1, PDF-21-1276) become the predominant in XRD pattern of the thermally oxidized sample. In the same time, α-Ti phase is almost disappeared. The results are generally in agreement with earlier observations by other investigators before [14–15], hence, a layer oxidation structure with an oxide layer on the surface and an oxygen diffusion zone (ODZ) in the subsurface were fabricated on Ti64 substrate after thermal oxidation treatment.

Fig. 1(b–d) shows the high-resolution Ti2p, Al2p and O1s XPS spectra of the thermally oxidized samples, respectively. In Fig. 1b, the position of the Ti2p1/2 peak at 463.9 eV and the Ti2p3/2 peak at 458.0 eV indicate the presence of Ti^{4+} oxidation states [28]. Fig. 1c shows the position of Al2p peak at 74 eV, which belongs to Al_2O_3 [29]. Fig. 1d illustrates the high-resolution O1s spectra. Two peaks appear. The peak with binding energy at 529.5 eV can be attributed to TiO_2 lattice oxygen [28], and the other peak at 531 eV represented the peak of Al_2O_3 [29].

From Fig. 2a for the cross-sectional morphology of thermally oxidized Ti64 sample, stratification characteristics could not be visible at all for thermally oxidized samples, which indicate that the layer for thermally oxidized sample has a good binding. The total thickness of these two zones is about 6.5 μm (Table 2). The oxide layer is about 1 μm thick with a high oxygen concentration close to TiO_2 stoichiometry from section A of Fig. 2b. Below this oxide layer is the ODZ of about 5.5 μm thickness with a gradually decreasing oxygen concentration and increasing titanuim concentration (section B of Fig. 2b). It is interesting to notice that Al_2O_3 peaks are absence in XRD pattern. This could be due to slow growth of Al_2O_3 as compared to TiO_2. Therefore, Al_2O_3 may only exist on the outer layer of the composite oxide layer which is too thin to be detected by XRD analysis [30].

The surface morphology of untreated and thermally oxidized samples is exhibited in Fig. 3. It can be seen that there are no oxide scales appearing on the surface of the untreated sample. However, many oxide scales and islands are formed on the surface of thermally oxidized