Wear 269 (2010) 747–756

Contents lists available at ScienceDirect

Wear

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

PEO layers obtained from mixed aluminate–phosphate baths on Ti–6Al–4V: Dry sliding behaviour and influence of a PTFE topcoat

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ARTICLE INFO

Article history:
Received 1 March 2010
Received in revised form 1 July 2010
Accepted 30 July 2010
Available online 7 August 2010

Keywords:
Sliding wear
Plasma Electrolytic Oxidation (PEO)
PTFE
Ti–6Al–4V

ABSTRACT

The present study focuses on the influence of PEO treatments (performed in the AC regime using mixed aluminate–phosphate baths) on the tribological behaviour of Ti–6Al–4V, dry sliding against EN100Cr6 steel. Three different sets of coatings were produced: (set 1) in an aluminate-rich electrolyte; (set 2) in a phosphate-rich electrolyte; and (set 3) identical to set 2, but with the addition of a spray-deposited PTFE topcoat. The topography, microstructure, phase constitution and surface microhardness of each set were characterized and dry sliding tests were carried out in the load range 5–120 N using a block-on-ring tribometer. For each set, a transition load which corresponds to the end of coating life has been identified. The highest transition loads were observed for coatings produced using the aluminate-rich electrolyte (set 1). Intermediate values of transition load were measured for duplex PTFE/PEO coatings (set 3). Single-layer PEO coatings produced in the phosphate-rich electrolyte (set 2) showed the lowest values of transition load, due to the low coating thickness and poor uniformity. The deposition of the PTFE topcoat proved to be beneficial in terms of both friction and wear resistance, particularly in an intermediate (30–50 N) load range.

1. Introduction

Titanium alloys, due to their excellent combination of high strength-to-weight ratio, high melting point, high corrosion resistance and biocompatibility, are widely used in the aerospace, automotive, chemical and biomedical industries. However, a major limitation is placed on the use of Ti alloys by their poor tribological behaviour, characterized by low abrasion resistance and strong adhesive wear, with a tendency to seizure [1,2]. For this reason, numerous surface treatments and coatings (e.g. surface modifications such as ion implantation and laser treatments, diffusion treatments such as thermal oxidation or aluminizing, as well as coatings obtained by chemical conversion, electroplating, thermal spraying, or PVD/CVD techniques [3]) have been developed for improving surface properties of Ti alloys. Among the most recent surface modification techniques, plasma electrolytic oxidation (PEO) has been successfully applied to titanium alloys [4–6], outperforming other surface modification treatments such as PVD coatings [7] and offering attractive combinations of mechanical properties, wear resistance, corrosion resistance and biocompatibility [4,8–10].

PEO is an electrochemical conversion treatment, mainly applied to light alloys, based on the modification of the growing anodic film by spark/arc micro-discharges, initiated at potentials above the breakdown voltage of the oxide film and rapidly moving over the treated surface [11]. PEO can be eco-friendly, quickly and economically produced on components of almost any shape and size, with a rather wide coating thickness and composition range, depending on the treatment conditions. As far as the composition of electrolytes is concerned, silicate-, phosphate- and aluminate-based electrolytes can provide strong passivation of the titanium surface and are therefore suitable for PEO treatment. In particular, PEO layers produced in mixed aluminate–phosphate electrolytes display a dense and uniform microstructure, with an optimum combination of thickness, hardness and adhesion [4].

The present study aims to evaluate the influence of PEO treatments, performed in the AC regime using mixed aluminate–phosphate baths (dilute alkaline solutions including sodium aluminate and sodium phosphate in varying proportions, to produce coatings with varying proportions of aluminium titanate and titania, accordingly) on the dry sliding behaviour of a Ti–6Al–4V alloy.

Whilst most tribological studies to date focus on a single applied load [4,12–15] or a limited load range [16,17], a wide range of loads (5–120 N) was employed in the present work. The reason for this was to investigate how the applied load

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0043-1648/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.wear.2010.07.011

affected the tribological behaviour of the PEO-treated Ti alloy, when sliding against EN100Cr6 steel. In addition, the PEO/steel tribological couple is reported [12,17] to generate rather high values of coefficient of friction (>0.6), especially when no removal of the reportedly weaker [16] outermost region of the coating has been carried out. In order to improve the tribological behaviour of PEO-treated alloys, a duplex approach, in which a low-friction top layer was deposited onto a load-bearing PEO layer, has been considered by other authors [15,18,19]. However, the use of PVD or PACVD techniques for depositing a top layer onto PEO-treated alloys [20,21] requires expensive equipment and non-negligible deposition times. As an alternative, simple and cost-effective approach, in the present work a PTFE layer was deposited by aerosol-spray on top of some PEO-treated surfaces, with a view to reduce the coefficient of friction. The tribological behaviour of the PEO/PTFE duplex coating in sliding wear with a EN100Cr6 steel counterpart was then evaluated and compared with those of the PEO coating and of the bare Ti–6Al–4V substrate.

2. Materials and methods

2.1. Sample preparation

Ti–6Al–4V substrates were used for all coatings. The Ti–6Al–4V alloy was supplied in the form of extruded bars, which were heat-treated at 900 °C for 30 min, then water-quenched and aged at 515 °C for 8.5 h. The aged alloy had a Rockwell hardness of 35 HRC.

The PEO coatings were produced using two electrolytes, with different concentrations of aluminates and phosphates (Table 1), with identical treatment conditions (AC regime with 50 Hz modulation; 60 min processing time; 20 A dm^{-2} initial current density, falling by up to 20% throughout the process; ~1 kW power output, maintained constant throughout the process).

Three sets of specimens were produced: (set 1) PEO coatings formed in the aluminate-rich electrolyte; (set 2) PEO coatings formed in the phosphate-rich electrolyte; and (set 3) PEO coatings identical to set 2, with the addition of a PTFE topcoat. The PTFE topcoat was deposited by spraying of a solvent-based aerosol suspension (Molykote PTFE-N-UV, Dow Corning product).

2.2. Microstructural and mechanical characterization

Surface and cross-sectional observations of the PEO-treated specimens were carried out by scanning electron microscopy (SEM) in low vacuum mode. The phase constitution of the coatings was determined by X-ray diffraction (XRD), performing θ–2θ scans from 10° to 90° with a 0.03° step size and a 18 s dwell time by a Philips PW 1820 diffractometer. A CuKα radiation source was used, with a 40 kV accelerating voltage and a 40 mA filament current. XRD traces were collected from coating free surfaces. Phase proportions were determined by Rietveld analysis [22].

Topographic measurements were carried out on coating free surfaces by optical and stylus profilometry, in order to measure the surface roughness and characterize surface morphology.

Hardness measurements were performed using a Vickers microhardness tester with a load of 200 g on free surfaces of PEO-treated samples. The applied load was selected so that the indentation depth amounted to approximately 1/10th of the coating thickness, beyond which the substrate would contribute significantly to the mechanical response [23].

Table 1
Main components of the electrolytes used for PEO treatments.

PEO treatment	$NaAlO_2$ ($g L^{-1}$)	Na_3PO_4 ($g L^{-1}$)
Set 1	12.5	4.5
Sets 2 and 3	2.0	4.5

Table 2
Average roughness values (R_a and R_z) measured on the free surface of untreated Ti–6Al–4V and PEO-treated samples.

	Ti–6Al–4V	Set 1	Set 2	Set 3
R_a (μm)	0.19 ± 0.05	5.0 ± 0.6	2.8 ± 0.2	2.4 ± 0.8
R_z (μm)	1.7 ± 0.5	28.8 ± 3.4	16.7 ± 2.3	13.5 ± 3.1

2.3. Dry sliding tests

The tribological performance of PEO layers was evaluated using a slider-on-cylinder test (block-on-ring contact geometry) described in more detail elsewhere [24]. In this test, a rotating cylinder of SAE52100 (EN100Cr6 steel) of hardness 62 HRC (and surface roughness $R_a = 0.10$ μm) slides against a stationary test piece, i.e. the untreated Ti–6Al–4V or PEO-treated slider (5 mm × 5 mm × 70 mm). Sliding tests were carried out on as-treated sliders (without removing the outermost region of the coating) at ambient conditions of temperature and humidity, under normal loads ranging from 5 to 120 N, at a sliding speed of 0.3 m/s, over a distance of up to 1000 m (unless otherwise indicated). The friction coefficient and the linear vertical displacement were monitored during the tests, whilst the maximum wear scar depth was measured at the end of each test by stylus profilometry (pick-up curvature radius: 5 μm). Worn surfaces and wear debris were observed and analyzed by SEM and EDX, in order to identify the dominant wear mechanisms.

3. Results

3.1. Surface topography

Representative SEM images of the PEO-treated surfaces are shown in Fig. 1, together with the corresponding topographies. The average values of R_a and R_z (measured according to [25]) are listed in Table 2. The free-surface coating morphologies shown in Fig. 1 result from physical phenomena occurring during growth of PEO layers and are responsible for the high coating surface roughness, relative to the untreated substrate (Table 2). On specimens from set 1 (Fig. 1a and b), formed in the aluminate-rich electrolyte, craters and regions of seemingly molten and re-solidified material are observed, which presumably result from localized discharge events. As a consequence, high values of roughness were measured (Table 2). Specimens from set 2 display an uneven, wavy surface with a high density of pits (Fig. 1c and d), which are likely to be the result of competition between aluminate and phosphate species, as was shown to occur between silicate and phosphate species [26]. The presence of pits affords an effective mechanical keying between the PTFE topcoat and the PEO layer in specimen from set 3, via filling of the pits by sprayed PTFE (Fig. 1e and f). The latter also leads to a lower surface roughness for the duplex coatings (Table 2).

3.2. Microstructure and phase constitution

Polished cross-sections of the PEO layers are shown in Fig. 2 (backscattered electron (BSE) mode). The average coating thicknesses derived from analysis of multiple cross-sections are 41 ± 6 μm (set 1), 22 ± 6 μm (set 2) and 24 ± 4 μm (set 3). PEO coatings formed in the phosphate-rich electrolyte (sets 2 and 3) are thinner than coatings formed in the aluminate-rich electrolyte (set 1) and less uniform, as denoted by the larger (relative) standard deviation.