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Evaluation of micromechanical behaviour of plasma electrolytic oxidation (PEO) coatings on Ti–6Al–4V

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ABSTRACT

This paper investigates the micromechanical behaviour and wear properties of coatings on a Ti–6Al–4V alloy generated using the plasma electrolytic oxidation (PEO) technique. Four different compositions of electrolyte were used: aluminate, phosphate, silicate, and mixed phosphate and silicate. The coatings' composition was characterised using X-ray diffraction and energy dispersive spectroscopy, and their morphologies were examined using SEM and optical interference profilometry. Following this, the micromechanical properties of the different coatings and the substrate alloy were examined using nanoindentation, nanoindentation scratch, nanoindentation impact, and modified grit blasting equipment. Correlations between these mechanical performance measures and observed structures are discussed. The aluminate-based coating, which contained a hard Al_2TiO_5 phase, was found to outperform other candidate systems and gave a performance enhancement over the bare substrate. However, it appears to be prone to delamination.

1. Introduction

Plasma electrolytic oxidation (PEO) involves the creation of relatively thick, oxide-based surface layers by oxidation of the substrate and/or deposition from the electrolyte. The high electrical fields generated across the growing oxide layer cause repeated local dielectric breakdown and plasma discharges which modify the structure of the layer. The coatings were developed primarily for wear-protection of aluminium [1–11]. Since it normally involves at least some conversion (oxidation) of the substrate, the interfacial adhesion tends to be superior to that of most deposited coatings [2,4]. The plasma discharges can result in high temperature conversion of the growing coating into crystalline phases such as corundum [12]. These phases confer higher hardness on the coating than the amorphous oxides grown during conventional anodising. PEO coatings also contain significant levels of surface-connected, fine-scale porosity [13,14] and, partly as a consequence of this, have a relatively low global stiffness [14–16] making them strain-tolerant.

The combination of good interfacial adhesion, high hardness, surface-connected porosity (giving good lubricant retention) and high compliance confers excellent tribological performance on PEO coatings in many modes of wear. In general, the wear performance is inferior under erosive or impact loading, particularly at normal incidence [11]. Of course, this is expected with ceramic coatings, which tend to fracture under these conditions, whereas a metallic coating or substrate tends to undergo plastic deformation. The shape, size and velocity of the erodent particles are often relevant, with large, high-speed, angular particles, incident at glancing angles, normally favouring excavation of metallic material.

While PEO coatings on aluminium and magnesium alloys are now in a relatively mature state, their development for use on titanium is still in its infancy. There has been some preliminary work in the area [17,18], but there are often problems of brittleness and relatively high levels of coarse porosity, possibly associated with gas evolution. There is nevertheless considerable interest in their development, particularly in the context of biomedical applications [19–23], and there have also been some reports concerning their microstructure [24] and their resistance to corrosion and wear [25–28]. Currently, they are not expected to enhance the wear resistance of the substrate, which is, of course, generally expected to be superior to that of Al and Mg alloys in any event.

The current work examines four different types of PEO coatings on a commercial titanium alloy (Ti–6Al–4V) with respect to their morphology, composition, and the consequent micromechanical properties, including impact, scratch wear, and erosion behaviour.

2. Experimental procedures

2.1. Specimen production

Coatings were produced on Ti–6Al–4V alloy, using a 10 kW, 50 Hz AC Keronite™ commercial PEO processing unit. Prior to coating, substrates of dimensions 50 × 30 × 1 mm were ground with 180 grit SiC paper and ultrasonically cleaned in acetone, followed by water.

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Four aqueous electrolytes were used, referred to here as “aluminate”, “phosphate”, “silicate” and “mixed”. Compositions are given in Table 1. These electrolytes are similar to those used by Yerokhin et al. [17]. Substrates were PEO-processed for a period of 60 min, with a constant power output and an initial current density of 20 A dm^{-2}. During the process, the anodic RMS voltage was in the range 270–300 V and the cathodic RMS voltage varied between −30 V and −90 V, depending on electrolyte composition. Once coated, specimens were ultrasonically cleaned in water and ethanol.

2.2. Specimen characterisation

The R_a surface roughness of the specimens was optically measured using a Wyko RST-2 interferometric surface profilometer. Coating thickness was measured using three methods; by measuring the coating thickness in representative cross-sectional images, with an Eban 2000 Mk2 eddy current thickness gauge, and by using a micrometer (the thickness of each sample was measured before and after PEO processing, and the half of difference between the two values was taken as the coating thickness, since both sides of the substrate were coated).

Secondary electron images of the surface and cross-sections of the coatings were obtained using a scanning electron microscope (SEM). Cross-sectional samples were metallographically mounted and progressively polished using SiC paper followed by a 1 µm diamond suspension. All samples were sputter coated with a ~40 nm gold layer to avoid surface charging. Energy dispersive spectroscopy (EDS) was used to quantify the elemental composition of the coatings. The probing depth was estimated at ~1 µm by a Monte-Carlo simulation. It should be noted that there is an inherent inaccuracy with using EDS for quantitative analysis of samples containing oxygen. Atomic percent values are generally only accurate to within ~7%.

X-ray diffraction (XRD) was used to identify the phases present in the coatings. A Philips PW1830 X-Ray generator with a beam current of 40 mA and an acceleration voltage of 40 kV was used. The Bragg–Brentano (θ–2θ) geometry was used, with 1° divergence and anti-scatter slits combined with a 0.3 mm receiving slit to maximise signal intensity. Diffraction data were collected using X'Pert Data Collector software, and X'Pert Highscore analysis software was used to identify the phases present.

2.3. Nanoindentation testing

Nanoindentation testing was performed using a Micro Materials Ltd. (MML) NanoTest NTX series system, fitted with a Berkovich diamond indenter tip. Grids of 10 by 10 indentations were performed across the mounted cross-sectional samples to a depth of 500 nm using a proportional loading constant of 0.1 and an unloading rate of 2 mN s^{-1}. Intra-indent spacing was adjusted to cover the local thickness of the coating at indentation, but remained >10 µm. The position of each indentation row relative to the position of the substrate interface was determined using a calibrated optical microscope. Due to the high variability in the coatings, groups of indents a similar distance from the interface were averaged and their standard deviations in both distances from interface and in mechanical properties were calculated.

Table 1
Electrolyte compositions for plasma electrolytic oxidation of Ti–6Al–4V.

Electrolyte	$NaAlO_2$ (g l^{-1})	Na_3PO_4 (g l^{-1})	$Na_2O\cdot SiO_2$ (g l^{-1})	NaOH (g l^{-1})	KOH (g l^{-1})
Aluminate	12.5	1.5	0	0	0
Phosphate	1.5	4.5	0	0	0
Silicate	0	0	5.0	2.0	0
Mixed	0	2.3	3.0	0	1.0

2.4. Multiple impact indentation testing

The nano-scale wear testing procedures employed (multiple impact indentation and scratch indentation) were designed to induce conditions closer to those of typical tribological service conditions than conventional, quasi-static indentation. Multiple impact and scratch indentation were performed using a 10 µm cono-spheroidal diamond indenter tip. In particular, they are likely to generate the types of high local strain rate and surface shear conditions that might be expected during various types of wear. For both nano-scale impact testing and scratch testing, a small piece was cut from each specimen. The coating surfaces of these were mounted freestanding and polished, using a South Bay Technology lapping fixture, with alumina and diamond lapping films of successive grades down to 0.3 µm.

Nanoimpact tests were conducted with 7 different acceleration loads, at logarithmic intervals: i.e. with impact forces of 1, 2, 5, 10, 20, 50, and 100 mN. All tests were performed with an initial standoff distance of ~15 µm, with a sampling rate of 5 Hz at a frequency of ~0.25 Hz, for 400 s, generating 100 impacts at each location. A solenoid, positioned at the base of the pendulum, was used to restrain the pendulum motion during load build-up. Once the desired acceleration load had been reached, the solenoid was released, allowing the pendulum to swing forward and impact the sample. Impact locations were spaced 50 µm apart, with each acceleration load applied in 3 different locations. The raw depth data were processed using a customised LabView analysis program which extracted depth as a function of impact number for each run and averaged the results for each accelerating load value.

2.5. Scratch indentation testing

Scratches 250 µm in length were performed with the load being linearly increased during the first 25 µm and then being held constant at the maximum loads, which were 10, 20, 50, and 100 mN. All scratches were performed parallel to each other, at 50 µm spacing. Surface profiles were taken using a very low load of 0.05 mN, along the length of each scratch, before and after scratching. The difference between these topology scans was taken as the plastic scratch depth. Loads indicated are the normal applied loads. Lateral forces were not monitored, and lateral displacement rates were held constant at 10 µm/s. Scratch hardness was calculated using William's [29] definition, with the load-bearing area being half of the projected area for the mean scratch depth, using an AFM measured diamond area function.

2.6. Erosive wear testing

Sandblast-type erosion testing was conducted using a Guyson Euro 2SF blast cleaning cabinet, with an inlet pressure of 3.2 bar and a gun-to-sample distance of 30 cm at 90° incidence. A shutter was used to ensure the samples were only exposed to a steady particle stream for the desired intervals. The particles used were spherical silica beads, with a diameter of 300 ± 23 µm. Particle velocity was estimated to be 13 m s^{-1}, 4 orders of magnitude faster than the indenter impact velocities, a maximum of 4 mm s^{-1}.

3. Characterisation results

3.1. Coating dimensions and morphology

Table 2 compares the coating thicknesses obtained using different measurement methods. There is good agreement amongst the measurements obtained with the different methods for the aluminate