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Surface modification of a Ti–6Al–4V alloy by thermal oxidation

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Abstract

In this study, the effect of thermal oxidation on the dry sliding wear resistance of a Ti–6Al–4V alloy has been examined. Oxidation has introduced hard surface layers composed of TiO_2 and oxygen diffusion zone beneath it. Hardness survey conducted under a load of 10 g with a Vickers pyramid indenter revealed that surface hardness increased from 450 to 1300 $HV_{0,01}$ upon oxidation at 600 °C for 60 h, which was accompanied by significant improvement in wear resistance. Thus, the dry sliding wear rate of thermally oxidised Ti–6Al–4V alloy was almost negligible when compared to the as-received condition.

Keywords: Diffusion; Oxidation; Titanium alloy; Wear

1. Introduction

Titanium and its alloys are widely used in a variety of engineering applications, where the combination of mechanical and chemical properties is of crucial importance. Low weight and good corrosion behaviour of titanium have stimulated research aiming to establish improved mechanical properties for structural applications. A great interest in titanium and its alloys began with the aerospace structures and has spread through other applications. Chemical and automotive industries, as well as the medical device manufacturers, also benefited from the outstanding properties of titanium alloys. Unfortunately, the insufficient performance of titanium and its alloys limits their use in wear-related applications, where contacting motion of counterparts is maintained. It has been reported that [1,2] excessive wear of titanium alloys is caused by their inherent characteristics leading to mechanical and chemical instability of the surface layers.

Because the poor tribological characteristics of titanium alloys are related to their electron configuration, crystal structure and lubrication characteristics, excessive wear of titanium and its alloys can be overcome only by changing the nature of the surface [3]. Various processes have been proposed to improve wear performance of titanium alloys including physical vapour deposition, thermal spray and thermochemical conversion treatments [4]. Thermal oxidation, which is usually carried out in a normal atmospheric condition containing oxygen as well as nitrogen, appeared to be very promising for producing hard surfaces on titanium alloys.

Ti–6Al–4V alloy is a widely used structural material among the titanium alloys because of its excellent mechanical and corrosion properties. This study aims to modify its surface through thermal oxidation and evaluate the dry sliding wear performance in comparison with untreated alloy. Previously, the wear performance of thermally oxidised Ti–6Al–4V alloy was mostly tested in oil, water and corrosive media [3,5–9]. Relatively few researchers conducted dry sliding wear tests on the oxidised alloy [10–12].

2. Experimental

Ti–6Al–4V alloy was received as an 8-mm diameter rod. Cylindrical samples (5 mm thick) were cut from the rod and prepared by a standard surface-finishing procedure. Samples were ground with SiC abrasive papers up to 1200 mesh and polished with fine grade Al_2O_3 paste to achieve a certain surface uniformity. Later, they were cleaned in acetone and dried in hot air. Isothermal oxidation

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treatments were conducted at 600 °C up to 60 h in normal atmospheric conditions. Characterisation of the untreated and oxidised surfaces was made by optical microscopic examinations, hardness measurements and X-ray diffraction (XRD) analysis.

Microstructural examinations were conducted with a Zeiss light optical microscope on the surfaces and on the cross-sections of the oxidised samples. Cross-sections were prepared by standard metallographic technique. After gentle grinding and polishing, samples were etched with 2% HF solution. Hardness tests were carried out with a Vickers pyramid indenter using a Fischer HP 100 XY-PROG ultra-microhardness tester. Hardness measurements were performed on the surfaces and on the cross-sections of the samples under the indentation loads of 10 and 5 g, respectively. A Philips RV 3710 X-ray diffractometer was used for phase identification of oxidised surfaces using the glancing incidence XRD technique, utilizing CuK_{α} radiation with the incidence beam angle of 2°. The diffraction angle range was between 10° and 90° with a step increment of 0.02° and a count time of 1 s.

Wear behaviour of untreated and oxidised samples was examined on a reciprocating wear tester designed according to ASTM G133. Wear tests were performed at ambient condition (room temperature and 40% relative humidity) under a normal load of 150 g with a 10-mm diameter Al_2O_3 ball, which created contact pressure of 31.5 kg/mm^2 on the surfaces. Wear test samples were sliced from the transverse section of the 8-mm diameter rod. Untreated samples were tested in as polished condition. Sliding speed of the ball on the samples was 20 mm/s with a stroke length of 9 mm. During the tests, the wear developed on the surfaces of the samples, and Al_2O_3 ball was examined at regular intervals with a light optical microscope and an optical profilometer (Mahr Perthen Perthometer S8P). At the end of the entire testing period (300 min), characteristic features of the worn surfaces were revealed by a JEOL JSM 6335 F-type scanning electron microscope (SEM).

3. Results

Thermal oxidation changed the surface colour to brown and increased the surface roughness of the samples. Average surface roughness value (R_a) increased from 0.17 to 0.96 μm at maximum oxidation time studied. Optical micrographs of the sample oxidised for 60 h are presented in Fig. 1. As seen in the 3-D figure (Fig. 1a), oxide layer consisted of numerous small grains, which caused dramatic increment in the R_a value. Beneath the oxide layer, oxygen diffusion zone appeared as white-coloured region after etching. Maximum oxidation time of 60 h resulted with an oxide layer thickness of 1 μm and oxygen diffusion zone depth of 8 μm (Fig. 1b). Even after oxidation of 60 h, no significant change was observed in the microstructure of the examined Ti–6Al–4V alloy.

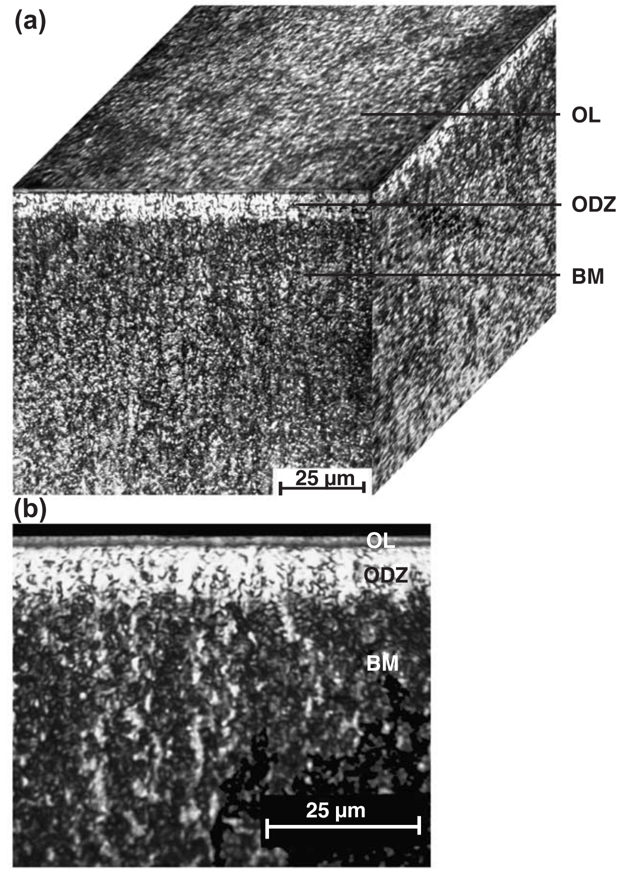

Fig. 1. (a) 3-D and (b) 2-D cross-section optical micrographs of the sample oxidised for 60 h (OL: oxide layer; ODZ: oxygen diffusion zone; and BM: base metal).

The results of microhardness measurements are shown in Fig. 2. Fig. 2a presents the variation of surface hardness with respect to oxidation time. "Hardness–depth" plot of the sample oxidised for 60 h is given in Fig. 2b. Hardness of untreated Ti–6Al–4V alloy utilized in this study was measured as 454 ± 30 $HV_{0.01}$ under a load of 10 g as depicted from Fig. 2a. A significant increase in surface hardness was achieved upon oxidation. However, it should be mentioned that relatively large scatter was observed in the hardness values measured on the oxidised surfaces than that of the untreated surface. Hardness measurements conducted on the cross-section depicted the gradual decrease of surface hardness through the core as presented on the "hardness–depth" profile (Fig. 2b), where the depth of the oxygen diffusion zone can be estimated as 8 μm. This is in good agreement with the results of the microscopic depth measurements conducted on the cross-sections of the oxidised sample (Fig. 1).

The XRD pattern of the oxidised alloy is shown in Fig. 3. As evidenced, the surface of the Ti–6Al–4V alloy was mainly covered by anatase and rutile modifications of TiO_2. After oxidation, peaks of the hcp (α) Ti phase also appeared on the XRD pattern. This was basically due to