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Tribological performance of surface engineered low-cost beta titanium alloy

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Abstract

Low-cost beta (LCB) alloy (Ti-6.8Mo-4.5Fe-1.5Al) is developed specifically for non-aerospace (e.g. automotive and motor sports) applications. However, as for all other titanium alloys, LCB alloy is characterised by a high and unstable coefficient of friction and a strong scuffing tendency. Hence, a new surface engineering process based on optimal integration of bulk heat treatment with surface ceramic conversion has been developed, and this paper reports the tribological performance of surface engineered LCB titanium alloy. TEM analysis carried out on the microstructure of the ceramic conversion layer. Reciprocating pin-on-disc sliding wear tests were conducted against both WC and hardened steel balls under unlubricated and oil lubricated conditions. Post-examination of the wear tracks, counterparts and wear debris was carried out to investigate the wear mechanisms involved.

The experimental results show that the wear resistance of the LCB alloy can be improved by 4-16 times by the novel combined bulk/surface treatment; the coefficient of friction is reduced from 0.8-1.0 for the untreated material to 0.2-0.4 for the treated samples. The wear mechanisms evolve from severe adhesive wear for the untreated material to mild abrasive wear for the treated material when sliding against a WC-Co ball in air. However, severe wear to the steel counterpart occurred and hence large frictional forces formed, which led to delamination wear of treated surfaces. It is also interesting to find that oil lubrication cannot reduce but rather increases the wear of treated surfaces especially when sliding against a hardened steel ball mainly due to oil pressure induced delamination wear.

Key words: Low-cost beta alloy; Combined bulk and surface treatment; Solution & ageing; Ceramic conversion; Reciprocating sliding wear

1. Introduction

The non-aerospace use of titanium alloys (such as in the motor sports industry) has become increasingly popular over the last 20 years due to their high specific strength, excellent corrosion resistance and outstanding biocompatibility. Titanium alloys are normally classified by their structure into the groups of alpha, alpha-beta and beta alloys. Advantages of β phase alloys include excellent workability, good hardening properties, high corrosion resistance and excellent fatigue/crack propagation behaviour [1,2]. TIMETAL LCB (Ti-6.8Mo-4.5Fe-1.5Al) is a low-cost beta (LCB) alloy developed specifically for non-aerospace (e.g. automotive) applications. TIMETAL LCB has been found to have a better combination of high strength (UTS>1500 MPa) and good ductility (total elongation >8%) than many other β alloys [3].

However, it has been reported that the natural oxide film that forms on titanium and its alloys has been found to easily rub off, thus leaving their substrate in a state of high friction and low wear resistance [4]. Consequently, titanium and its alloys are characterised by inferior tribological properties including a high and unstable coefficient of friction and a strong scuffing tendency [5]. This is a problem for titanium and its alloys in all tribological applications, and surface engineering is an essential requirement for the tribological applications of titanium components.

To this end, many surface engineering methods have been developed to improve the poor tribological properties of titanium and its alloys [6,7]. These range from surface coatings such as laser deposition, PVD and plasma electrolytic oxidation to surface modifications such as ion implantation, plasma nitriding and thermal oxidation [8, 9, 10]. However, there is little research on the surface engineering of TIMETAL LCB alloy within the current literature which is an issue needing to be addressed.

Research carried out by Li and Dong and [11] on the titanium alloy Ti-6Al-4V demonstrated the effectiveness of the ceramic conversion treatment (CCT) through controlled thermal oxidation (TO) in enhancing the wear resistance of the alpha/beta alloys. During the treatment, the titanium alloy surface can be converted through controlled thermal oxidation processes into a diffusionally bonded ceramic (rutile TiO_2) layer and an oxygen strengthened diffusion zone underneath. Typical CCT for most $\alpha+\beta$ alloys is normally carried out at about 600 °C in air for a long time (50-100h). However, this process cannot be directly applied to the TIMET LCB alloy since it is a metastable beta alloy. The long-time CCT at high-temperature will cause undue growth of the beta grains and excessive precipitation and growth of the alpha phase, thus leading to the degradation of the core mechanical properties of the β -alloy [12].

Therefore, a novel surface engineering technology combining bulk heat treatment with surface ceramic conversion treatment has been developed in order to enhance the tribological properties of TIMETAL LCB alloy without evoking a loss of core mechanical properties. This paper reports the tribological performance of the surface engineered TIMETAL LCB alloy.

2. Experimental

2.1 Materials and sample preparation

The substrate material used for research purposes was TIMETAL LCB titanium alloy supplied by Titanium Metals Corporation. It had been previously solution treated and then aged for 4 hours at

565.5 °C. The nominal composition of the material was (wt %): 6.8%Mo, 4.5%Fe, 1.5% Al and balance Ti.

A rod of 27mm in diameter was cut into 5mm sections to produce the coupon samples. Standard sample preparation procedure was used to grind the surface of the samples up to 1200 grit and polish to a fine finish, after which they were cleaned with acetone and dried under hot air.

2.2 Design of combined bulk and surface treatments

A new surface engineering approach tailored for beta titanium alloys were designed by combining solution treatment and aging (STA) with thermal oxidation based ceramic conversion treatment. For solution treatment, samples were loaded into an Elite electric furnace, heated at a ramp rate of 10 °C/min from 23 °C to 850 °C and then held for either 0.5 or 6 hours. Immediately after the holding time finished, samples were removed from the furnace and dropped into cold water for quenching. Based on the outcomes of surface morphology and microstructure characterisation, one of the conditions was selected for solution treatments. Samples solution treated with the selected condition were then aged at 500, 550 or 600 °C for 8 hours. The preliminary evaluation revealed that the 500 °C aged samples possessed the best surface oxide layer quality among these aged samples. Then, different aging periods of 4, 16 or 32 hours were carried out at this temperature to identify the optimal aging time for the tribological performance. A summary of the treatment matrix and sample codes are given in Table 1 and the parametric study procedure is shown in Figure 1.

Table 1 Treatment parameters and specimen codes

Specimen code	Solution treatment time (at 850°C), hrs	Aging temperature ,°C	Aging time, hrs
ST6	6	-	-
ST0.5	0.5	-	-
STA500_8	0.5	500	8
STA550_8	0.5	550	8
STA600_8	0.5	600	8
STA500_4	0.5	500	4
STA500_16	0.5	500	16
STA500_32	0.5	500	32

Figure 1 Parametric study procedure of combined bulk and surface treatments.

2.3 Microstructure characterisation

Metallographic cross-sections of the treated samples were prepared using the standard procedures described in Section 2.1. An etching solution of 2% HF, 10% HNO₃, and 88% H₂O was used to reveal the layer structures of the treated samples.

Surfaces and cross-sections of the samples were examined under a Phillips XL30 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) for composition analysis. The phase constituents of the as-received and treated samples were studied by X-ray diffraction (XRD) from 20-100°. Sample STA500_8 was XRD scanned on the top surface and the interface by removing the surface layer precisely. The X-Pert Highscore software was used to analysis the diffraction peaks for identifying the phases presented.

STA500_8 sample was prepared in cross-sectional for transmission electron microscope (TEM) analysis. The sample was cut and thinned by using a Quanta 3D FEG focused ion beam (FIB) miller. A JEOL TEM-2100 LaB6 transmission electron microscope with the operating voltage of 200 kV was used to characterise the microstructure and the phase constituent of the surface layers.

2.4 Mechanical and tribological property evaluation

MVK-H1 hardness testing machine was used with a Vickers indenter at 100g load for microhardness measurements. Load bearing capacity tests were also carried out by measuring the surface hardness from 10g to 1000g load, individually, to find the critical load at which the oxide layer cracked. Three indentations were inserted under each load and the average value was taken. Polished cross-sectional mounted samples were used to generate hardness-depth profiles from the oxygen diffusion zone to the substrate beneath the top oxide layer. Nano-indentation was carried out to measure the surface hardness and the Young's modulus with a Nano-Test 600 machine (Micromaterials, UK).

Reciprocating ball-on-disc sliding wear tests on as-received (untreated) and the optimally treated STA500_4, 8, 16 and 32 samples were conducted using the TE79 multi-axis tribology machine. A schematic view of reciprocating-wear tribometer is shown in Figure 2. The reciprocating sliding wear tests were carried out against two different counterparts, 8 mm tungsten carbide (1800HV0.1) and hardened steel (830HV0.1) balls in air (dry) and in oil (lubricated) under a load of 10 and 20 N. The reciprocating amplitude was 10mm, the average sliding speed was 10 mm/s and the tests were repeated for 3750 cycles with an equivalent sliding distance of 7.5 meters.

The resultant wear tracks were measured using an Ambios XP-200 profilometer and the wear volume loss was calculated by integrating the cross-sectional area of the wear track and then timing the length of wear track. The friction force was recorded and the coefficient of friction (CoF) was calculated according to the recorded friction force and the applied normal load. Post-examination of the wear tracks and the wear scars formed on the counterpart ball surfaces by SEM observation and EDX analysis was carried out to investigate the wear mechanisms involved.

Figure 2 Schematic view of reciprocating-wear tribometer.

3. Results

3.1 Microstructure

Solution treatment and aging (STA), a two-step procedure, is often carried out for LCB titanium alloys to increase the mechanical properties of the bulk materials. When the surface tribological properties were concerned, it is not only the matrix but also the surface layers formed during the treatments need to be studied.

a) Solution treatment time effect

The cross-section SEM images of ST treated ST0.5 and ST6 samples (Fig 3) showed a thin oxide top layer, an oxygen diffusion zone (ODZ) and the grain structure of the substrate. It can be seen that the microstructure beneath the surface oxide layer differs greatly from that of the substrate with secondary phase in the beta matrix. This is the alpha phase, confirmed by XRD analysis (Fig. 6), formed during the solution treatment when oxygen diffused into the beta matrix since it is well-known that oxygen is an alpha stabiliser. The sample treated for 0.5 hours (ST0.5) had an average ODZ thickness of 61 μm and a surface layer of 2.1 μm (Figs. 3 a, b). The sample treated for 6 hours (ST6) had an average ODZ thickness of 117 μm and a thin surface layer of 1.7 μm (Figs. 3 c, d). It is understandable that the thickness of the ODZ increased with the solution treatment time. However, the surface layer of the ST6 sample is thinner than that of the ST0.5 sample and the observation of the surface revealed the spallation of the top layer (Fig 3e). This suggests a short solution treatment time of 0.5 hours at 850 °C as the optimal solution treatment condition for further aging treatments.

b) Aging temperature effect

The cross-sectional SEM images taken from the ST0.5 samples after ageing at 500, 550 and 600°C for 8 h are shown in Figure 4. It can be seen that a white surface layer and an oxygen diffusion zone featured with strong contrast of two-phase structures formed after the aging treatments. In general, the thickness of the surface oxide layer and the ODZ increased with increasing the ageing temperatures. However, spallation of the surface oxide layer was observed for 600°C aged sample. It can be also found by comparing the high magnification images of Figures 4 b and d that the size of the α -Ti precipitates are smaller and more finely distributed in the β -Ti matrix of 500°C aged samples than 550°C aged samples. Hence, 500°C could be selected as the optimal aging temperature considering both the oxide layer and ODZ microstructure.

Figure 3 SEM images of the cross-section view at low and high magnifications: (a) and (b) for ST0.5 sample; (c) and (d) for ST6 sample. (e) top view SEM image of the ST6 sample.

c) Aging duration effect

As described in section 2.2, the effect of different aging durations of 4, 8, 16 and 32 h on the microstructure and surface properties were studied. SEM observations on these samples revealed that they possessed a similar layer structure with a top rutile layer and a beneath ODZ. In general, the thickness of these two sublayers increased with the aging time but marginally. Figure 5 shows the surface hardness and the critical load, at which surface cracking appeared around the indents, against the aging durations. It can be seen that a high hardness value, >1200HV0.025, was gained for all the aged samples compare with the substrate hardness of 530HV0.025. Between the aged samples, 8 hours aged samples possess the highest surface hardness. The critical load decreased with increasing the ageing time mainly due to reduced interface bonding between the surface oxide layer and the ODZ. Nano-indentation measured Surface hardness and Young's modulus for the as-received and STA500_8 surface treated samples are listed in Table 2 with the calculated E/H values.

Figure 4 SEM micrographs of the oxygen diffusion zone at different magnifications from samples STA500_8 (a&b), STA550_8 (c&d) and STA600_8 (e&f)

Figure 5 Critical load and surface hardness as a function of ageing time.

Table 2 Surface hardness and Young's modulus measured for the as-received and STA500_8 surface treated samples

	As-received	STA500_8 Treated
H, GPa	5.0	18
E, GPa	115.0	147
E/H	23.0	8.2

3.2 XRD and TEM characterisation of the oxide layers

Figure 6 shows XRD patterns of sample STA500_8 taken from surface, ODZ and matrix. XRD patterns taken from the surfaces of samples, STA0.5 with different aging durations, showed similar features as the one denoted as 'Surface' in Figure 6. It can be seen that rutile TiO_2 phase formed on the surface and HCP α -Ti phase was detected from both the ODZ and matrix surfaces. When comparing the α -Ti peaks, the ODZ ones are shifted to the left sides of the matrix ones, indicating oxygen diffusion into hexagonal interstices and causing α -Ti hexagonal unit expansion.

Cross-sectional TEM microstructure of sample STA500_8 is shown in Figure 7. It can be seen that the oxidized surface layer consists of three sub-layers as noted in Figure 7 a): an outer oxides layer, an inner oxide layer and an oxygen diffusion layer (zone). Analysing the SAD patterns taken from the outer oxide layer revealed that it mainly composed of nano-grains (100-200 nm) of TiO_2 oxide. However, the outmost area about 250 nm depth from the surface developed relatively coarse (500-700nm) TiO_2 grains with Al_2O_3 nano-particles beneath, see notations in Fig 7 a). It was also found that an interface layer between the nano-oxide of TiO_2 and the ODZ was formed in columnar structures, and a low oxygen containing phase, Ti_3O_5 oxide was identified by SAD patterns analysis. No oxides were found in the oxygen diffusion zone but oxygen expanded α -Ti and β -Ti phases were evidently identified (Figs 7 c) and d)), consistent with the XRD results of the left shifting of the relevant peaks (Fig.6).

Figure 6 XRD patterns taken from different surfaces of sample STA500_8, as denoted.

Figure 7 Cross-sectional TEM microstructure of sample STA500_8 (a) and corresponding SAD patterns of (b) top TiO_2 oxide layer; (c) β -Ti and (d) α -Ti phases in ODZ.

3.3 Tribological properties

(a) Unlubricated (dry) wear under 10N

The friction coefficient of the as-received TIMETAL LCB was about 0.8-1.0 whilst all surface treated samples showed a significantly reduced friction coefficient of about 0.2-0.4. Figure 8 displays the wear area losses calculated from the 2D profiles of the wear tracks formed during the ball-on-disc reciprocating sliding against WC and hardened steel balls. Compared with the as-received material, STA500_4, 8, 16 and 32 samples all showed significantly reduced wear loss. Comparing the wear performance of the samples against different counterparts, it is of interest to find that the hard WC ball (1800HV0.1) has resulted in less wear than the relatively soft steel ball (830HV0.1) for the same treated samples and the reason behind the seemingly abnormal results will be discussed in Section 4. Among these treated samples, more wear was observed for the long time (16 & 32 h) aged samples than the short time (4 & 8 h) aged ones.

The typical 2D profiles of the wear tracks formed on the as-received and a typical STA500 aged sample against a WC ball in air (Fig. 9a) showed that the as-received sample experienced severe wear loss as evidenced by the wide (1.8 mm) and deep (~14 microns) wear track and, in contrast, the wear track formed on the treated surfaces was very narrow and shallow. It was also noted that the bottom of the wear track formed in the as-received material was very rough with large fluctuation. This implies that severe adhesive wear and abrasive wear may have occurred.

After sliding against a hardened steel ball, the untreated sample showed similar wear track features as to against the WC ball, as shown in Fig 9a. However, the 2D profiles of the wear tracks for all the treated samples presented a rectangle shape as shown in Fig 9b with a depth and a width of about 2 and 800 μm respectively.

Figure 8 Wear area loss of treated and as-received LBC (10N, dry)

Figure 9 2D wear track profiles produced against (a)WC balls and (b) steel balls without lubrication.

(b) Dry and wet wear under 20N

The reciprocating sliding wear tests were also conducted against two different counterparts, a WC ball and a hardened steel ball, under a load of 20 N with and without oil lubrication and the typical results are compared in Figure 10. It can be seen that under unlubricated (dry) condition, the steel ball produced more wear than the WC ball to the surface treated samples, which confirmed the similar observation as shown in Fig 8 under 10N. It is also very interesting to observe that when sliding against both the WC and steel balls more wear was produced in oil (i.e. lubricated wear) than in air (i.e. dry wear). This indicates that oil lubrication increased rather than reduced wear of surface treated samples.

Figure 10 Wear area loss of STA500_16 against WC and hardened steel (HS) balls in dry and oil lubricated conditions under 20N.

(c) Examination of wear tracks and wear scars

SEM observations of wear tracks formed on the tested surfaces were conducted and the typical wear morphologies are exemplified in Figure 11. Severe wear occurred to the as-received material under both dry and oil lubricated conditions against WC or steel balls as evidenced by a deep groove with large adhesive craters and parallel scratches within the wear track formed in the sample surface (Fig. 11a). This is in line with the observation that normal oil lubrication is ineffective in reducing adhesive wear of titanium and its alloys [12,13].

Figure 11b shows a typical wear track produced on the surface treated samples after sliding against a WC ball in air. It can be seen that the outer oxide layer was partially removed but with no appreciable wear to the underneath oxide layer as the original machining marks continuously across the wear tracks are still evident. Figure 11c represents a typical wear track formed on the treated samples during the dry sliding wear tests against a hardened steel ball. It is clearly seen that the surface oxide layer was removed and the track is very wide (about $800 \mu\text{m}$) but shallow with a depth of $2 \mu\text{m}$ as evidenced in the 2D profile shown in Fig. 9b. It can also be seen from the wear track that material transfer was formed during the wear test and EDX composition analysis confirmed transfer of the elements of Fe, Cr from hardened steel ball to the wear track. When wear was carried out under oil lubrication condition with both counterpart balls, the wear track was featured a similar morphology with a wide and shallow wear track. It is alike the wear track produced by hardened steel ball in dry condition but without counterpart's materials transfer. This is evidenced by the original parallel machining marks left at the bottom of the wear track as shown in Fig. 11d. This implies that the oil lubricant has to a large extent prevented the adhesion and material transfer between the tribopaire.

Figure 11 Typical wear morphologies observed from the wear tracks formed under 20N on (a) as-received material after sliding against WC ball in air; (b) treated surface against WC ball in air; (c) treated surface against steel ball in air; (d) treated surface against steel ball with oil lubrication.

The wear scars formed on the counterpart surfaces after sliding against the treated surface were examined using SEM/EDX. The observations on the WC and steel balls after wear tests revealed very different worn surface features. As shown in Figure 12a, the wear scar formed on the surface of tungsten carbide balls is about 200μm in diameter; no sign of wear scratches but wear debris were observed. EDX analysis confirmed that the wear debris attached around the scar come from the titanium surface. Figure 12b shows the wear scar of the steel ball after dry wear testing. It evidently shows a circular flattened area, 800 μm in diameter, where steel material had been worn away. The severe scratch lines on the scar surface indicates abrasive wear on the steel ball. EDX analysis on the debris around the circular flat scar confirmed the presents of elements from Ti sample and the steel ball.

Figure 12 Wear scars formed on wear counterparts of (a) WC ball and (b) Hardened steel ball.

4. Discussion

As have been reported above, the novel hybrid bulk/surface treatment combining bulk solution treatment and aging (BSTA) with surface ceramic conversion treatment (SCCT) can effectively enhance the wear properties of low-cost beta (LCB) alloy. The tribological study has also revealed some seemingly abnormal and hence interesting phenomena and this section is devoted to advance scientific understanding of the mechanisms involved.

4.1 Improved wear properties

As shown in Figures 8 and 10, the developed novel hybrid bulk/surface treatment by combining bulk solution treatment and ageing (BSTA) with surface ceramic conversion treatment (SCCT) can effectively increase the wear resistance of LCB titanium alloy under both 10 and 20 N sliding against WC and steel balls in air.

Typical adhesive wear features, such as adhesive craters and deep ploughing grooves, were seen from wear tracks on as-received material (Fig. 11a). This strong adhesive wear tendency is related to the nature of titanium in terms of electron configuration and crystal structure (Dong & Bell, 2000). The removed titanium then became work-hardened under the repeated sliding, resulting in abrasive wear damage on the titanium surface. Oil lubrication provided limited, if any, effect in reducing the wear of LCB. This indicates that oil lubrication is ineffective for titanium alloys, which is in line with the results reported for other titanium alloys.

By contrast, the wear morphologies of the treated surfaces differ greatly from that of the above untreated material and mild abrasive wear was observed for all treated samples. As shown in Figure 11a, although spallation or delamination wear occurred, the wear is limited in the near surface layer. This is as evidenced by the parallel original machining marks extended continuously from the unworn surface across the wear track. No any features of adhesive wear could be observed from the wear track and the wear is dominated by mild oxidative wear. The changed wear mechanism should be attributed to the formation of a hard surface oxide layer supported by a strong interface oxide layer and an oxygen diffusion zone beneath.

According to Bowden and Tabor's theory [14], adhesive wear is closely related to the nature of the deformation between two contact surfaces because high plasticity would promote the formation of cold weld and the growth of junctions. The plasticity index is proportion to the ratio of Young's modulus (E) to hardness (H) [15]. The E/H for the as-received LCB material is 23.0, which has been reduced to 8.2 (Table 2) after the novel hybrid surface treatment. This dramatically reduced plasticity explains the elimination of adhesive wear following the surface treatment.

Abrasive wear is expected in view of the large hardness difference between the WC ball (1800HV0.1) and the oxide layer on the treated surface (1060HV0.1). Abrasive wear occurred from the sliding motion of the hard WC ball which caused the formation of wear particles. As revealed by the XTEM shown in Figure 7, the outer oxide layer consisted of a superficial large sized TiO_2 layer (250nm) followed by an Al_2O_3 enriched thin layer and, most probably, the reciprocating motion caused spallation of the superficial layer. These wear particles were then catalysts for three-body abrasive wear [16]. A diagrammatic explanation of this mechanism is given in Figure 13a.

4.2 Effect of counterpart balls

It is of great interest to note that the wear of the surface treated samples increased rather than decreased as expected when the hard (1800HV0.1) WC balls were replaced by relatively soft (830HV0.1) hardened steel balls (Fig.8). Clearly, this cannot be explained from an abrasive wear point-of-view because abrasive wear mainly depends on the hardness difference between the sample surface and the sliding ball.

Therefore, with this change in counterpart material, an entirely different wear mechanism could have taken place. As shown in Figures 9b and 11c, the wear track is wide and shallow with a relatively flat bottom; the width of the wear track is similar to the diameter of the wear scar on the steel ball; and the depth of the wear track is close to the thickness of the outer oxide layer (Figs 4 & 9b). The above observations suggest that fatigue or delamination wear could have dominated the wear of the treated surface by a relatively soft steel ball.

According to tribology theory, fatigue wear of a material is caused by cyclic loading during friction. Microcracks form at or below the surface, which then spread and cause wear particles to delaminate. When steel ball reciprocated against the treated surface, abrasive wear preferentially occurred to the steel ball due to its relatively low hardness (830HV0.1) as compared to the hard surface oxide (1060HV0.1) and the continues interaction with the sample surface. This resulted in a large contact area between the articulating surfaces as evidenced in Figure 12b and hence large frictional forces (0.6-0.8) [ref]. Therefore, a high level of shear stress will generate and hence microcracks would have been initiated within the rutile layer. These cracks would then spread parallel to the surface as a result of repeated stress by the steel ball. Eventually the rutile layer delaminated from the surface (Fig. 13b). This new rougher surface increased the rate of the wear on the ball and widened the wear tracks. This wear of the ball was caused by abrasion from spalled rutile particles. Material transfer then occurred from the steel counterpart to the wear track it was creating (Fig. 11c).

4.3 Effect of oil lubrication

The effect of lubrication on the wear of surface engineered samples sliding against WC and steel balls was investigated. It was surprising to find that wear of surface treated LCB samples by both counterpart balls increased by oil lubrication (Fig. 10). The wear tracks were wider than in a dry environment but there was however no adhesion of the removed steel ball material within the wear tracks (Fig. 11d) as had been seen without oil (Fig. 11c). The increased wear could be attributed to the penetration of high-pressure oil within the contact area into the oxide layer via such micro-defects as pinholes and micro-cracks, which speeded up the delamination of the outer oxide layer.

The proposed mechanism is schematically shown in Figures 13c and d. When a WC (Fig.13c) or hardened steel ball (Fig.13d) is sliding across the oxide layer in an oil lubricated environment, the ball firstly undergoes wear which widens the contact area between the two articulating surfaces and forces oil downwards into the microcracks of the outer oxide layer, and repeated stress and high oil pressure causes growth of cracks at the interface mainly due to the relatively low bonding strength of the outer oxides layer to the inner oxide layer (Fig 6). Most probably, this is related to the micro-defects observed at the interface of the outer TiO_2 and inner Ti_2O_3 layers (Fig. 7). Finally sections of the outer oxide layer to be delaminated and severe wear loss from the hardened steel ball causes wide track to be formed. As discussed in Section 4.2, the relatively soft steel ball was worn faster

than the hard WC ball and hence larger spallation of oxide layer would be expected by the steel ball (Fig.13d) than by the WC ball (Fig.13c).

However, wear does not proceed into the inner oxide layer and ODZ (both are included in the hatched area on the diagrams). This is supported by the observation that the wear tracks have almost vertical sides and the depth of the wear track formed in the treated surfaces is the same as the thickness of the outer oxide layers on these samples.

Figure 13 Schematics of the wear mechanisms of WC (a), (c) and hardened steel balls (b), (d) against oxidised surfaces under dry (a) (b), and oil lubricated (c), (d) conditions.

5. Conclusions

A novel hybrid bulk/surface process has been developed to combat wear of TIMETAL low-cost beta titanium alloy (Ti-6.8Mo-4.5Fe-1.5Al) by combining bulk solution treatment/ageing with surface ceramic conversion treatment. The tribological performance of the hybrid bulk/surface treated low-cost beta titanium alloy was studied and based on the experimental results and discussion, the following conclusions can be drawn:

- The wear resistance of TIMETAL LCB alloy can be improved by more than 4 times by the novel combined bulk/surface treatment when sliding against WC-Co and hardened steel balls under unlubricated conditions. The coefficient of friction is reduced from 0.8-1.0 for the untreated material to 0.2-0.4 for the treated samples under the same test conditions.
- The severe adhesive wear tendency of the untreated LCB alloy can be effectively addressed by the novel hybrid bulk/surface treatment due to the formation of a hard (1060HV0.1) titanium oxide layer supported by an oxygen diffusion hardened case beneath. The ratio of Young's

modulus (E) to hardness (H), E/H a measure of plasticity index, is reduced from 22.9 for the untreated LCB alloy to 13.9 for the treated surface, thus reducing the severe adhesive wear of the untreated LCB alloy.

- The wear mechanisms evolve from severe adhesive wear for the untreated material to mild abrasive wear (under low-load) and mixed abrasive/delamination wear (under high loads) for the surface treated material when sliding against a WC-Co ball in air. However, severe wear to the steel counterpart occurred and a large flat contact surface and hence large frictional forces formed. This led to delamination wear of the treated surfaces because of the large shear stress at the oxide/substrate interface.
- Oil lubrication can prevent material adhesive transfer, but cannot reduce (and rather increases) the wear of treated surfaces especially when sliding against a hardened steel ball. This is largely because the oil at the contacting area will penetrate into the interface, thus promoting the delamination of surface oxide layer. However, there is no appreciable wear to the dense and adherent Ti3O5 beneath.

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