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Author post-print (accepted) deposited by Coventry University's Repository

Original citation & hyperlink:

Xu, Y, Qi, J, Nutter, J, Sharp, J, Bai, M, Ma, L & Rainforth, WM 2021, 'Correlation between the formation of tribofilm and repassivation in biomedical titanium alloys during tribocorrosion', Tribology International, vol. 163, 107147.

<https://dx.doi.org/10.1016/j.triboint.2021.107147>

DOI 10.1016/j.triboint.2021.107147

ISSN 0301-679X

Publisher: Elsevier

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Correlation between the formation of tribofilm and repassivation in biomedical titanium alloys during tribocorrosion

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Abstract

Titanium alloys are widely used in the field of orthopaedics, however, poor tribological performance arising from the low shear resistance and weak protection of the oxide layer limits their applicability. In this work, the tribocorrosion behaviour of novel β and $\alpha + \beta$ biomedical titanium alloys were studied in bovine serum solution under open circuit potential. Ti-5Mo-Fe-3Sn and Ti-6Al-4V ELI alloys were found to have the capability to repassivate when testing at a slower sliding speed. Scanning and transmission electron microscopy results revealed that the repassivation was mainly associated with the greater tribofilm formation on the worn surface, rather than an oxide film. The tribolayer performed as a solid lubricating film, which stabilised the coefficient of friction.

Keywords: Titanium alloys; Tribocorrosion; Repassivation; Tribofilm; Electron microscopy

1. Introduction

Metallic implants have received much attention due to the unprecedented trend of population ageing around the world. According to the newest projection from 2020 to 2040, the number of primary total hip and knee arthroplasty (THA and TKA) in the USA will increase by 284% and 401%, respectively, which may result in over three million cases in total [1]. *In-vivo* tribological performance of implant determines postoperative feeling and the lifespan of the product. The tribological contact mode is directly related to their specific function and relative distance of motion that normally ranged from tens of micrometres to millimetres [2]. The lubricating condition *in-vivo* is much more complicated due to the electrochemically active environment in the human body. The surface of the implant undergoes both mechanical and corrosive damage, resulting in a synergistic effect on material degradation. Titanium alloys have been widely studied with the emphasis on their corrosion and tribocorrosion performance [3–6]. However, the poor wear resistance compared to ceramic and CoCrMo precludes them as bearing surface materials [7]. Nevertheless, they are still important orthopaedic components because of the superior corrosion resistance and specific strength. There remains, therefore, considerable importance to understand the tribocorrosion performance of biomedical Ti alloys, which must take into account every aspect of the dynamic changes, including the origin of passivation (where present) and the dynamic surface microstructural changes.

The formation of a tribofilm has been widely reported in the metal hip prosthesis. A tribofilm may improve the corrosion resistance by hindering the transport of oxygen [8]. If a graphite-like structure is present in the tribofilm it is also believed to act as a solid lubricant and is responsible for a lower coefficient of friction (COF), but this requires that protein is present in the simulated body lubricant [9–14]. Various factors can affect the formation of a bio-tribofilm. Zeng et al. [15] reported that a mechanically polished CoCrMo could form thicker bio-tribofilm compared to electropolished samples. In other words, the residual stress and difference in

surface topography have significant effects on the formation of bio-tribofilm. Wang et al. [16] also found that rubbing at cathodic potential was more likely to form a thicker bio-tribofilm than at anodic potential because the increased potential decreased the adhesion between protein and surface. This was also believed to explain the reason for the discontinuous distribution of the bio-tribofilm on the test surface. However, the majority of studies have been on CoCrMo alloys, whereas the formation of bio-tribofilm on Ti alloys is not fully understood. Therefore, the present work aims to investigate and compare the tribocorrosion behaviour of biomedical titanium alloys in protein-containing solutions, particularly to understand the nature of tribofilm and corresponding effects on material degradation.

The titanium alloy traditionally used in orthopaedic applications is Ti-6Al-4V, an $\alpha + \beta$ alloy originally developed for aerospace applications. There has been interest in β titanium or near β titanium alloys because they exhibit lower elastic modulus than the $\alpha + \beta$ alloys, and have excellent corrosion and fatigue resistance. In this paper, we report on two newly developed β titanium alloys, Ti-4Mo-Fe-3Sn and Ti-5Mo-Fe-3Sn (at%), which are known to provide low modulus and high strength. These are compared to the conventional commercial Ti-6Al-4V ELI (Extra Low Interstitial) [17]. The tribocorrosion behaviour was examined using a ball-on-disc reciprocating apparatus in simulated physical solution at two sliding speeds. The worn surface and microstructure of the subsurface were analysed by scanning electron microscopy (SEM), and a detailed analysis of the worn surface was undertaken using transmission electron microscopy (TEM) with associated electron energy loss spectroscopy (EELS).

2. Experimental

2.1. Materials and electrolyte

Ti-Mo-Fe-Sn alloys were prepared through a non-consumable arc melter (Arcast Arc200, USA) in a high-purity argon atmosphere. The description of the thermal-mechanical process has been

reported previously [17]. A plate of annealed Ti-6Al-4V ELI (ASTM F136, Grade 23) was obtained from Ti-shop (UK) with a dimension of 250 mm × 250 mm × 4 mm. The Ti-4Mo-Fe-3Sn, Ti-5Mo-Fe-3Sn and Ti-6Al-4V ELI samples are denoted as Ti413, Ti513 and Ti64 ELI hereafter.

All experimental tests were carried out in phosphate-buffered saline (PBS) solution containing 25 vol.% of new-born calf serum (BCS, supplied by Fisher Scientific, UK) at a temperature of $37 \pm 1^\circ\text{C}$. One PBS tablet was dissolved in 50 ml BCS and mixed with 200 ml ultra-pure water (High-Performance Liquid Chromatography, HPLC, Sigma-Aldrich, UK), followed by the addition of 0.4 g sodium azide to prevent protein degeneration.

2.2. *Sample preparation*

Square discs with a dimension of 25 × 25 mm were cut from the as-annealed plate and subjected to the same metallurgical polishing procedures. First, plane grinding using 400 grit SiC papers was used to achieve a flat surface. After that, fine polishing on MD-Largo cloth (Struers, USA) with 9 μm diamond suspension ensures complete removal of the grinding scratches. Lastly, a mirror-like surface can be acquired through polishing on MD-Chem (Struers, USA) with 0.5 μm colloidal silica suspension containing 20 vol.% H₂O₂.

2.3. *Electrochemical characterization*

Electrochemical tests were carried out in a three-electrode cell connected to a potentiostat. The sample, a pure platinum rod and an Ag/AgCl electrode, were used as the working electrode, counter electrode and reference electrode, respectively. The open circuit potential (OCP, E_{ocp}) measurements were performed for 30 minutes. Potentiodynamic polarization was carried out at a scan speed of 0.1 mV/s. According to the Tafel extrapolation method, corrosion potential E_{corr} and current I_{corr} were determined at the intersection of cathodic and anodic current curves extrapolated from the Tafel region.

2.4. Tribocorrosion test

Ball-on-disc reciprocating tests were carried out in a Universal Mechanical Tester (Tribolab, Bruker, USA). A Grade10 alumina ball with a diameter of 4 mm was chosen as the counterface. The stroke length was set 2 mm, and a normal load of 0.5 N was applied. The specimen was rubbed at reciprocating frequencies of 5 Hz and 2.5 Hz. The total sliding distance was 216 m, corresponding to 54000 cycles. All tests were conducted under OCP condition and repeated at least three times to ensure the repeatability of the data. Each test consisted of the following stages:

- OCP stabilization for 1800 s before sliding.
- Sliding for 10800/21600 s.
- Subsequent potential measurement for 1800 s when sliding stopped.

Total wear volume was measured through 3D optical microscopy (Contour GT, Veeco Instruments). To minimize the number of no-measurement points (main error in non-contact technique), the as-received data was modified through a post-process software: Mountains Map (Digital Surf, France). The surface was levelled, and non-measurement points were filled based on infinitesimal calculus. After that, the corrected volume was estimated, and the corresponding specific wear rate could be calculated.

2.5. Surface and subsurface characterization

Samples after heat treatment and tribocorrosion tests were initially investigated by scanning electron microscopy (Inspect F50, FEI company) with an operating voltage of 10 kV (secondary electron mode, SE) and 20 kV (backscattered electron mode, BSE). Site-specific FIB samples were prepared using an FEI Helios (SEM/FIB, the Netherlands). Prior to etching, a rectangular platinum (Pt)/carbon (C) coating with a thickness of 2 μm was patterned to prevent the surface from ion damage. TEM investigation, including scanning transmission

electron microscopy (STEM) and EELS analysis, were performed in a cold-field emission transmission electron microscope JEM-F200 (JEOL, Japan) operating at 200 kV. The JEM-F200 was equipped with a Nanomegas ASTAR, automated crystal orientation and phase mapping tool using precession electron diffraction. For mapping, the TEM was in spot size 7, with a 10 μm condenser aperture, a precession angle of 0.7 degrees and a step size of 2.5-10 nm depending on the scan area. Diffraction patterns were recorded using the external camera, with an exposure time of 20 ms. Precession electron diffraction (PED) is a technique to collect quasi-kinematical diffraction patterns suitable for crystal structure determination using direct methods algorithms.

3. Results

3.1. Microstructural characterization

Fig.1 shows the microstructure of the as-polished surface for titanium alloys. Ti413 and Ti513 displayed a fully β equiaxed grain structure with a mean grain size of 48 and 61 μm , respectively. Meanwhile, Ti64 ELI exhibited an $\alpha + \beta$ equiaxed microstructure and β phase (bright) homogeneously dispersed between primary α grains (dark).

3.2. Electrochemical behaviour

Fig.2 shows the evolution of OCP versus time for Ti413, Ti513 and Ti64 ELI. Note that all alloys exhibited similar behaviour in which potentials slightly changed in the positive direction upon immersion in the BCS solutions. As previously suggested, monitoring the evolution of OCP versus time at static conditions could provide information about the thermodynamic tendency of surface oxidation. For most Ti alloys, this pathway involves the spontaneous formation of TiO or Ti₂O₃, anodic transformation to TiO₂ and corresponding oxide growth [18,19]. Thus, a more positive value represents a better ability of passivation. Table 1

summarises the mean OCP values obtained for alloys after three tests. It is seen that Ti513 has the noblest OCP (-162 ± 17 mV) compared to Ti413 and Ti64 ELI, indicating a better protection characteristic of the passive film.

Fig.3 shows the potentiodynamic polarization for Ti413, Ti513 and Ti64 ELI. All samples exhibited a similar active-passive transition and self-passivation behaviour. There was no observed breakdown potential or pitting until the upper limit of the scanning potential, suggesting the formation of a stable and compact passive film in BCS solution at 37 °C. Ti413 presented a wider passive region (0.28 ~ 1.5 V) compared to Ti513 (0.56 ~ 1.5 V) and Ti64 ELI (0.59 ~ 1.5 V). However, Ti513 and Ti64 ELI possessed a more positive E_{corr} (-0.50 V for Ti513 and -0.66 V for Ti64 ELI) and notably lower I_{corr} ($0.05 \mu\text{A}/\text{cm}^2$ for Ti513 and $0.03 \mu\text{A}/\text{cm}^2$ for Ti64 ELI). The mean values of their corrosion parameters with standard deviation are shown in Table 1. E_{corr} of Ti413, Ti513 and Ti64 ELI are -0.957 ± 0.036 V, -0.493 ± 0.023 V and -0.632 ± 0.045 V respectively. It was also found that Ti513 had the lowest I_p , implying faster repassivation kinetics without mechanical disruption. Thus, given these observations, it could be concluded that the Ti513 sample presented a better corrosion resistance.

3.3. Tribocorrosion behaviour

The tribocorrosion behaviour of Ti413, Ti513 and Ti64 ELI was examined under the OCP condition at frequencies of 2.5 and 5 Hz. Fig.4 shows the time dependence of the OCP and COF variation during reciprocating motion at 5 Hz. At the start of the mechanical disruption, the potential instantaneously moved to negative values in all alloys, corresponding to the breakdown of the passive film, i.e., depassivation (Fig.4a). Then, spontaneous repassivation was observed, as expected for passive metallic materials such as Ti alloys. The potential was observed to oscillate, i.e., the actual surface degradation could be described as a dynamic depassivation and repassivation [20–22]. The potential oscillation for Ti513 and Ti413 was

larger than Ti64 ELI. Similarly, the oscillation in the COF curves for the Ti513 and Ti413, Fig.4b and c, was larger than in the Ti64 ELI curve, Fig.4d, which appeared to mirror the changes in the potential. The average COF for the Ti513 and Ti413 remained approximately constant throughout the test (~0.2), while there was a slight decrease from 0.3 to 0.2 for the Ti64 ELI.

The OCP and COF results for the 2.5 Hz tests are shown in Fig.5. As with the 5 Hz test, the potential dropped at the initial point of testing, after which there was a competition between depassivation and repassivation. The oscillations in the potential were greater at 2.5 Hz than at 5 Hz. This is not surprising because a slower reciprocating speed gives more time for repassivation. For the Ti64 ELI, the repassivation was much stronger at 2.5 Hz than 5 Hz and much greater than for the Ti513 and Ti413. Moreover, the repassivation events lasted much longer for this alloy, Fig.5a. Interestingly, both Ti513 and Ti64 ELI exhibited potential recovery over the duration of the test, indicating that these two alloys can regain the passive state. The corresponding COF curves at which potential recovery occurred are indicated by arrows in Fig.5b which was associated with a more stable COF with reduced signal noise. This supports the assumption that the formation of debris, as well as ploughing effects from hard asperities, are suppressed. As with the 5 Hz test, the COFs of Ti413, Ti513 and Ti64 ELI tested at 2.5 Hz exhibited oscillations that tended to mirror the potential behaviour, Fig.5b-d. The average COF values are summarized in Table 2, which shows that speed did not significantly alter the average COF. The lowest average COF was 0.23 ± 0.03 for Ti513 tested at 5 Hz, and the highest value was 0.34 ± 0.11 for Ti413 tested at 2.5 Hz.

3.4. Wear rates and morphologies of the worn surface

The specific wear rates are presented in Fig.6. Ti513 exhibited the lowest wear rate ($K = 1.80 \times 10^{-4} \pm 0.28 \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$) when tested at 5 Hz. Decreasing the sliding speed to 2.5 Hz led to

a lower total material loss for all samples. A significant reduction in wear rate was observed for Ti513 ($0.77 \times 10^{-4} \pm 0.03 \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$) and Ti64 ELI ($0.31 \times 10^{-4} \pm 0.05 \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$), and this was mainly attributed to potential recovery during tribocorrosion, which could play an important role in enhancing resistance to mechanical, as well as corrosive damage.

In order to gain a better understanding of the wear mechanism, the morphologies of the worn surfaces were investigated using secondary electron imaging in the SEM. For Ti413 samples, there were visible grooves along the sliding direction for both test conditions (Fig.7). However, the worn surface tested at 2.5 Hz displayed more pronounced abrasive features than the 5 Hz test, including grooves and the flake-like debris near the edge of the grooves. It is clear that the formation of wear debris can act as third-body particles and eventually accelerates material loss in simulated body fluid (SBF) [23]. Additionally, a region exhibiting dark contrast was heterogeneously distributed on both worn surfaces, the extent of which was larger at the slower sliding speed. It is known that the organic matter has poor conductivity and so would exhibit dark contrast in the SEM, and previous studies suggest that the dark region on the worn surface could be attributed to the formation of protein-enriched tribofilm [24–26] or an oxide film or both [27,28]. A more detailed investigation of the tribofilm is described later.

The wear tracks of Ti513 and Ti64 ELI are also shown in Fig.7, with similar abrasion-dominated morphologies also observed. A closer examination of the Ti513 wear track at 2.5 Hz showed that the region with dark contrast was raised up from the surface and generally had a much smoother surface.

3.5. The structure of the tribofilm

To further investigate the structure of the tribofilm and surface oxide, a FIB sample for TEM was prepared from the Ti513 tested at 2.5 Hz. As shown in Figs.8a-c, a smooth region exhibiting darker contrast and raised up from the surface was located from the centre of the

wear track. The surface was then covered by a protective carbon coating, and a lamella perpendicular to the worn surface along the sliding direction was milled by the ion beam. The polishing current was decreased step by step from 200 to 50 pA, which promoted the final thickness of ~50 nm and avoided the ion damage as much as possible.

Fig.9a and b show bright-field TEM images of the cross section of the surface of the Ti513 sample. It can be seen that a tribofilm with a thickness of ~200 nm was formed on the topmost surface and a high density of nano-sized particles embedded inside. These smooth and oval particles were found to have a homogeneous distribution in the tribofilm with a diameter ranging from a few to tens of nanometres. Underneath the tribofilm, a nanocrystalline layer was present, with the corresponding selected area electron diffraction (SAED) pattern showing a wide range of crystal orientations within the crystallites. Nanocrystalline layers form in response to the shear loading during reciprocating contact [29,30].

To understand the material constituents comprising the tribofilm, EELS point analysis was performed from the deposition through to the substrate. Fig.9c displays the normalized EEL spectra obtained from three sites of interest marked in black, red and blue circles (Fig.9b). It should be noted that the red circle was selected to cover an embedded particle, but the collected information also contained the inelastic scattering electrons from the surrounding matrix. In the carbon coating, only the C-K characteristic edge was present, and there was no evidence of other metallic components or oxygen. For the target particle, the Ca-L_{2,3}, Ti-L_{2,3} and O-K edges were seen with a weak C-K edge. The sample often drifted a small amount (few nm) during EELS measurements so that the Ca-L_{2,3} and C-K represented the main constituents of the matrix of the tribofilm. The O-K edge was only found in this region and was not associated with titanium and so did not arise from titanium oxides. Rather it must have come from the tribofilm. In the substrate, only Ti-L_{2,3} edges were observed, and there was no trace of C-K edges, implying that the specimen contamination during FIB thinning was negligible.

As shown in Fig.10, a heterogenous tribofilm with a thickness around 100 nm was formed on the worn surface of the Ti64 ELI tested at 2.5 Hz. The tribofilm comprised inner and outer layers. It was found that the outer part of the tribofilm (region 2) displayed weak contrast with a small number of nanoparticles within it. C-K, Ti-L_{2,3} edges and a weak O-K edge were observed in EEL spectra taken from region 2. The stronger strength of the C-K edge suggested that this layer became enriched in absorbed protein from the BCS solution. It is known that in high angle annular dark-field (HAADF) images, the contrast is approximately proportional to the square of atomic number, i.e., Z contrast [31]. Thus, the dark contrast of this region 2 was consistent with a proteinaceous layer. The inner part of the tribolayer (region 3) had a similar characteristic to that observed on the surface of the Ti513 (Fig.9b), also with nanoparticles inside. The corresponding EEL spectra exhibited a weak C-K and O-K edge, with a clear Ti-L_{2,3} present, while the HAADF contrast was similar to the titanium substrate. The weak O-K edge was found in various places, including the substrate, indicating it arose from the expected mild oxidation of the FIB sample and not the formation of titanium oxides. This suggests that this tribolayer is primarily nanocrystalline titanium.

3.6. Structural evolution of the subsurface

The largest difference in wear rate was between the Ti64 ELI tested at 5 Hz and 2.5 Hz. To understand the difference in substrate evolution, FIB cross-sections were examined using ion channeling contrast and also in the TEM. As illustrated in Fig.11a, the region of interest in the centre of the wear track was firstly covered by a protective coating to prevent ion beam damage. A half-sided hole with a dimension of 20 μm × 20 μm × 20 μm was drilled, and the section parallel to the sliding direction was carefully polished until the microstructure appeared. It was found that both samples displayed a near-surface nanocrystalline layer, but the nanocrystalline layer was much thicker at 2.5 Hz compared to 5 Hz (Fig.11b and c, the measured thickness for 5 Hz was 1-1.5 μm and for 2.5 Hz was ~2-3 μm).

Fig.12 shows STEM images from a FIB TEM lift-out sample taken from the 2.5 Hz test to obtain a more detailed examination of the surface microstructure. An ultra-fine nanocrystalline structure is visible underneath the tribofilm. In Fig.12a, the grain size in the nanocrystalline layer gradually increases with depth below the contact surface. Fig. 12b shows a region where there was a thinner nanocrystalline layer when the tribofilm comprises just the outer part. In this region, a thinner nanocrystalline layer (average grain size <50 nm) was observed, which had a more abrupt interface between the nanocrystalline layer and the substrate. The same observations were made in other places, namely that a thicker tribofilm, having both inner and outer parts, coincided with a thicker nanocrystalline layer. Fig.13 shows the abrupt interface between the nanocrystalline layer and substrate in more detail, with the precession electron diffraction, which shows crystal orientation, revealing this interface much more clearly than was evident in the bright-field image.

4. Discussion

4.1 The effect of speed on contacting interface conditions

The wear rate of Ti413, Ti513 and Ti64 ELI was about 39 %, 57 % and 85 % respectively, lower at 2.5 Hz compared to 5 Hz. The lower wear rates at 2.5 Hz were also associated with a much smoother worn surface morphology. Also, alloys tested at 2.5 Hz exhibited a more widespread tribofilm compared to the tests at 5 Hz. Thus, it can be concluded that the greater formation of tribofilm may be the key factor to the improved wear resistance. To explain the greater formation of a tribofilm at 2.5 Hz and its effect on material degradation, the difference in interfacial conditions between 2.5 Hz and 5 Hz must be understood.

Firstly, the effect of sliding speed on interface temperature must be considered. In non-conforming contacts, such as ball-on-disc configuration, rubbing surfaces with very small

contact area will experience a localised rapid increase in temperature when two asperities are in contact, i.e., the flash temperature. Under lubricated conditions, based on a steady-state heating model, the averaging temperature of the lubricant film T_L (°C) can be given as follows [32,33]:

$$T_L = 0.1665 \frac{\mu W U}{\pi a^2} \frac{h}{2k_{lub}} + T_{surface} \quad (1)$$

Where μ is the coefficient of friction, W is the normal load, U is the speed of heat source or sliding speed, h is the lubricant film thickness, k_{lub} is the thermal conductivity of the lubricant and a is the contact area.

Furthermore, the surface temperature $T_{surface}$ can be expressed by:

$$T_{surface} = T_{lub} + \Delta T \quad (2)$$

Where T_{lub} represents the bulk temperature of the lubricant, taken here as 37 °C. ΔT is the surface temperature increase due to reciprocating contact, which can be further evaluated based on the dimensionless Peclet number (L):

$$\Delta T = \frac{\mu W U}{4ka}, \quad L = \frac{Ua}{2\chi} \quad L < 0.1, \quad (3)$$

$$\Delta T = [0.35 + (5.0 - L) \frac{0.5}{4.9}] \frac{\mu W U}{4ka} \quad 0.1 < L < 5.0, \quad (4)$$

$$\Delta T = \frac{0.308 \mu W U}{4ka} \sqrt{\frac{\chi}{Ua}} \quad L > 5.0, \quad (5)$$

Where χ is the thermal diffusivity at the asperity contact and k is the thermal conductivity. The Peclet number describes the speed criterion of a single contact area [32]. The temperature

distribution is locally inhomogeneous across the various asperity contacts and it is difficult to calculate the absolute value of T_L . But in simpler terms, assuming mixed lubrication with comparable h , it is clear that the temperature T_L is proportional to the normal load and sliding speed. 5 Hz is therefore expected to provide a greater heat generation leading to a higher interfacial temperature between contacting asperities. It has been reported that viscosity of globular protein solution is very sensitive to the temperature [34]. Thus, an increase in speed would be expected to increase flash temperature and decrease the viscosity of the lubricant and thereby weaken the protein aggregation. In other words, the tribofilm formation could be suppressed. As discussed later, it was far less at 5 Hz compared to 2.5 Hz.

Secondly, the effect of strain rate on lubricant should also be taken into account. Currently, there is some controversy about the effects of strain rate on shear denaturation. The denaturation of globular protein has been found to require an extraordinary high shear rate of up to $\sim 10^7 \text{ s}^{-1}$ [35]. This suggests the difference in strain rate between 5 Hz and 2.5 Hz is insignificant. However, an increase in strain rate can lead to an increase in viscosity of the bovine serum, which may enhance protein aggregation and be responsible for the greater formation of the tribofilm [34,36]. This effect would be offset by the increase in flash temperature at a higher speed. It would appear that the effect of strain rate on the lubricant was minimal as the tribofilm formation was much less at 5 Hz compared to 2.5 Hz.

Finally, the change in speed could change the lubrication conditions with a change in the Hersey number in going from 2.5 to 5 Hz. For the Ti513 and Ti64 ELI, the change in speed had no discernible impact on the friction, meaning that the lubrication conditions had not changed. Indeed, changes in friction were controlled far more by passivation/depasivation events rather than sliding speed. However, for the Ti413, friction decreased from ~ 0.5 at 2.5 Hz to ~ 0.3 at 5 Hz. This may suggest a change from boundary lubrication towards a mixed lubrication regime at a higher speed [37,38].

4.2 *On the nature of repassivation*

The surface of Ti alloys can form a local galvanic couple as a result of the passive film being removed by the wear process while the surrounding area remains passivated. At 5 Hz, all materials in this study depassivated at the start of the test, Fig.4a. The Ti64 ELI exhibited a marginally more cathodic potential than the two β titanium alloys. Although the potential oscillated for the two β titanium alloys during the test, there was no real evidence of repassivation. The potential of the Ti64 ELI gradually increased as the test progressed, becoming the same as the two β titanium alloys at the end, but there was no evidence of repassivation. Thus, at this sliding speed, the time between asperity contact was too short for passivation to occur. Moreover, the general absence of a tribofilm at 5 Hz limited the ability to repassivate.

The observed oscillation of the potential for the 2.5 Hz test (Fig.5) is attributed to the dynamic depassivation and repassivation process. Major differences were seen in the extent of repassivation and the time for repassivation between the Ti413, Ti513 and the Ti64 ELI, Fig.5a. As shown in Fig.5a, Ti413 depassivated at the start of the test and, although there were major fluctuations in the potential during the test, it remained depassivated throughout. The increases in friction appeared to be associated with the production of plate-like wear debris, Fig.7. The extent of depassivation for Ti513 was less, with a gradual increase in potential throughout the test, reaching near (but unstable) repassivation towards the end of the test after 20 ks sliding. In comparison, the Ti64 ELI test at 2.5 Hz exhibited extended periods of repassivation, but periodic events occurred, leading to depassivation. In all cases, the friction coefficient tended to follow the same trend as the potential; for example, the Ti64 ELI exhibited abrupt increases in the friction coefficient associated with the depassivation events.

The extent of depassivation of the Ti413 was similar to that expected from its corrosion behaviour, Table 1, with this material exhibiting the poorest corrosion resistance. However, the Ti64 ELI exhibited superior repassivation compared to the Ti513, in contrast to the expectations from the corrosion tests, where Ti513 had the lowest I_p implying a faster repassivation kinetic without mechanical disruption. This result is consistent with that observed by Khan et al. [39,40], where the extent of repassivation was shown to not follow the corrosion resistance under wear conditions. Indeed, several researchers have shown that proteinaceous solutions affect the dynamic recovery of the rubbing potential, which can lead to better than expected wear resistance [4,22,41,42]. In the current work, there was therefore some additional reasons for the difference in repassivation behaviour between Ti513 and Ti64 ELI, most probably associated with the manner in which each material reacted with the bovine serum during rubbing. It is believed that this was associated with the difference in materials ability to form a tribofilm on the surface, as discussed below.

4.3 Tribofilm formation and relationship to passivation

SEM images of the worn surface showed regions of darker contrast, e.g., Fig.7. As discussed below, these regions of darker contrast were associated with the formation of a tribofilm. The extent of the tribofilm was a strong function of sliding speed, with the tribofilm extensively found on surfaces tested at 2.5 Hz, but much less so on surfaces tested at 5 Hz, for example, compare the worn surfaces for Ti513. As discussed in section 4.1, the primary effect appeared to be that the increase in speed increased flash temperature, thereby decreasing the viscosity of the lubricant and thereby weakening the protein aggregation, resulting in a suppression of the formation of the tribofilm.

TEM examination of site-specific surface cross sections showed that the regions of dark contrast in the SEM images corresponded to the formation of a surface tribofilm, Figs. 9, 10.

Detailed chemical analysis by EELS indicated that the tribofilm consisted of carbonaceous material containing nanoparticle wear debris. The main composition of the matrix of the tribofilm was graphite-like carbon, as shown by the fine structure in the EEL spectra, suggesting that the protein underwent carbonisation/denaturation during tribological contact. It has been reported that the structural stability of a protein is associated with various parameters, such as temperature and ionic strength [43]. There were also minor amounts of oxygen in this film which might be thought to be associated with repassivation events of the titanium surface. The oxygen was associated with very fine particles within the carbon-based matrix. For the Ti513, these particles contained calcium and titanium as well as oxygen. This suggests some form of mechanical mixing between titanium wear debris and the bovine serum. It is known that nanoparticles can rapidly interact with proteins because of a higher surface area and enhanced chemical reactivity [44]. The incorporation of these hard oxide particles could reinforce the soft carbonaceous layer. This may produce a more robust tribofilm, enhancing the staged repassivation behaviour.

It could be assumed that these oxide nanoparticles in the tribofilm were mainly from the breakdown of the compact titanium oxide-based passive film, which was continuously formed when the fresh surface was exposed to BCS solution during tribocorrosion. However, despite extensive TEM investigation, no evidence was found of a passivating titanium oxide layer. Thus, mechanical disruption and chemical action together contribute to this complicated tribofilm, with the formation of the tribofilm illustrated in Fig. 14.

The structure of the tribofilm also appeared to be a function of the material, with a two-layer tribofilm found on the surface of the Ti64 ELI (Fig. 10) compared to the single-layer tribofilm found on the Ti513 (Fig. 9). The extent of formation of the tribofilm therefore appears to be closely correlated with the extent of repassivation observed during the sliding tests (Figs. 4, 5) and with the material type. Thus, the current work strongly suggests that the tribofilm formation

is the precondition for repassivation and is responsible for the stronger and stable passive recovery. The formation of the tribofilm and associated repassivation leads to less material loss, implying the tribofilm offers protection of the surface to the wear induced mechanical disruption. This is consistent with the work of Khan and Williams [45], who found that the presence of protein reduced the wear rate of all alloys but that the extent was very much alloy dependent.

4.4 The effects of sliding speed on the nanocrystalline layer

Apart from the tribofilm, the subsurface microstructure can play a crucial role in controlling wear performance through friction-induced changes that alter the mechanical properties of the surface. As summarised in a review of the effect of fine and ultra-fine grained structures on wear, Gao et al. [46] showed how such structures could sometimes improve wear resistance, while under different conditions can reduce wear resistance. Improvements in wear resistance are associated with the refined microstructure leading to the greater strength of the surface. However, decreased wear resistance can be a result of decreased ductility, reduced work hardening capability, a greater grain boundary area accelerating corrosion/oxidation and a strain incompatibility with the substrate. There are several examples where a nanostructured surface can give greatly enhanced wear resistance. For example, Chen et al. [47] found that a gradient nanostructure possessed a better capacity of strain accommodation, which reduced ploughing and delamination during dry sliding, leading to a lower COF and superior wear resistance.

In the current work, all samples underwent the same number of cycles and so surface structures can be directly compared. The cross-sectional view of Ti64 ELI worn surface found the thicker nanocrystalline layer formation at 2.5 Hz than at 5 Hz, Fig. 11. The lower sliding speed was associated with a significantly smaller material loss, Fig. 6, giving a smaller wear track

geometry. This would reduce the Hertzian contact pressure compared to the test at 5 Hz, which would be expected to give less surface deformation and therefore, a thinner nanocrystalline layer. However, the opposite was observed.

An interesting observation, particularly for the Ti64 ELI, was that the depth of the nanocrystalline layer was greater where there was a thicker tribofilm on the surface. In particular, the nanocrystalline layer was much thicker when the double tribolayer was present, Fig. 12. The tribofilm was more extensive for all materials at 2.5 Hz compared to 5 Hz, which was coincident with a thicker nanocrystalline layer and a lower wear rate. There are several reports for thicker nanocrystalline layers being coincident with a surface film, such as an oxide or tribofilm. For example, Mischler and co-workers [48,49] have shown a much thicker nanocrystalline layer in the friction of stainless steel for anodic conditions, where an oxide was present, compared to cathodic conditions in the absence of an oxide. It was believed that the surface film acts as a barrier to dislocation glide and dislocation annihilation at a free surface, leading to the formation of a nanocrystalline layer to a greater depth.

5. Conclusions

In this paper, the tribocorrosion performance of β -type Ti alloys and Ti64 ELI was investigated at 5 Hz and 2.5 Hz under the OCP condition. The lower sliding speed was found to result in repassivation in the form of potential recovery and stabilization of COF in Ti513 and Ti64 ELI.

This recovery was associated with the greater formation of tribofilm, which could perform as a solid lubricant film and prevent cumulative material degradation during tribocorrosion.

The tribofilm had a complex structure, which differed with material type. For the Ti513, a single-layer tribofilm was observed, comprising an amorphous carbon matrix containing small oxide-based particles that contained calcium and titanium as well as oxygen. The Ti64 ELI

exhibited a double layer tribofilm. The outer layer was predominantly carbon-based, with few particles in it. The inner layer was similar in structure to that found on the Ti513.

A more pronounced nanocrystalline layer was formed beneath the worn surface. The thickness of this nanocrystalline layer was much greater at 2.5 Hz than at 5 Hz. The nanocrystalline layer was also thicker, where a tribofilm was present on the surface. This is consistent with earlier suggestions that surface layers block the dislocation loss. The presence of a tribofilm and a thicker nanocrystalline layer appeared to coincide with lower wear rates.

Acknowledgements

This work was supported by the Henry Royce Institute for Advanced Materials under EPSRC grant EP/R00661X/1 and also the EPSRC Programme Grant, Friction: The Tribology Enigma, EP/R001766/1. The authors would like to thank Mr Neil Hind for heat treatment and hot rolling.

References

- [1] J.A. Singh, S. Yu, L. Chen, J.D. Cleveland, Rates of total joint replacement in the United States: Future projections to 2020-2040 using the national inpatient sample, *J. Rheumatol.* 46 (2019) 1134–1140.
<https://doi.org/10.3899/jrheum.170990>.
- [2] Y. Yan, *Bio-tribocorrosion in biomaterials and medical implants*, Elsevier, 2013.

- [3] W. Xu, M. Chen, X. Lu, D. wei Zhang, H. preet Singh, Y. Jian-shu, Y. Pan, X. hui Qu, C. zong Liu, Effects of Mo content on corrosion and tribocorrosion behaviours of Ti-Mo orthopaedic alloys fabricated by powder metallurgy, *Corros. Sci.* 168 (2020).
<https://doi.org/10.1016/j.corsci.2020.108557>.
- [4] I. Hacisalihoglu, A. Samancioglu, F. Yildiz, G. Purcek, A. Alsaran, Tribocorrosion properties of different type titanium alloys in simulated body fluid, *Wear.* 332–333 (2014) 679–686.
<https://doi.org/10.1016/j.wear.2014.12.017>.
- [5] J. Ureña, S. Tsipas, A.M. Pinto, F. Toptan, E. Gordo, A. Jiménez-Morales, Corrosion and tribocorrosion behaviour of β -type Ti-Nb and Ti-Mo surfaces designed by diffusion treatments for biomedical applications, *Corros. Sci.* 140 (2018) 51–60.
<https://doi.org/10.1016/j.corsci.2018.06.024>.
- [6] Z. Wang, Y. Zhou, H. Wang, Y. Li, W. Huang, Tribocorrosion behavior of Ti-30Zr alloy for dental implants, *Mater. Lett.* 218 (2018) 190–192.
<https://doi.org/10.1016/j.matlet.2018.02.008>.
- [7] K.G. Budinski, Tribological properties of titanium alloys, *Wear.* 151 (1991) 203–217. [https://doi.org/10.1016/0043-1648\(91\)90249-T](https://doi.org/10.1016/0043-1648(91)90249-T).

- [8] M.T. Mathew, C. Nagelli, R. Pourzal, A. Fischer, M.P. Laurent, J.J. Jacobs, M.A. Wimmer, Tribolayer formation in a metal-on-metal (MoM) hip joint: An electrochemical investigation, *J. Mech. Behav. Biomed. Mater.* 29 (2014) 199–212. <https://doi.org/10.1016/j.jmbbm.2013.08.018>.
- [9] M.T. Mathew, M.J. Runa, M. Laurent, J.J. Jacobs, L.A. Rocha, M.A. Wimmer, Tribocorrosion behavior of CoCrMo alloy for hip prosthesis as a function of loads: A comparison between two testing systems, *Wear.* 271 (2011) 1210–1219. <https://doi.org/10.1016/j.wear.2011.01.086>.
- [10] Z. Wang, Y. Yan, Y. Su, L. Qiao, Effect of proteins on the surface microstructure evolution of a CoCrMo alloy in bio-tribocorrosion processes, *Colloids Surfaces B Biointerfaces.* 145 (2016) 176–184. <https://doi.org/10.1016/j.colsurfb.2016.05.002>.
- [11] Y. Liao, R. Pourzal, M.A. Wimmer, J.J. Jacobs, A. Fischer, L.D. Marks, Graphitic Tribological Layers in, *Science (80-.)*. 334 (2011) 1687–1690. <https://doi.org/10.1126/science.1213902>.
- [12] A. Erdemir, G. Ramirez, O.L. Eryilmaz, B. Narayanan, Y. Liao, G. Kamath, S.K.R.S. Sankaranarayanan, Carbon-based tribofilms from lubricating oils, *Nature.* 536 (2016) 67–71. <https://doi.org/10.1038/nature18948>.

- [13] Y. Xu, Q. Zheng, R. Abuflaha, D. Olson, O. Furlong, T. You, Q. Zhang, X. Hu, W.T. Tysoe, Influence of dimple shape on tribofilm formation and tribological properties of textured surfaces under full and starved lubrication, *Tribol. Int.* 136 (2019) 267–275.
<https://doi.org/10.1016/j.triboint.2019.03.047>.
- [14] Y. Xu, Q. Zheng, T. You, L.L. Yao, X. Hu, Laser-induced improvement in tribological performances of surface coatings with MoS₂ nanosheets and graphene, *Surf. Coatings Technol.* 358 (2019) 353–361.
<https://doi.org/10.1016/j.surfcoat.2018.11.063>.
- [15] P. Zeng, A. Rana, R. Thompson, W.M. Rainforth, Subsurface characterisation of wear on mechanically polished and electro-polished biomedical grade CoCrMo, *Wear.* 332–333 (2015) 650–661.
<https://doi.org/10.1016/j.wear.2015.02.007>.
- [16] Z. Wang, Y. Yan, Y. Su, L. Qiao, Effect of electrochemical corrosion on the subsurface microstructure evolution of a CoCrMo alloy in albumin containing environment, *Appl. Surf. Sci.* 406 (2017) 319–329.
<https://doi.org/10.1016/j.apsusc.2017.02.152>.
- [17] Y. Xu, J. Gao, Y. Huang, W.M. Rainforth, A low-cost metastable beta Ti alloy with high elastic admissible strain and enhanced ductility for orthopaedic application, *J. Alloys Compd.* 835 (2020) 155391.
<https://doi.org/10.1016/j.jallcom.2020.155391>.

- [18] C.E.B. Marino, E.M. de Oliviera, R.C. Rocha-Filho, S.R. Biaggio, On the stability of thin-anodic-oxide films of titanium in acid phosphoric media, *Corros. Sci.* 43 (2001) 1465–1476. [https://doi.org/10.1016/S0010-938X\(00\)00162-1](https://doi.org/10.1016/S0010-938X(00)00162-1).
- [19] M. V. Popa, I. Demetrescu, E. Vasilescu, P. Drob, A.S. Lopez, J. Mirza-Rosca, C. Vasilescu, D. Ionita, Corrosion susceptibility of implant materials Ti-5Al-4V and Ti-6Al-4Fe in artificial extra-cellular fluids, *Electrochim. Acta.* 49 (2004) 2113–2121. <https://doi.org/10.1016/j.electacta.2003.12.036>.
- [20] N. Diomidis, S. Mischler, N.S. More, M. Roy, S.N. Paul, Fretting-corrosion behavior of β titanium alloys in simulated synovial fluid, *Wear.* 271 (2011) 1093–1102. <https://doi.org/10.1016/j.wear.2011.05.010>.
- [21] M.P. Licausi, A.I. Muñoz, V.A. Borrás, N. Espallargas, Tribocorrosion Mechanisms of Ti6Al4V in Artificial Saliva by Zero-Resistance Ammetry (ZRA) Technique, *J. Bio- Tribo-Corrosion.* 1 (2015) 1–11. <https://doi.org/10.1007/s40735-015-0008-x>.
- [22] N. Diomidis, S. Mischler, N.S. More, M. Roy, Tribo-electrochemical characterization of metallic biomaterials for total joint replacement, *Acta Biomater.* 8 (2012) 852–859. <https://doi.org/10.1016/j.actbio.2011.09.034>.

- [23] S. Cao, S. Mischler, Modeling tribocorrosion of passive metals – A review, *Curr. Opin. Solid State Mater. Sci.* (2018) 1–15.
<https://doi.org/10.1016/j.cossms.2018.06.001>.
- [24] R. Yazdi, H.M. Ghasemi, M. Abedini, C. Wang, A. Neville, Mechanism of tribofilm formation on Ti6Al4V oxygen diffusion layer in a simulated body fluid, *J. Mech. Behav. Biomed. Mater.* 77 (2018) 660–670.
<https://doi.org/10.1016/j.jmbbm.2017.10.020>.
- [25] M.A. Wimmer, M.P. Laurent, M.T. Mathew, C. Nagelli, Y. Liao, L.D. Marks, J.J. Jacobs, A. Fischer, The effect of contact load on CoCrMo wear and the formation and retention of tribofilms, *Wear.* 332–333 (2015) 643–649. <https://doi.org/10.1016/j.wear.2015.02.013>.
- [26] R.J.K. Wood, Tribo-corrosion of coatings: A review, *J. Phys. D. Appl. Phys.* 40 (2007) 5502–5521. <https://doi.org/10.1088/0022-3727/40/18/S10>.
- [27] Y. Zhou, S. Wang, W. Chen, W. Jiang, L. Wang, K. Chen, X. Cui, Comparative research on the effect of an oxide coating and a tribo-oxide layer on dry sliding wear of Ti–6Al–4V alloy, *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* 232 (2018) 1569–1580.
<https://doi.org/10.1177/1350650118757329>.

- [28] L. Wang, Q.Y. Zhang, X.X. Li, X.H. Cui, S.Q. Wang, Dry sliding wear behavior of Ti-6.5Al-3.5Mo-1.5Zr-0.3Si alloy, *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* 45 (2014) 2284–2296.
<https://doi.org/10.1007/s11661-013-2167-z>.
- [29] C. Greiner, J. Gagel, P. Gumbsch, Solids Under Extreme Shear: Friction-Mediated Subsurface Structural Transformations, *Adv. Mater.* 31 (2019).
<https://doi.org/10.1002/adma.201806705>.
- [30] M.A. Wimmer, A. Fischer, R. Büscher, R. Pourzal, C. Sprecher, R. Hauert, J.J. Jacobs, Wear mechanisms in metal-on-metal bearings: The importance of tribochemical reaction layers, *J. Orthop. Res.* 28 (2010) 436–443. <https://doi.org/10.1002/jor.21020>.
- [31] D.B. Williams, C.B. Carter, The transmission electron microscope, in: *Transm. Electron Microsc.*, Springer, 1996: pp. 3–17.
- [32] J.F. Archard, The temperature of rubbing surfaces, *Wear.* 2 (1959) 438–455. [https://doi.org/10.1016/0043-1648\(59\)90159-0](https://doi.org/10.1016/0043-1648(59)90159-0).
- [33] M.D. Marko, J.P. Kyle, Y.S. Wang, E.J. Terrell, Tribological investigations of the load, temperature, and time dependence of wear in sliding contact, *PLoS One.* 12 (2017) 1–20.
<https://doi.org/10.1371/journal.pone.0175198>.

- [34] Z. Zhang, Y. Liu, Recent progresses of understanding the viscosity of concentrated protein solutions, *Curr. Opin. Chem. Eng.* 16 (2017) 48–55.
<https://doi.org/10.1016/j.coche.2017.04.001>.
- [35] J. Jaspe, S.J. Hagen, Do protein molecules unfold in a simple shear flow?, *Biophys. J.* 91 (2006) 3415–3424.
<https://doi.org/10.1529/biophysj.106.089367>.
- [36] M.M. Castellanos, J.A. Pathak, R.H. Colby, Both protein adsorption and aggregation contribute to shear yielding and viscosity increase in protein solutions, *Soft Matter*. 10 (2014) 122–131.
<https://doi.org/10.1039/c3sm51994e>.
- [37] J. Williams, *Engineering tribology*, Cambridge University Press, 2005.
- [38] J.P. Davim, *Tribology for engineers: A practical guide*, Elsevier, 2011.
- [39] M.A. Khan, R.L. Williams, D.F. Williams, The corrosion behaviour of Ti–6Al–4V, Ti–6Al–7Nb and Ti–13Nb–13Zr in protein solutions, *Biomaterials*. 20 (1999) 631–637.
[https://doi.org/https://doi.org/10.1016/S0142-9612\(98\)00217-8](https://doi.org/https://doi.org/10.1016/S0142-9612(98)00217-8).
- [40] M.A. Khan, R.L. Williams, D.F. Williams, In-vitro corrosion and wear of titanium alloys in the biological environment, *Biomaterials*. 17 (1996) 2117–2126. [https://doi.org/https://doi.org/10.1016/0142-9612\(96\)00029-4](https://doi.org/https://doi.org/10.1016/0142-9612(96)00029-4).

- [41] F. Contu, B. Elsener, H. Böhni, A study of the potentials achieved during mechanical abrasion and the repassivation rate of titanium and Ti6Al4V in inorganic buffer solutions and bovine serum, *Electrochim. Acta.* 50 (2004) 33–41. <https://doi.org/10.1016/j.electacta.2004.07.024>.
- [42] V. Pejaković, V. Totolin, M. Rodríguez Ripoll, Tribocorrosion behaviour of Ti6Al4V in artificial seawater at low contact pressures, *Tribol. Int.* 119 (2018) 55–65. <https://doi.org/10.1016/j.triboint.2017.10.025>.
- [43] V.A. Borzova, K.A. Markossian, N.A. Chebotareva, S.Y. Kleymenov, N.B. Poliansky, K.O. Muranov, V.A. Stein-Margolina, V. V. Shubin, D.I. Markov, B.I. Kurganov, Kinetics of thermal denaturation and aggregation of bovine serum albumin, *PLoS One.* 11 (2016) 1–29. <https://doi.org/10.1371/journal.pone.0153495>.
- [44] M. Lundqvist, J. Stigler, G. Elia, I. Lynch, T. Cedervall, K.A. Dawson, Nanoparticle size and surface properties determine the protein corona with possible implications for biological impacts, *Proc. Natl. Acad. Sci. U. S. A.* 105 (2008) 14265–14270. <https://doi.org/10.1073/pnas.0805135105>.
- [45] M.A. Khan, R.L. Williams, D.F. Williams, Conjoint corrosion and wear in titanium alloys, *Biomaterials.* 20 (1999) 765–772. [https://doi.org/https://doi.org/10.1016/S0142-9612\(98\)00229-4](https://doi.org/https://doi.org/10.1016/S0142-9612(98)00229-4).

- [46] N. Gao, C.T. Wang, R.J.K. Wood, T.G. Langdon, Tribological properties of ultrafine-grained materials processed by severe plastic deformation, *J. Mater. Sci.* 47 (2012) 4779–4797. <https://doi.org/10.1007/s10853-011-6231-z>.
- [47] X. Chen, Z. Han, X. Li, K. Lu, Lowering coefficient of friction in Cu alloys with stable gradient nanostructures, *Sci. Adv.* 2 (2016) 1–8. <https://doi.org/10.1126/sciadv.1601942>.
- [48] J. Perret, E. Boehm-Courjault, M. Cantoni, S. Mischler, A. Beaudouin, W. Chitty, J.P. Vernot, EBSD, SEM and FIB characterisation of subsurface deformation during tribocorrosion of stainless steel in sulphuric acid, *Wear.* 269 (2010) 383–393. <https://doi.org/10.1016/j.wear.2010.04.023>.
- [49] M. Favero, P. Stadelmann, S. Mischler, Effect of the applied potential of the near surface microstructure of a 316L steel submitted to tribocorrosion in sulfuric acid, *J. Phys. D. Appl. Phys.* 39 (2006) 3175–3183. <https://doi.org/10.1088/0022-3727/39/15/S07>.