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Short communication

## Fretting corrosion behaviour of Ti–6Al–4V alloy in artificial saliva containing varying concentrations of fluoride ions<sup>☆</sup>

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## ABSTRACT

The present communication addresses the fretting corrosion behaviour of Ti–6Al–4V alloy in artificial saliva containing 0, 190, 570 and 1140 ppm of fluoride ions. The fretting corrosion behaviour of Ti–6Al–4V alloy was evaluated based on the change in free corrosion potential (FCP) measured as a function of time. The wear morphology and surface profile of the fretted zone, assessed by scanning electron microscopy and non-contact optical profilometer, were used to ascertain the wear mechanism. The cathodic shift in FCP observed with the onset of fretting indicates damage of the passive film. After the fretting motion is ceased, an instantaneous repassivation of Ti–6Al–4V alloy is observed only in artificial saliva. The negative influence of fluoride ions on passive film formation hinders instantaneous repassivation of the damaged areas of the fretted zone. The morphology of the fretted zone reveals the occurrence of adhesive galling in all the cases. The wear volume of the fretted zone of Ti–6Al–4V alloy in artificial saliva free of fluoride ions is  $3.26 \times 10^{12} \text{ nm}^3$ . In presence of 190 ppm of fluoride ions in artificial saliva, the wear volume is increased from  $3.26$  to  $9.87 \times 10^{12} \text{ nm}^3$ . However, the wear volume is reduced to  $6.95 \times 10^{12} \text{ nm}^3$  and  $3.60 \times 10^{11} \text{ nm}^3$  at 570 and 1140 ppm of fluoride ions, respectively. The change in contact configuration from alumina–titanium to titanium-coated alumina–titanium reduced the mutual solubility between alumina and titanium, the extent of trapping and grinding of the wear debris and the wear rate of Ti–6Al–4V alloy in artificial saliva containing 1140 ppm of fluoride ions. The study reveals that the fretting corrosion behaviour of Ti–6Al–4V alloy in artificial saliva shows a strong dependence on the fluoride ion concentration.

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### 1. Introduction

Titanium and titanium alloys are widely used as orthopaedic and dental implants due to their low density, excellent biocompatibility, corrosion resistance and mechanical properties [1–3]. One of the important reasons for choosing them is the ability of the naturally formed highly stable passive oxide layer, typically of 4–6 nm thickness that provides an excellent corrosion protection. However, this passive oxide layer possesses inferior mechanical properties. It has been shown that the naturally formed passive oxide layer could be disrupted at very low shear stresses, even by rubbing against soft tissues [4]. Fretting and sliding wear conditions lead to fracture of the passive oxide layer [5–12].

Fretting corrosion is the deterioration of materials that occurs at the interface of contacting surfaces due to the occurrence of small oscillatory movements ( $<100 \mu\text{m}$ ) between them in pres-

ence of a corrosive medium. Fretting corrosion is a major mode of failure of hip and knee implants as well as in dental implants [9]. In orthopaedic implants, fretting corrosion causes accumulation of wear debris in the surrounding tissues, release of metal ions into the human body and loosening of the femoral stem that eventually leads to failure of the total joint prosthesis [10]. In dental implants, fretting motion is induced by the biting force, mastication on the implant/abutment or on the abutment/ceramic crown [9,11]. Fretting corrosion would lead to toxicity, reddening and allergic reactions of the skin, inflammation of tissues, etc. [12]. The tribocorrosion behaviour of bare and surface modified stainless steel, CP-Ti, Ti–6Al–4V alloy and CoCrMo alloy in simulated body fluids/artificial saliva were studied by many researchers [13–28]. These *in vitro* studies on tribocorrosion provides a good understanding of the stability of the passive film, susceptibility of the material for corrosion upon removal of the passive film, extent of damage of the material, nature of particulate debris generated and the repassivation ability. It is evident from these studies that fracture of the passive oxide layer and its subsequent removal, damage of the contact zone and, the extent of particulate debris generation are mainly influenced by the mechanical forces while corrosion and repassivation of the material is largely influenced by the corrosivity of the

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medium. Damage of the passive oxide layer present on these materials would occur by any mechanical force. Hence, repassivation assumes significance in terms of the stability of the material.

In recent years, there has been a rapid increase in the utilization of fluorinated prophylactic gels and rinses in the odontological field. Many commercially available fluorinated gels contain very high concentrations of fluoride ions, up to 10,000 ppm (1 wt.%), with a pH, ranging between 7.2 and 3.2 [29]. The regular use of fluoride-containing toothpastes and mouthwashes is recommended to reduce the risk of dental caries [30,31]. However, fluoride ions have been shown to cause a deleterious influence on the corrosion resistance of titanium and its alloys [29,32–40]. These studies were performed under static conditions in which in spite of the negative influence of fluoride ions, titanium and its alloys exhibit passive film formation. Hence, it will be of much interest to ascertain whether the fluoride ions would allow passive film formation under fretting conditions. In this perspective, the present study aims to evaluate the influence of fluoride ions (190, 570 and 1140 ppm) on the fretting corrosion behaviour of Ti–6Al–4V alloy in artificial saliva.

## 2. Experimental details

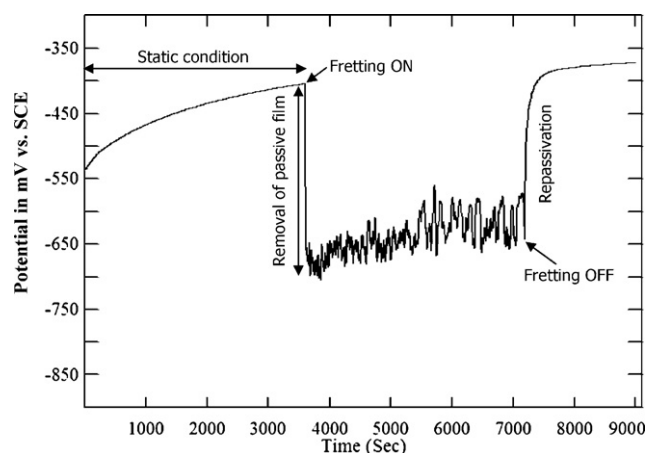
The fretting corrosion behaviour of Ti–6Al–4V alloy in artificial saliva containing varying concentrations of fluoride ions was studied using a fretting corrosion test assembly (Wear and Friction Tech., Chennai, India). The details of the fretting corrosion test assembly were described in our earlier papers [25–27]. Artificial saliva, having a chemical composition (in kg/m<sup>3</sup>) of 0.4 KCl, 0.4 NaCl, 0.6841 CaCl<sub>2</sub>, 0.69 NaH<sub>2</sub>PO<sub>4</sub>, 0.004 Na<sub>2</sub>S and 1 NH<sub>2</sub>CONH<sub>2</sub> (pH: 5.3) (commonly referred as Fusayama Meyer solution) was used as the base electrolyte solution. The fluoride ions having a concentration of 190, 570 and 1140 ppm were added to the base electrolyte as NaF. A normal load of 3 N, an oscillating frequency of 5 Hz and a linear peak-to-peak displacement amplitude of 180 μm were used as the fretting corrosion test parameters. All the tests were performed for 18,000 fretting cycles. Ti–6Al–4V alloy discs (composition in wt.-%: N: 0.02; C: 0.03; H: 0.011; Fe: 0.22; O: 0.16; Al: 6.12; V: 3.93 and Ti: balance) having a dimension of 20 mm diameter and 2 mm thick were used as the substrate. Before performing the fretting corrosion studies, the Ti–6Al–4V alloy discs were mechanically polished using various grades of SiC paper followed by 0.3 μm alumina paste to a mirror-like finish ( $R_a = 0.02 \mu\text{m}$ ) and rinsed with deionized water. Subsequently, they were pickled using a mixture of 35 vol.% HNO<sub>3</sub>–5 vol.% HF–60 vol.% H<sub>2</sub>O at 313 K for 60–70 s, thoroughly rinsed with deionized water and dried using a stream of compressed air. The cleaned Ti–6Al–4V alloy discs formed the working electrode while a saturated calomel electrode (SCE) and a graphite rod served as the reference and auxiliary electrodes, respectively. These electrodes were placed in the fretting corrosion cell in such a way that only 2 cm<sup>2</sup> area of the working electrode was exposed to the electrolyte solution. A ball-on-flat contact configuration that involves an 8 mm  $\varnothing$  alumina ball (G 10 finish; hardness: 1365 HV) moving against the stationary Ti–6Al–4V alloy disc was chosen so that large contact stresses could be achieved under low loads. The alumina ball/Ti–6Al–4V alloy flat contact was arranged in such a way that they were totally immersed in the electrolyte solution. The fretting corrosion cell was connected to a potentiostat/galvanostat/frequency response analyzer of ACM instruments (model: Gill AC). The fretting corrosion experiments were performed under conditions involving free (open circuit) potential and no additional potential was imposed by the potentiostat. The change in free corrosion potential (FCP), (i.e., potential of Ti–6Al–4V alloy measured after immersion in the electrolyte solution in open circuit conditions) measured as a function of time was used to

evaluate the performance of Ti–6Al–4V alloy under fretting conditions. Before performing the fretting corrosion experiment, the Ti–6Al–4V alloy was kept in the electrolyte solution and allowed to stabilize for 60 min. The fretting corrosion experiments were repeated at least three times to check the reproducibility of the test results. It is important to maintain uniformity in mechanical polishing using various grades of SiC paper and alumina paste, surface finish ( $R_a = 0.02 \mu\text{m}$ ), etching using HNO<sub>3</sub>–HF–H<sub>2</sub>O mixture at the recommended temperature and time, rinsing using deionized water, drying and stabilization by immersing the sample in the electrolyte solution for 60 min to ensure reproducibility of the test results. The variation in FCP of Ti–6Al–4V alloy measured as a function of time and, the restoration ability after the fretting motion ceases, were used to assess its performance under fretting corrosion conditions. The morphological features of the fretted zone were assessed using scanning electron microscopy (SEM). The 3-dimensional surface profile and depth of the fretted zone was assessed using a non-contact optical surface profilometer (Zygo NewView™ 6000 Series). The diameters of the wear scar, both in the direction of fretting and in perpendicular to it was measured to calculate the according to the equation proposed by Klaffke [41]. The wear scar on the alumina ball was assessed by optical microscopy.

## 3. Results and discussion

### 3.1. Change in FCP as a function of time

The change in FCP of Ti–6Al–4V alloy in artificial saliva measured before the onset of fretting, during fretting and after the fretting motion is ceased, as a function of time, is shown in Fig. 1. The measurements made in triplicate confirm reproducibility of the trend as well as the magnitude of change in FCP with time. Before the onset of fretting, the Ti–6Al–4V alloy was allowed to stabilize in artificial saliva for 60 min. During this period, the FCP of the alloy exhibits an anodic shift (from –535 to –404 mV vs. SCE), suggesting thickening of the passive film. With the onset of fretting, a sudden drop (cathodic shift) in FCP (from –404 to –698 mV vs. SCE) is observed. A surge in the anodic current is also observed at this point (not shown in Fig. 1). A similar trend of decrease in FCP and an increase in anodic current with the onset of fretting have been made earlier by many researchers [15–18]. It has been established that the potential of an electrode shifts in the noble direction when a passive film grows on the surface with a conse-



**Fig. 1.** Change in free corrosion potential (FCP) of Ti–6Al–4V alloy measured as a function of time during fretting corrosion in artificial saliva [conditions: load: 3 N; frequency: 5 Hz; peak-to-peak amplitude: 180 μm; number of fretting cycles: 18,000].

quent decrease in anodic current. On the contrary, the potential of an electrode shifts in the active direction upon damage or under partial/complete removal of the passive film, with a consequent increase in the anodic current [20]. Hence, the sudden drop in FCP (from  $-404$  to  $-698$  mV vs. SCE in about 30 s) observed with the onset of fretting (Fig. 1) is due to the removal of the passive oxide layer induced by fretting, suggesting the increase in susceptibility of Ti-6Al-4V alloy for corrosion. Ponthiaux et al. [21] have reported that the FCP of titanium during corrosion-wear test is quite close to that of a freshly ground material in the electrolyte. The extent of cathodic shift in FCP (294 mV) observed in this study further confirms the removal of the passive layer with the onset of fretting and increase in corrosion susceptibility of Ti-6Al-4V alloy in artificial saliva. During fretting, some fluctuations in FCP of Ti-6Al-4V alloy are observed. This is due to the periodic removal (depassivation) and growth (repassivation) of the passive film in the fretted zone. The fluctuations in FCP observed during fretting are due to the establishment of a dynamic equilibrium between depassivation and repassivation [17,18,20–22]. When the fretting motion is ceased, the FCP of Ti-6Al-4V alloy exhibits an anodic shift, suggesting the occurrence of repassivation of the active area of the fretted zone.

The change in FCP of Ti-6Al-4V alloy in artificial saliva containing 190, 570 and 1140 ppm of fluoride ions, measured as a function of time, are shown in Fig. 2(a)–(c), respectively. The measurements made in triplicate confirm the reproducibility of the trend as well as the magnitude of change in FCP with time. During the initial stabilization period of 60 min, a shift in FCP towards the anodic direction (from  $-586$  to  $-470$  mV vs. SCE) following thickening of the passive film is observed only in artificial saliva containing 190 ppm of fluoride ions. The extent of anodic shift in FCP is marginal (from  $-630$  to  $-606$  mV vs. SCE) when the concentration of fluoride ion is 570 ppm while a reversal in trend (cathodic shift in FCP from  $-614$  to  $-687$  mV vs. SCE) is observed when the fluoride ion concentration is increased to 1140 ppm. This observation suggests the negative influence of fluoride ions on passivation of the alloy, a fact that has been reported earlier by many researchers [29–40]. Similar to the observations made in artificial saliva (Fig. 1), a sudden cathodic shift in FCP is observed with the onset of fretting at all concentrations of fluoride ions (Fig. 2(a)–(c)). The extent of cathodic shift in potential, however, is relatively less in presence of fluoride ions ( $\sim 175$ – $250$  mV) and it decreases with increase in concentration of fluoride ions from 190 to 1140 ppm. This is due to the negative influence of fluoride ions, which did not allow thickening of the passive film during the initial stabilization period of 60 min. Similar to the observations made in artificial saliva (Fig. 1), some fluctuations in FCP of Ti-6Al-4V alloy are observed at all concentrations of fluoride ions (Fig. 2(a)–(c)). However, the extent of fluctuation in FCP is relatively less in presence of fluoride ions and it decreased with increase in concentration of fluoride ions in artificial saliva. The negative influence of fluoride ions on the formation of passive film can be considered responsible for this behaviour. When the fretting motion is ceased, an anodic shift in FCP of Ti-6Al-4V alloy is observed at all concentrations of fluoride ions due to repassivation of the active area of the fretted zone. However, the rate of repassivation is not instantaneous in presence of fluoride ions. During the first 10 s of repassivation, the extent of anodic shift in FCP is 45, 10 and 9 mV for 190, 570 and 1140 ppm of fluoride ions as opposed to 100 mV in artificial saliva free of fluoride ions. The FCP fails to reach the initial steady state value (i.e., potential before the onset of fretting) when the concentration of fluoride ions are 190 and 570 ppm. Restoration of the passive film in the fretted zone depends on the extent of damage caused by fretting wear and, corrosion of the Ti-6Al-4V alloy accelerated by the formation of galvanic cell between the 'active' fretted zone and the 'passive' unworn area. In presence of fluoride ions, the formation of a gal-

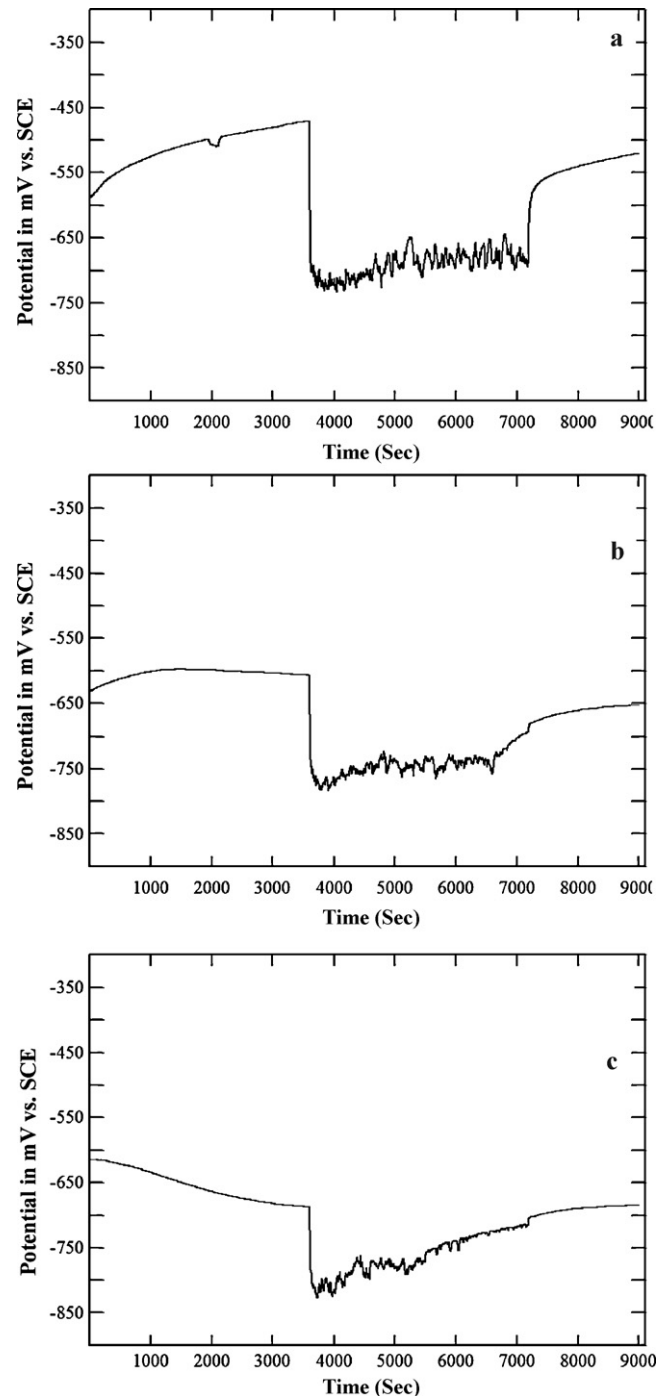
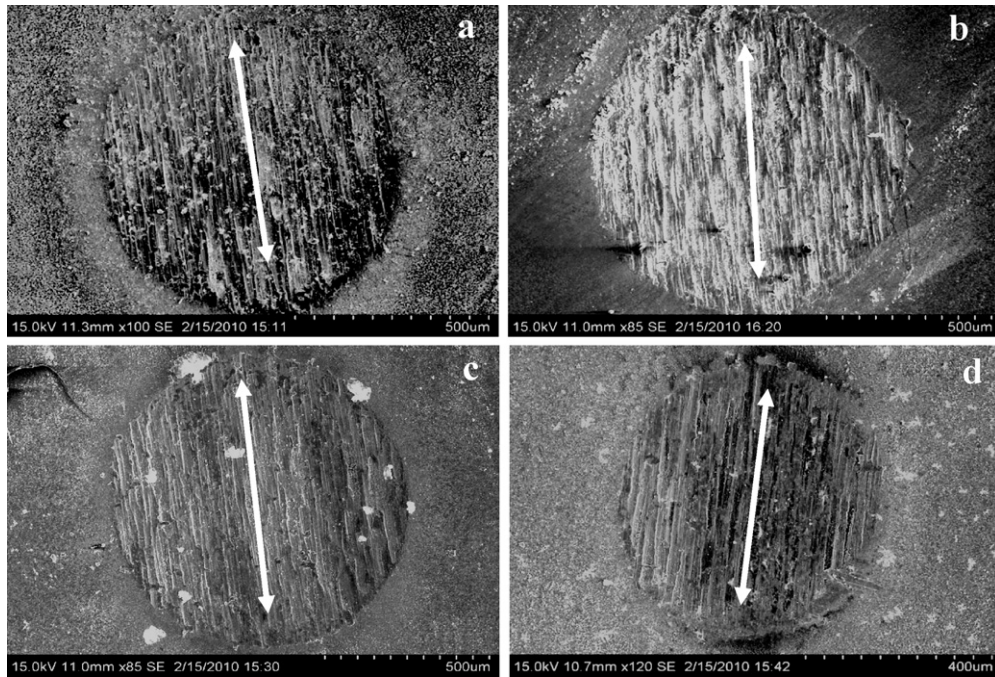


Fig. 2. Change in free corrosion potential (FCP) of Ti-6Al-4V alloy measured as a function of time during fretting corrosion in artificial saliva containing varying concentrations of fluoride ions: (a) 190 ppm  $F^-$ ; (b) 570 ppm  $F^-$ ; and (c) 1140 ppm  $F^-$  [conditions: load: 3 N; frequency: 5 Hz; peak-to-peak amplitude: 180  $\mu\text{m}$ ; number of fretting cycles: 18,000].

vanic cell, cathodic to anodic area ratio and the potential difference between them is further compounded by the higher corrosivity of the medium. Obviously, this would induce a strong influence on the extent of corrosion of Ti-6Al-4V alloy from the fretted zone. When the fretting motion is ceased, two competing reactions, corrosion that would cause a cathodic shift in potential and, repassivation of Ti-6Al-4V alloy in the electrolyte solution that would enable an anodic shift in potential, are likely to occur. These two processes will be in dynamic equilibrium and reach a steady state. The extent of damage of the fretted zone caused by fretting wear compounded



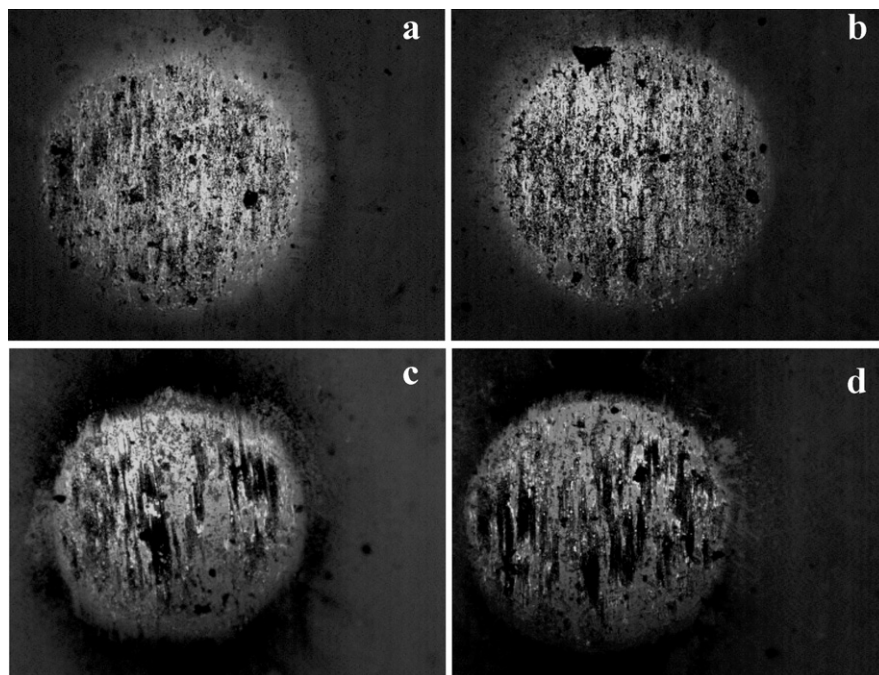


**Fig. 3.** Secondary electron images of fretted zone of Ti-6Al-4V alloy after subjecting it to fretting corrosion in artificial saliva containing varying concentrations of fluoride ions: (a) 0 ppm F<sup>-</sup>; (b) 190 ppm F<sup>-</sup>; (c) 570 ppm F<sup>-</sup>; and (d) 1140 ppm F<sup>-</sup> (fretting direction is indicated by double headed arrow) [conditions: load: 3 N; frequency: 5 Hz; peak-to-peak amplitude: 180  $\mu$ m; number of fretting cycles: 18,000].

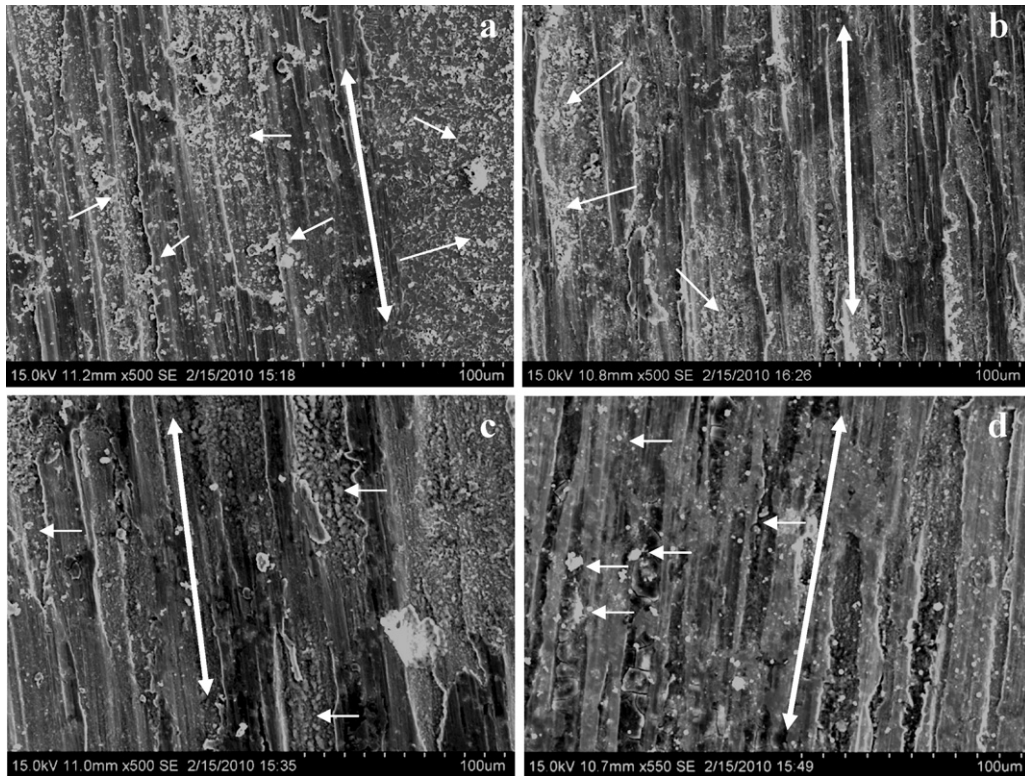
by the corrosive effect of fluoride ions limit the FCP of Ti-6Al-4V alloy to reach the initial steady state value when the concentration of fluoride ions are 190 and 570 ppm. The ability of the alloy to reach the initial steady state value at 1140 ppm of fluoride ions suggest that in spite of the increase in corrosivity of the medium, the rate of repassivation is increased possibly due to a decrease in the extent of damage of the fretted zone. Surface analytical characterization of the fretted zone by SEM and non-contact optical profilometer would provide a better insight on this phenomenon.

### 3.2. Surface analytical characterization of the fretted zone

The secondary electron images of the fretted zone of Ti-6Al-4V alloy, after subjecting it to fretting corrosion in artificial saliva containing 0, 190, 570 and 1140 ppm of fluoride ions are shown in Fig. 3(a)–(d), respectively. The fretted zone has experienced severe damage due to extensive shear deformation and ploughing action of the alumina ball while the surrounding areas of the fretted zone is relatively smooth in which particulate debris is smeared all around.



**Fig. 4.** Wear scar on the Al<sub>2</sub>O<sub>3</sub> ball fretted against Ti-6Al-4V alloy in artificial saliva containing varying concentrations of fluoride ions: (a) 0 ppm F<sup>-</sup>; (b) 190 ppm F<sup>-</sup>; (c) 570 ppm F<sup>-</sup>; and (d) 1140 ppm F<sup>-</sup> [conditions: load: 3 N; frequency: 5 Hz; peak-to-peak amplitude: 180  $\mu$ m; number of fretting cycles: 18,000] (images were acquired at  $\times 50$  in optical microscopy).



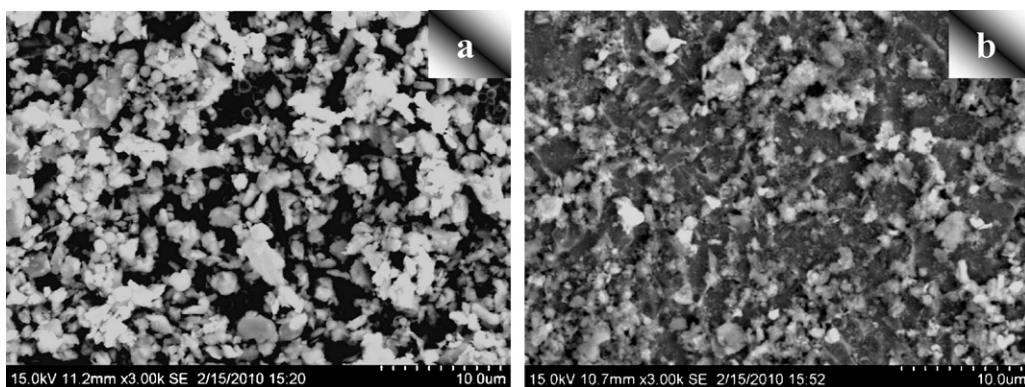
**Fig. 5.** Secondary electron images of the central region of the fretted zone of Ti-6Al-4V alloy after subjecting it to fretting corrosion in artificial saliva containing varying concentrations of fluoride ions: (a) 0 ppm F<sup>-</sup>; (b) 190 ppm F<sup>-</sup>; (c) 570 ppm F<sup>-</sup>; and (d) 1140 ppm F<sup>-</sup> (fretting direction is marked by double sided arrow; debris particles are marked by arrow marks) [conditions: load: 3 N; frequency: 5 Hz; peak-to-peak amplitude: 180 µm; number of fretting cycles: 18,000].

The morphological features of the central region of the fretted zone indicate transfer of material from Ti-6Al-4V alloy to the alumina ball. This type of morphological feature, commonly called as “prows” has been observed for systems that involves adhesive wear failure. Hence, it is evident that adhesive galling is the predominant wear mechanism when Ti-6Al-4V alloy is fretted against alumina ball in artificial saliva containing 0, 190, 570 and 1140 ppm of fluoride ions. Micro-welding between surface asperities, which occurs during the initial stages gets sheared and plucked away in the subsequent stages. Evaluation of the wear scars on the alumina ball confirms material transfer and the involvement of adhesive galling (Fig. 4).

A large number of particulate debris (size range: nano to sub-micron) are observed at the central region of the fretted zone of Ti-6Al-4V alloy (indicated by arrow marks in Fig. 5). Trapping of particulate debris between the contacting surfaces enables grind-

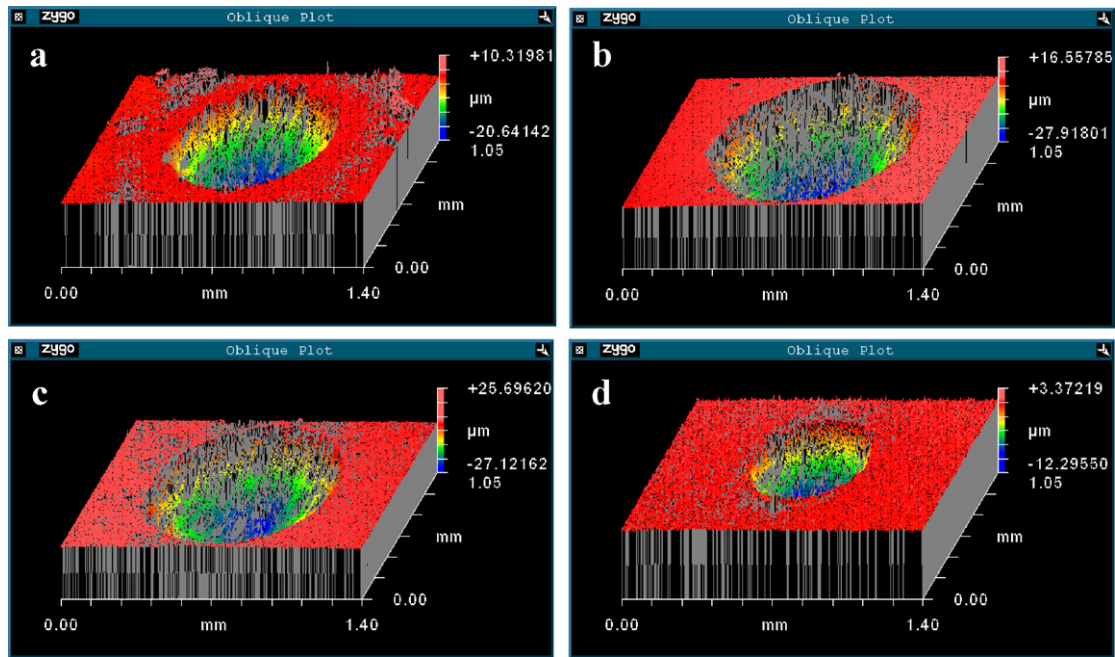
ing of the particles and a reduction in their size. The abrasive nature of these particles could promote an abrasive wear mechanism. The amount of particulate debris, however, is relatively less when the concentration of fluoride ions is 1140 ppm than at 0, 190 and 570 ppm. A comparison of the extent of accumulation of particulate debris at the edges of the fretted zone (Fig. 6) reveals that they are relatively less in artificial saliva containing 1140 ppm of fluoride ions than in other cases. Some of the particulate debris is agglomerated.

The 3-dimensional images of the fretted zone of Ti-6Al-4V alloy in artificial saliva containing varying concentrations of fluoride ions and the corresponding surface profiles (measured perpendicular to the fretting direction) are shown in Figs. 7 and 8, respectively. The wear volume of the fretted zone of Ti-6Al-4V alloy in artificial saliva free of fluoride ions is  $3.26 \times 10^{12}$  nm<sup>3</sup>. When 190 ppm of fluoride ions are added to artificial saliva, the wear volume is increased

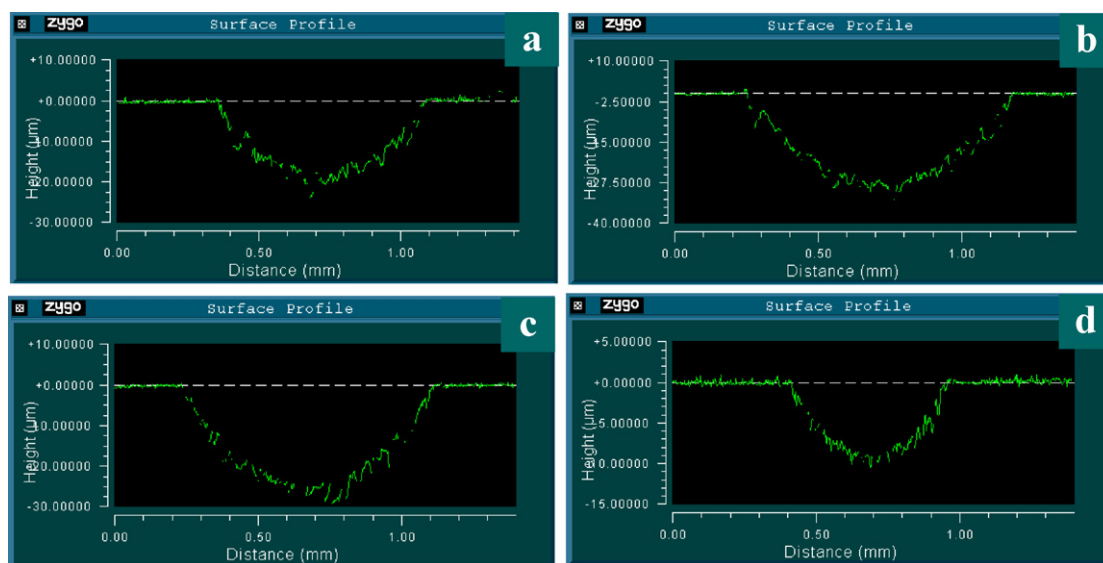


**Fig. 6.** Secondary electron images of the particulate debris generated during fretting corrosion of Ti-6Al-4V alloy in artificial saliva containing varying concentrations of fluoride ions: (a) 0 ppm F<sup>-</sup>; and (b) 1140 ppm F<sup>-</sup>; [conditions: load: 3 N; frequency: 5 Hz; peak-to-peak amplitude: 180 µm; number of fretting cycles: 18,000].





**Fig. 7.** 3-Dimensional image of the fretted zone of Ti-6Al-4V alloy after subjecting it to fretting corrosion in artificial saliva containing varying concentrations of fluoride ions: (a) 0 ppm F<sup>-</sup>; (b) 190 ppm F<sup>-</sup>; (c) 570 ppm F<sup>-</sup>; and (d) 1140 ppm F<sup>-</sup> [conditions: load: 3 N; frequency: 5 Hz; peak-to-peak amplitude: 180 μm; number of fretting cycles: 18,000].



**Fig. 8.** Surface profile of the fretted zone of Ti-6Al-4V alloy after subjecting it to fretting corrosion in artificial saliva containing varying concentrations of fluoride ions: (a) 0 ppm F<sup>-</sup>; (b) 190 ppm F<sup>-</sup>; (c) 570 ppm F<sup>-</sup>; and (d) 1140 ppm F<sup>-</sup> [conditions: load: 3N; frequency: 5 Hz; peak-to-peak amplitude: 180 μm; number of fretting cycles: 18,000].

from  $3.26$  to  $9.87 \times 10^{12} \text{ nm}^3$ . A reversal in trend is observed at 570 and 1140 ppm of fluoride ions. The wear volume is reduced to  $6.95 \times 10^{12} \text{ nm}^3$  and  $3.60 \times 10^{11} \text{ nm}^3$  at 570 and 1140 ppm of fluoride ions, respectively. This can be explained based on the effect of fluoride ions in artificial saliva to promote delamination. The highly corrosive fluoride ions seeps through the damages in the passive oxide layer induced by fretting and enables delamination of the oxide layer. This effect is well pronounced with increasing concentration of fluoride ions from 190 to 1140 ppm (Fig. 3). The extent of material transfer on the alumina ball is relatively high in artificial saliva containing 1140 ppm of fluoride ions (Fig. 4(d)), which supports the view that the presence of fluoride ions in artificial saliva tends to promote delamination of the oxide film. As a result, a major portion of the contacting bodies is changed from alumina-titanium

to titanium-coated alumina-titanium. This type of contact configuration would reduce the mutual solubility between alumina and titanium. Moreover, the change in contacting bodies decreased the extent of trapping and grinding of the wear debris and decreased the wear rate. The lower amount of particulate debris trapped at the central region (Fig. 5(d)) and the decrease in their extent of accumulation at the edges of the fretted zone (Fig. 6(b)) observed at 1140 ppm of fluoride ions further supports this phenomenon.

#### 4. Conclusions

During the initial stabilization period of 60 min, an anodic shift in FCP of Ti-6Al-4V alloy is observed in artificial saliva containing 0 and 190 ppm of fluoride ions due to thickening of passive film.

This effect is nullified at 570 ppm and reversed at 1140 ppm of fluoride ions in the electrolyte solution. With the onset of fretting, a rapid cathodic shift in FCP of Ti–6Al–4V alloy following damage of the passive film induced by fretting is observed in all the cases studied. The extent of cathodic shift in FCP is decreased with increase in fluoride ion concentration in the electrolyte solution. During fretting, fluctuations in FCP of Ti–6Al–4V alloy due to the periodic removal (depassivation) and growth (repassivation) of the passive film in the fretted zone is observed in all the cases studied. The extent of fluctuation is decreased with increase in fluoride ion concentration in the electrolyte solution. After the fretting motion is ceased, Ti–6Al–4V alloy exhibit repassivation in artificial saliva. The rate of repassivation is not instantaneous in presence of fluoride ions. During the first 10 s of repassivation, the extent of anodic shift in FCP is 45, 10 and 9 mV in artificial saliva containing 190, 570 and 1140 ppm of fluoride ions as opposed to 100 mV in the absence of fluoride ions. After the fretting motion is ceased, the FCP of Ti–6Al–4V alloy tends to reach the initial steady state value (i.e., potential before the onset of fretting) in artificial saliva. The extent of damage of the fretted zone caused by fretting wear compounded by the corrosive effect of fluoride ions limit the FCP of Ti–6Al–4V alloy to reach the initial steady state value when the concentration of fluoride ions are 190 and 570 ppm. In spite of the increase in corrosivity of the medium, the FCP of Ti–6Al–4V alloy reaches the initial steady state value at 1140 ppm of fluoride ions. Adhesive galling is the predominant wear mechanism of Ti–6Al–4V alloy when fretted against the alumina ball in artificial saliva containing 0, 190, 570 and 1140 ppm of fluoride ions. The occurrence of adhesive galling is supported by the material transfer on the alumina ball. The wear volume of the fretted zone of Ti–6Al–4V alloy subjected to fretting corrosion in artificial saliva free of fluoride ions is  $3.26 \times 10^{12} \text{ nm}^3$ . When 190 ppm of fluoride ions are added to artificial saliva, the wear volume is increased from  $3.26$  to  $9.87 \times 10^{12} \text{ nm}^3$ . The wear volume is reduced to  $6.95 \times 10^{12} \text{ nm}^3$  and  $3.60 \times 10^{11} \text{ nm}^3$  at 570 and 1140 ppm of fluoride ions, respectively. The highly corrosive fluoride ions seeps through the damages in the passive oxide layer induced by fretting and enables delamination of the oxide layer, which is supported by the higher amount of material transfer on the alumina ball at 1140 ppm of fluoride ions. The change in contact configuration from alumina–titanium to titanium–coated alumina–titanium reduced the mutual solubility between alumina and titanium, the extent of trapping and grinding of the wear debris and the wear rate of Ti–6Al–4V alloy in artificial saliva containing 1140 ppm of fluoride ions. Hence, it can be concluded that the fretting corrosion behaviour of Ti–6Al–4V alloy in artificial saliva is largely a function of the fluoride ion concentration present in it.

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