This is a repository copy of *Fretting corrosion of hafnium in simulated body fluids.*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/88416/

Version: Accepted Version

Article:

Rituerto Sin, J, Suñer, S, Neville, A et al. (1 more author) (2014) Fretting corrosion of hafnium in simulated body fluids. Tribology International, 75. 10 - 15. ISSN 0301-679X

https://doi.org/10.1016/j.triboint.2014.03.003

(c) 2014, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International http://creativecommons.org/licenses/by-nc-nd/4.0/

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

Fretting corrosion of hafnium in simulated body fluids

J. Rituerto Sin[a], S. Suñer[a], A. Neville[b], N. Emami[a]

[a] Division of Machine Elements, Department of Engineering Sciences and Mathematics, Luleå University of Technology, 971 87 Luleå, Sweden

[b] Institute of Engineering Thermofluids, Surfaces and Interfaces, School of Mechanical Engineering, University of Leeds, LS2 9JT Leeds, UK

Abstract

Hafnium has been suggested as an interesting material for biomedical applications due to its good biocompatibility and osteogenesis. However, its behaviour under fretting corrosion conditions, found in applications such as dental and joint implants, has not been studied in depth. A three-electrode electrochemical cell integrated with a ball-on-flat reciprocating tribometer was used to investigate the corrosion of hafnium and commercially pure (CP) titanium in simulated body fluids. An increased susceptibility to pitting corrosion was observed when hafnium was subjected to fretting. Open circuit potential measurements showed a more severe mechanical depassivation due to fretting in the case of CP titanium in comparison to hafnium. In addition, the anodic currents measured during potentiostatic tests were also higher for CP titanium.

Keywords: Hafnium; Biomaterial; Corrosion; Fretting corrosion

1. Introduction

The majority of metals used for biomedical applications owe their corrosion resistance to the formation of an oxide layer on their surface that isolates the bulk material from the corrosive media. In some applications, metals are exposed to small relative motion (fretting), which, combined with the corrosiveness of biological environments, leads to enhanced material degradation [1]. Mechanical damage could cause disruption of the passive layer which would leave the bulk material exposed to the corrosive media, leading to the release of metallic particles and ions into the body. The released degradation products can induce a number of biological responses such as inflammation, hypersensitivity reactions or allergy that can lead to the failure of the implant [2]. In addition, fretting corrosion can accelerate crack initiation on the materials and lead to early failure of metallic devices [1].

Fretting corrosion can be found in fracture fixation screws and plates, dental implants and joint implants [3] and [4]. Titanium and titanium alloys are used for some of these applications due to their excellent corrosion resistance and biocompatibility. However, they show relatively poor wear characteristics that may lead to the release of degradation products under wear-corrosion conditions [5]. The protective oxide film can be damaged not only when rubbed against a hard surface but also against soft tissues [6]. In spite of their good biocompatibility, titanium particles can induce the release of osteolytic cytokines involved in implant loosening [7] and [8]. In addition, metallic particles can be disseminated in the body and accumulated in organs such as the liver and kidneys [9]. Research on the possibilities of new biocompatible materials that generate less degradation products could lead to a reduced risk of adverse biological reactions and improved outcomes.

Hafnium is a transition metal with high ductility and strength, and good resistance to corrosion and mechanical damage [10]. A very protective oxide layer, mainly formed by HfO_2 [11], provides excellent corrosion resistance. Various studies have shown that hafnium has a good biocompatibility and osteogenesis [12] and a tissue response similar to that observed for titanium [13]. However, there is limited information about the behaviour of hafnium in biological environments. Despite the passive state and the good corrosion behaviour of the material in simulated body fluids, a tendency to suffer from pitting corrosion has been reported in previous studies [14]. To date, the behaviour of hafnium in biological environments under fretting corrosion conditions has not been studied in depth. In the present study, electrochemical techniques have been used in order to investigate the effect of fretting on the corrosion behaviour of hafnium, and to assess the potential of the material to be used in biomedical applications.

2. Materials and methods

2.1. Preparation of specimens and electrolyte solutions

Commercially pure titanium (Grade 2) and commercially pure hafnium rods (GfE Metalle und Materialien GmbH, Germany) were used in this study. Plates of 6 mm thickness and 25 mm diameter were prepared from the initial rod. Samples were polished with silicon carbide (SiC) paper up to 1200 grit followed by a 9 µm and a 3 µm diamond paste. Colloidal silica suspension was employed for the final polishing. Samples were cleaned and rinsed with distilled water and ethanol before they were assembled into the measurement cell.

In order to simulate body fluids, 25% bovine calf serum solution (Sigma-Aldrich, USA) was used. In addition, 0.9% NaCl solution was used in to isolate the effect of the organic species (proteins, amino acids, etc.) from the saline environment. All tests were conducted at 37 °C.

2.2. Microhardness measurements

A Matsuzawa MXT-CX microhardness tester (Matsuzawa Co., Japan) was used to study the microhardness of CP titanium and hafnium. Five measurements were performed on each sample to ensure repeatability.

2.3. Fretting corrosion tests

A ball-on-flat reciprocating tribometer (CETR-UMT-2, Bruker Nano Inc., USA) was used to perform the fretting corrosion experiments. Samples were mounted on a polyoxymethylene holder and were fretted against a stationary silicon nitride ball (grade 10) of 12 mm diameter (Redhill Precision, Czech Republic). A normal load of 10 N was used (490 MPa and 530 MPa Hertzian initial mean contact pressure for CP titanium and hafnium, respectively). The frequency was controlled at 1 Hz and the maximum stroke length was 120 µm. Tests were performed for 3600 cycles. A three-electrode electrochemical cell was integrated into the system to perform the fretting corrosion tests. The schematic diagram of the fretting corrosion set up is shown in Fig. 1. The electrochemical cell consisted of a platinum wire used as the counter-electrode, an Ag/AgCl electrode (3 M KCl) used as the reference electrode, and the studied material was used as the working electrode. All potentials are given with respect to the Ag/AgCl electrode, which is 196 mV on the standard hydrogen electrode scale. Three different electrochemical tests were performed in this study.

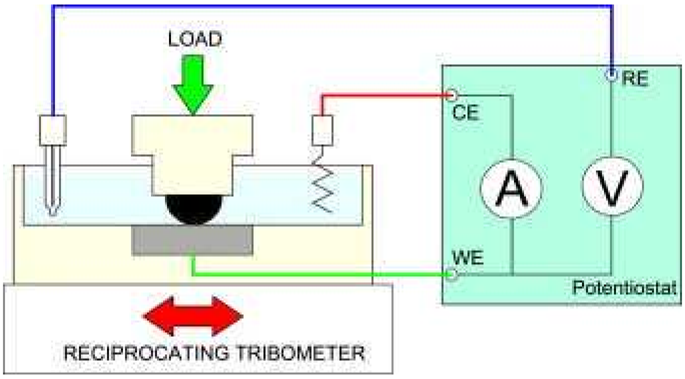

Fig. 1. Schematic representation of the experimental set up.

2.3.1. Cyclic polarisation scans

Cyclic polarisation scans were performed on hafnium under fretting conditions in 0.9% NaCl and 25% serum solution. Before the cyclic polarisation scan, samples were immersed in each solution for 3600 s to stabilise them. Thereafter, fretting was started and the open circuit potential (OCP) was measured until a stable value was reached. Samples were polarised in the cathodic direction down to −1 V (vs Ag/AgCl) at a scan rate of 10 mV s^{-1}. Finally, the cyclic polarisation test was performed at a scan rate of 2 mV s^{-1} up to a potential of 3 V (vs Ag/AgCl) or until the current density limit (800 µA cm^{-2}) was reached. Tests were repeated three times.

2.3.2. Open circuit potential (OCP)

The OCP of the studied materials was measured as a function of time. The test consisted of three different phases. First, the sample was immersed in static conditions for 3600 s. Second, the specific load was applied and the fretting was started. Finally, after 3600 cycles fretting was stopped and the sample was unloaded. Tests were repeated three times. Scanning electron microscopy (HR-SEM Merlin Zeiss, Germany) was used to analyse the worn surfaces.

2.3.3. Potentiostatic tests

A constant potential of 0 V (vs Ag/AgCl), which is in the passive regime for the metals [14], was applied to monitor the current as a function of time and the effect of the mechanical depassivation due to fretting. The tests consisted of three phases:

first, the current was monitored at 0 V for 3600 s before the start of fretting; the sample was fretted for 3600 s. Finally, fretting was stopped and currents were monitored for 3600 s. Tests were repeated three times.

3. Results

3.1. Microhardness measurements

Table 1 shows the microhardness values measured for each material. Hafnium showed higher microhardness (HV500 g) in comparison to CP titanium.

Table 1. Microhardness ($HV_{500\ g}$) of hafnium and CP titanium.

	$HV_{500\ g}$
Hf	213±3
CP Ti	163±6

3.2. Cyclic polarisation measurements

The potentiodynamic scans of hafnium in 0.9% NaCl and 25% serum solutions (Fig. 2) showed a breakdown of the passive layer due to the formation of pits on the surface. The formation of the pits and the subsequent corrosion appeared to be retarded in 25% serum solution (Table 2). Once the potential scan was reversed, pit propagation would cause currents to continue increasing. The currents reached in the saline solution were generally higher than in the serum solution. The repassivation potential, at which currents reached the original passive values, was slightly higher in the case of 25% serum solution.

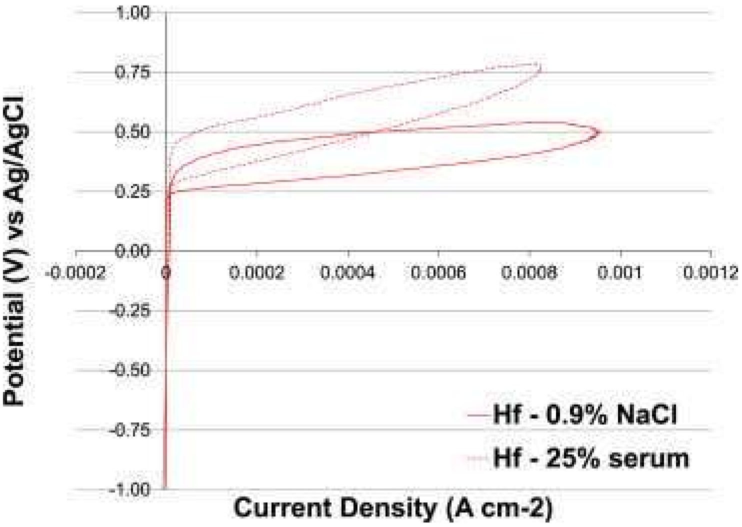

Fig. 2. Cyclic polarisation of hafnium in fretting conditions in 0.9% NaCl and 25% serum solution.

Table 2. Comparison of the breakdown potential of hafnium in fretting conditions ($E_b^{fretting}$) and in static conditions (E_b^{static}) in 0.9% NaCl and 25% serum.

	$E_b^{fretting}$ (V)	E_b^{static} (V) [13]
0.9% NaCl	0.273±0.003	1.387±0.080
25% serum	0.405±0.007	2.331±0.128

3.3. Open circuit potential (OCP) measurements

The OCP measurements are shown in Fig. 3. The tests can be divided in three phases: from A to B (in Fig. 3), which represents the period before fretting started. An anodic shift was observed which suggested a thickening of the passive layer. At point B (in Fig. 3), fretting started and the OCP values dropped towards more active values. The OCP reached a minimum value immediately after the onset and it tended to increase towards less active values due to the equilibrium between the mechanical depassivation and electrochemical repassivation. Once the fretting was stopped at point D (in Fig. 3), the OCP recovered towards more positive values indicating repassivation of the material. The values of the maximum variation of the OCP and the average variation during fretting are shown in Table 3. Despite titanium showing more noble OCP values in static conditions, the variation of the values due to fretting was larger than in the case of hafnium in the two studied solutions. The average drop in the OCP (ΔE_{avg}) due to fretting was found to be greater for CP titanium, being more pronounced in 25% serum than in the saline solution. The initial depassivation peak (ΔE_{max}) was more acute in the case of CP titanium in both solutions. Furthermore, the depassivation peak was more pronounced in 25% serum for hafnium and CP titanium.

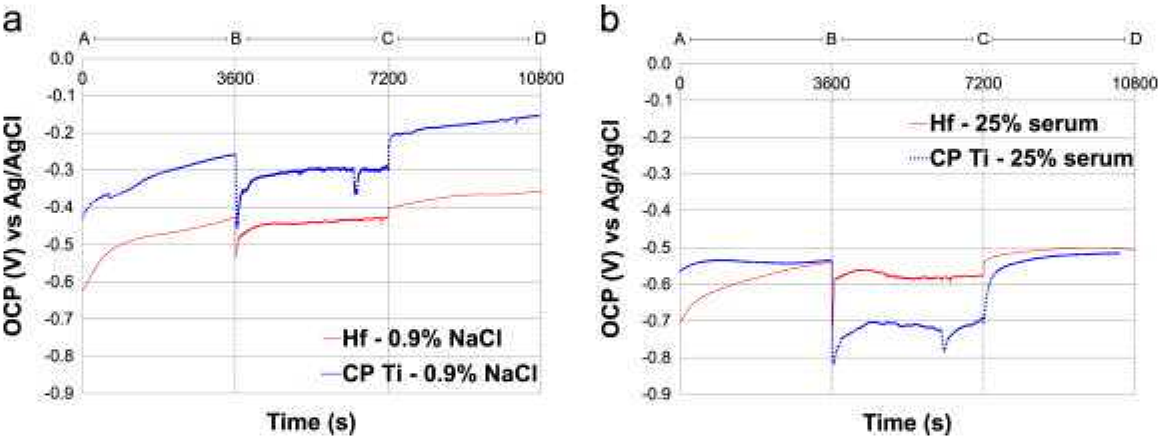

Fig. 3. Effect of fretting on the open circuit potential of hafnium and CP titanium in (a) 0.9% NaCl and (b) 25% serum.

Table 3. Maximum drop (ΔE_{max}) and average variation (ΔE_{avg}) of the OCP due to mechanical depassivation caused by fretting.

	ΔE_{max} (mV)	ΔE_{avg} (mV)
Hf		
0.9% NaCl	79.2±25.9	36.9±1.6
25% serum	151.9±36.3	39.9±19.7
CP Ti		
0.9% NaCl	227.3±43.6	81.3±5.5
25% serum	260.4±22.0	171.9±21.3

The secondary electron images of the fretted zones after 3600 cycles (Fig. 4 and Fig. 5) show an extended worn area due to penetration of the counterface and wear of the materials. The internal zone of the wear scar shows a more severe degradation whereas material accumulation was observed on the external zones. The wear scar observed in the case of hafnium was smaller than that of CP titanium in 0.9% NaCl solution (Fig. 4a and c). Although both materials showed similar abrasion marks in the direction of the movement (Fig. 4b and d), CP titanium showed a more acute material detachment in the centre of the scar. In the case of the 25% serum solution (Fig. 5), both hafnium and CP titanium show marks of material detachment and accumulation of wear debris in the craters. Cracking is observed in zones of accumulated debris (Fig. 5b and d), as well as on the surface of the craters. In addition, abrasive wear of the materials can be observed.

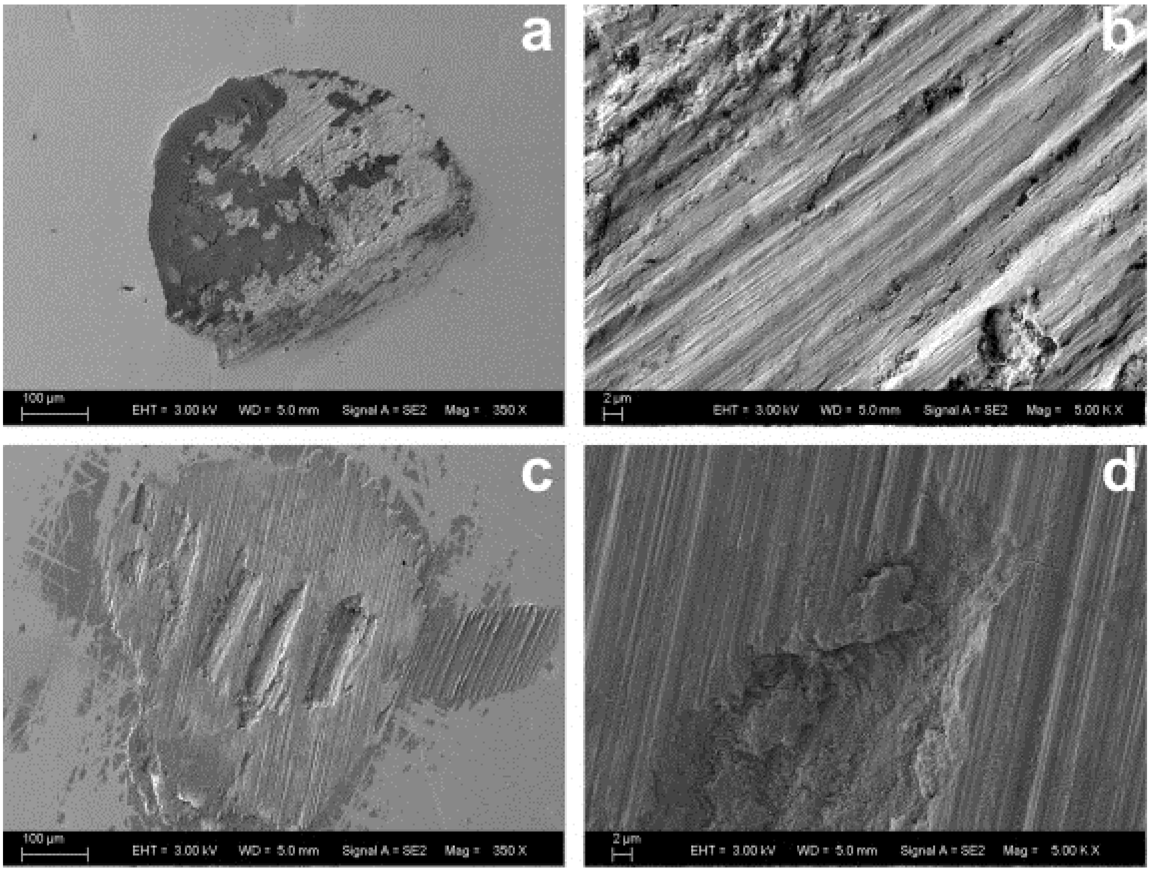

Fig. 4. SEM images of the worn surface of (a, b) hafnium and (c, d) CP titanium in 0.9% NaCl solution.

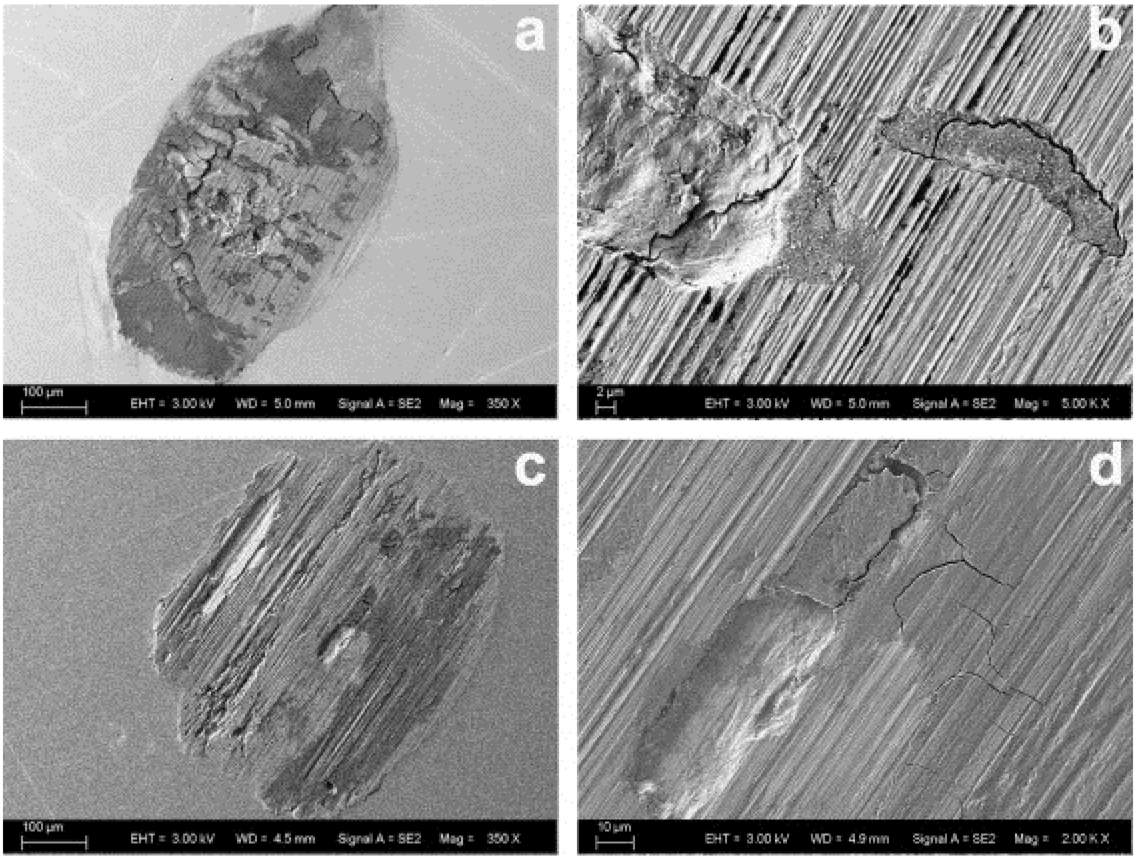

Fig. 5. SEM images of the worn surface of (a, b) hafnium and (c, d) CP titanium in 25% serum solution.

3.4. Potentiostatic tests

The evolution of the current measured in CP titanium and hafnium at a constant passive potential (0 V vs Ag/AgCl) is shown in Fig. 6. The test can be divided in three phases: from A to B, the samples were immersed in the solution and a potential in the passive range (0 V vs Ag/AgCl) was applied. The low currents indicated that both materials were in a passive state, as also shown in a previous study [14]. After that, from B to C, the onset of the fretting led to removal of the passive film, causing a sudden increase in the current due to the exposition of the unprotected metal to the media. After an initial peak, the current decreased towards lower values due to the equilibrium between mechanical repassivation and electrochemical depassivation. Finally, from C to D, the low currents were quickly recovered when the mechanical damaging stopped, indicating that the passive layer had reformed.

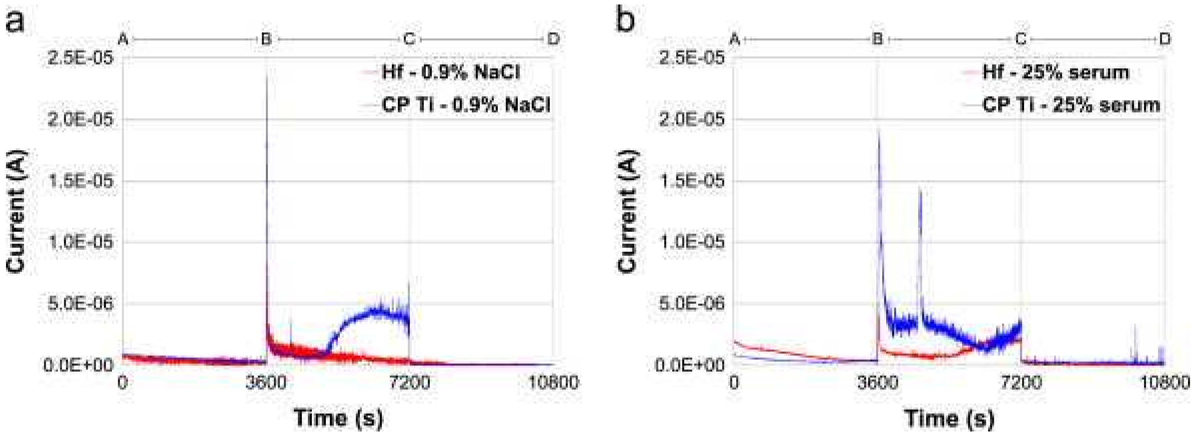

Fig. 6. Evolution of the current as a function of time at a potential of 0 V in (a) 0.9% NaCl and (b) 25% serum.

The peak current and the average current measured are summarised in Table 4. The peak currents measured in the case of CP titanium were higher compared to hafnium, indicating a more severe initial depassivation. The average currents were higher in the case of CP titanium as well; however, Fig. 6a shows that initially the currents measured were similar in both materials, increasing after this initial stage in the case of CP titanium. This could have been caused by a higher wear and an increased depassivated area.

Table 4. Anodic peak current (I_{peak}) and average current (I_{avg}) measured during fretting at a potential of 0 V (vs Ag/AgCl) for Hf and CP Ti.

	I_{peak} (μA)	I_{avg} (μA)
Hf		
0.9% NaCl	6.01±3.24	0.86±0.25
25% serum	4.35±2.15	1.03±0.22
CP Ti		
0.9% NaCl	14.42±6.16	2.82±0.55
25% serum	23.67±6.35	3.57±0.52

4. Discussion

The behaviour of hafnium and CP titanium in fretting corrosion conditions has been studied in order to assess the corrosion of hafnium under a tribological action in simulated body fluids. Previous studies have shown a tendency of hafnium to suffer from pitting corrosion in simulated body fluids [14]. The effect of fretting on the breakdown potential of hafnium was studied by means of cyclic polarisation scans. The breakdown potential observed when hafnium was subjected to fretting was drastically reduced in comparison to the values observed in static conditions (Table 2). Breakdown potential was higher in the serum solution, which suggested that the presence of organic species retarded the formation of corrosion pits and increased the repassivation potential when the pits were formed. This could be due to the negative charge of proteins at the pH of the studied solutions (pH 7.4) [15], which would lead to attractive forces towards the anodically polarised surface. Negatively charged proteins and chlorides, which are known to be a cause of localised corrosion [16], would compete to adsorb on the surface, retarding the formation of pits [17]. The currents reached due to the propagation of the pits were reduced when proteins were present in the media. Similar effects of the organic species have been reported in static conditions in previous studies [14].

The open circuit potential is commonly used as a qualitative indication of the corrosion regime in which a material resides [18]. Both CP titanium and hafnium were in the passive state when immersed in saline and serum solutions. Both materials showed an anodic shift before the onset of the fretting that suggested thickening of the passive film. When fretting started a sudden cathodic shift was observed. The mechanical damage on the surface exposed the bulk metal to the corrosiveness of the media; therefore the OCP value was much closer to that of the fresh material [19]. The OCP values measured correspond to the mixed potential between the fretted and the unfretted areas. An initial peak in the cathodic direction was observed with the onset of the fretting. The initial peak was more prominent in the case of CP titanium, which suggested a more severe mechanical depassivation when fretting started. After the initial cathodic peak the OCP increased towards more anodic values due to the balance between the mechanical depassivation due to fretting and the electrochemical repassivation or reformation of the oxide layer due to the reaction of the materials with the oxygen in the solution [20]. The difference between the OCP value on the passive state and under fretting was smaller in the case of hafnium, suggesting less mechanical damage, which could be related to the higher hardness of the material (Table 1). This is also observed in the scanning electron micrographs (Fig. 4 and Fig. 5), where craters formed due to material detachment were detected, especially in the case CP titanium. The formation of such craters could be due to an accelerated crack formation caused by fretting, together with the corrosive action of the media. In the case of hafnium, a more severe damage is observed when immersed in 25% serum solution in comparison with the saline solution, which would also indicate the higher corrosiveness of the first solution. In addition to the cracking and delamination of the material, abrasive wear was also observed.

The evolution of the anodic current during the tribological tests under passive potential (0 V vs Ag/AgCl) showed higher corrosion currents for CP titanium under the studied conditions. A drastic increase of the current was observed with the onset of the fretting. The initial peak was higher for CP titanium in both 0.9% NaCl and 25% serum solutions, which could be caused by a more severe initial depassivation due to the lower hardness of the material. After the initial peak, the current values reached lower values and a tended to decrease, which could be due to the higher conformity of the contact due to wear of the material. The average currents measured for hafnium were lower than those for CP titanium in the saline solution and the 25% serum solution. In the case of hafnium in 0.9% NaCl solution, the currents remained relatively low during the time of the test; however, in the case of hafnium in 25% serum solution and CP titanium in both solutions, an increase of the current was observed during the test. Proteins could have had an effect on the passivation of the materials by restricting the diffusion of oxygen to the surface and making repassivation of the metal more difficult [15]. This negative effect of proteins on the repassivation of the metal would increase not only the corrosion but also the wear induced by corrosion; more severe crack propagation and delamination could take place and cause an increase in total wear-corrosion damage. In the case of CP titanium, the lower surface hardness might lead to increased mechanical damage and therefore more severe mechanical damage.

5. Conclusions

- The fretting corrosion behaviour of hafnium and CP titanium has been investigated. The main conclusions of this study are:
- Hafnium tended to suffer from pitting corrosion; its resistance was drastically decreased when the material was subjected to fretting. However, the organic species contained in the serum solution retarded the formation of pits and limited their propagation.
- Hafnium showed a passive state in both 0.9% NaCl and 25% serum solution under static conditions. The passive layer was damaged due to fretting; however, the mechanical depassivation was more severe in the case of CP titanium in comparison to hafnium. Both hafnium and CP titanium repassivated in the studied solutions when the fretting damage ceased.
- The damage produced due to fretting resulted in increased currents and therefore higher corrosion of the materials. Hafnium showed lower anodic currents in fretting than CP titanium.

Acknowledgements

This work was funded by the Centrum för Medicinsk Teknik och Physic (CMTF) and Kempe Stiftelserna.

References

[1] Hiromoto S, Mischler S. The influence of proteins on the fretting – corrosion Behaviour of a Ti6Al4V alloy. Wear 2006; 261:1002–11.

[2] Hallab NJ, Jacobs JJ. Biologic effects of implant debris. Bull NYU Hosp Jt Dis 2009; 67:182–8.

[3] Upadhyay D, Panchal MA, Dubey R, Srivastava V. Corrosion of alloys used in dentistry: a review. Mater Sci Eng A 2006; 432:1–11.

[4] Jacobs JJ, Gilbert JL, Urban RM. Current concepts review—corrosion of metal orthopaedic implants. J Bone Jt Surg 1998; 80:268–82.

[5] Geetha M, Singh A, Asokamani R, Gogia A. Ti based biomaterials, the ultimate

choice for orthopaedic implants—A review. Prog Mater Sci 2009; 54:397–425.

[6] Kumar S, Sankara Narayanan TSN, Ganesh Sundara Raman S, Seshadri SK. Evaluation of fretting corrosion behaviour of CP–Ti for orthopaedic implant applications. Tribol Int 2010; 43:1245–52.

[7] Taki N, Tatro JM, Nalepka JL, Togawa D, Goldberg VM, Rimnac CM, et al. Polyethylene and titanium particles induce osteolysis by similar, lymphocyte independent, mechanisms. J Orthop Res 2005; 23:376–83.

[8] Suñer S, Tipper JL, Emami N. Biological effects of wear particles generated in total joint replacements: trends and future prospects. Tribol—Mater Surf Interfaces 2012; 6:39–52.

[9] Urban RM, Tomlinson MJ, Hall DJ, Jacobs JJ. Accumulation in liver and spleen of metal particles generated at non-bearing surfaces in hip arthroplasty. J Arthroplast 2004; 19:94–101.

[10] Cerreta E, Yablinsky C, Gray G, Voge IS, Brown D. The influence of grain size and texture on the mechanical response of high purity hafnium. Mater Sci Eng A 2007; 456: 243–51.

[11] Badawy W, Al-Kharafi F. The electrochemical behaviour of naturally passivated hafnium inaqueous solutions of different pH. J Mater Sci 1999; 34:2483–91.

[12] Matsuno H, Yokoyama A, Watari F, UoM, Kawasaki T. Biocompatibility and osteogenesis of refractory metal implants, titanium, hafnium, niobium, tantalum and rhenium. Biomaterials 2001; 22:1253–62.

[13] Mohammadi S, Esposito M,Cucu M, Ericson LE, Thomsen P. Tissue response to hafnium. J Mater Sci: Mater Med 2001; 12:603–11.

[14] RituertoSin J, Neville A, Emami N. Corrosion and tribocorrosion of hafnium in simulated body fluids. J Biomed Mater Res Part B: Appl Biomater 2013

[15] Khan MA, Williams RL, Williams DF. The corrosion behaviour of Ti–6Al–4V, Ti–6Al–7Nb and Ti–13Nb–13Zr in protein solutions. Biomaterials 1999; 20:631–7.

[16] Macdonald DD. The point defect model for the passive state. J Electrochem Soc 1992;139:3434–49.

[17] Valero Vidal C, Igual Muñoz A. Electrochemical characterisation of biomedical alloys for surgical implants in simulated body fluids. Corros Sci 2008; 50: 1954–1961.

[18] Yan Y, Neville A, Dowson D. Tribo-corrosion properties of cobalt-based

medical implant alloys in simulated biological environments. Wear 2007; 263: 1105–1111.

[19] Sivakumar B, Kumar S, Narayanan T.Comparison of fretting corrosion behaviour of Ti–6Al–4V alloy and CP–Ti in Ringer's solution. Tribol—Mater Surf Interfaces 2011; 5:158–64.

[20] Dimah M, Devesa Albeza F, Amigó Borrás V, Igual Muñoz A. Study of the biotribocorrosion behaviour of titanium biomedical alloys in simulated body fluids by electrochemical techniques. Wear 2012; 294:409–18.