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Corrosion and tribocorrosion of hafnium in simulated body fluids

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Abstract: Hafnium is a passive metal with good biocompatibility and osteogenesis, however, little is known about its resistance to wear and corrosion in biological environments. The corrosion and tribocorrosion behavior of hafnium and commercially pure (CP) titanium in simulated body fluids were investigated using electrochemical techniques. Cyclic polarization scans and open circuit potential measurements were performed in 0.9% NaCl solution and 25% bovine calf serum solution to assess the effect of organic species on the corrosion behavior of the metal. A pin-on-plate configuration tribometer and a three electrode electrochemical cell were integrated to investigate the tribocorrosion performance of the studied materials. The results showed that hafnium has good corrosion resistance. The corrosion density currents measured in its passive state were lower than those measured in the case of CP titanium; however, it showed a higher tendency to suffer from localized corrosion, which was more acute when imperfections were present on the surface. The electrochemical breakdown of the oxide layer was retarded in the presence of proteins. Tribocorrosion tests showed that hafnium has the ability to quickly repassivate after the oxide layer was damaged; however, it showed higher volumetric loss than CP titanium in equivalent wear-corrosion conditions.

Key Words: hafnium, titanium, biomaterials, corrosion, tribocorrosion

INTRODUCTION

Hafnium is a metal included in the group 4 in the periodic table, together with titanium and zirconium. The metal was first identified by Dirck Coster and Georges de Hevesy in Copenhagen in 1923,[1] and owes its name to 'Hafnia', the Latin name for Copenhagen. Hafnium is always found associated with zirconium in ores and is primarily found in zircon, with a ratio Hf/Zr of about 2.5%.[2] Due to a number of interesting properties such as high ductility and strength, and resistance to corrosion and mechanical damage,[3] it has attracted interest for various applications. For instance, it is used as a control material for nuclear reactors and as an alloying element in some superalloys used in aircrafts engines.[4]

In 1984, Marcel Pourbaix included hafnium among the group of metals to be considered for surgical implants due to the passive state presented by the metal. However, due to the lack of information about its toxicity in the human body at that time, it was discarded from the final list of 13 metals to be theoretically considered.[5] The passive layer found on hafnium's surface, mainly formed of HfO2, is highly stable in neutral solutions.[6]

More recently, the properties of hafnium as an implant material have been investigated.[7,8] Matsuno et al.[7] implanted a number of refractory materials (titanium, hafnium, niobium, tantalum, and rhenium) in subcutaneous tissue and femoral bone marrow of rats, and performed histological observation and elemental mapping to evaluate the biocompatibility and osteogenesis of such materials. The results of the in vivo study showed that hafnium had good biocompatibility and osteogenesis. A different study on the tissue response to hafnium[8] showed similar response in soft and hard tissues in two different animal species (rat and rabbit), which suggests that hafnium could be an interesting material for biomedical applications.

Hafnium has also been investigated as an alloying element for titanium alloys. Titanium alloys are commonly used for biomedical applications such as dental implants, bone plates, and hip and knee implants. Titanium6%Aluminum-4%Vanadium (Ti-6Al-4V) is usually the material of choice. However, there are concerns regarding the toxicity of the alloying elements. Aluminium has been pointed out as a growth inhibitor of bone and possible cause of Alzheimer's disease.[9] In addition, studies have shown that vanadium shows cell toxicity[10] and this material could lead to cardiac and renal dysfunction.[11] These concerns enhance the need to investigate new alloying elements. Different Ti-Hf binary alloys have been reported in the literature. Wrought Ti-Hf alloys have shown a gradually increase in yield and tensile strength with increased amount of hafnium, up to 40%, at the same time the ductility decreased.[12] More recent studies also showed an increased yield and tensile strength and bulk hardness for cast Ti-Hf alloys.[13,14] The electrochemical behavior of this type of alloys is similar to pure titanium, showing excellent corrosion resistance.[15,16]

Titanium–Niobium–Hafnium–Zirconium (Ti-Nb-Hf-Zr) alloys have also been investigated.[17] These alloys have shown a low elastic modulus, which is beneficial to reduce the stress shielding effect and to enhance bone ingrowth. It has also been shown that cold work can be used to decrease the elastic modulus of this type of alloys, reaching values close to the elastic modulus of cortical bone.[18]

To date, the behavior of pure hafnium in a biological environment has not been studied in great depth. Little is known about the resistance of the passive layer under wear-corrosion conditions and the effect of proteins on its corrosion and tribocorrosion behavior. Thus, there exists a need for further studies of hafnium under biological conditions to determine the suitability of this material for biomedical applications. The present work studies the corrosion resistance of hafnium in simulated body fluids and the effect of wear on the system.

MATERIALS AND METHODS

Preparation of specimens and electrolyte solutions

CP titanium (grade 2) and commercially pure hafnium rods (GfE Metalle und Materialien GmbH, Germany) were used in this study. An abrasive cut-off machine

and a silicon carbide (SiC) cut-off disc were used to prepare plates of 6 mm thickness by 25 mm diameter from the initial rods. Specimens were cast in an epoxy mount and the epoxy-metal borders were sealed with silicon to avoid the presence of crevices. The plates were polished with SiC paper up to 1200 grit followed by a 9 mm and a 3 mm diamond paste. Finish polishing was accomplished with a colloidal silica suspension. Specimens were cleaned and rinsed with distilled water and ethanol before they were assembled into the measurement cell. Two different surface finishes were investigated to assess the effect of surface imperfections on the corrosion resistance of hafnium. The first group of specimens were studied immediately after polishing. The second group of specimens were scratched after polishing by means of a spherical stainless steel tip with a radius of 0.4 mm. An example of the resulting surface is shown in Figure 1.

To simulate body fluids, 25 and 50% bovine calf serum (Harlam Sera-Lab[VR], UK) solutions were used. In addition, 0.9% NaCl solution was used to isolate the effect of the organic species (proteins, amino acids, etc.) from the saline environment. All tests were conducted at 37 6 1°C.
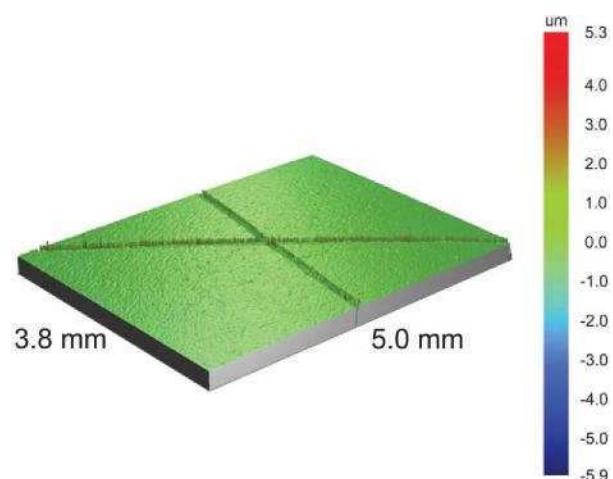

FIGURE 1. Resulting surface finish of a scratched specimen.

Electrochemical tests

All electrochemical measurements were performed using an Autolab PGSTAT302N potentiostat (Metrohm Autolab, The Netherlands). A three electrode electrochemical set-up was used. A platinum wire was used as a counter electrode, a Ag/AgCl electrode (3.0M KCl) was used as a reference electrode [196 mV vs. standard hydrogen electrode (SHE)] and the studied material acted as a working electrode. All potentials are given with respect to the Ag/AgCl electrode. Specimens were immersed in the solution at open circuit potential (OCP) for 60 min to stabilize them. Cyclic polarization tests were performed at 2 mV s^{-1} scan rate. The current density was limited to a maximum of 500 µA cm^{22}. All tests were repeated at least three times to ensure repeatability. Optical microscopy (Olympus Vanox-T, Olympus Optical, Japan) was used to analyze the surface of the specimens before and after measurements. A range of magnifications between 2.53 and 1003 was used.

Tribocorrosion tests

A tribocorrosion cell consisting of a three electrode electrochemical cell and a reciprocating tribological tester was used. All electrochemical measurements were performed using a potentiostat VersaSTAT 4 (Princeton Applied Research). The three-electrode cell configuration is the same as the earlier described, with a Ag/AgCl electrode as the reference electrode, a platinum (Pt) wire as counter electrode and the specimen as the working electrode. The sliding wear tests were performed in a reciprocating wear tester that conforms to ASTM G133. The materials were rubbed against a silicon nitride ball with 12 mm diameter. A normal load of 40 N was used. The frequency was controlled at 1 Hz and the stroke length was set at 10 mm. Specimens were passivated in 30% HNO_3 for 30 min before each test. The mass of the specimens was gravimetrically determined by using a digital microbalance (Mettler Toledo AT201, UK) with 0.01 mg resolution. Each plate was weighed before and after each test at least five times to ensure repeatability. Specimens were immersed in the selected solution in static conditions before the onset of the tribological test and the OCP was monitored for 60 min. After that, the tribological test was started and the OCP was measured for 60 min. Finally, the sliding was stopped and the OCP was measured for 60 min to study the repassivation kinetics of the materials in different environments. A 3D optical profilometer (Wyko 1100NT, Veeco Instruments) was used to study the cross-section profile of the wear tracks after the tribocorrosion tests. Vertical Scanning Interferometry mode (vertical resolution 1 nm) was used to acquire the surface images.
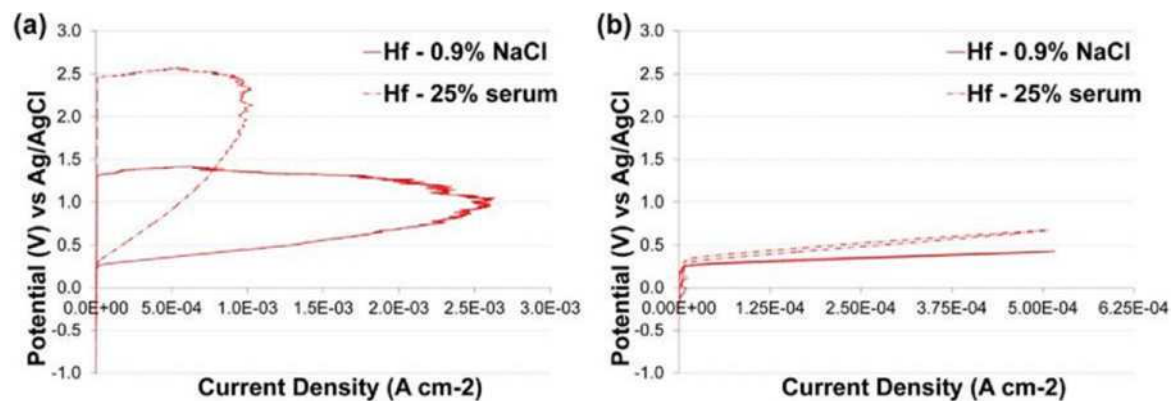

FIGURE 2. Cyclic polarisation curve of (a) mirror polished and (b) scratched hafnium in 0.9% NaCl solution and 25% serum solution

RESULTS

Electrochemical behavior

The potentiodynamic polarization curves of hafnium in 0.9% NaCl solution and 25% serum solution are shown in Figure 2(a). A sudden increase of the current density was observed in both solutions due to the breakdown of the passive layer. The

breakdown potential increased in presence of proteins, as shown in Table I. Once the current density reached the current limit (500 µA cm^{-2}), the potential slope was reversed, however the current density kept increasing after the reversal point was reached, showing typical pit propagation behavior.[19] The pit propagation curve was larger in 0.9% NaCl solution. The repassivation potential in the case of 25% serum solution was slightly higher than in the saline solution. As shown in Figure 2(b), the breakdown potential showed a large decrease when the surface of the material was scratched.

Formation of pits due to localized corrosion was observed under optical microscopy. The pits observed on the polished specimens [Figure 3(a,b)] were larger than in the case of the scratched surfaces, where small pits were preferentially formed on the surroundings of the surface imperfections [Figure 3(c,d)].

TABLE I. Breakdown Potential of Hafnium in 0.9% NaCl Solution and 25% Serum Solution

	0.9% NaCl	25% Serum
$E_{breakdown}$/V	1.38 ± 0.11	2.33 ± 0.18
	± Standard Deviation	

The anodic polarisation curve was extracted from the cyclic polarisation tests. Figure 4 shows the anodic polarisation curves of hafnium and CP titanium in 0.9% NaCl and 25% serum solution, which could be divided in four zones: at potentials below the corrosion potential (E_{corr}), the current density was dominated by the cathodic reaction; at potentials around the E_{corr} there was a transition from cathodic to anodic currents; when the potential was increased above the E_{corr}, both materials showed a passive plateau where a stable oxide layer was formed on their surface; finally, when the potential was further increased the passive film was disrupted and the current rapidly increased. In the case of CP titanium, breakdown of the oxide layer was not observed and the passive layer remained stable at high potentials. The current densities of hafnium showed slightly lower current density values than titanium in its passive state (Table II) before the breakdown potential was reached. The values of corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of titanium and hafnium in 0.9% NaCl solution and 25% serum solution, extracted from the Tafel plots fitted on the potentiodynamic curves, are shown in Table III. Hafnium showed a lower E_{corr} than titanium in both solutions. The i_{corr} observed for hafnium was slightly lower than that for CP titanium in both 0.9% NaCl solution and 25% serum. Both materials showed lower i_{corr} in 25% serum.

Tribocorrosion behavior

The evolution of the OCP value during the tribocorrosion tests is shown in Figure 5. Stable passive OCP values were observed for the first 60 min, when the specimens

were immersed in the electrolyte solution. With the onset of the reciprocating test a shift of the OCP value toward more active values was observed, indicating that the passive layer was being mechanically damaged. When the mechanical damaging ceased the OCP rapidly increased, indicating that the oxide layer was rebuilt on the surface.

The evolution of the OCP of hafnium and CP titanium after mechanical depassivation ceased is shown in Figure 6. The percentage of repassivation was calculated according to Eq. (1).
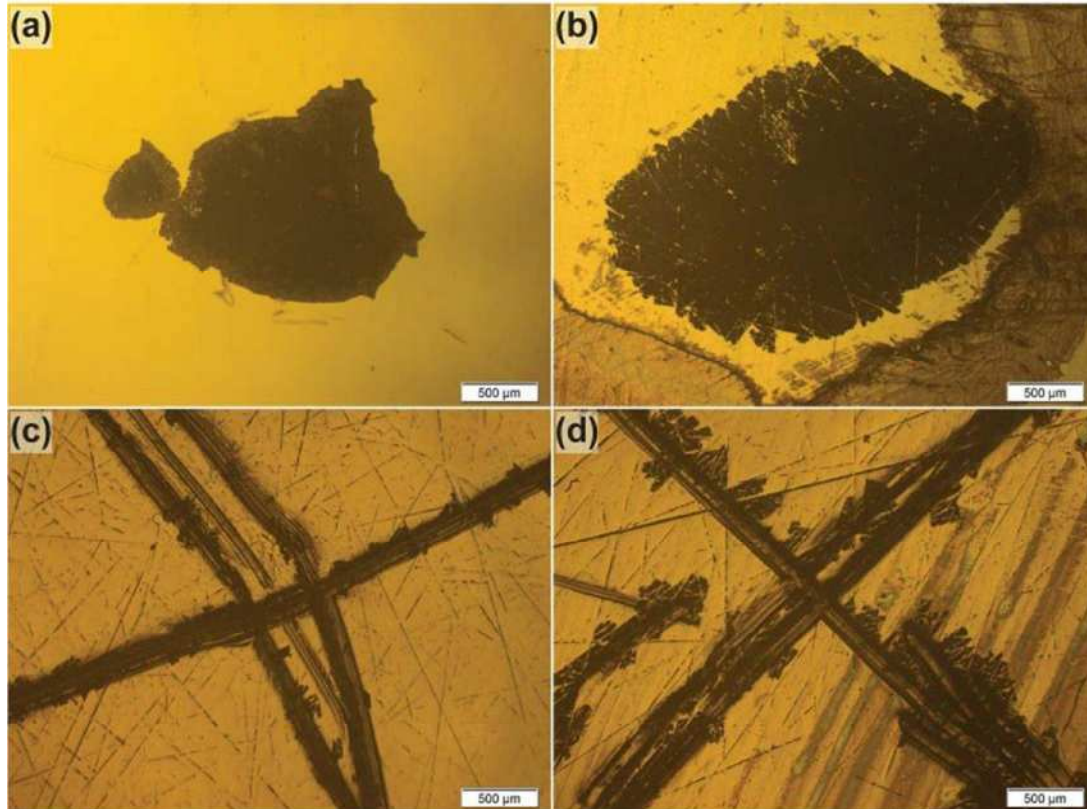

FIGURE 3. Corrosion pits were observed on the surface of hafnium after cyclic polarization tests on the mirror polished surface in (a) 0.9% NaCl and (b) 25% serum and on the scratched surface in (c) 0.9% NaCl, and (d) 25% serum.

$$Repassivation\ (\%) = \frac{E_t - E_{wear}}{E_{passive} - E_{wear}}. \qquad (1)$$

Where E_t is the OCP value at a time t; E_{wear} is the OCP value during wear-corrosion before the mechanical damage ceased; and $E_{passive}$ is the OCP value before the mechanical damaging starts. After the first quick increase, the potential kept rising at a lower rate due to the growth of the protective film. The OCP increased slightly faster in the case of hafnium in all fluids.

The measured volumetric loss of hafnium and titanium in 0.9% NaCl solution, 25% serum, and 50% serum are shown in Figure 7. Hafnium showed higher volumetric loss in 0.9% NaCl solution and 25% serum solution. The volu¬metric loss was

generally higher for 25% serum than for 0.9% NaCl solution; however, it did not increase in the case of 50% serum in comparison with 25% serum. The depth of the wear scars measured for hafnium was larger in the case of hafnium [Figure 8(a)] than for CP titanium [Figure 8(b)] in all solutions.
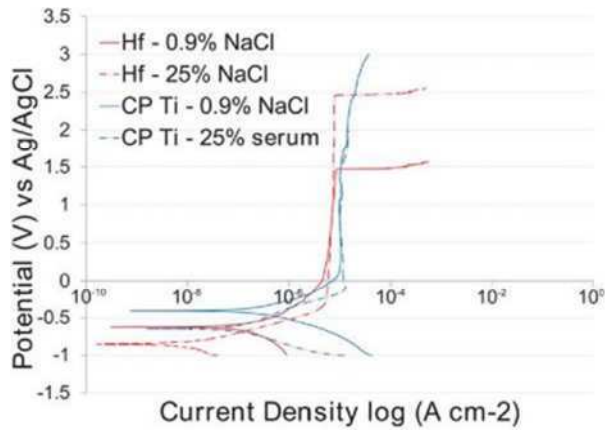

FIGURE 4. Anodic polarization curves of titanium and hafnium in 0.9% NaCl and 25% serum solution.

DISCUSSION

Corrosion resistance of hafnium

The pH of the human body is normally around 7.4, however, it can be affected by different factors such as infections or surgery, where the pH can vary from values around 5.6 up to 9.[5] A preliminary study of the potential-pH curves of hafnium and titanium showed that these two materials are in passive state in the body's pH range.[5] Hafnium is spontaneously passivated in aqueous environments by forming a hafnium oxide layer on the surface.[6] Titanium is well known to be in the passive state in biological environments. A titanium oxide layer provides this material with excellent corrosion resistance. Titanium and hafnium are generally passivated by the reaction with water according to the Eqs. (2) and (3), respectively.

TABLE II. Current Density of Hafnium and CP Titanium in the Passive Region at Different Applied Potentials in 0.9% NaCl and 25% Serum Solution

	Hafnium		CP Titanium	
	0.9% NaCl	25% serum	0.9% NaCl	25% serum
Potential (mV)	Passive Current Density (mA cm^{22})			
0	4.26 ± 0.18	5.65 ± 0.02	5.95 ± 1.52	11.99 ± 0.24
250	5.36 ± 0.03	6.08 ± 0.05	9.66 ± 0.79	11.17 ± 0.16
500	6.25 ± 0.24	6.43 ± 0.01	10.21 ± 0.02	10.90 ± 0.31
750	6.97 ± 0.38	6.78 ± 0.19	10.31 ± 0.49	10.46 ± 0.50

| 1000 | 7.44 ± 0.38 | 7.15 ± 0.10 | 10.2 ± 0.96 | 10.28 ± 0.07 |
| 1250 | 7.82 ± 0.07 | 7.34 ± 0.06 | 10.8 ± 0.31 | 10.33 ± 0.28 |

±: Standard Deviation

TABLE III. Tafel Extrapolation of the Corrosion Potential and Corrosion Current Density in 0.9% NaCl Solution and 25% Serum Solution

	Hafnium		CP Titanium	
	0.9% NaCl	25% serum	0.9% NaCl	25% serum
E_{corr} (V)	-0.638 ± 0.016	-0.881 ± 0.045	-0.415 ± 0.011	-0.613 ± 0.051
Icorr (nA cm^{-2})	163.9 ± 40.9	15.3 ± 3.5	395.9 ± 114.9	146.0 ± 32.0
±: Standard Deviation				

$$Ti + 2H_2O \leftrightarrow TiO_2 + 4H^+ + 4e^- \quad (2)$$

$$Hf + 2H_2O \leftrightarrow HfO_2 + 4H^+ + 4e^- \quad (3)$$
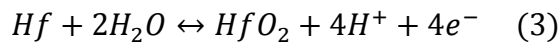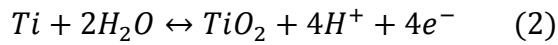
In simulated body fluids, such as the studied solutions, both titanium and hafnium formed a stable passive layer and OCP values were in the passive domain. The oxide layer formed on hafnium has been shown to be protective, showing slightly lower current densities than those for titanium. Both materials also showed low corrosion current density in the presence of organic species. The i_{corr} values extracted from the Tafel plots showed lower corrosion currents densities in 25% serum solution, indicating that proteins might be acting as a cathodic inhibitor[20]; however, no considerable difference was observed in the corrosion current densities measured in the passive region in the saline and in the serum solutions.
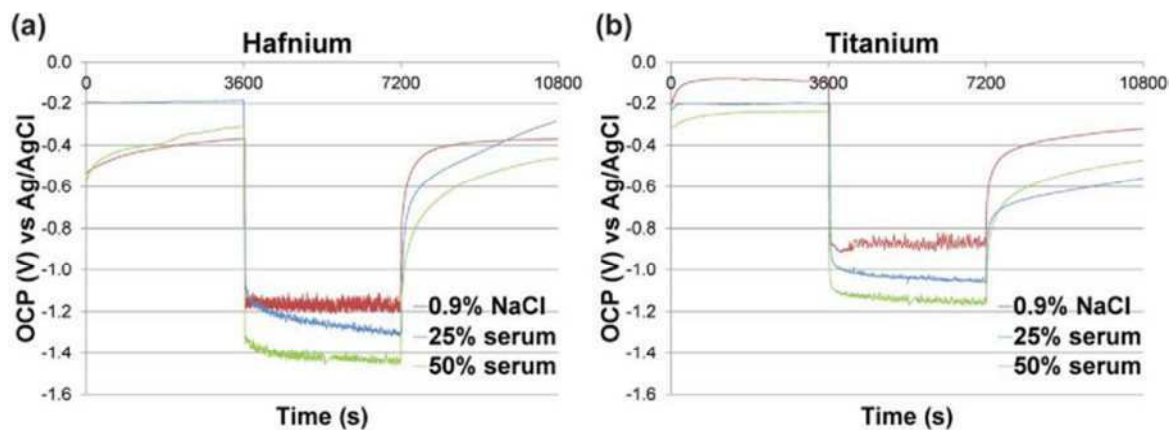

FIGURE 5. Evolution of the OCP during tribocorrosion tests of (a) hafnium and (b) CP titanium.
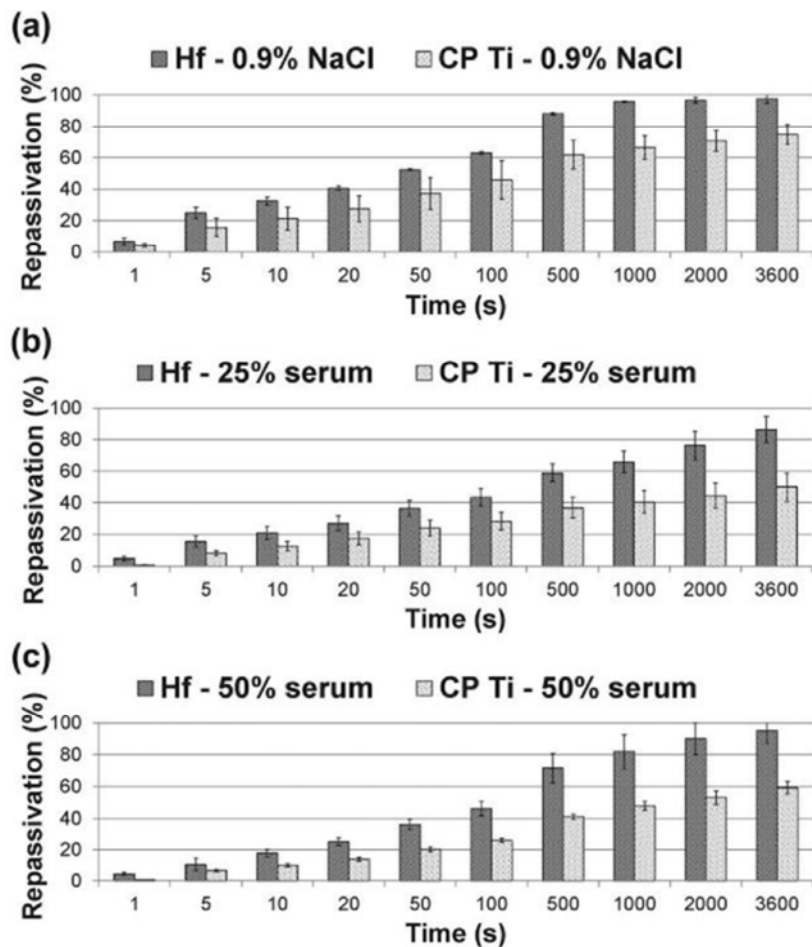
FIGURE 6. Evolution of the potential of hafnium and CP titanium after the mechanical damaging stopped, with respect to the OCP value under wear-corrosion conditions, in (a) 0.9% NaCl, (b) 25% serum, and (c) 50% serum solutions.

Cyclic polarisation tests revealed that hafnium tends to suffer from localized corrosion at higher potentials. The results showed that the presence of organic species increased the breakdown potential of the film, which could be due to the positive charge of proteins at the pH of the test solutions (pH 7.4).[21] In the polarisation scan, specimens were anodically polarised, therefore the negatively charged species tended to be attracted toward the surface of the specimen. Proteins would compete with chlorides to adsorb on the surface, which would retard the formation of pits. Similar effects have been reported for AISI 316L stainless steel.[22] The breakdown potential measured in both 0.9% NaCl and 25% serum solution exceeded the anodic oxygen evolution potential; however this reaction could not be detected, due to the insulating effect of HfO_2 for anodic reactions.[23] The pit propagation curve was also limited in the presence of organic species. Proteins would be attracted toward the region were positively charged ions were released.[22] The presence of proteins could act as a diffusion barrier; therefore the current density values reached when the pits were formed in serum solution were lower than those in the case of saline solution. A strong correlation between the surface finish and resistance to localized corrosion was also observed. When surface imperfections were present on the surface of hafnium, its resistance to localized

corrosion was largely decreased, and corrosion pits were formed around the surface imperfections.
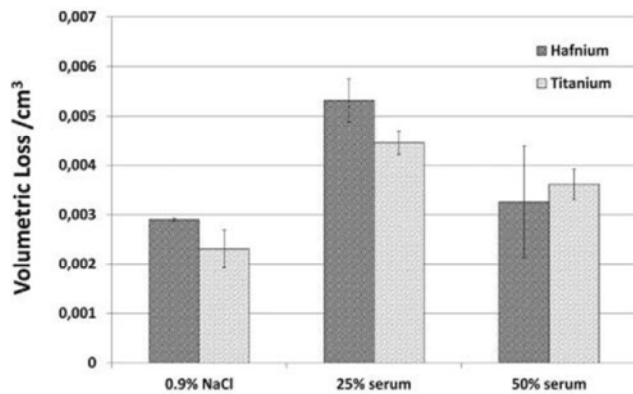

FIGURE 7. Total volumetric loss of hafnium and CP titanium after the tribocorrosion test in 0.9% NaCl, 25% serum, and 50% serum solutions.

Tribocorrosion of hafnium

As discussed earlier, both hafnium and titanium show a passive state when immersed in aqueous solution. The passive state was also observed in the presence of organic species, which provided them with excellent corrosion resistance. The mechanical damage, to which the materials were exposed caused damage to the passive layer and the bulk material to be in contact with the media, therefore the OCP dropped toward more active values. When the mechanical damage ceased, both materials had the ability to repassivate, and the oxide layer was quickly reformed on their surface, which could be observed by a quick increase on the OCP. Hafnium showed a slightly faster repassivation that was observed by a faster increase of the OCP in all solutions. The presence of organic species slowed down the reformation of the passive layer in both cases.

The volumetric loss measured in the case of hafnium was higher in 0.9% NaCl and 25% serum under the studied conditions. This was influenced by the higher elastic modulus of hafnium (138 MPa)[24] as compared to CP titanium (102.7 MPa),[25] which yields an initial Hertzian contact pressure of approximately 850 MPa in the case of hafnium and approximately 750 MPa in the case of CP titanium in this study. However, the volumetric loss decreased in 50% serum for both materials in comparison with 25% serum solution, which suggests that the increase of the protein content of this solution may improve the lubrication of the system.[26,27]
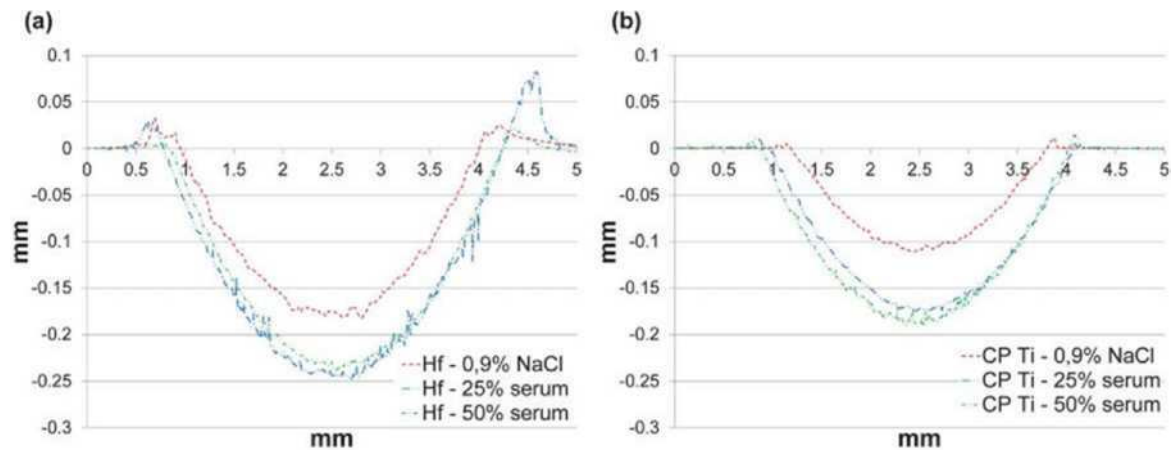
FIGURE 8. Wear scar cross-section profiles measured on (a) hafnium and (b) CP titanium after the tribocorrosion tests.

CONCLUSIONS

Hafnium has been pointed out as an interesting material for biomedical applications due to its good biocompatibility and osteogenesis.[8] However, its corrosion and tribocorrosion behavior in the biological environment have not been fully studied. In the current study, the corrosion and tribocorro¬sion behavior of hafnium have been investigated using CP titanium as the reference material.

- Hafnium showed a passive state in the presence of proteins. The oxide layer formed provided high protection to corrosion. Hafnium had a higher tendency to suffer from localized corrosion than CP titanium. The presence of proteins retarded the formation of pits and reduced their propagation.
- Mechanical damage could disrupt the passive layer of hafnium preventing its protective effect. However, the oxide layer was quickly reformed on the surface when the damaging ceased. Hafnium showed a slightly faster repassivation than titanium.
- The wear rate shown by hafnium was higher in comparison to CP titanium in 0.9% NaCl solution and 25% solution under the studied conditions.

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