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Fretting corrosion of hafnium in simulated body fluids

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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.

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 [3,4]. 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 [7,8]. 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

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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.

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.

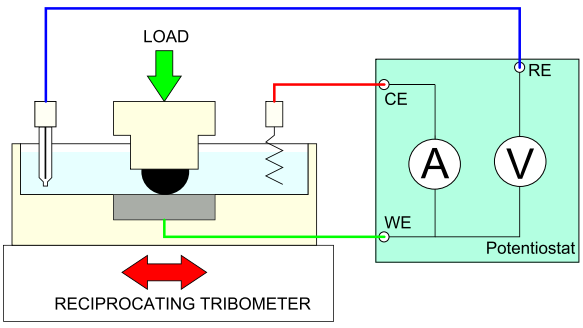

Fig. 1. Schematic representation of the experimental set up.

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 ($HV_{500\ g}$) 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

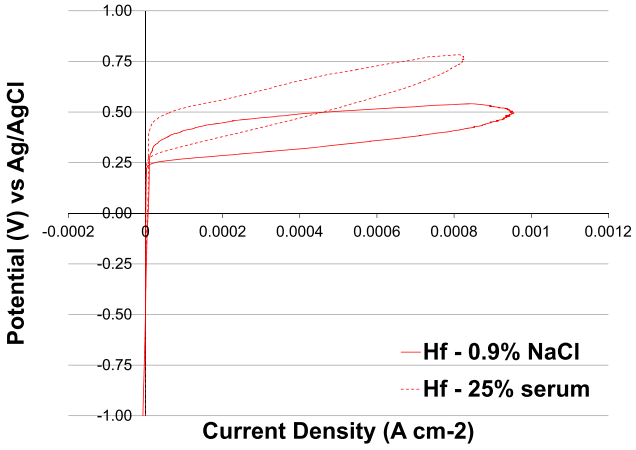

Fig. 2. Cyclic polarisation of hafnium in fretting conditions in 0.9% NaCl and 25% serum solution.

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