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ScienceDirect

Biosurface and Biotribology 1 (2015) 130–134

www.elsevier.com/locate/bsbt

Nanocrystalline layer on the bearing surfaces of artificial hip implants induced by biotribocorrosion processes

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Received 12 March 2015; received in revised form 8 April 2015; accepted 20 May 2015

Abstract

Orthopedic prostheses are lubricated by a pseudosynovial fluid that contains proteins. Under regular movements, bearing surfaces would suffer wear and corrosion. More importantly, their interaction controls the material degradation process. Nanocrystalline layer was found on the surface of CoCrMo alloy surface after tribocorrosion tests. Tribocorrosion tests were taken in 0.9% NaCl and 0.9% NaCl with 1% bovine serum albumin (BSA) solution. Small angle X-ray Scattering was applied to measure the size distribution of the nano-crystals. As a general conclusion, proteins can absorb on prosthesis materials and act as a lubricant during sliding. The negative charge distribution on the material surface can promote the adsorption of protein. The average size of the nano-crystals on the bearing surface was 5 nm.

Keywords: Wear; Corrosion; Protein adsorption; SAXS

1. Introduction

In recent years, total hip replacements have obtained great attraction in research field as an effective treatment for millions of patients worldwide. CoCrMo alloys have become one of the most used metals for total joint replacements due to its appropriate hardness and elastic modulus. Research has been done to analyze the reasons of loosening for both of metal-on-metal and metal-on-polyethylene total hip replacements [1,2]. For metal-on-metal (MoM) joints [3,4], wear debris and released toxic ions have become main causes of failure. Pseudocyst caused by nano-sized debris was found during the use of CoCrMo alloy prosthesis [5]. In the previous studies [6–9], the effect of albumin, the major synovial protein, on the tribological behavior of the prosthesis materials was investigated, which has drawn a conclusion that the adsorption of proteins can interpret the differences in the friction behavior of different materials. The microstructure of the joint surface would have some unusual changes when compared in the normal environment and was considered as a key factor in the wear of MoM joints. This study aims to analyze the effect of surface potential on the protein adsorption on CoCrMo alloy. Small angle X-Ray Scattering was used to compare the size of nano-crystals under different conditions.

2. Materials and methods

2.1. Wear test

The main material used in the experiment was a CoCrMo alloy, the composition of which is listed in Table 1. Ultra-high molecular weight polyethylene was chosen as the counterpart. The diameter of the UHMWPE pin was 5 mm. The sliding wear tests were carried with a UMT-II friction wear tester. The coefficient of friction was recorded during sliding. The test parameters were set as follows: the average speed of sliding: 30 mm/s; the frequency of sliding: 1 Hz; the applied load was 5 N (corresponding to a nominal contact pressure of 200 MPa) and the longest sliding time was 8 h. 0.9% NaCl and 0.9% NaCl + 1% bovine serum albumin (BSA) solution were used as lubrication medium.

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http://dx.doi.org/10.1016/j.bsbt.2015.05.001

Table 1
The chemical composition of the materials in this study (wt/%).

Materials	Co	Cr	Mo
CoCrMo alloy	Bal.	28	5

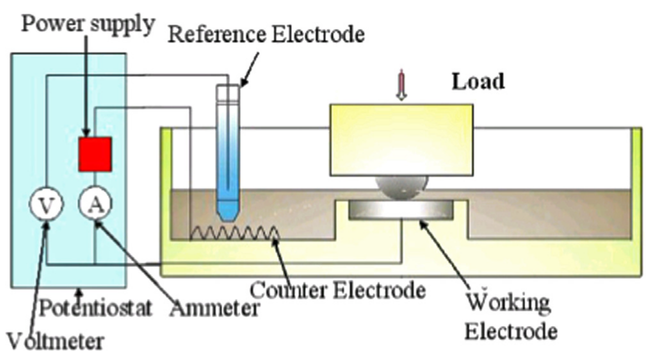

Fig. 1. Schematic representation of the integrated three-electrode cell.

The three-electrode electrochemical cell was used, in which the specimen acted as working electrode(WE), a platinum wire as the counter electrode(CE) and a silver/silver chloride electrode as the reference electrode(RE). Fig. 1 shows the integrated tribocorrosion tester so that the tribological and electrochemical data can be obtained synchronously.

2.2. Scanning electron microscopy (SEM)

SEM experiments were carried out with a ZEISS EV018 special edition microscope. Backscattered electron imaging mode was used to analyze the surface components of the CoCrMo alloy under different conditions.

2.3. Small Angle X-ray scattering(SAXS)

SAXS was used to determine the size, shape, and distribution of the nano-sized crystals in the wear track in different solutions and different conditions (at open circuit and under cathodic protection). The experiment was carried out at BRSF small-angle scattering station in the Institute of High Energy Physics, Chinese Academy of Sciences, 1W2A beamline. The storage ring of electronic energy was 2.5 GeV and the average beam intensity was 60 mA. The wavelength of the X-Ray used was 0.153 nm. The synchrotron radiation beamlines from electron–positron collider storage ring was focused and collimated before it irradiate on the specimen. The two-dimensional imaging plate(IP) CCD detector (Mar 165) was used to detect the changes of the light intensity with the scatter angle. The image pixels were 2048×2048, with each pixel 79 μm. The distance from the specimen to the detector was 1.58 m [10].

The specimens were removed directly after tribological tests. Table 2 shows the tribological conditions in SAXS experiment.

Table 2
The tribological conditions in SAXS experiments.

Specimen number	Lubricant	Applied potential	Time (h)
1	0.9% NaCl	OCP	8
2	0.9% NaCl	CP(−0.8 V)	8
3	0.9% NaCl+1%BSA	OCP	8
4	0.9% NaCl+1%BSA	CP(−0.8 V)	8
5 (Blank)	–	–	–

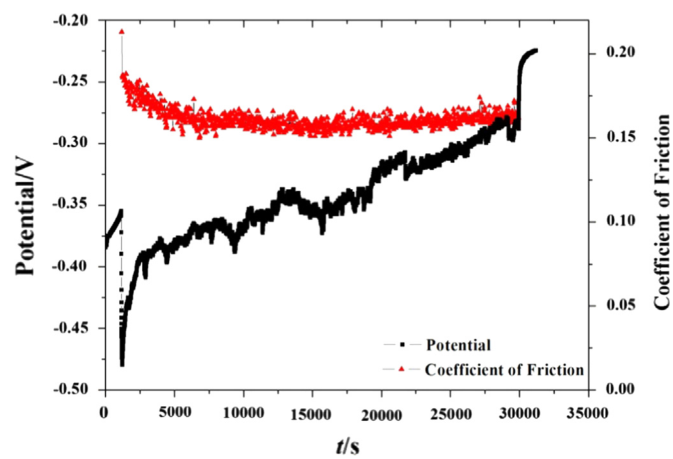

Fig. 2. Open circuit potential change vs. time for CoCrMo alloy in 0.9% NaCl solution.

3. Results and discussion

3.1. Open circuit potential(OCP) and cathodic protection(CP) measurements

A passive film can form on the surface of the material spontaneously. During sliding, this passive film was removed and then re-established. The shift of the open circuit potential with time can depict this process. Fig. 2 shows the coefficient of friction and the OCP during sliding for CoCrMo alloy disk and UHMWPE pin in 0.9% NaCl solution. When the load was added on the material, a shift was seen on the potential curve, which indicates that the passive film was removed and the metal surface was in an active status. And after 8 h sliding, the load was removed and the passive film was rebuilt on the metal surface, which caused a positive shift of the potential. There was a dynamic equilibrium of the removal and the re-establishment of the passive film during sliding, the relative velocity of the two procedures determined the value of the open circuit potential. A constant positive shift can be seen during sliding, indicated that the velocity of the re-establishment process was faster than the removal of the passive film.

Fig. 3 shows SEM images of CoCrMo alloy samples tested in different solutions and potentials. The dark region indicated the aggregation of light elements such as C, S, O, etc., which are the elements that protein contains. Protein adsorption can be observed on the surface of the samples sliding in protein environments (Fig. 3(a)), which is different from the sample sliding in 0.9% NaCl solution. The adsorption of proteins is