Journal of the mechanical behavior of biomedical materials 68 (2017) 124–133

Contents lists available at ScienceDirect

Journal of the Mechanical Behavior of Biomedical Materials

journal homepage: www.elsevier.com/locate/jmbbm

Release of metal ions from nano CoCrMo wear debris generated from tribo-corrosion processes in artificial hip implants

Yang Wang, Yu Yan*, Yanjing Su, Lijie Qiao

Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, 100083, China

ARTICLE INFO

Keywords:
CoCrMo alloy
Wear debris
Corrosion
Wear
TEM

ABSTRACT

CoCrMo alloys have been widely used in metal-on-metal (MoM) hip replacements due to their superior wear and corrosion resistance properties. However, metal ions like Co^{2+} and Cr^{3+}, or even Cr^{6+} released from CoCrMo hip prostheses can induce macrophage apoptotic vs. necrotic mortality and damage the surrounding tissues. Simultaneously, osteolysis induced by the wear debris can be a cause of failure. Nano wear debris is more active than the bulk material, due to its small size. In this study, to accurately analyse the fresh wear debris retrieved from the hip simulator and the interaction between the particles and tribocorrosion of CoCrMo, wear debris was observed without protein digest, using a combined experimental approach involving the employment of TEM and ICP-MS. The results suggest that nanoscale wear debris generated from a hip simulator in bovine serum albumin (BSA) lubrication was Cr-rich, containing crystalline and amorphous structures; meanwhile, without any proteins, the wear particles mostly had an hcp-Co crystalline structure.

1. Introduction

CoCrMo hip prostheses have been used for more than 50 years due to their superior wear and corrosion resistance properties (Mckee and Watson-Farrar, 1966). A CoCrMo hip replacement is subjected to long-term wear and corrosion through body fluids in vivo, resulting in the formation of tribological films, wear particles, and metal ions. At present, studies about CoCrMo hip replacements mainly include two areas: one is the formation and construction of the tribofilm; another is the characteristics of wear particles (Hart et al., 2010; Liao et al., 2011, 2012a, 2012b). It has been reported that the tribological films are composed of a graphene-like structure which may comprise denatured proteins and the nano-crystalline (NC) hcp ε-Martensite region. Metal-on-metal hip replacements have experienced a sharp decline in use in the last five years, due to biocompatibility issues related to wear and corrosion products, which have been established as the main reasons for the degradation of such prostheses. Despite their lower volumetric wear compared to conventional metal-on-polyethylene bearings, all metal implants have been reported to generate a large number of nanometre-sized particles. The total number of particles generated within one year in MoM total hip replacement lies between $6.7\times\ 10^{12}$ and $2.5\times\ 10^{14}$ (Doorn et al., 1998).

Great attention has been paid to the potential biological effects of metal nanoparticles and ions (Brodner, 2003; Ingham and Fisher, 2000), and many studies have been conducted to determine the exact size, morphology, and chemical composition of wear particles generated in MoM hip implants. Specimens of wear particles have been retrieved from three sources: revision hip-implant surgeries, reciprocating sliding-wear tribometers, and hip simulators. Different methods have different merits or deficiencies. Many different techniques and approaches have been used over the years towards establishing a reliable and repeatable methodology for the isolation and characterization of metal wear particles from tissues or lubricants used for wear simulations. Though there is still no consensus as to which method should become the standard for routine application, most particle analysis protocols essentially consist of four parts: digestion and isolation, display and image acquisition, morphological and chemical characterization, and statistical analysis (Billi et al., 2009).

Some studies have reported that in vitro or in vivo wear particles are chromium oxide (Catelas et al., 2003, 2004b; Pourzal et al., 2011; Topolovec et al., 2013a), whereas a minority have appeared to be CoCrMo alloy or possibly of carbide origin. Studies have shown that CoCrMo nanoparticles may cause damage to DNA and chromosomes (Sood et al., 2011), and that the presence of metal ions in the tissues around implants could cause carcinogenicity, hypersensitivity, allergy, local tissue toxicity, inflammation, and genotoxicity (Bauer, 2002). It

* Corresponding author.
E-mail address: yanyu@ustb.edu.cn (Y. Yan).

http://dx.doi.org/10.1016/j.jmbbm.2017.01.041
Received 1 December 2015; Received in revised form 12 December 2016; Accepted 25 January 2017
Available online 30 January 2017
1751-6161/

Table 1
The nominal chemical composition of the tested alloy.

wt.%	Cobalt	Chromium	Molybdenum	Carbon	Iron	Silicon
HC CoCrMo	Bal.	28	5	0.05	< 1.0	< 1.0

Table 2
The concentration of different metal elements of wear debris after 24 h wear tests.

	Co (ppm)	Cr (ppm)	Mo (ppm)
In BSA containing PBS	6.59 ± 0.55	82.87 ± 0.25	0.49 ± 0.06
In PBS	46.82 ± 2.42	19.38 ± 0.90	2.14 ± 0.11

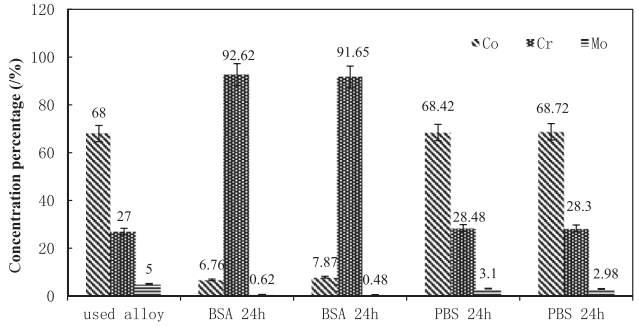

Fig.1. The concentration percentage of different elements in wear particles produced in different wear media.

has been reported that nano-sized particles, ranging from 25 to 50 nm (Firkins et al., 2001a) for MoM bearings, could be phagocytosed and/or subjected to pinocytosis more easily than micro-particles, and cause more mitochondrial and DNA damage (Papageorgiou et al., 2007). Morphology and composition may be different under different conditions, but there is some general agreement. Particle size of MoM implants ranges from 30 to 500 nm (Catelas et al., 2001a), the shape of wear particles including round, oval, and needle. As for chemical composition, most studies assume that the particles are chromium oxide, although a minority appear to be Co matrix, oxide, carbide, or all of these.

It is important to address the characterization of the wear particles: different periprosthetic tissue responses might be explained by differences in particle characteristics, as suggested by in vitro studies on the effects of particle size, concentration, and composition on cellular response (Catelas et al., 1998; Lloyd et al., 2013). Given these considerations, a detailed characterization of metal wear particles is crucial to help predict and study the periprosthetic tissue response to all metal prostheses. The present study examines the chemical composition and the original state of the wear particles generated in a wear tester with bovine serum albumin (BSA) and in phosphate-buffered saline (PBS) with no proteins.

2. Material and methods

2.1. Test conditions and sample preparation

Particles were retrieved from a reciprocating sliding-wear tester with a CoCrMo disc and a CoCrMo bar, respectively. The tribocorrosion equipment has been described in detail elsewhere (Yan et al., 2013). The applied load was 3 N (the Herzian contact stress was about 200 MPa) and the sliding distance was 30 mm/cycle. All the samples were made of wrought HC (high carbon, 0.2% wt. C content) CoCrMo (DePuy International Ltd., UK). Table 1 details the chemical composition of the CoCrMo alloy. All HC CoCrMo discs were 20 mm in diameter and 5 mm in thickness. The counterparts to the CoCrMo disc samples were bars also made from CoCrMo. The counterparts had a 10 mm diameter and a smooth hemisphere on one side. They were 25 mm in length, and were machined from rods of wrought CoCrMo. Before implanting into the patient, it was ensured that the MoM implants had highly polished surfaces with minimal scratches, and that they incurred the expected low wear and caused minimal osteolysis (Jacobsson et al., 1996).

One side of each disc was ground with SiC emery paper up to 2000 grit and polished with 2.5 μm diamond paste until a mirror-like surface (R_a about 10 nm) was achieved (no scratching under an optical microscope). After sonification with acetone and rinsing with deionized water, the disc samples were fixed in the cell using 704 RTV silicone. Here, the mirror-like surface side of the disc samples simulated the acetabular cup, and the smooth hemisphere of the bar represented the cup of the femoral head.

Tests were run in 30 mL 0.01 g/mL BSA in PBS solution (1 L PBS containing 8 g NaCl, 0.2 g KCl, 1.42 g Na_2HPO_4, 0.27 g KH_2PO_4) at pH 7.4. In order to compare the effect of proteins on the characterization of the wear particles, PBS solution with no proteins was employed as lubricant in another test where other experimental conditions were not changed. In order to reduce the influence of the chemical reagent on the particles, no antibiotics or preservative-like EDTA were added to the test medium during the test procedure. After 24 hours, the test fluid containing the metal wear particles was retrieved from the cell.

2.2. Metal-ion-concentration characterization

Fluid samples were aliquoted into a 20 mL centrifuge tube and spun separately at 4000 rad/min for 60 min. All samples were centrifuged three times. A Malvern High Performance Particle Sizer (Zetasizer) was used to detect whether any wear debris remained in the supernatants. The size of particles can be obtained based on the dynamic light scattering theory. The range of the measurement of the apparatus is from 0.3 nm to 10 μm. All supernatants were discarded except the dreg containing almost all the particles. Protein disturbs the image contrast, increases the degree of agglomeration, and inhibits the identification of single particles; therefore, the particles were isolated from the protein-rich environment. The literature (Billi et al., 2009; Brown et al., 2007; Catelas et al., 2003, 2001b; Doorn et al., 1998; Firkins et al., 2001b) provides several different protocols, such as the use of enzymatic digestion for example with papain and proteinase-k, causing minor damage to the particles (Catelas et al., 2003, 2001b). It is known that nano-sized particles have a very high surface energy and are more than usually reactive and sensitive to changes in environmental conditions, such that they have a tendency to agglomerate at elevated temperatures and to dissolve at extremes of pH; when using acid or alkaline chemical reagents, metal particle size, shape, and characterization may change – therefore, to acquire the characterization of the fresh and primitive wear particles, the particles were surveyed directly without protein digestion.

0.2 mL deionized water was injected into the centrifuge tube only with the deposit, then placed into the sonification centrifuge tube for 10 min to homogenize the wear particles, while the metal particles were surrounded by the protein or the denatured protein compound. Then, the samples were analysed by Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM) (phase identification). These results were compared to those achieved in bulk techniques like Inductively Coupled Plasma Mass Spectrometry (ICP-MS), demonstrating the evolutionary process of different elements from matrix to wear particles or lubrication under simulator wear in different test media. Our analysis of the macroscopic