Tribology International ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Tribology International

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

Nano-scale wear characterization of CoCrMo biomedical alloys

V. Martinez-Nogues [a,*], J.M. Nesbitt [b], R.J.K. Wood [a], R.B. Cook [a]

[a] National Centre for Advanced Tribology, nCATS, Faculty of Engineering and the Environment, University of Southampton, University Road, Southampton SO17 1BJ, UK

[b] RedLux Ltd, 3/7 Avenger Close, Chandlers Ford, Southampton SO53 4DQ, UK

ARTICLE INFO

Article history:
Received 6 October 2014
Received in revised form
12 February 2015
Accepted 26 March 2015

Keywords:
Nano-wear
Single asperity contact
Femoral stem–cement interface
White-light-interferometry

ABSTRACT

Low amplitude motions at the micro and the nano-scale at the femoral stem–cement interface under physiological loads can result in fretting and nano-wear on the stem surface. These are important wear processes in cemented total hip replacements as the release of metal debris and ions can trigger adverse local tissue reactions within the body, bone resorption and subsequent aseptic loosening of the femoral component resulting in the implant failure. However, the influence of the microstructure and manufacturing processes on the nano-wear behaviour of different cobalt chromium molybdenum (CoCrMo) alloys has not been studied extensively. Four CoCrMo alloys were tested under reciprocating wear conditions at the nano-scale level. Tangential friction forces, coefficient of friction and plastic deformation values were recorded. A new white-light-interferometer system was validated against atomic force microscopy and Nano Vantage Test System measurements to analyse the permanent plastic deformation caused in each of the samples. Significant differences were found in the total plastic deformation achieved by the as cast alloy compared to the forged, as cast single thermal treated and as cast double thermal treated samples. In addition thermal treated samples presented a tendency to produce a higher quantity of wear debris around the nano-wear scars. These findings indicate a possible relation between the wear resistance at the nano-scale and the manufacturing and thermal processes applied on the CoCrMo biomedical alloys.

1. Introduction

In vivo wear of metallic materials have been demonstrated to result in the generation of metal particles and metallic ions which can cause adverse tissue reactions or bone resorption [1] and therefore the loosening of the implant and its revision. Wear particles are generated at the articular surface of total hip arthroplasties (THA), [2], but they can also be generated at other interfaces, in particular the femoral stem–cement or the taper–trunnion interfaces [3–5].

In cemented total hip replacements, (THR), the difference between the mechanical properties of the cement and the metallic femoral stem under loading, results in motion between the two surfaces. This motion generates cement or metallic particles which can act as single asperities increasing the maximum contact pressure applied that combined with the micromotions can accelerate the nano-scale wear happening at the femoral–cement interface [6]. Retrieval studies [2,6–8] have shown that the most affected zones are mainly localised in the posterior and medial regions in the femoral stem. The level of damage has been found been dependent of the final surface roughness of the stem, the pores produced after the polymerization of the cement in contact with the metallic surface [9,10], the type of cement [11,12] and/or the presence of hard radiopacifier particles in it which can produce ploughing at the CoCrMo stem surface accelerating the fretting wear processes [13].

Different fretting and nano-scale wear mechanisms affecting both polished and matte femoral stems have been observed previously, [2]. Ductile wear together with pitting of the surface was found in polished stems, while abrasive wear processes were found in the matte ones. Recently, Bryant et al. quantified the tribochemical reactions occurring at the stem–cement interface and their influence on the stem degradation and the debris released into the biological environment [8,14]. They proposed a mechanism for the formation and transfer of the oxidised metallic debris from the metallic stem to the bone cement. The motion between the two contacting surfaces remove the passive film created on the CoCrMo alloy exposing a new reactive surface in contact with the liquid environment causing the oxidation of the metallic substrate and metallic debris. Due to the cyclic loading and the contact between the surfaces these particles

* Corresponding author.
E-mail address: vm1y11@soton.ac.uk (V. Martinez-Nogues).

http://dx.doi.org/10.1016/j.triboint.2015.03.037
0301-679X/Crown Copyright © 2015 Published by Elsevier Ltd. All rights reserved.

get compacted creating Cr_2O_3 layers which remain between both surfaces. This type of mechanism was also observed at the taper–trunnion interface as reported by Gilbert et al. [15].

The findings by Cook et al. [13] of hard zirconium dioxide radiopacifier particles between the femoral stem and the cement surfaces provides a field of investigation on the plastic deformation produced by these hard asperities in the metallic surface at the nanoscale. The existence of different CoCrMo biomedical alloys due to manufacturing processes and thermal treatments history provide an extensive range of microstructures and mechanical properties which can affect the deformation behaviour and therefore the nano-wear-corrosion processes. The role of the size grain, the presence or absence of the carbides in addition to their morphology has been reported playing an important role in the sliding or abrasive wear of CoCrMo at the articular surfaces and also in their corrosion processes [16–20]. Nano-wear testing of different biomedical materials, accelerated micro-wear of silicon or nano-scratch testing of different Stellite-21 alloys have been studied previously [21–23], proving the capability of nano-mechanical testing to optimise biomaterials and compare the different mechanical properties, wear resistance and wear processes at the micro and nano-scale.

This present study aims to establish a better understanding of the wear mechanisms at the nano-scale by comparing four CoCrMo alloys commonly used as implantable materials in total hip replacements. Investigations include mechanical properties measurements, coefficient of friction (COF) evaluation during the running-in and steady state periods, dispersed energy value calculation, plastic deformation measurements validated by the following methods: atomic force microscopy (AFM), (MFP-3D, Asylum Research, USA), white-light-interferometry (OptiLux, Red-Lux Ltd, UK) and by a mechanical system (NanoTest Vantage System, MicroMaterials Ltd, UK) and nano-wear scar morphology observation by optical microscopy (Alicona Infinite Focus, Alicona, Austria) and scanning electron microscopy (SEM), (JSM 6500F, JEOL, Japan). Knowing the processes which affect the different microstructure of CoCrMo alloys can be essential for the correct choice of the material for future cemented total hip replacement.

2. Material and methods

Mirror polished biomedical CoCrMo samples, $R_a = 12 \pm 0.5$ nm, were used for the present study. Two CoCrMo alloys with different thermal and manufacturing history were used: forged (ASTM F1537), as cast (ASTM F75), as cast single thermal treated (as cast-TT), and as cast double thermal treated (as cast-2TT).

2.1. Mechanical properties

Micro Vickers hardness values (*HV*) were obtained using a square based pyramidal indenter holding a 1 N load constantly during 15 s, (Matzsuzawa Seiki Co. Ltd, Japan). *HV* values were converted into indentation hardness (H_{IT}) values using Eq. (1) according to Annex F from ISO 14577-1:2002 [24]. Where *HV* is the Vickers hardness, H_{IT} is the indentation hardness, A_p is the projected area of the indenter, A_s is the contact surface area and *g* is the acceleration due to gravity.

$$HV = \frac{H_{IT} \times A_P}{g_n \times A_s} = 0.0945 H_{IT}\ (\mathrm{GPa}) \tag{1}$$

Indentation maps of 20 by 20 indents, under depth control up to 500 nm, were performed on the samples using a diamond Berkovich tip to determine the hardness and elastic modulus. Loading and unloading rates were set at 2 mN/s and a dwell time of 60 s was established at the maximum depth. Thermal drift values were recorded during 40 s before and after the experiment to correct the obtained values.

2.2. Nano wear experiments

Nano-wear experiments were performed using the NanoTest Vantage System. Two different experimental conditions were used to assess the frictional behaviour and the nano-wear resistance of the CoCrMo alloys. To monitor the tangential friction forces a friction probe was attached to the rig during the experiments. A spherical diamond tip of 200 μm was used while the normal loads applied were 5, 10 and 20 mN, which corresponds to maximum contact pressures of 0.97, 1.2 and 1.5 GPa, respectively. COF values were calculated from the ratio of tangential force to the normal force at each load during running-in and steady state periods. Dispersed energy values were calculated from the hysteresis area of the force–displacement curves as a measure of the interfacial mechanical energy dissipated during the wear experiments.

The reciprocating nano-wear resistance experiments were performed using a spherical 5 μm radius diamond tip, with a load range from 1 to 30 mN, providing contact pressures from 6.6 to 20.70 GPa, respectively. This range is representative of a single asperity contact between hard inert ceramic ZrO_2 radiopacifier agglomerates present in the cement and the CoCrMo stem surface [25]. The radiopacifier agglomerates typically have a mean diameter between 5 and10 microns in size [26,27] although bigger size agglomerates have been found as well due to mixing inhomogeneity's [28]. The diamond tips were observed under optical microscope before and after wear experiments without observing any geometry changes which might affect the results.

Depth measurements were monitored throughout the duration of the experiments and pre and post thermal drift values were collected during 60 s to correct the obtained depth data. Displacement of the tip was measured by means of a two parallel capacitor plates situated behind the diamond tip. One plate is attached to the tip holder and moves with it while the second plate is fixed. When the tip is pressed into the test specimen, the spacing between the parallel plates changes, hence the capacitance changes. By measuring it using a capacitance bridge, the depth changes are measured. The system stiffness was calculated by indenting on a fused silica reference sample over a broad range of loads using the reciprocating nano-wear holder and using that values to correct the depth values measured by the capacitor plates.

A fixed displacement amplitude of 10 μm was used on the basis of clinical studies which demonstrated that micro-motions between the femoral stem and the cement are typically below 40 μm [29,30]. To shorten the test duration, tests were carried out using a oscillation frequency of 7.5 Hz rather than a physiologically 1 Hz frequency. Each test ran for 3000 cycles.

The instrument uses a multi-layer piezo-stack to generate the oscillating sample motion. The piezo movement is magnified by means of a lever arrangement to achieve larger amplitudes [31]. Track length values depend on the frequency and voltage applied to the piezo-stack inside the nano-wear stage. The piezo voltage is produced by a signal generator+amplifier+transformer combination. During the calibration, it is mounted perpendicularly to the experimental oscillation axis so that the magnitude of the oscillation (track length) can be measured by the depth sensor and the voltage applied can be correlated to the length of the wear track produced.

As is shown in Fig. 1, an initial low contact load of 0.1 mN was applied for 15 s to record the initial contact depth. The load is then linearly increased over 10 s until the maximum test load was reached (1). This load was kept constant during the 3000 cycles (400 s), (2). Finally the samples were unloaded linearly in 10 s to 0.1 mN and held for the next 15 s to record the final non-loaded