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Tribological characterization of NCD in physiological fluids

M. Amaral [a], C.S. Abreu [b], F.J. Oliveira [a], J.R. Gomes [c], R.F. Silva [a,*]

[a] CICECO, Glass and Ceramics Eng. Deparment, Univ. of Aveiro, Portugal
[b] Physics Department, Porto Superior Eng. Institute, ISEP, Portugal
[c] Mech. Eng. Deparment, CIICS, Univ. of Minho, Portugal

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Abstract

NCD films deposited on silicon nitride (Si_3N_4) ceramic substrates by hot-filament chemical vapour deposition (HFCVD) technique were biotribologically assessed under lubrication of Hank's balanced salt solution (HBSS) and dilute fetal bovine serum (FBS), using a pin-on-flat test configuration. The reciprocating tests were conducted under an applied load of 45 N during 500,000 cycles using a NCD coated Si_3N_4 biocompatible ceramic substrates with two different surface preparations: i) polished (P) and ii) polished and plasma etched (PE). Friction coefficient values of 0.02 and 0.12 were measured for the P samples under HBSS and FBS lubrication, respectively. PE samples showed increased adhesion relatively to P ones and withstood 6 km of sliding distance without any evidence of film fracture but with friction coefficients of 0.06 for HBSS and 0.10 for FBS experiments. Evidences of protein attachment and salt deposition were found, being the responsible for the enhancement of friction under FBS relatively to HBSS. The wear rates measured for the NCD films are in the range of $\sim 10^{-9}$–10^{-8} $mm^3 \cdot N^{-1} m^{-1}$, values that are similar to the best values found for ceramic-on-ceramic combinations.

Keywords: Nanocrystalline; Diamond film; Hot filament CVD; Biotribology

1. Introduction

"Total hip replacement is one of the most challenging types of human implants from the materials science's point of view" [1]. In fact, the selection of materials for artificial hip joint is not always straightforward and mechanical properties (strength, elasticity, toughness and ductility), tribological features (low friction and low wear), biocompatibility and corrosion resistance are just some aspects that must be considered [2,3]. For hip prosthesis, the femoral head is usually made of metallic alloys (stainless steel, CoCr or some Ti-based alloys) or ceramics (Al_2O_3 or ZrO_2). The acetabular cup (socket) is made of ultra-high molecular weight polyethylene (UHMWPE), alumina (Al_2O_3) or zirconia (ZrO_2), or CoCr alloys. In this kind of prostheses, one of the main causes of failure is the production of wear debris [1,3–6], which enhance the wear rate through a three-body wear mechanism when deposited between the two bearing surfaces. These residues are generally responsible for osteolysis and aseptic loosening of the implant [4–6].

The search for new materials that potentially improve the wear resistance and minimize the generation of harmful debris of artificial hip joints has been an objective in the past few years. Coating the implants with protective functional films may be a successful way of reducing wear and corrosion of the components of hip prosthesis and of avoiding adverse biological reactions with the surrounding tissues. Nanocrystalline diamond (NCD) coatings have the required properties to play this role. The super hardness of this film ensures low wear rates while the innocuous nature of any wear debris prevents inflammatory responses. In this work, silicon nitride (Si_3N_4) ceramics were used as substrate material due to the well-proven adhesion of NCD to this ceramic [7]. A screening analysis is performed using pin-on-flat tribological tests under lubrication with simulated physiological fluids: Hanks's balanced salt solution (HBSS) and dilute fetal bovine serum (FBS). The experiments are self-mated, considering that articulating surfaces, acetabular cup and femoral head, can both be coated with NCD films.

* Corresponding author. Department Ceramics & Glass Eng., University of Aveiro, 3810-193 Aveiro, Portugal. Tel.: +351 234370243; fax: +351 234425300.
E-mail address: rsilva@cv.ua.pt (R.F. Silva).

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2. Experimental

A Si_3N_4 ceramic, whose composition and preparation has been described elsewhere [8], was used as substrate material. Square plates ($10 \times 10 \times 3$ mm^3) and cylindrical and flat ended pins (diameter = 4 mm; thickness = 3 mm) were polished with colloidal silica until a mirror-like surface was obtained. Two sets of samples were used in the tribological tests: one composed only by polished samples (P) and other comprising polished and tetrafluoromethane (CF_4) plasma etched substrates (PE). Prior to NCD deposition, all the substrates were scratched for 1 h in an ultrasonic suspension with 1 µm diamond powder in *n*-hexane (1 g/100 ml), followed by ultrasonic cleaning with ethanol for 10 min.

NCD films were grown by hot-filament chemical vapour deposition (HFCVD) technique using an $Ar–H_2–CH_4$ gas mixture and the following conditions: $Ar/H_2 = 0.1$, $CH_4/H_2 = 0.04$, tungsten (W) filament/substrate distance = 5 mm, filament temperature = 2300 °C, substrate temperature = 750 °C, total gas flow = 50 $ml \cdot min^{-1}$, total pressure = 5 kPa and deposition time = 22 h.

The tribological testing of self-mated NCD coatings on the Si_3N_4 ceramic was performed in a reciprocating sliding tribometer. The oscillating arrangement consisted on a pin-on-flat geometry and tests were performed under lubricated conditions at room temperature. The liquids used were: i) Hank's balanced salt solution (HBSS, Cambrex, Belgium) containing 8 $g \cdot L^{-1}$ NaCl, 1 $g \cdot L^{-1}$ glucose, 0.4 $g \cdot L^{-1}$ KCl, 0.35 $g \cdot L^{-1}$ $NaHCO_3$, 0.09 $g \cdot L^{-1}$ $Na_2HPO_4.7H_2O$ and 0.06 $g \cdot L^{-1}$ KH_2PO_4 as main components; and, ii) fetal bovine serum (FBS, Cambrex, Belgium) diluted to 50% to contain 18.5 $mg \cdot ml^{-1}$ protein, complying with synovial fluid plus 0.2 wt.% of a biocide (NaN_3, Merck, Germany).

A constant stroke of 6 mm and frequency of 1 Hz were imposed to give a sliding velocity that lies in the range typically found for a working hip joint [9]. The tests lasted for 500,000 cycles, giving a total sliding distance in the order of 6 km, under 45 N of normal load, the friction coefficient being continuously recorded. The tests with HBSS lubrication were uninterrupted while the experiments using FBS needed to be periodically stopped to replace the liquid and minimize serum degradation.

The morphology of the NCD coated ceramics and of the worn surfaces was observed by scanning electron microscopy (SEM) in order to characterize the microstructure and the wear processes. This analysis was complemented by atomic force microscopy (AFM), used to assess topographical features and wear. Wear rates were calculated using the AFM bearing function for volume loss quantification data [10].

3. Results and discussion

A parameter of decisive importance in NCD coatings relates to the surface conditioning prior to the deposition as it will affect the adhesion, the surface roughness and even the growth rate [7]. The SEM micrographs in Fig. 1 exemplify the microstructure of as-deposited NCD films on polished (P), Fig. 1a, and on etched (PE) ceramics, Fig. 1b. The lower surface roughness of the P samples relatively to the PE ones was confirmed by AFM analysis, Fig. 1c and d. The former have RMS values in the range 70 nm to 130 nm, while for PE samples the RMS values lie between 200 nm and 400 nm due to the CF_4 etching. The insets of Fig. 1a and b also reveal differences in the growth rate of NCD, due only to distinct surface conditioning as the deposition conditions are the same. For P samples the measured growth rate is about 0.6 $\mu m \cdot h^{-1}$ while it is nearly the double

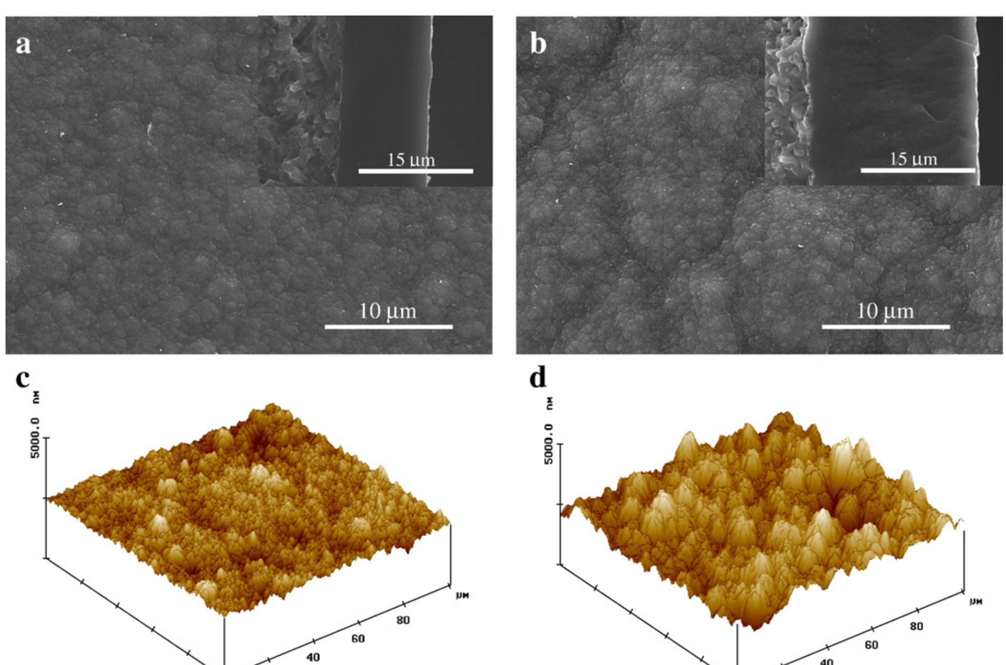

Fig. 1. SEM micrographs of NCD coated samples with inset micrographs of fracture cross-section showing the thickness of the NCD films for: a) P samples; b) PE samples. AFM micrographs evidencing the surface roughness differences between P (c) and PE (d) NCD coated substrates.