Applied Surface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

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

The stability of DLC film on nitrided CoCrMo alloy in phosphate buffer solution

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ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form 18 April 2014
Accepted 19 April 2014
Available online xxx

Keywords:
CoCrMo alloy
Diamond like carbon
Stability
Nitrogen implantation
Corrosion
Adhesion

ABSTRACT

CoCrMo alloy is often used as the material for metal artificial joint, but metal debris and metal ions are the main concern on tissue inflammation or tissue proliferation for metal prosthesis. In this paper, nitrogen ion implantation and diamond like carbon (DLC) film composite treatment was used to reduce the wear and ion release of biomedical CoCrMo substrate. The mechanical properties and stability of N-implanted/DLC composite layer in phosphate buffer solution (PBS) was evaluated to explore the full potential of N-implanted/DLC composite layer as an artificial joint surface modification material. The results showed that the DLC film on N implanted CoCrMo (N-implanted/DLC composite layer) had the higher surface hardness and wear resistance than the DLC film on virgin CoCrMo alloy, which was resulted from the strengthen effect of the N implanted layer on CoCrMo alloy. After 30 days immersion in PBS, the structure of DLC film on virgin CoCrMo or on N implanted CoCrMo had no visible change. But the adhesion and corrosion resistance of DLC on N implanted CoCrMo (N-implanted/DLC composite layer) was weakened due to the dissolution of the N implanted layer after 30 days immersion in PBS. The adhesion reduction of N-implanted/DLC composite layer was adverse for in vivo application in long term. So researcher should be cautious to use N implanted layer as an inter-layer for increasing CoCrMo alloy load carrying capacity in vivo environment.

1. Introduction

Joint prosthesis has been successfully used to cure the osteoarthritis, rheumatoid arthritis, bone tumors or traumas. Metal-on polymer (MOP), ceramic-on-polymer (COP) and ceramic-on-ceramic (COC) joint bearings are used widely in clinical application [1]. However, the MOP and COP artificial joint have a problem in long term service. The debris worn from the polymer, ultra high molecular weight polyethylene (UHMWPE), may cause the process of osteolysis and aseptic loosening [2–4]. Comparing with MOP and COP bearings, COC type joint prosthesis has the best wear resistance. But ceramic material is brittle and sensitive to stress concentration. So the unexpected catastrophic failure, such as brittle fracture, has to be concerned for COC type joint prosthesis in clinical even though the possibility is small [5].

Metal-on-metal (MOM) bearing is another type of artificial joint with good toughness and anti-wear properties. The wear resistance of MOM type joint is better than MOP and COP joint. The wear rate of MOM is in the range of 1–3 mm^3/year while the MOP is 5–30 mm^3/year [6]. And MOM type joint has good toughness and wear resistance, it allows big femoral head size leading to large range of motion [7]. These advantages make MOM type joint suitable for young and active patients. In the United States, more than 500,000 patients have received MOM hip prosthesis [8]. But the MOM joint is still imperfect because the metal debris and metal ions will be produced after long-term service in vivo. These debris and ions may induce tissue inflammation or tissue proliferation, which would cause further failure of the joint prosthesis [9].

In order to reduce the wear and ion release of the metal component, surface treatment has been used to improve the lifetime of the MOM joint prosthesis. Diamond like carbon (DLC) film is a kind of hard film with chemical inertness, wear resistance and biocompatibility. And it is considered as a promising coating to reduce the wear and ion release of MOM joint. In vitro studies, DLC coated MOM joint has revealed much better wear-resistance than the traditional MOP and MOM ones [10–12]. But in clinical application, DLC coated artificial joints perform below expectation. In 2003, Taeger et al. reported that 45% of the DLC coated artificial joint failed in 8.5 years due to the delamination of DLC film [13]. The DLC coated artificial joint should serve in human body for a long

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http://dx.doi.org/10.1016/j.apsusc.2014.04.117
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time and the adhesion, especially the long-term adhesion of DLC film is crucial for its application. If the DLC delamination happens, the fragments will cause severe three body abrasion and accelerate the failure of the implants [14].

In this paper, N ion implantation and DLC film were used to improve the wear-resistance of CoCrMo alloy (Cr: 28.02%, Mo: 6.11%, Ni: 0.2%, C: 0.062%, Co: bal. It is widely used as MOM joint material). The load bearing capacity, friction and the stability (structure, adhesion and corrosion resistance) of DLC film in phosphate buffer solution (PBS) were investigated to explore the full potential application of N-implanted/DLC composite layer in vivo environment.

2. Experiment

2.1. Samples preparation

Pins (cylinders with Φ 6 mm ball heads) and discs (1.2 mm thickness, Φ 14 mm) made of biomedical CoCrMo alloy were ground and polished to a mirror like finish. In order to improve the load bearing capacity, the samples (pins and discs) were firstly nitrided by high frequency and low voltage plasma immersion ion implantation (HLPIII) with nitrogen (N_2) as process gas [15]. The chamber was pumped down to 5.0×10^{-3} Pa. Prior to the implantation, Ar plasma was used to sputter and clean the samples at −1300 V dc bias voltage for 30 min. Then N_2 was introduced into the chamber and ionized under 800 W radio frequency (RF) power. The N ions were implanted into the substrates at a 3.5 kV bias pulse voltage (duty ratio 25%, frequency 15.15 kHz) for 3 h. The substrate temperature during the HLPIII is about 350 °C. The depth of the N implanted layer is about 3.2 μm and the indentation hardness of the nitrided layer is 23 GPa. After N implantation, the roughness of CoCrMo alloy samples increased from 25 nm to 70 nm. Then DLC films were deposited on the N implanted (CoCrMo/N) and virgin CoCrMo samples (pins and discs) by magnetic filtered cathodic vacuum arc source (MFCVA) [16]. The base pressure was less than 3.0×10^{-3} Pa. Before the deposition, all the samples were sputter cleaned in Ar plasma at a −1200 V dc bias voltage for 15 min. Before DLC deposition, a 50 nm Ti interlayer was deposited on the N implanted and virgin CoCrMo substrates with a titanium cathode for better adhesion. Then 360 nm DLC film was deposited by magnetic filtered cathodic vacuum arc source with a carbon cathode.

2.2. Mechanical properties of DLC film

Micro indentation hardness of DLC films were evaluated using a Dynamic Ultra-Micro Hardness Tester (DUH-211S, SHIMADZU, Japan). Load–unload curve was obtained in the experiment to analyze the load bearing capacity of virgin CoCrMo, CoCrMo/Ti/DLC (labeled as DLC) and CoCrMo/N/Ti/DLC (labeled as NDLC) sample. The applied load was 20 mN and the loading speed was 0.89 mN/s. The indentation hardness was calculated by the method described in Ref. [17].

The wear resistance of the samples was evaluated with a pin-on-disc rotation tribometer (CSEM, Switzerland). Three groups of pin-on-disc friction pairs (CoCrMo–CoCrMo, DLC–DLC and NDLC–NDLC) were tested in this paper. The pins were fixed in the upper sample holder and the discs were fixed into a sample holder where the phosphate buffered saline (PBS) covered the samples. The discs performed the rotation motion with the sliding velocity of 3 cm/s, the track radius was 3 mm and the sliding distance was 471 m. The normal force applied for the pins was 2 N.

After the friction experiments, microscopy and profilometer were used for wear volume assessment. The pin wear volume was evaluated based on the size of wear scar obtained by optical microscopy (Axio Lab.A1, ZEISS, Germany). The disc wear was assessed according to the cross section outline of the wear track which was obtained by a profilometer (XP2, AMBIOS, USA).

2.3. The stability of DLC film-substrate system

Film coated joint will suffer the corrosion of the synovial fluid during the long time service, thus the structure and adhesion stability of DLC film is essential. In this paper, in order to research the stability of the DLC film on the virgin and N implanted CoCrMo alloy substrate in physiological environment, the samples were immersed in PBS (NaCl: 8 g/L, KCl: 0.2 g/L, Na_2HPO_4: 1.44 g/L, KH_2PO_4: 0.24 g/L) at room temperature (10–15 °C) for 30 days. And after that the samples were rinsed with distilled water and dried in air. The structure change of DLC film was characterized by Raman spectroscopy (InVia Raman Microscope, RENISHAW, Britain) and Fourier transform infrared spectroscopy (FTIR, Nicolet 5700, USA).

The adhesion and the corrosion properties of DLC film were evaluated by scratch test and dynamic polarization experiments. The scratch test was performed using a MFT-2000 scratch tester (Lanzhou, China). A GCr15 steel ball with 3 mm diameter was chosen as the indenter and the scratch length was 5 mm. The loading speed of the steel ball was 100 N/min and the maximal load was 100 N. The scratch morphologies were observed by an optical microscope (Axio Lab.A1, ZEISS, Germany) to evaluate the adhesion of DLC films.

Dynamic polarization experiments were carried out in the 0.9% NaCl solution using an electrochemical workstation (IM6, Zahner, Germany) to evaluate the corrosion resistance of the films. Before the polarization, the samples were kept in the solution for 15 min to establish a relative stable open circuit potential (OCP). The potential of the electrode was scanned from −500 mV to 1000 mV with a scan rate of 0.2 mV/s.

3. Results

3.1. The mechanical properties of the as-deposited DLC film

Indentation tests were performed to evaluate the micro-hardness of the DLC films. Load–unload curves are shown in Fig. 1. The virgin CoCrMo alloy shows the largest indentation depth (0.31 μm) corresponding to an indentation micro-hardness of 10 GPa. The indentation depth of the DLC film deposited on virgin CoCrMo substrate (DLC sample) is about 0.25 μm, and the composite indentation micro-hardness is 20 GPa. Meanwhile, the indentation depth of NDLC sample is only about 0.18 μm and the

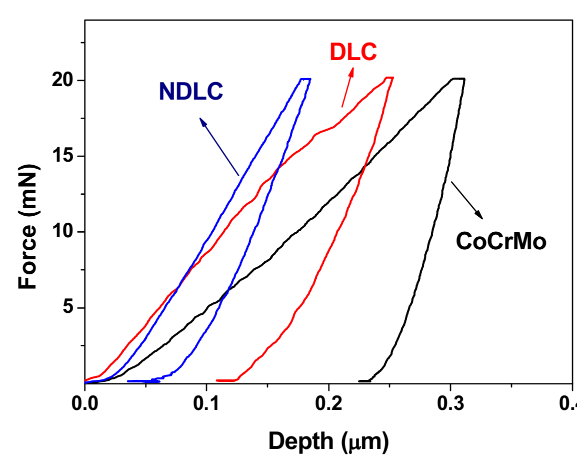

Fig. 1. Load–unload curves of CoCrMo, DLC and NDLC samples at the maximum indention load of 20 mN.

Please cite this article in press as: T.F. Zhang, et al., The stability of DLC film on nitrided CoCrMo alloy in phosphate buffer solution, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.04.117