ORIGINAL PAPER

Tribocorrosion of Diamond-Like Carbon Deposited on Ti6Al4V

T. M. Manhabosco · I. L. Müller

Abstract Tribological and corrosion properties of Ti6Al4V alloy both bare and coated by diamond-like carbon (DLC) were investigated in PBS solution. The films obtained by a PACVD technique present high hardness, good corrosion and wear resistance and lower friction coefficient compared to bare alloy. Tribocorrosion tests on bare alloy showed that when wear stops, the alloy rapidly passivates. DLC films present superior wear resistance under dry conditions. However, film life is greatly reduced during tribocorrosion tests.

Keywords Corrosive wear · Corrosion · Carbon

1 Introduction

In a tribological contact, the coefficient of friction and the wear are the main parameters to describe the performance of this system, i.e., the tribological system. The wear characteristics of the system define the lifetime of the materials and the amount of wear products produced. In the last decade, there has been an increasing interest in diamond-like carbon (DLC) films mainly as a biomaterial due to their very good properties such as high hardness, low wear rates, low friction coefficient, bio and hemocompatibility. Under tribological contact, some authors [1, 2] suggest that the DLC coating produces a so-called transfer layer to the partner surface that promotes an extremely low wear rate of the DLC coating. Other authors propose a chemisorption of hydrogen or other chemically species on sliding interfaces [3, 4] and the occupation of the dangling bonds on the surface of the films by hydrogen and oxygen [5], thus reducing the friction force. Also, the wear products can act as a solid lubricant as they are graphitic products according Edemir et al. [6].

With these interesting properties, DLC coatings are promising candidates for biomedical applications like load-bearing implants, for example, knee and hip replacements. However, a disastrous example occurred with knee-joints commercially which in a short period of time showed delamination, increased wear and implant loosening [7]. In this case, the materials forming the tribological contact are not only exposed to wear but also to a corrosive environment, therefore constituting a tribocorrosion system, which can strongly affect the wear and so the work life. Tribocorrosion is defined as an irreversible transformation of material resulting from simultaneous physico-chemical and mechanical surface interactions occurring in a tribological contact [8].

Despite extensive research done in the field of DLC coatings, few works account for the wear of the coatings in the presence of humidity, water or lubricant environments [9–14] and the wear–corrosion synergism in a corrosive environment [15, 16]. Most of the works carried out in aqueous environment (like in NaCl or other simulated physiological solutions) show a catastrophic failure of the films and try to explain this occurrence [9–11, 13, 15]. Aiming to contribute to increased research on tribocorrosion and to understanding the action of the degradation mechanism in the field of DLC coatings, the present work shows some results of tribocorrosion performance of a DLC-coated Ti alloy, in a simulated physiological environment.

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2 Experimental

The substrate material was obtained from a Ti6Al4V (grade 5) bar with a mean thickness of 17 mm and 38 mm diameter. The sample surfaces were ground with SiC emery paper to 800 grit and polished with colloidal silica to a surface roughness of R_a 0.025 μm. After polishing, the samples were ultrasonically cleaned in acetone for 10 min followed by rinsing in methanol and deionized water.

The DLC films were deposited on the polished samples using an RF (13.56 MHz) PACVD technique. Prior to deposition, samples were cleaned by sputtering with Ar. The deposition was performed at 1.5 Pa with acetylene (C_2H_2) flowing at a rate of 50 sccm for 2 h. The negative self-bias voltage of the RF powered electrodes was 1000 V.

The coatings were analyzed by Raman spectroscopy performed with a NTEGRA Spectra Nanofinder (NT-MDT) operating with a blue laser (488 nm) at room temperature.

Electrochemical tests were performed with an EG&G PAR Model 273 potentiostat. In order to simulate the physiological environment, the phosphate buffer saline solution (PBS) was used, which is composed by 8 g/L NaCl, 0.2 g/L KCl, 0.594 g/L Na_2HPO_4 and 0.2 g/L KH_2PO_4, pH = 7.1. All corrosion experiments were carried out in the same electrochemical cell, including the tribocorrosion tests, with a platinum wire as counter-electrode and a saturated calomel electrode as reference electrode at a temperature of 37 °C controlled by a thermostatic bath. Prior to the experiments, the system was maintained for 1 h at open circuit potential (OCP). Potentiodynamic polarization curves were performed at a scan rate of 0.167 mV/s and potentiostatic essays at 400 mV, an anodic potential located in the passive region of the titanium alloy. The total coating porosity was estimated from electrochemical measurements using the empirical equation [17]:

$$P = \left(R_{pm(substrate)} / R_{p(coating-substrate)} \right) \times 10^{-|\Delta E_{cor}/\beta_a|} \qquad (1)$$

where R_{pm} is the polarization resistance of the substrate, R_p the measured polarization resistance of the coated alloy, ΔE_{cor} is the potential difference between the corrosion potentials of the coated alloy and the bare substrate and β_a the anodic Tafel slope for the substrate. The protective efficiency of the coating was also determined from the polarization curve by the following equation [18]:

$$P_i = 100(1 - i_{cor}/i_{cor}^{\circ}) \qquad (2)$$

where i_{cor} and i_{cor}° are the corrosion current densities in the presence and absence of the coating.

Wear tests were carried out in a reciprocating motion pin-on-plate tribometer with an alumina ball ($\varnothing$ 5 mm,

Saphirwerk). These tests were achieved in two conditions, setting normal load, sliding velocity and sliding distance to 4 N, 8 mm/s, 8 mm or 16 N, 32 mm/s, 8 mm, respectively. Tribocorrosion tests, with the same electrochemical and wear parameters used in the other tests, were performed coupling the electrochemical cell to the pin-on-plate tribometer with the reference electrode no more than 1 cm distant from the wear track.

At the end of each wear test, the wear track was analyzed by optical microscopy and scanning electron microscopy (SEM); the wear track profile was recorded by a profilometer (MicroGlider, Fries Research & Technology).

3 Results and Discussion

The film morphology, observed by SEM, reveals a smooth structure composed by well-compacted grains. Cross-sectional images were used to determine a 4 μm film thickness.

Raman spectroscopy, one of the most used techniques to characterize DLC coatings, was performed. The spectra (Fig. 1) reveal two peaks located at approximately 1380 and 1598 cm^{-1} that can be related to the D and G bands typical of DLC films. The D band is assigned to the "disordered carbon", the bond-angle disorder in the sp^2 graphite-like microdomains, induced by linking with sp^3 atoms, as well as the finite crystalline sizes of sp^2 microdomains, while the G band is ascribed to sp^2 trigonal bonding related to the graphite phase [19]. The Raman spectrum was deconvoluted and the I_D/I_G ratio, a qualitative indicator of the nature of the bond and degree of graphitization, was calculated as being 0.64.
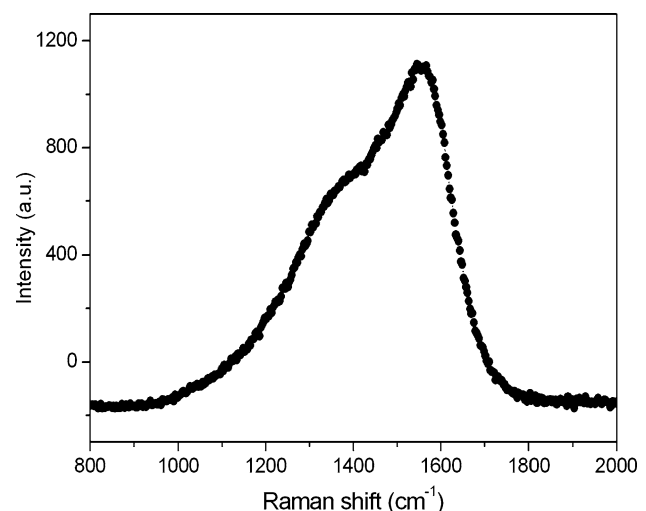

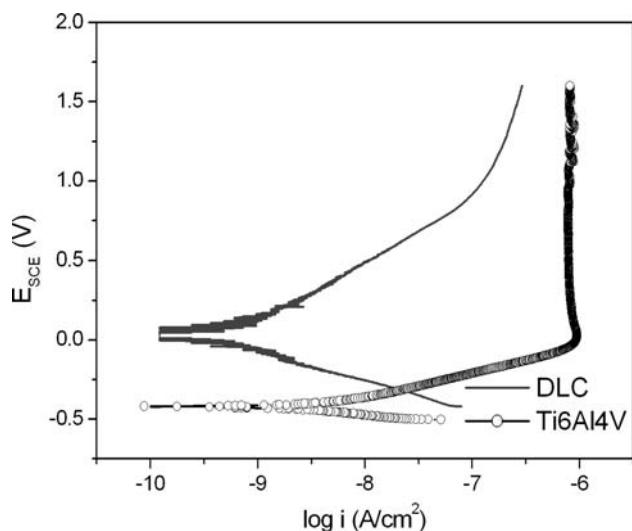**Fig. 1** Raman spectrum of DLC films

Fig. 2 Potentiodynamic polarization curves in PBS solution. Scan rate: 0.167 mV/s

Potentiodynamic polarization curves were performed in PBS solution for Ti6Al4V sample, both uncoated and DLC coated, and are shown in Fig. 2. The bare alloy presents a corrosion potential of about −0.4 V and a passivity current density of about 8×10^{-7} A/cm^2 from 0.02 V in the anodic direction. The DLC-coated samples present a nobler behavior with lower anodic current density. A protective efficiency of about 97% and a porosity of 0.01 were calculated from the potentiodynamic polarization tests, indicating superior corrosion protection; however, the presence of porosity, even at a low index, may facilitate the diffusion of water and aggressive agents through the coating that can lead to local corrosion, blistering of the coating and delamination.

Figure 3a shows the evolution of the E_{cor} over time in tribocorrosion tests, realized in PBS solution, for the bare alloy and DLC-coated alloy, while Fig. 3b shows the current density developed by a coated sample exposed to a 400 mV potentiostatic test and also tribocorrosion tests at the same 400 mV, with reciprocating sliding at 4 N, 8 mm/s and 16 N, 32 mm/s, respectively. A sudden decrease in corrosion

potential was observed for the bare alloy at the beginning of the wear that destroys locally the TiO$_2$ passive surface film exposing the alloy to the electrolyte. After stopping sliding, a rapid increase in the potential is observed as repassivation of the metal takes place. The coated samples also present a lowering of the corrosion potential as the tests run, probably due to the combined action of normal force and corrosive environment since the films contain pores. Figure 3b shows the influence of the normal force applied on the corrosion current density. The highest normal forces must induce an important tension in the film and substrate, which increases the corrosion process through coating pores and/or promotes the formation of microcracks in the coating, thus facilitating the diffusion of corrosive species throughout the film. At the end of wear, the current and potential values go to values slowly higher than that before wear, showing the influence of the wear load and the possible presence of a greater number of small defects in the coating than before the tests.
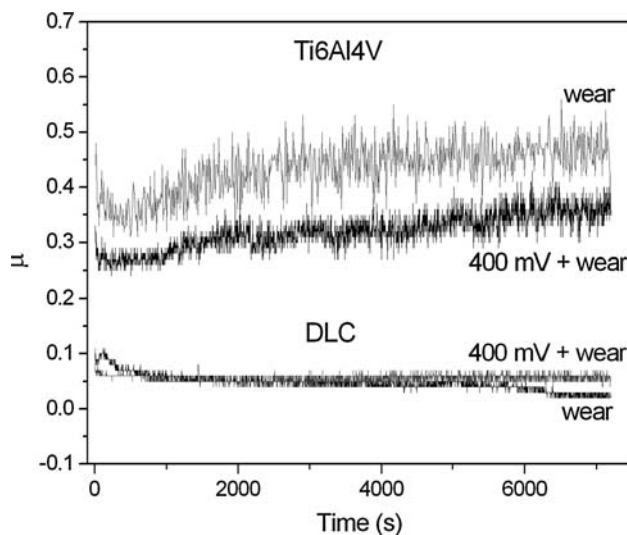

Fig. 4 Friction coefficients obtained from wear and tribocorrosion tests

Fig. 3 Evolution of E_{cor} (**a**) with time in tribocorrosion test at OCP. Developed current density (**b**) with time in potentiostatic and tribocorrosion tests
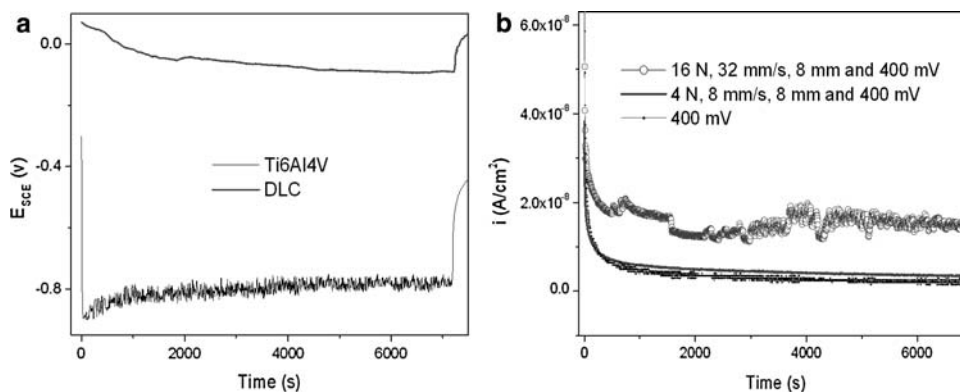
Figure 4 shows the friction coefficients from wear and wear–corrosion tests for bare and DLC-coated alloy. For the tribocorrosion tests, the same mechanical parameters for wear tests were used simultaneously with an applied corrosion potential of 400 mV. The alloy presents a high friction coefficient of about 0.44 at ambient air condition that is reduced to 0.33 in the wear–corrosion tests due the lubricant action of the PBS solution. The DLC coatings present a much lower friction coefficient that after a run-in stage becomes 0.04 in ambient air. As observed, in PBS solution, the initial run-in stage becomes much shorter and the friction coefficient exhibits a value of around 0.05.

After wear and tribocorrosion tests during 2 h, at a normal force of 16 N and sliding velocity of 32 mm/s, the wear track and the counterbody profile were acquired by profilometry and the wear volume was estimated from the profiles. Figure 5 shows the wear track and counterbody profiles for blank Ti6Al4V (a) and DLC coatings (b) after wear and tribocorrosion tests. The wear volume at dry conditions for the bare alloy was about 1.2×10^{-10} m^3 while in tribocorrosion tests, the wear volume was lower (1.03×10^{-10} m^3) probably due the lubricant action of the fluid that reduces the third body action by dispersing the wear debris. Also, the counterbody suffered greater damage under dry conditions. As can be seen in Fig. 5a, the presence of PBS solution changes the profile of wear track mainly on the bare alloy, when it becomes deeper and narrower than that from wear tests in air. Under the same conditions tested, DLC coatings present superior wear resistance, indicating that the substrate is protected from abrasive wear by the hard coating. The wear volume in DLC coatings after 2 h of rubbing was about 4×10^{-13} m^3 in air and 9×10^{-14} m^3 in PBS solution with no visible damage and no detectable transfer layer to the counterbody.

Wear and wear–corrosion tests were carried out until coating failure occurred. At ambient air, the failure occurred after 4.1 km of wear. However, when wear–corrosion was performed, the life of the coating was reduced and failure occurred after covering different distances, from 0.37 to 2 km. Some tribocorrosion tests were achieved more than once in the same sample resulting in different distances of rubbing to failure. As the coatings may present dispersed defects (pores), which cannot hinder the diffusion of aggressive agents through the coating, the distance of rubbing to failure is also related to the probability that the rubbing may find some defect. Figure 6 shows the beginning of a failure in tribocorrosion tests with a neighboring region detached around the failure. From these observations, this study seems to agree with Drees et al. [9], who propose that the catastrophic failure of the coating in the corrosive environment is due to the loss of adhesion between the substrate and coating by the simultaneous action of both load and corrosive environment and that the life of the coating would be improved by decreasing porosity. Park et al. [11] effectively proved that the reduction of porosity increases the life of the coatings in an aqueous environment. We also propose, as the films contain pores and a rise in the normal force during tribocorrosion tests produces an increase in the corrosion current, that the tension induces a higher metal/DLC coating interface degradation.

The results showed that DLC coatings can improve the corrosion and wear resistance of titanium alloy-made devices. However, when these films were tested with
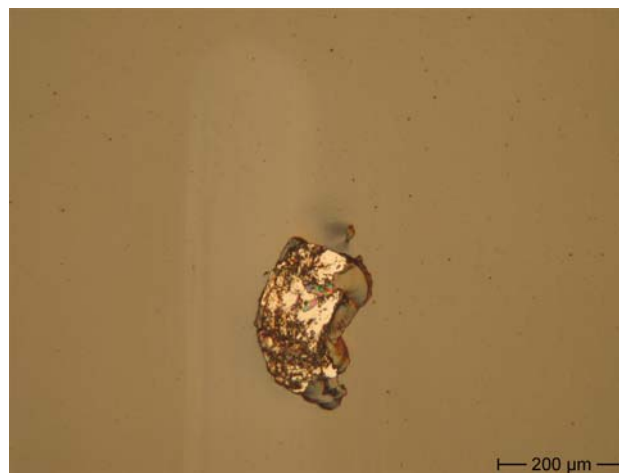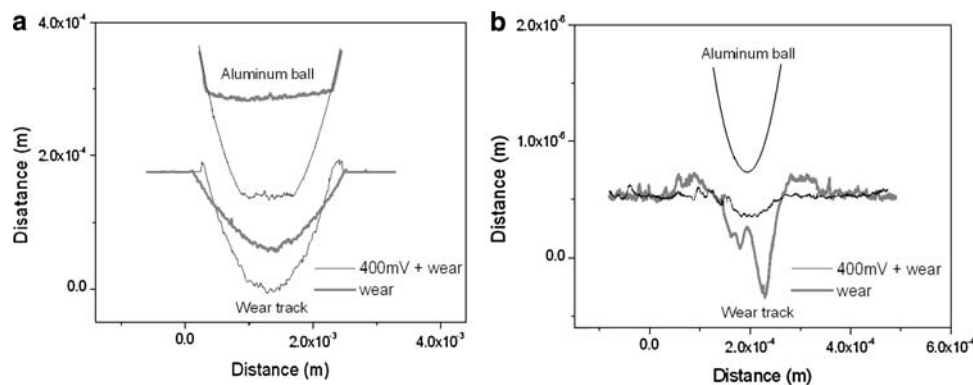

Fig. 6 Optical microscopy image of an initial failure on the coating

Fig. 5 Wear track and counterbody's profiles for blank (**a**) and DLC coated (**b**) Ti6Al4V after wear and tribocorrosion tests

simultaneous corrosion and wear, an important reduction in the lifetime of the films was observed. Despite the significance of this research, it is important to point out that these results cannot be directly extrapolated to an in vivo situation where proteins and different kinds of cells are present.

4 Conclusions

The passive surface oxide TiO_2 offers good corrosion protection for Ti6Al4V and a tendency to repassivate when this oxide is damaged. Despite its good corrosion resistance, the bare alloy has poor tribological properties.

DLC coatings demonstrate high protection efficiency (about 97%) against corrosion of the substrate, drastically reducing the corrosion current density in static conditions compared to the base alloy. The tribological properties were greatly improved under dry conditions. However, the life of DLC films was reduced 2–10 times in the tribo-corrosion tests by the simultaneous action of corrosion and wear mechanisms.

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