Kovove Mater. 50 2012 277–284
DOI: 10.4149/km_2012_4_277

The properties of diamond-like carbon coatings used for artificial joints

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Received 20 July 2011, received in revised form 2 December 2011, accepted 7 December 2011

Abstract

The paper presents the results of the tribological tests for materials used in elements of hip and knee endoprostheses. The tests were conducted for a Co-Cr-Mo alloy and the same material with a diamond-like coatings (DLC) coating produced by applying the plasma assisted chemical vapor deposition (PACVD) method. The materials to be tested were selected because of their good biocompatibility and high resistance to corrosion and sliding wear. The coating structure was determined by applying scanning electron and atomic force microscopes. The tribological characteristics were obtained with a T-17 tester operating in the pin-on-plate configuration under lubricated friction conditions. The friction pair consisted of a cobalt-based alloy plate, or alternatively, a cobalt-based alloy plate with a diamond-like carbon coating, and an ultra-high molecular weight polyethylene (UHMWPE) pin. The model lubricant used in the tests was Ringer's solution. The results indicated that the mechanisms of wear of the endoprosthesis elements were dependent mainly on the material used for the working surfaces in the friction joint. The wear resistance and friction coefficient of a cobalt-based alloy disc, or alternatively, a cobalt-based alloy disc with a diamond-like carbon coating, and an alumina ball were also determined by means of a T-01M tester during technically dry friction and lubrication in Ringer's solution. The comparative analysis confirmed different tribological effectiveness of the cobalt-based alloy and DLC coatings during friction.

Key words: AFM, biotribology, coatings, diamond, EDS, friction, SEM, wear resistance

1. Introduction

Materials based on carbon, either in the diamond or graphite form, play an important role in modern science and technology. In the recent thirty years, considerable progress has been made in the research and the application of diamond and diamond-like carbon coatings produced with the PVD and CVD methods, the discovery of fullerenes, carbon nanotubes, and single-layer graphenes [1]. Amorphous carbon is also increasingly used and has been reported suitable for coatings of orthopedic prosthesis. These coatings are known as corrosion resistive and biocompatible with good bearing capacity, wear resistance, and low friction. Hard amorphous carbon coatings have attracted considerable interest for mechanical applications because of their favourable tribological properties. Diamond-like carbon coatings cover a wide range of different types of carbon-based coatings.

Generally speaking, amorphous carbon is a mixture of sp^3, sp^2 and even sp^1 hybridized bonds; it may also contain hydrogen. Amorphous carbon materials possess a characteristic heterogeneous structure, and their properties are dependent on the method and parameters of the production process [1–3]. The composition of diamond-like coatings is not uniform, they have amorphous structure with micro-crystalline regions [4]. Hydrocarbon gases as precursor are often used in some deposition methods, therefore, hydrogen is incorporated into the diamond-like coatings

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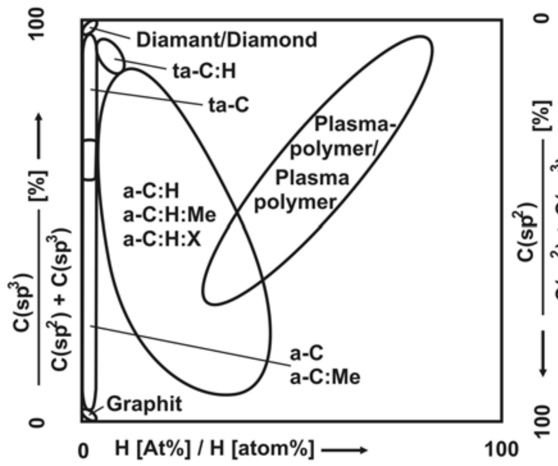

Fig. 1. Relationship between the ratio of sp^2 to sp^3 bonds and the hydrogen content.

(DLC) structures which are referred to as hydrogenated amorphous carbon films (a-C : H). Hydrogen atoms play a critical role in promoting and stabilizing sp^3 tetrahedral bondings, which is the typical structure of natural diamond [5–7].

The ratio of sp^2 to sp^3 bonds, with the former being typical of graphite and the latter characteristic of diamond, is an important factor determining the properties of these materials. The DLC coatings can be more diamond-like, with a large percentage of sp^3 bonded carbon atoms, or more graphite-like, with a small percentage of sp^3 bonded carbon atoms. Usually DLC coatings are amorphous or nano-crystalline and they are sometimes called a-C or, if they contain hydrogen, a-C : H. The coatings with a dominant content of sp^3 bond type are denoted as DLC. The properties of DLC coatings can be improved or modified by doping with metals (W or Cr) or non-metals (e.g. Si). The metal containing amorphous carbon coatings are denoted as Me-C : H (or a-C : H : Me), and the coatings modified with non-metals, like S or Si, are denoted as X-C : H (or a-C : H : X) [8].

Figure 1 presents the relationship between the ratio of bonds and the concentration of hydrogen [9].

For the last few decades, there has been close cooperation between engineers and physicians on friction and other complex processes occurring in natural and artificial joints. The core literature are works describing natural placentae; there are definitely fewer studies dealing with the design and maintenance of endoprostheses. The service life is dependent mainly on the friction system applied [10, 11]. The mobility system of a prosthesis consists of a polyethylene acetabulum and a metal or ceramic head. As the head has to be biocompatible and resistant to corrosion and sliding wear, it is made of a Co-Cr-Mo alloy. The materials of the friction pair, i.e. Co-Cr-Mo and UHMWPE, were characterized by relatively low wear resistance.

Although designs of endoprostheses are constantly being improved, the wear processes have not been reduced sufficiently. The recent research has focused on the application of more advanced materials.

DLC coatings deposited on elements for biotribological systems have to meet substantially higher quality requirements than industrially applied DLC coatings. The desirable properties include high adhesion, high mechanical and physicochemical stability, and high concentration of carbon atoms with sp^3 hybridized covalent bonds [12]. This analysis was conducted for DLC coatings deposited by the PACVD method, which are characterized by high quality and high structure homogeneity.

2. Apparatus and method

2.1. Metallographic analysis

The specimens made of the Co-Cr-Mo alloy and, alternatively, the Co-Cr-Mo alloy with a : C : H-type diamond-like carbon coatings were analyzed using an FEI XL30 E-SEM microscope equipped with a GEMINI 4000 EDAX energy dispersive X-ray spectrometer capable of performing measurements even in low vacuum. The spectrometer was equipped with an Si(Li) detector with a super ultra thin window (SUTW) ≤ 133 in resolution. The EDAX system was responsible for controlling an electron beam in the SEM microscope and acquiring images and maps using a scan generator.

2.2. AFM parameters

An NT-MDT atomic force microscope with a Smena (NT-MDT) probe was used to measure the material surfaces in the tapping mode. It was possible to visualize the topography of most surfaces, $(50 \times 50)\ \mu m^2$ and $(20 \times 20)\ \mu m^2$ in dimensions. The cantilever used for surface scanning (NSG 11 by NT--MDT) had $k = 5.5–22.5\ N\ m^{-1}$ and resonance frequency of 223.2 kHz.

2.3. Tribological tests

The tribological tests were conducted by means of a T-17 tester operating in the pin-on-plate configuration. It was possible to assess the friction coefficient and wear in the function of the number of cycles. The friction system consisted of a UHMWPE pin, and a plate made of the Co-Cr-Mo alloy, and alternatively the Co-Cr-Mo alloy coated with DLC. The tribological system was composed of:

– test machine,
– control and measurement system,

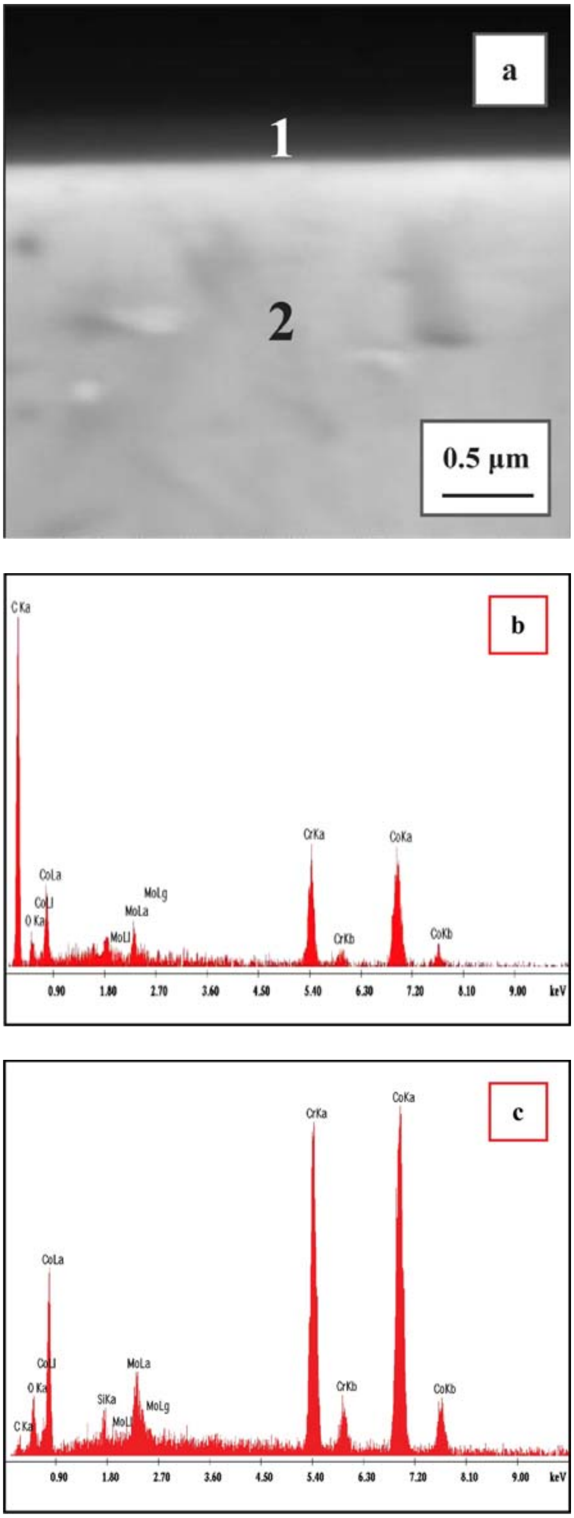

Fig. 2. SEM cross-sectional microstructure of the a : C : H coating: a) a SEM view and point analysis of the elementary composition of: b) the coating, c) the substrate.

– registration and archiving system,
– circulation system responsible for temperature stabilization and fluid filtration.

Long test time was necessary because the materials to be used for endoprosthesis elements were characterized by a very low wear ratio [4]. The metallic-polymer systems used for joint endoprostheses were tested at the following parameters:

– test duration/number of cycles: 1000000 s/1000000,
– amplitude: 12.5 mm,
– frequency: 1 Hz,
– average sliding velocity: 0.05 $\mathrm{m\,s^{-1}}$,
– load: 225 N,
– lubricating fluid: Ringer's solution,
– fluid temperature: 37 ± 1 ℃.

Tribological investigations were also carried out on T-01 M machine running in ball-on-disc configuration, enable assessment of friction and wear character in time, at constant load, temperature and surroundings humidity value, on the basis of friction force and wear intensity recording. Tribological curves were obtained during the tests in technically dry friction and boundary lubrication in Ringer's solution.

Conditions for friction pair are as follows:

– ball: Al_2O_3,
– disc: CoCrMo alloy, and alternatively the Co-Cr-Mo alloy coated with DLC,
– load $P = 9.81$ N,
– sliding speed $v = 0.1\ \mathrm{m\,s^{-1}}$,
– relative humidity conditions 55 ± 5 % ,
– surroundings temperature $T_0 = 23 \pm 1$ ℃.

3. Results and discussion

3.1. SEM analysis

Figure 2 shows the SEM view of cross-sectional microstructure of the a : C : H coating and point analysis of the elementary composition of: the coating (b) and the substrate (c).

The DLC coating possesses a highly homogeneous structure; no defect or non-discontinuity was found.

3.2. AFM analysis

The materials were analyzed also by means of an atomic force microscope to illustrate their surface topography. The microscope operated at atmospheric pressure in the tapping mode. The samples were scanned at an area of 50 × 50 µm^2 using an Si cantilever coated with Si_3N_4. The topographies and cross-section images of Co-Cr-Mo alloy and a-C : H coating with thickness of 2 µm are shown in Fig. 3.

3.3. Tribological tests

The tribological tests were performed using a T-17 tester operating in the reciprocating motion. The fric-

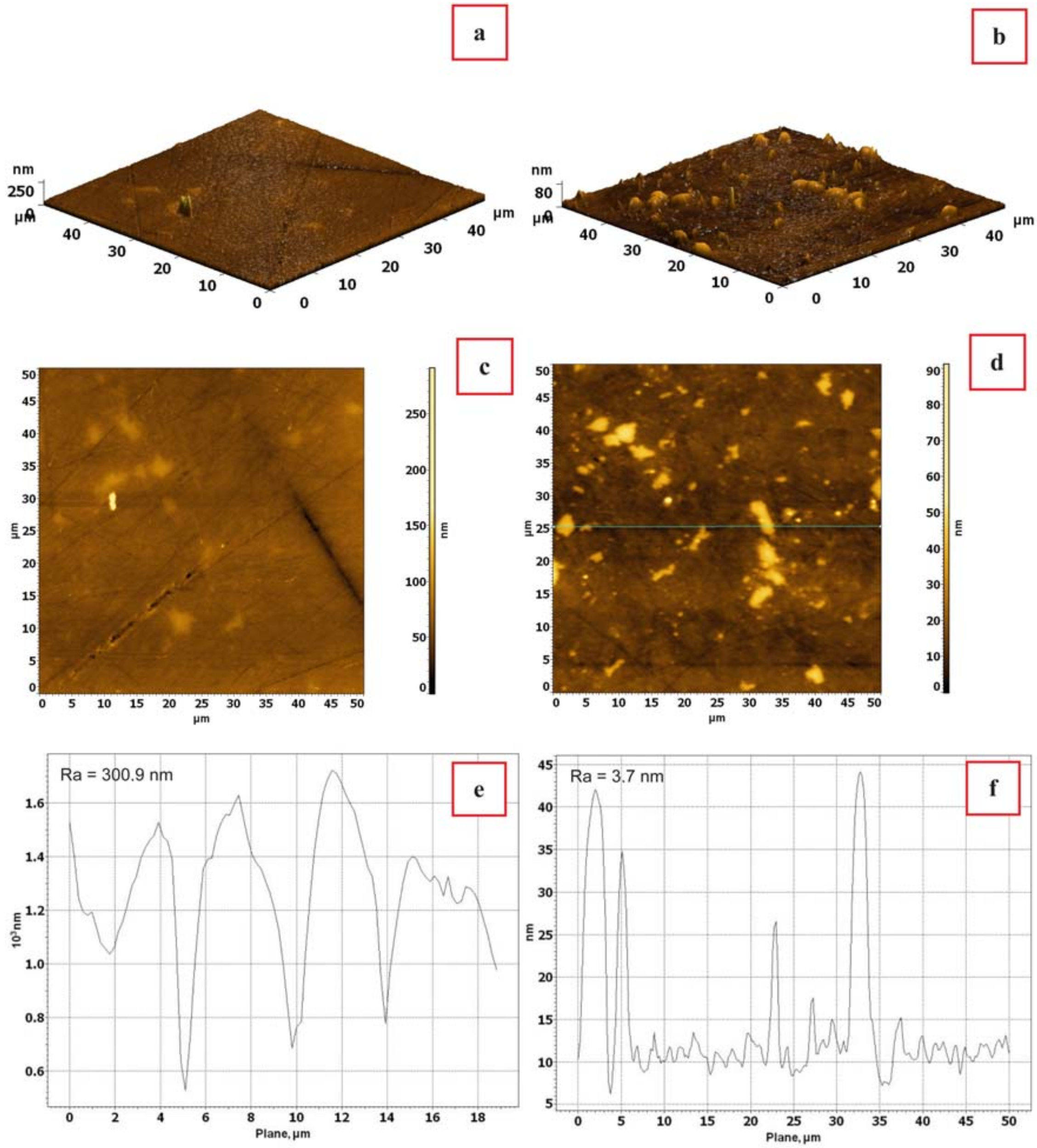

Fig. 3. AFM topography surface images of the investigated materials and their cross section with R_a parameters of: a), c), e) the Co-Cr-Mo alloy and the DLC coating b), d), f).

tion pair comprised a stationary pin made of ultra-high molecular weight polyethylene and a mobile plate made of Co-Cr-Mo, or alternatively, Co-Cr-Mo coated with DLC. The tests were conducted in accordance with the ASTM 732-82 standard [13]. The characteristics of the friction coefficient and linear wear versus the number of cycles were presented in Figs. 4 and 5, respectively.

As can be seen from Fig. 4, the value of the friction coefficient reported in the initial stage for the Co-Cr-Mo alloy was lower than that for the DLC coating. It should be noted that during the cycle, it was more stable, while, at the end, it was lower for the DLC coating. The average friction coefficient calculated for the period between cycles 300000 and 900000 was as follows: $\mu = 0.212$ for the Co-Cr-Mo and UHMWPE system, and $\mu = 0.207$ for the DLC and UHMWPE system.

Figure 5 demonstrates that the linear wear was higher for the Co-Cr-Mo alloy in the initial stage in the period of up to cycle 13600; then, it increased gradually till the end of the test. For the DLC specimen, however, there was a gradual increase in the linear wear up to cycle 360000; then, it remained stable.

The images of the wear areas presented in Fig. 6 confirm the above findings. The results concerning the

Table 1. Weight loss of the metallic-polymer friction joint

Friction element	Specimen weight		Wear	
	Prior to test	After test	(g)	(%)
Co-Cr-Mo				
Plate	56.9395	56.9378	0.0017	0.17
Pin	0.6994	0.6908	0.0086	0.86
DLC				
Plate	56.9993	56.9981	0.0012	0.12
Pin	0.6998	0.6918	0.0080	0.80

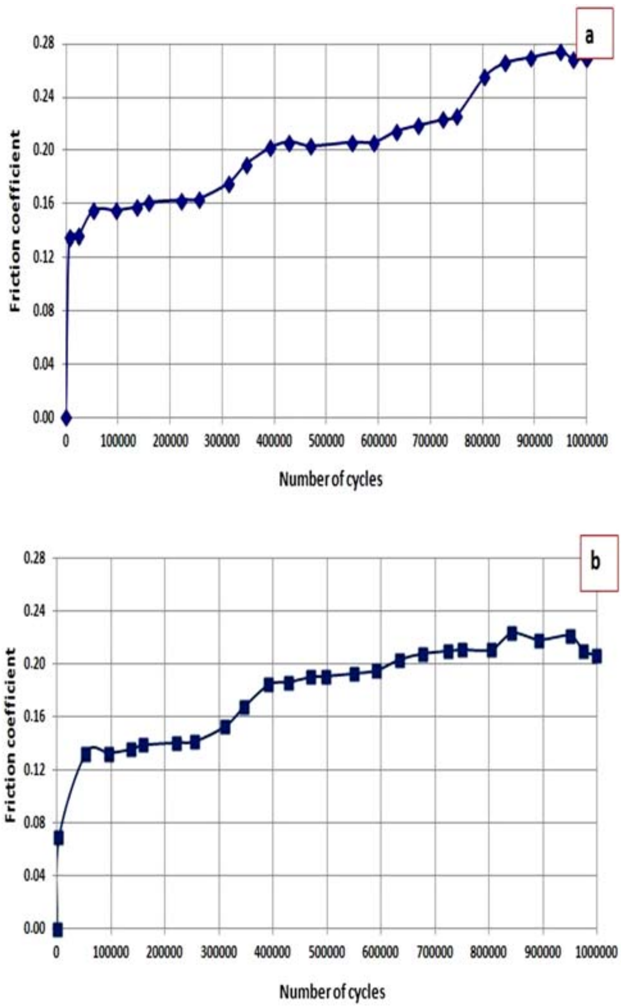

Fig. 4. Friction coefficient in the friction joint versus the number of cycles: a) the Co-Cr-Mo alloy, b) DLC coating.

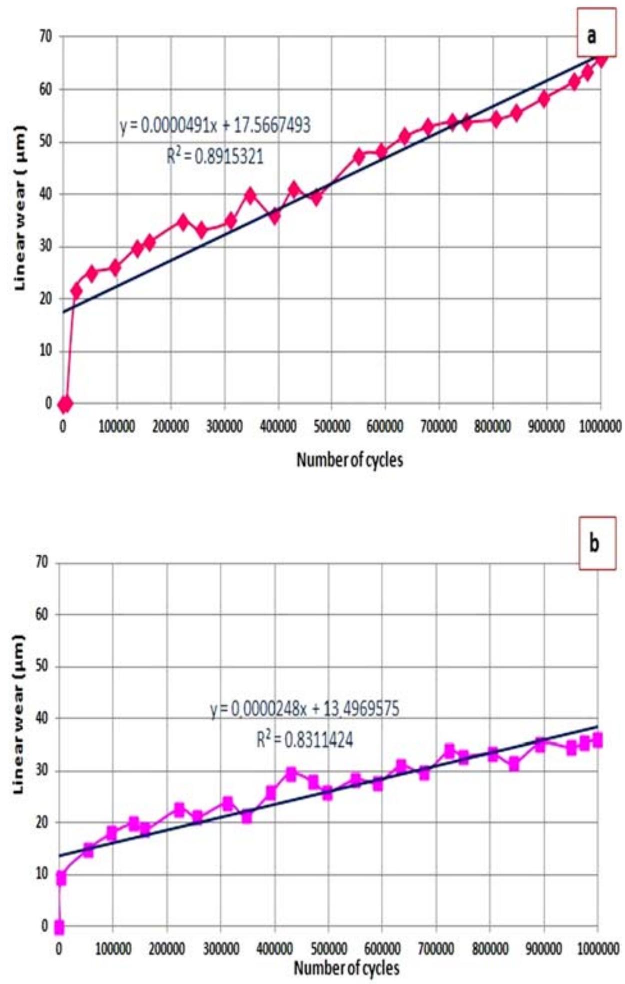

Fig. 5. Linear wear in the friction joint versus the number of cycles: a) the Co-Cr-Mo alloy, b) the DLC coating.

wear in the friction joint are included in Table 1.

The images show the rate and extent of tribological wear, which is considerably lower for the DLC coating (Fig. 6b) than for the base material. Analyzing the results, one can see that the a-C : H-type DLC coating demonstrated better tribological properties than the base material, i.e. the Co-Cr-Mo alloy, at the same pre-determined test parameters.

The tribological tests were also carried out with a T-01 M machine running in a ball-on-disc configura-

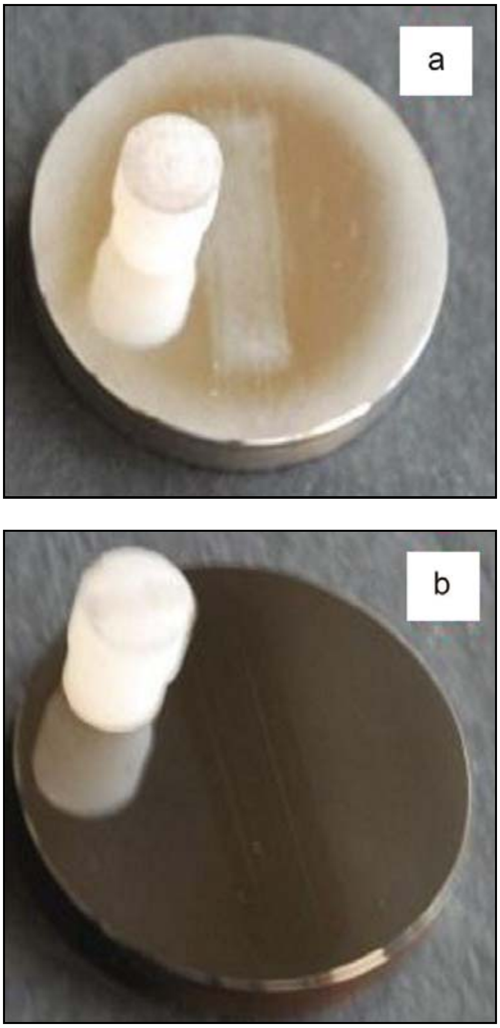

Fig. 6. View of the metallic-polymer friction joint after the tribological tests: a) the Co-Cr-Mo alloy and UHMWPE system, b) the DLC coating and UHMWPE system.

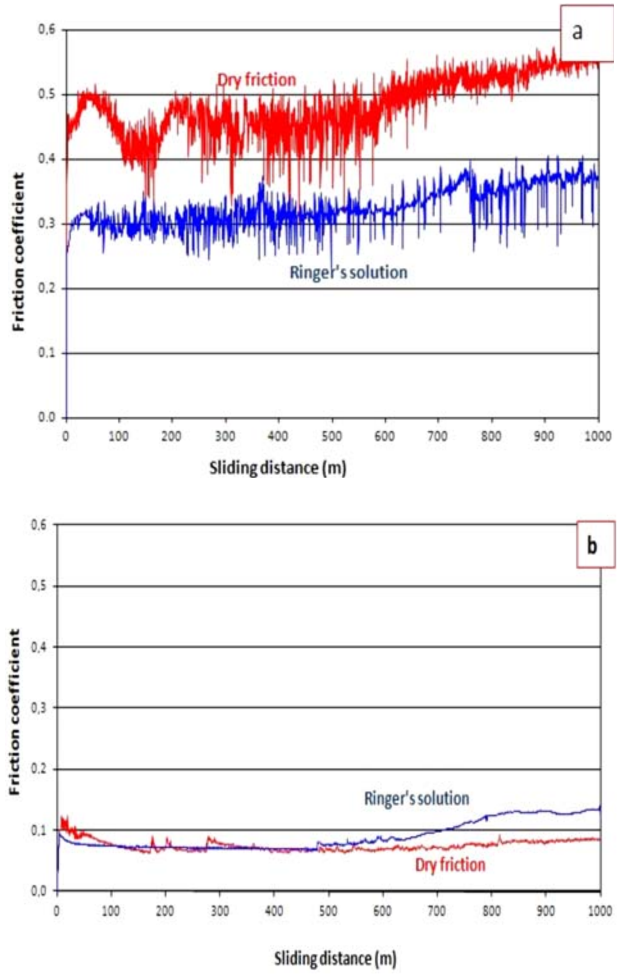

Fig. 7. Friction coefficient versus the sliding distance during technically dry friction and boundary lubricated friction using Ringer's solution: a) the Co-Cr-Mo alloy, b) the DLC coating.

tion. Figure 7 shows the relationship between the friction coefficient and the sliding distance during technically dry friction and boundary lubricated friction using Ringer's solution for the Co-Cr-Mo alloy, or alternatively, the Co-Cr-Mo alloy coated with DLC. The linear wear versus the sliding distance is presented in Fig. 8.

The friction coefficient obtained for the Co-Cr-Mo alloy during technically dry friction was 0.44 at the initial stage and 0.56 at the final stage. The changes in the friction coefficient observed during the test were due to the influence of the surroundings on the surfaces in contact. For the Co-Cr-Mo alloy, the friction coefficient during boundary lubricated friction using Ringer's solution was considerably lower; at the beginning of the test, it was 0.27, and, at the end, it reached 0.38. The changes in the friction coefficient were slightly more stable compared to the results obtained under technically dry friction conditions. However, the friction coefficient was significantly lower for the DLC coatings than for the Co-Cr-Mo alloy both during technically dry friction and boundary lubricated friction using Ringer's solution. The values of the friction coefficient ranged from about 0.12 to 0.09, and from 0.09 to 0.13, respectively; the changes during the tests were small, which testified the stability of the tribological system.

The changes in the coefficient of friction correspond to the changes in the linear wear. After 160 m of the sliding distance, there was an increase in the linear wear for the Co-Cr-Mo alloy, particularly under technically dry friction conditions. Higher stability was reported during boundary lubricated friction. Similar changes in the linear wear were observed for the DLC coating. The linear wear during technically dry friction was reported to be lower than that during boundary lubricated friction. The

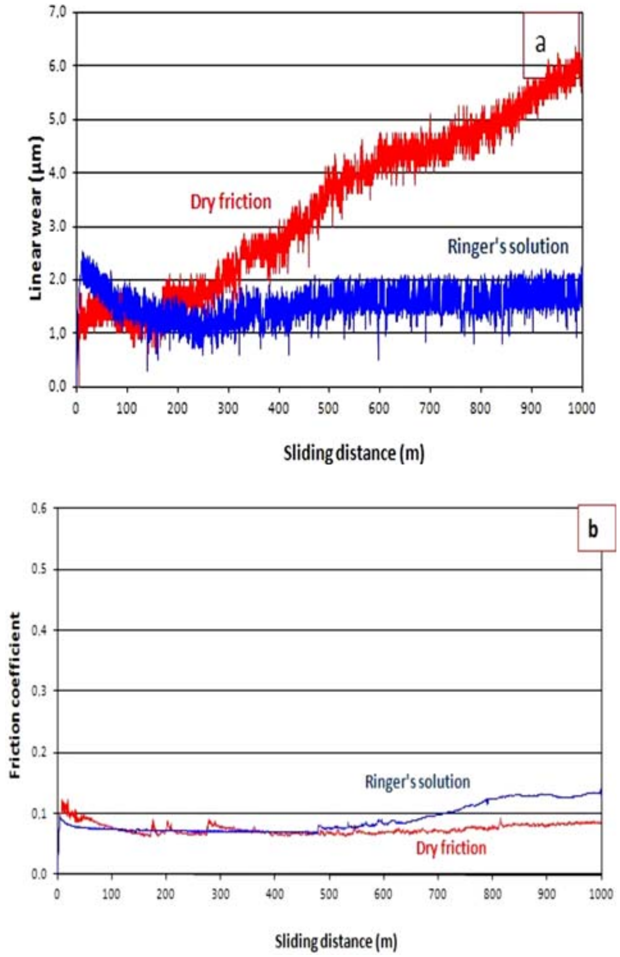

Fig. 8. Linear wear versus the sliding distance during technically dry friction and boundary lubricated friction using Ringer's solution: a) the Co-Cr-Mo alloy, b) the DLC coating.

initial slight decrease in wear followed by stability suggests higher tribological stability of the coating.

4. Conclusions

The behavior of the cobalt-based alloy with a diamond-like carbon coating in the UHMWPE tribosystem was compared to that of the uncoated cobalt-based alloy. Analyzing the properties of the materials applied to the tests, one can conclude that:

– a further study is required to determine the properties of the DLC coatings deposited by the PACVD method and UHMWPE with a view to increasing their biotribological applications;

– from the SEM and AFM analyses it is clear that the DLC coatings deposited by the PACVD method possessed a more homogeneous structure;

– the AFM analysis showed there was a decrease in roughness, parameter R_a, after the deposition of the DLC coating;

– the tribological tests using a T-17 machine and Ringer's solution showed that the average friction coefficient was lower and more stable for the DLC coating than for the Co-Cr-Mo alloy;

– the linear wear was more stable for the DLC coating than for the Co-Cr-Mo alloy both at the initial phase and during the whole test; the trend line was described by an equation used for determining the wear ratio coefficient measured in micrometers per one million cycles;

– the wear rate is considerably lower for the DLC coating than for the Co-Cr-Mo alloy;

– the tests were conducted in accordance with the ASTM standard; the DLC coatings showed better tribological properties and more stable operating conditions than the base material;

– the tests conducted with a T01-M showed that the tribological stability of the DLC coating was significantly higher than that of the substrate;

– lower values of the friction coefficient were reported for the DLC coating during technically dry friction as well as boundary lubricated friction using Ringer's solution.

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