Beneficial silver: antibacterial nanocomposite Ag-DLC coating to reduce osteolysis of orthopaedic implants

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Abstract. Silver-containing diamond-like-carbon (DLC) is a promising material for biomedical implants due to its excellent combination of antibacterial and mechanical properties. In this work, a dual-cathode pulsed filtered cathodic arc source containing silver and graphite rods was employed in order to obtain DLC samples with various silver contents. Chemical composition of the samples was analyzed by acquiring their compositional depth-profiles using radio-frequency Glow Discharge Optical Emission Spectroscopy (rf-GDOES), while the microstructural properties were analyzed by X-ray diffraction and Raman spectroscopy. Tribological studies carried out against UHMWPE balls in fetal bovine serum indicate that the presence of silver in DLC could be beneficial to reduce the wear of the polymeric surfaces.

Keywords. Silver, amorphous carbon, Raman, GDOES, wear, biotribology.

1. Introduction

Diamond-like carbon (DLC) films are of interest to many applications due to their favorable mechanical and tribological properties [1]. They have also generated interest in the biomedical field because of their high biocompatibility and perform well as a surface that will support appropriate cellular activity [2-6]. Strictly speaking, the term “DLC” includes a broad range of metastable amorphous carbon materials with variable sp^2/sp^3 and H contents. In this manuscript, we will employ the broad term “DLC” to refer to hydrogen-free amorphous carbon with an overall sp^3 content around 30%, and deposited by the plasma immersion implantation and deposition technique. Amorphous carbon films can be functionalized using plasma treatments [7] and by embedding metallic elements, which can also add functionality by providing an antimicrobial effect [8-13]. However the use of DLC-coated implants has not been widely employed due to the increased wear observed in ultra-high molecular weight polyethylene (UHMWPE) in polymer/coated metal implants. The formation of worn particles of UHMWPE has been found to cause a medical condition called osteolysis, which refers to bone resorption due to removal or loss of calcium from the bone near the joint implant [14]. In this work, we carry out a set of tribological tests in order to determine the influence of silver embedded in a DLC matrix on the reduction of the wear of the UMWPE balls.

2. Experimental

Amorphous carbon films doped with silver were prepared on TiAl6V4 disc substrates by pulsed dual-cathode filtered cathodic vacuum arc (PDC-FCVA). Pulsed arc discharges on individual cathodes were triggered by a computer control system using a “triggerless” system [15]. The pulses used in the production of carbon plasma were 100 A and had a duration of 5 ms, while the metal plasma was made using pulses of 1 ms long and a current of 700 A. The plasma stream produced by the source is injected into a 90-degree filter to remove most of the macroparticles which were formed during the cathodic arc process. After exiting the filter, the plasma expanded through a homogenizer device composed of concentric magnets and allowed to have homogeneous thickness and composition in the substrates over an area of 80 cm^2. During the deposition of carbon pulses, the substrates were biased with negative 1 kV pulses that were 2 μs long with an off time between pulsed of 14 μs. The substrate was kept at ground potential during the deposition of the metal plasma (hence “species selective bias”) [16]. The pulse repetition rate was set at 2 pulses per second and the number of pulses per deposition was 5000. During the deposition, the substrate holder was rotated at a speed of 2 rpm. The residual gas pressure was typically in the 10^{-4} Pa range. The thicknesses of the deposited films ranged from 50 nm to 100 nm.

Raman spectroscopy was used to characterize the microstructure of the carbon films and the changes caused by the silver addition. Raman spectra were acquired with a Jobin Yvon HR 460 monochromator and a nitrogen-cooled CCD (charge coupled device) detector. The excitation light was the 514.5 nm line of an Ar–Kr laser. The incident and scattered beams were focused using an Olympus microscope, and a Kaiser Super-Notch filter was used to suppress the elastically scattered light. The structural characteristics of the Ag-DLC films were probed by Grazing Incidence X-ray Diffraction (GIXRD) at an incident angle of 2º with respect to the substrate surface. The experiments were done with a Co Kα source. Glow Discharge Optical Emission Spectroscopy (GDOES) depth-profile analysis of the deposited films was done using a Jobin Yvon RF GD Profiler equipped with a 4 mm diameter anode. The GDOES was operating at a typical radio-frequency discharge pressure of 650 Pa and power of 40 W. Quantified profiles were obtained automatically using the standard Jobin Yvon QUANTUM Intelligent Quantification software.

The tribological properties were studied by reciprocating motion following the guidelines of the standard test method ASTM F732 for evaluating the friction and wear of materials for use in total joint prosthesis. UHMWPE 10-mm balls were rubbed against coated TiAl6V4 specimens in diluted fetal bovine serum (proteins content 20-23 g/l) in a CSM tribometer. Preliminary trials were attempted using flat-ender circular cylinders or conical shape tips but the difficulties to estimate the worn volume caused by different surface finishing made advisable the employment of balls to ensure similar contact conditions. The test parameters were set at 10 N of applied load (average contact pressure 30 MPa); 50 mm/s of linear speed; frequency 1 Hz and 75000 cycles (3.5 km of sliding distance). The tests were repeated at least twice to check the reproducibility. The worn surfaces were examined by using a Scanning Electron Microscope (SEM) JEOL JSM-5400 at 0.5 kV. The specific ball wear rate was estimated after dividing the worn cap volume by the applied load and the sliding distance.

3. Results

3.1 Composition and structural properties

Fig. 1 shows the GDOES compositional profile of silver for samples obtained with C:Ag pulse ratios of 24:1, 12:1, 6:1 and 3:1 (pulses of carbon:pulses of silver). There is a monotonous increase of the Ag content when decreasing the C:Ag ratio. The overall amount of silver was below 5 at.% for all composite samples, except in the case of 3:1 where the overall amount of silver was around 15 at.% and contained a large peak at the surface where the silver was concentration reached ~55 at.%. The segregation of certain amounts of silver to the surface is an expected effect due to the lower surface energy of silver compared to DLC. Fig. 2 shows the XRD patterns of the Ag-containing DLC samples. Crystalline silver peaks were only observed in samples containing 4 at.% and 15 at.%. of silver. These results are consistent with the formation of silver nanocrystals inside an amorphous carbon matrix.

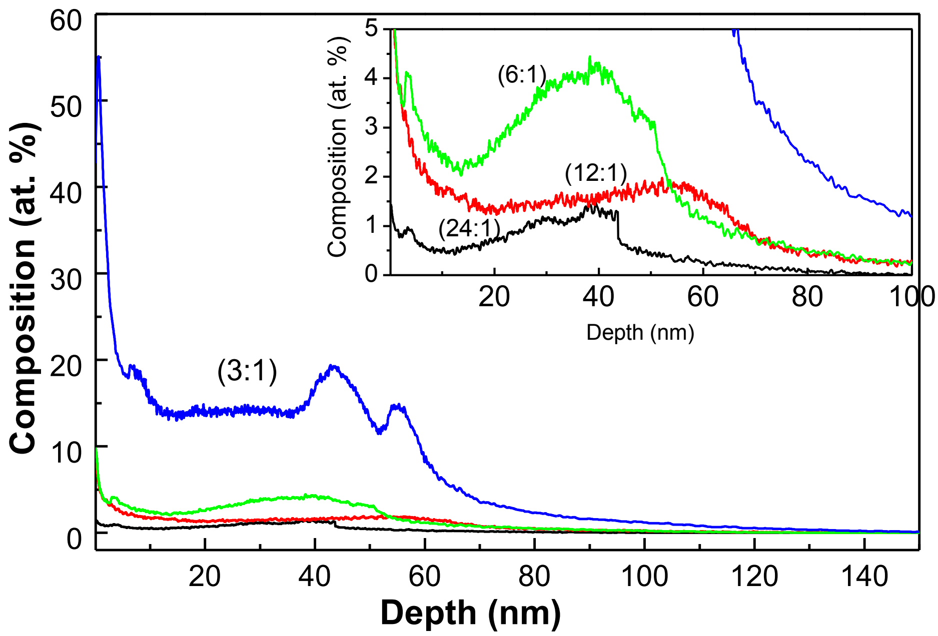

Figure 1. GDOES profile of silver in Ag-DLC coatings deposited by dual-cathode filtered cathodic arc.

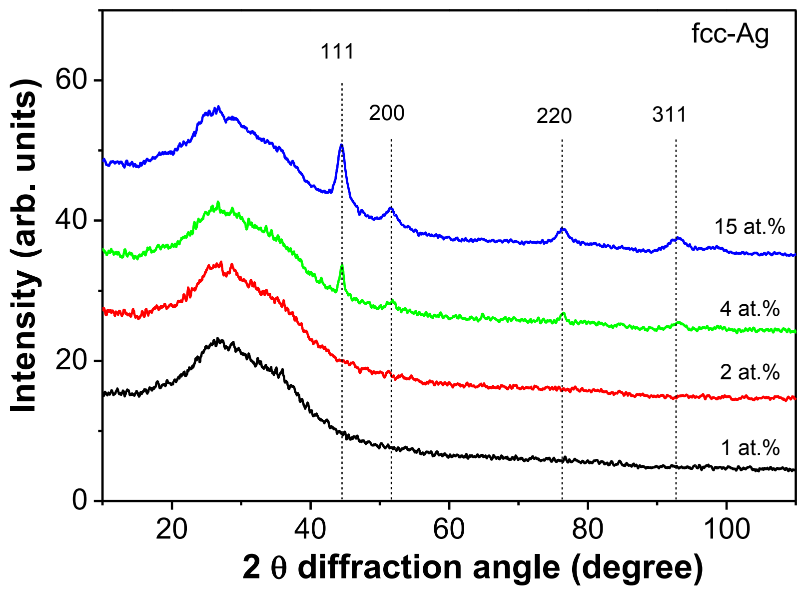

Figure 2. X-ray diffraction patterns of Ag-DLC coatings with various silver contents.

Normalized Raman spectra for the mixed Ag-DLC samples along a pure a-C sample are shown in Fig. 3. The Raman spectra for all the samples are featureless and have just one asymmetric broad peak with a maximum at around 1530 cm^{-1}. The only remarkable difference is the decrease of the total intensity of the peak with increasing the Ag content in the coating. The spectra which has been fitted before using two Gaussians centered at frequencies around 1350 cm^{-1} and 1530 cm^{-1}, commonly named as the D (disorder) and G (graphite) bands [17, 18], clearly shows that the peak position, full widths at half maximum (FWHM) and the ratio between the intensities of D and G peaks does not change significantly and implies that the amount of sp^3 and structural order in the amorphous carbon matrix remains intact and independent of the silver content. This is in good accordance with the formation of nanocomposite Ag-DLC.

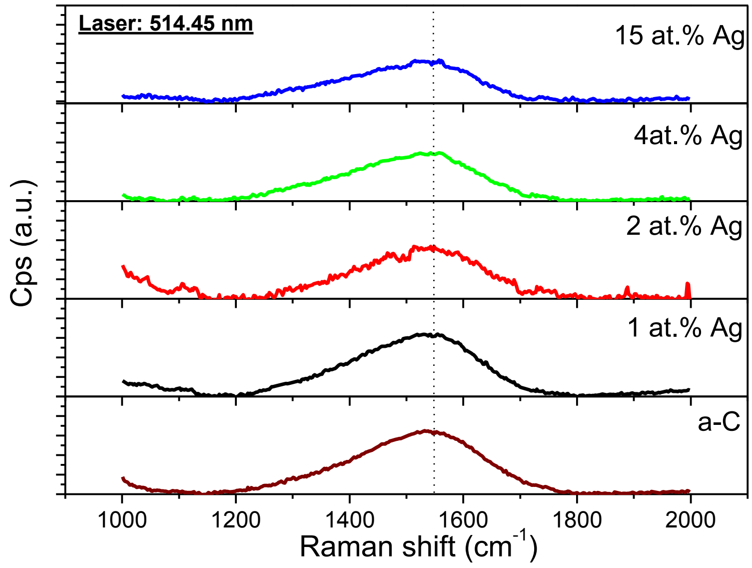

Figure 3. Raman spectra of Ag-DLC coatings collected at 514.45nm wavelength

3.2 Tribological Properties

The friction coefficients (shown in Fig. 4) of the Ag-DLC coatings varied between 0.07 and 0.09 being higher than the pure silver film whose friction value was about 0.04. They did not exhibit a clear dependence on the Ag content although an optimum was found for a small silver addition (2 at. %). Regarding the ball wear rate values, although the differences were not very significant (5 to 6.5×10^{-7} mm^3/Nm), a decreasing trend is observed upon incorporating silver in the carbon coatings.

Fig. 5 shows the optical micrographs taken from the ball counterfaces for the undoped carbon and with Ag (15 at.%) samples at the end of the friction tests. The rough surfaces of the UHMWPE balls appear smoothed in the contact region. The presence of silver seems to decrease the wear damage as can be denoted from the picture taken of the Ag (15 at.%)-DLC coating. The wear mechanism seems to be abrasive in all the cases identified by the presence of parallel groves onto the surface along the sliding direction. Under compression, the PE ball suffers plastic deformation and removal by the harder counterface. The slight diminution of the wear can be explained by a softening of the coatings when increasing the Ag content as reported by other authors [19,20].

Nevertheless, in order to determine whether the presence of silver on the top surface could have a tribochemical effect, a SEM analysis was carried out on the scar obtained with the pure Ag film. Fig. 6a illustrates the smoothing of the ridges originally present on the surface of the PE ball along the sliding direction. An EDX analysis carried out in this area (not shown) did not find evidence of silver eventually being transferred from the counterpart. One can conclude that wear progresses mainly by plastic deformation of the soft polymer material. This can be further confirmed in Fig. 6b showing the smearing of the PE ridges on the scar edge.

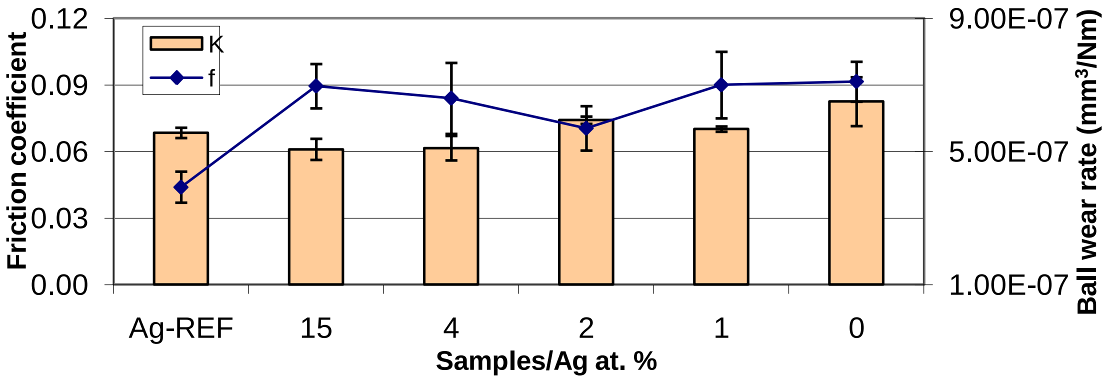

Figure 4. Friction coefficient and ball wear rates for the Ag-doped diamond-like carbon coatings against PE balls. The results obtained with a pure silver and amorphous carbon coating are included for comparison.

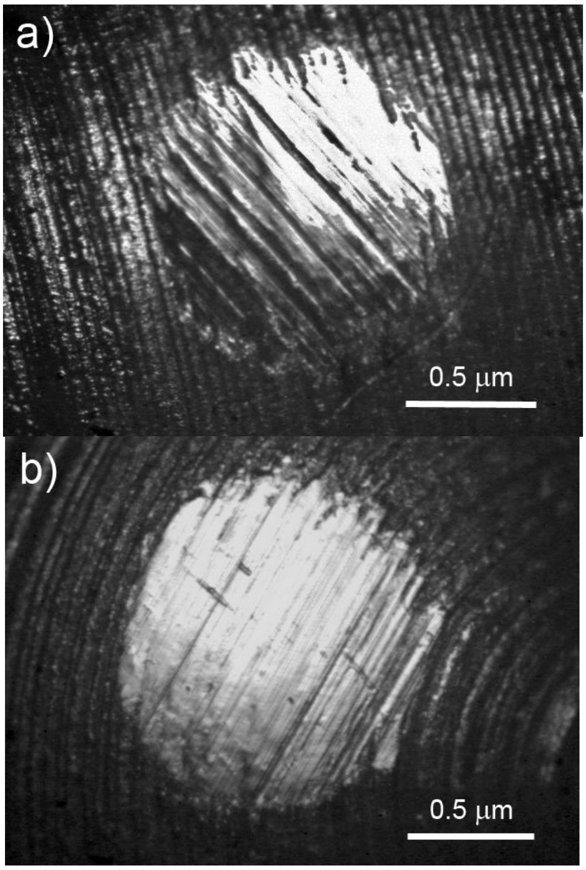

Figure 5. Optical micrographs taken from the ball scars after testing the following samples: a) Ag (15 at.%)-DLC and b) undoped a-C.

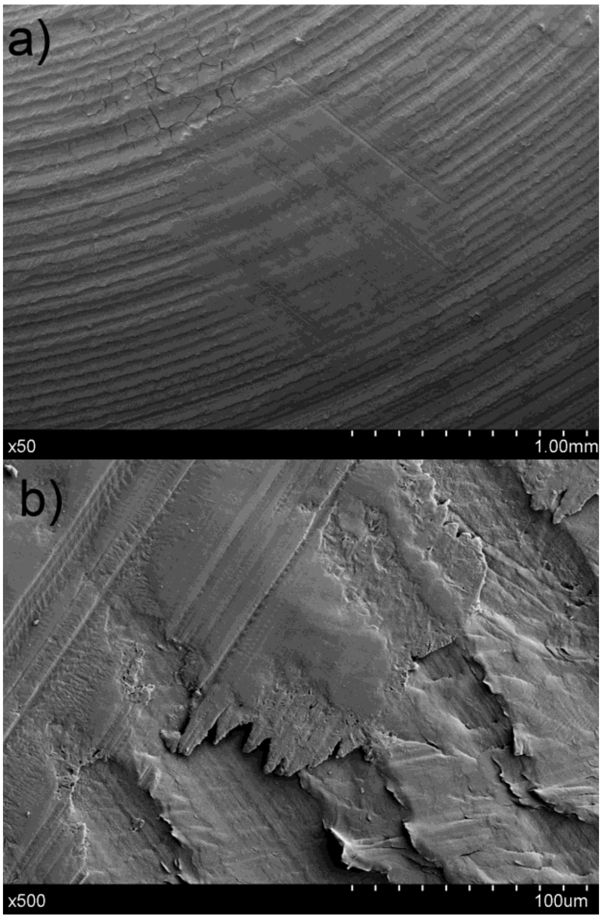

Figure 6. SEM micrographs from UHMWPE ball rubbed against the Ag film: a) wear scar; b) detail on the edge.

4. Conclusions

In this study, the influence of the silver content on the tribological properties of hydrogen-free Ag-DLC films against UHMWPE lubricated with fetal bovine serum was investigated. The incorporation of silver into DLC by means of “selective bias” pulsed dual-cathode cathodic arc results in nanocomposite coatings composed of nanocrystalline silver grains embedded in an amorphous carbon matrix, as indicated by both XRD and Raman spectra, where the structural characteristics of the amorphous carbon matrix are independent of silver content. There was a slight reduction in the wear volume of the UHMWPE balls for DLC containing 4 at.% or more of silver. SEM investigations of wear ball scars indicated this effect is due to a less abrasive interaction between the UHMWPE ball and the softer surface of silver-containing DLCs.

Acknowledgements

The authors thank J.M. Albella (ICMM, CSIC) for his helpful comments, A. Espinosa and A. de Andrés for the collection of the Raman spectra and M.C. Jiménez de Haro for taking the SEM pictures. This work was partially supported by MICINN project CSD 2008-0023 FUNCOAT. A.A. acknowledges support by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. JLE also acknowledges Spanish MICINN Project FIS2009-12964-C05-04.

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