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# Comparison of hydrogenated and unhydrogenated carbon films obtained by FCVA onto Ti6Al4V: Structure, hardness and biocompatibility study

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**Abstract**

This work compares hydrogenated and unhydrogenated carbon films as surfaces for implants. Thin films are deposited by a filtered cathodic vacuum arc (FCVA) process in a variable methane pressure in order to obtain very close sets of deposition conditions for the hydrogenated and unhydrogenated films. Ti6Al4V alloy is used as substrate. The structure is investigated by XRR, ERDA-RBS and Raman spectroscopy. The mechanical and physico-chemical properties such as adherence load, hardness and wettability are studied for the two sets of coatings on the metallic substrate. The biological approach is a study of the cytocompatibility of these films with MC3T3-E1 osteoblast-like cells and in particular the adhesion kinetics. The carbon coatings influence neither the morphology nor the early adhesion behaviour of these target cells on the substrates. This is probably due to similar hydrophilic surface energies of the tested control and carbon-coated test samples.


*Keywords:* DLC films; Titanium alloy; Biomaterials; Hydrogen; MC3T3-E1 cell

## 1. Introduction

From the earliest step of tissue repair, cell adhesion is a particularly important phenomenon in the optimal integration of medical devices. A maximum knowledge of the surface characteristics is required for a better understanding of the multiple cell–material interactions. The characteristics of the implant/tissue interface play a primary role in the integration with immediate complexity. In order to improve the reactive nature of the surface, many advanced surface modification techniques have been proposed, before studying the biocompatibility of a surface. The topography of a surface with a constant chemical composition induces the adhesion of different cell types: some cells prefer deep grooves in a rough surface and some cells not [1] and other prefer rough surfaces or not [2,3]. An understanding of cell–material interactions is very complex because interactions of the cells are not easy to identify and so difficult to analyse such as cell migration [4], cell adhesion [5,6] or all other mechanisms involved in the cell function [7–10].

In this work, we elaborated two sets of carbon films by filtered cathodic vacuum arc (FCVA), one set contains 8 at.% hydrogen and the other contains 1 at.% hydrogen. Carbon is a biomaterial, possess good characteristics as a low friction coefficient, good chemical inertness and hardness, and can improve an implant surface. In order to evaluate the influence of the hydrogen content in the carbon films as implant surfaces, after characterization of the carbon coatings, we studied the adhesion kinetics of the MC3T3-E1 osteoblastic cells. To compare the two films, deposition conditions must be similar. We introduced methane gas during the arc discharge to produce the ta-C:H films. The chemical composition and structure of the films are investigated by both X-rays reflectometry (XRR) and elastic recoil of $He^+$ detection spectroscopy (ERD) to obtain the density of the film and Raman spectroscopy for the determination of the $sp^2$ tendency. Mechanical properties of the films are studied by indentation or scratching techniques.

## 2. Films preparation and characterizations

The carbon films were prepared by arc discharge in a commercial FCVA system (RHK Technology Company) where the arc was controlled by the trigger voltage (10–25

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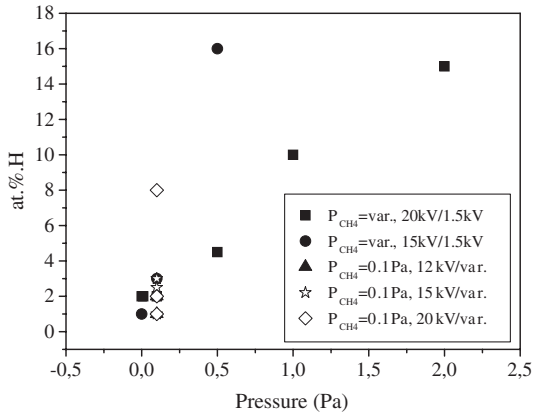


Fig. 1. Influence of the methane pressure and the electrical parameters of the arc discharge on the atomic hydrogen content of the carbon films. The first voltage indicates the trigger voltage and the second voltage indicates the substrate holder voltage (bias voltage) [12].

kV) and filtered. We introduce methane in the chamber to incorporate hydrogen in the coating. The films are prepared with varying the trigger voltage from 12 kV to 20 kV and the substrate bias voltage to −750 V from −2500 V. The pulse frequency is kept constant at 1 Hz and 2000 pulses are counted for all the depositions. The films are deposited onto the Ti6Al4V alloy, mirror polished discs with 15 mm diameter and 2 mm thickness and titanium-coated. Roughnesses are evaluated by XRR and are in the 1–1.5 nm range for all the non-hydrogenated carbon films and slightly higher for hydrogenated films (1–2 nm).

Fig. 1 shows the hydrogen incorporation in the carbon films as a function of some parameters conditions. Two sets of carbon films were chosen for the evaluation of the cell adhesion kinetics after immersion test and completely characterized. The deposition conditions are 20 kV trigger voltage, 2 kV bias voltage and 0.1 Pa methane pressure for the hydrogenated films. Raman $I_D/I_G$ ratio, hydrogen content and density, hardness and normal load for a delamination are summarized in Table 1; the extended experimental details on structural characterizations can be found in Refs. [11,12]. Fig. 2 is a two-part figure, one part for the 800–2000 $cm^{-1}$ range used for $I_D/I_G$ ratio determination and the other part (2000–3600 $cm^{-1}$) for the bonded hydrogen existence. Wettability tests were carried out by using the sessile drop angle method and the surface energy has been evaluated by linear extrapolation of the wettability coefficients ($\cos\theta$) with three liquids (diiodomethane, ethylene glycol and water). These two sets of carbon and the metallic substrate are sterilized under gamma radiations (40 kGy $Co^{60}$). Negative control sample of tissue culture polystyrene (TCPS) was UV sterilized.

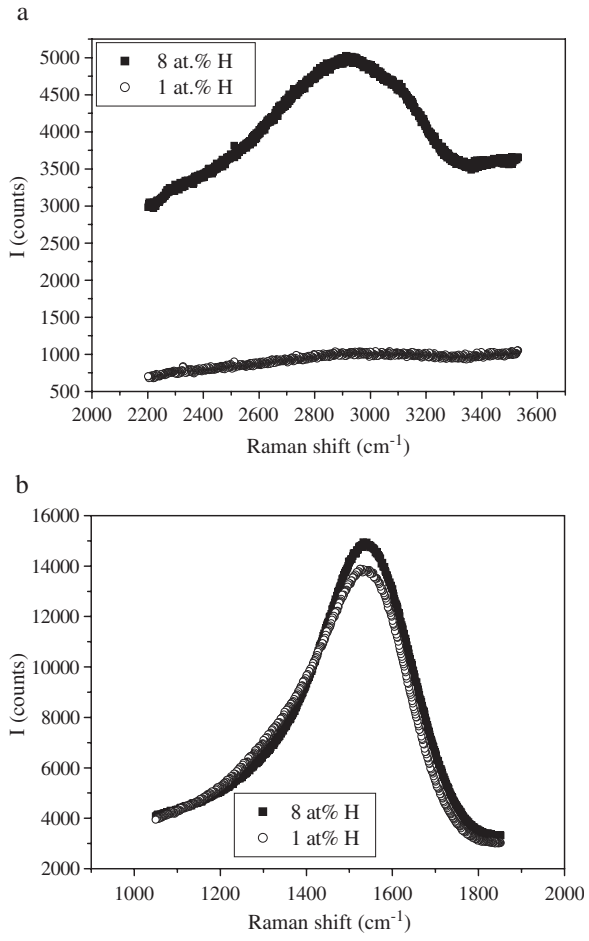


Fig. 2. (a) Raman Shift in the region of the C–H oscillator. (b) Raman shift for the C–C oscillator.

We used nano-hardness tester (NHT) and nano-scratching tester (NST) from CSM Instruments for the mechanical evaluation of the carbon films.

## 3. Cell adhesion kinetics

MC3T3-E1 cells derived from mouse calvarium tissue are an immortalized cell-line [13]. These cells described as osteoblast-like cells are characterized by alkaline phosphatase activity and the synthesis of an extracellular matrix containing osteocalcin, osteopontin, osteonectin and type-1 collagen [14,15]. The original stem cells and the immortalized cells have an identical morphology. The cells are seeded in T75 plastic bottles (Nunc) in alpha MEM medium with Glutamax (Gibco BRL) supplemented with 10% foetal calf serum (Eurobio). The medium also contained penicillin (100 IU $mL^{-1}$), streptomycin (0.1 g $L^{-1}$) and mycostatin (100 IU $mL^{-1}$) [5].

Table 1
Some physico-chemical characteristics evaluated for the two carbon films

| $P$ (Pa) | at.% H | $I_D/I_G$ | Average mass density ($g/cm^3$) | Thickness (nm) | $\gamma_s$ ($mJ/m^2$) | Hardness (GPa) | Nano-scratch |
|---|---|---|---|---|---|---|---|
| $10^{-5}$ | 1 | 0.45 | 2.5 | 200 | 41 | 35 | No delamination (>50 mN) |
| 0.1 | 8 | 1.02 | 1.7 | 160 | 40 | 15 | No delamination (>50 mN) |