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# Functional carbonic structures with applications in cardio-vascular implantology

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The hemocompatibility of an implant is determined by its surface properties. Diamond like carbon surfaces (DLC) are slowing thrombin development due to their low values of surface energy. Magnetron sputtering (MS) and plasma enhanced chemical vapor deposition (PECVD) are the techniques successfully used in this type of applications. In this paper we have studied carbonic hemocompatible adherent structures onto metallic substrates of stainless steel and titanium. The carbonic structures have been characterized by FTIR, AFM, scratch test and pull-test adherence test. Surface energy was estimated by the contact angle method and the clotting time by the droplet method.

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*Keywords*: DLC, MS, PECVD, Surface energy, Thromboplastin time, Functional carbonic structures

## 1. Introduction

The replacement of tissues in contact with human blood requires biomaterials able to maintain their mechanical integrity for a long term. As modern implants there are tested functional structures made of titanium alloys and stainless steel substrates covered with hemocompatible thin films, which assure also a buffer against the metallic atoms diffusion. Among these materials, encouraging results have been obtained with diamond-like structures. Related to the hemocompatible feature has been observed that the high clotting times require low surface energies [1]. As preparation methods for hemocompatible structures there were reported MS, PECVD, PLD [2] and recently PSIID [3]. In this paper we have studied two deposition routes by combining the MS and PECVD deposition methods in order to produce adherent hemocompatible structures with DLC coatings.

## 2. Methods

### 2.1. Substrates preparation

Ti6Al4V and 316L stainless steel polished plates, with a dimension of 10×10 mm were used. The substrates were cleaned in an ultrasonically bath – 5 minutes in acetone and 5 minutes in alcohol and finally dried in argon flow. Previously deposition, an outgassing (for 10 minutes) and a corrosion procedure (for 5 min) of the substrates were performed.

In order to investigate the properties of functional films, similar carbonic films have been deposited onto silicon substrates.

### 2.2. Deposition routes for preparing the functional graded structures

In order to prepare the hemocompatible structures, we have used an YBN-75P-I -type deposition system. This is equipped with two RF magnetron cathodes (one with vertical target and the other with a horizontal one) and also a capacitive PECVD position. This configuration allows the producing of multi-layer or graded functional structures by using both deposition methods. The MS method was used to prepare the adherence graded layer and the PECVD method to obtain the functional top layer. We have used two deposition routes - the first one in a single working session (for the stainless steel substrates), and the second one in two sessions (for the titanium alloys substrates).

### 2.3. Deposition of functional structures onto stainless-steel substrates

The functional structures were prepared in a single work session starting with a MS adherence-graded layer, which was functionalized by covering it with a PECVD DLC carbon film. A stainless steel target was mounted on the vertical cathode and the substrates were bonded using silver paste onto PECVD position at a distance of 40 cm to the target.

The buffer layer with a thickness 50 nm was deposited in 10 minutes through MS-RF method. The initial deposition atmosphere (2 mbarr) of argon was progressively enriched with methane up to a composition of 20% methane in argon. This structure was finally functionalized by the PECVD deposition of a DLC-type film of about 300 nm in an atmosphere of 20% methane diluted in argon. The $DC_{bias}$ value has been maintained at about 440 V during the deposition process.

### 2.4. Deposition of functional structures onto Ti6Al4V substrates

The adhesion layer was prepared by co-sputtering from two targets, titanium (Ti) and titanium carbide (TiC) in argon atmosphere (3mTorr) by using the magnetron co-sputtering deposition method. First target (Ti) was fixed on the vertical cathode, while the second one (TiC) on the horizontal cathode. Initially, the holder with the substrates was placed in a parallel position with the first target at a distance of 47 mm. During the deposition process, it has been gradually displaced towards the second target using a planetary movement. In this way we have obtained a structure with composition gradient finished with titanium carbide surface.

Afterwards, the Ti6Al4V substrates have been taken down from the holder and fixed with silver paint onto the capacitive PECVD position. The next step was the deposition of a DLC layer in 20% methane diluted in argon atmosphere, similarly to that reported for the stainless steel structures.

### 2.5. Structural, morphological and mechanical characterization of the DLC films

The DLC carbonic films deposited onto silicon substrates have been measured in IR (400-8000 $cm^{-1}$) using a Perkin Elmer – Spectrum BX spectrophotometer.

Atomic Force Microscopy have been used to characterize the surfaces morphology and estimate surfaces roughness ($R_{rms}$-root mean square roughness and $R_{abs}$ – absolute roughness) for Ti6Al4V, 316L substrates and functional carbonic structures on these substrates. The AFM system works in the tapping mode in air with a commercial standard silicon nitride cantilever (NSC35) having a force constant of 7.5 N/m, 240 kHz resonance frequency and tips with radius less 10nm. The AFM images cover various areas, from 30*µm* x 30*µm* to 3*µm* x 3*µm*. A low-pass filtering to remove the statistical noise without loss of information is performed. AFM measurements are performed on different points of the sample, keeping the same conditions of room temperature and ambient atmosphere.

The adherence of the prepared structures was estimated using a pull-test home-made measurement system (dynamometer- UWE HS type – 30 kg linked to a poinson Φ 4 mm by glue – Bison type). A set of 5 measurements were performed for every structure.

### 2.6. Characterization of the DLC films hemocompatibility

***Surface energy***

The surface energy measurements of the prepared DLC structures were performed at 25 °C, by using goniometric method; three solvents (water, diiodomethane and ethylene glycol) were carefully dropped on surface (drops volume and distance kept constant) and contact angle values were measured.

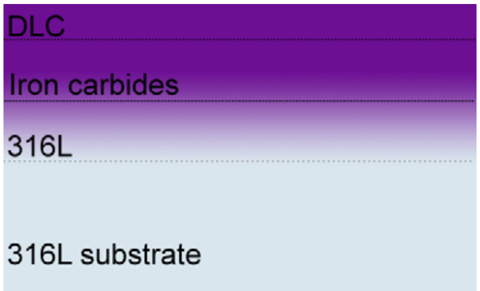
***Partial thromboplastin time measurements***

The partial thromboplastin time was estimated by using the drop method as the time for the fresh blood coagulation, deposited on the biomaterial surface. Surfaces were cleaned with ethyl alcohol and ethyl ether and then dried at 25°C, for 4hours. The used blood was freshly harvested in a heparinized syringe from a healthy and non-smoking volunteer. Samples were deposited on a plane surface and drops of blood (50 µl) were deposited from a distance of 2 cm. The partial thromboplastin time was considered as the time for blood clotting on surface. Three measurements were made for each surface.

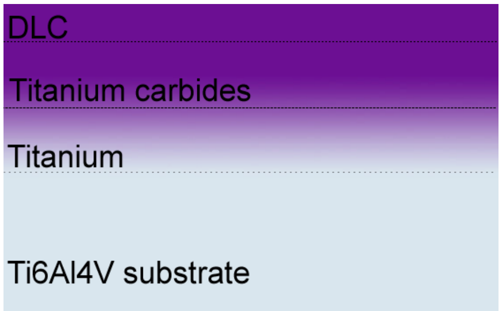
## 3. Results and discussion

### 3.1 The structure of the functional graded hemocompatible materials

The obtained functional structures are schematically shown in Fig.1 (a, b). It can be seen that both functional structures are graded with practically no interface between metallic substrate and buffer adhesion layer.




a




b

*Fig. 1. Functional structures onto 316L stainless steel (a) and Ti6Al4V titanium alloy (b)*

The as-prepared DLC structures demonstrated good values of adherence of 42.64 ± 6.5 MPa for the 316L stainless steel substrates and of 66.6 ± 1.1 MPa for Ti6Al4V ones (Fig 2). A value of 40 MPa is a minimum required for the hemocompatible applications.

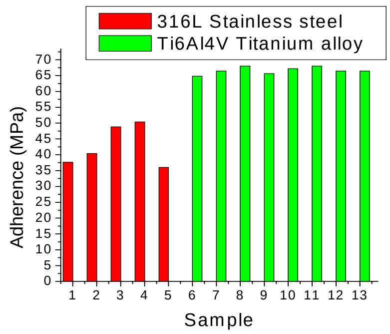



*Fig. 2. Adhesion values estimated for the two types of structures.*

### 3.2 Morphological and structural characterizations onto the functional DLC films

FTIR spectrometric analysis of the DLC silicon structures has revealed a typical DLC signature One can see (Fig. 3) that the DLC film is IR transparent in the 1000-8000 $cm^{-1}$ range and it presents only a low absorption in 2800 – 3000 $cm^{-1}$ region with a maximum value of 140 $cm^{-1}$ (Fig. 4).

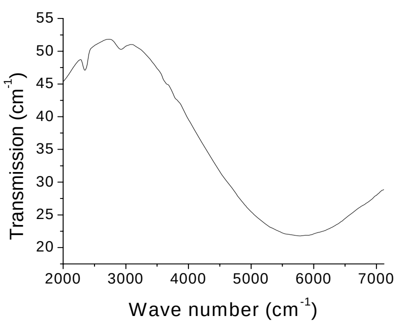



*Fig. 3. IR spectra for the DLC film deposited onto silicon substrate.*

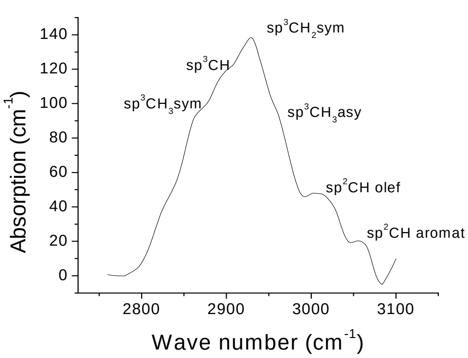
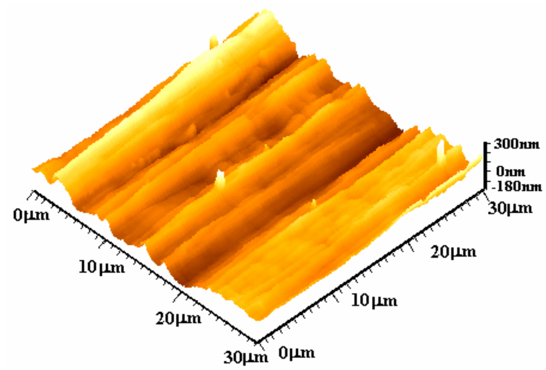
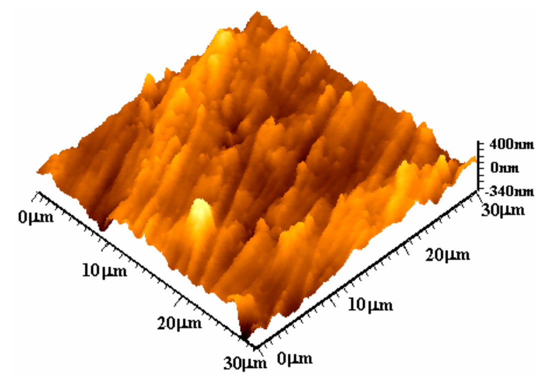



*Fig. 4. IR absorption on stretching absorption zone.*

Phase and topographic AFM images revealed homogeneous surfaces with a very low variation of color and contrast, which demonstrate that both type of structures, are relatively smooth (Fig. 5). The values of rms were of 63,3nm for the 316L steel structures and of 89,3 nm for the Ti6Al4V ones.




a




b

*Fig. 5. 3D AFM topographic images for 316L (a) and Ti6Al4V (b) both surfaces covered with functional carbonic structures.*

As a general observation, the shape and features of functional carbonic structures are following the features of substrates surfaces.

### 3.3. Surface energy and partial thromboplastin time measurements

One can notice that by coating the Ti6Al4V with DLC functional coatings the surface energy is decreasing determining an increasing of the thromboplastin time. These values are comparable with those corresponding to the PMMA medical grade material. The surface energy and thromboplastin times for the analyzed carbonic structures are shown in Table 1.

*Table 1. Surface energy and thromboplastin times for 316L stainless steel, Ti6Al4V titanium alloy and PMMA comparative with our structures.*

| Material | Surface energy ($mJ/m^2$) | | Partial thromboplastin time (min) | |
|---|---|---|---|---|
| | Before DLC | After DLC | Before DLC | After DLC |
| 316 L | - | 31.42 | - | 16.66 |
| Ti6Al4V | 38.65 | 32.12 | 13.66 | 15.33 |
| PMMA | 35.42 | | 14.50 | |

A major issue in the case of DLC films deposition onto metallic substrates is the very low adherence of these materials. In order to eliminate this drawback there were used various solutions for the preparation of structures with a composition gradient at the metal –DLC interface [4]. The method we have chosen consists in a deposition of an adherence layer with a composition gradient, without an actual interface layer to metallic substrates. Even more, the latter contains, in its surface layer, carbon atoms in a significant ratio that assure its adherence to DLC functional films. We can affirm that carbon atoms are both part of a TiC surface layer of the functional structures deposited on the Ti6Al4V, and also in a mixture of surface iron carbides layer in the case of structures onto 316L stainless steel.

For both analyzed structures and for the PMMA substrate, one can notice that the clotting times values are increasing with the lowering of the surface energy, similar to what has previously reported [5].

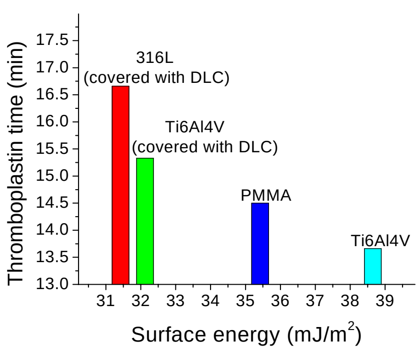



*Fig. 6. Correlation of the surface energy vs. thromboplastin time for some types of hemocompatible surfaces.*

The hemocompatibility tests have proven that we succeeded in obtaining structures with good thromboplastin times (Fig. 6). The obtained results demonstrate the utility of further in vitro research with more detailed studies of the clotting phenomena in modified sanguine fluids.

## 5. Conclusions

We have succeeded in obtaining graded hemocompatible carbonic structures onto 316L stainless steel and Ti6Al4V substrates. The adherence of the carbonic films to the Ti6Al4V substrates was situated in the range 65-70 MPa, at the limit accepted for medical application. The obtained surface energy (31.42mJ/$m^2$) and clotting times (16.66 min) values were comparable to those of PMMA material frequently used in hemoclinical applications. There has also been noticed a normal correlation between the values of the surface energy and those of partial thromboplastin times.

**Acknowledgments**

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