

were presented in the FIG.4. Different surface morphology of layers on samples could be one of the reasons to growth preference of cells on individual samples. It may be the cause of the growth preference of cells on the edge areas of samples with comparison to the middle areas of samples, where on day 1 and 3 after seeding rather isolated cells were found.

### Conclusion

In this study growth and proliferation of osteoblast-like cells MG 63 on four carbon films deposited under different process conditions in MW/RF reactor were investigated. In this paper the comparison of cell growth on coated, uncoated, glass and tissue culture polystyren was performed. We have noticed potential dependence of cell adhesion on surface morphology on edges and in the middle of sample. This study may be helpful in a selection of coating conditions in MW/RF reactor to create suitable carbon films for biological application.

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## ELECTRIC POTENTIAL OF BIOMATERIALS COATED WITH DIELECTRIC CARBON LAYER AND NON-COATED IN WATER AND SERUM

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### Abstract

*Electric potentials, established in water and human blood serum, of the electrodes made of platinum, graphite, Ti6Al4V alloy, TiN, AISI316L steel, oxidized steel and the materials coated with diamond like carbon layer (DLC) and a nanocrystalline-diamond layer (NCD) were determined. The values of the potentials of non-coated materials increased with increasing electron work function ( $\Phi$ ) of investigated materials in reasonable accordance. The difference between the potentials measured in serum and in water was ascribed to the differing molecular electron structure of the proteins in contact with the electrodes. Electrode potentials of different materials coated with the same thin dielectric carbon layer varied significantly depending on the  $\Phi$  value of the substrate. In this way the selection of a substrate material permits influencing on the interaction between NCD (DLC) coating and serum compounds. The potential of an electrode has appeared to be a simple but sensitive indicator of the phenomena that take place on the biomaterial surface.*

**Keywords:** electrode potential, electron work function, Pt, TiN, carbon, Ti6Al4V, AISI316L, DLC, NCD. **[Engineering of Biomaterials, 56-57,(2006),21-24]**

### Introduction

The bulk biocompatibility of implant materials (i.e., the similarity of their mechanical, magnetic etc. properties to the properties of the human body) can be evaluated in the macro-scale in a quite simple way by in vitro examinations. The interaction between the surface of the implant material and the tissues, blood and cells is usually examined in vitro by observing the phenomena in the microscopic scale using biological methods. The specific drawback of the biological methods carried out in vitro lies in the necessity of using certain additional substances, absent in the living organism, that ensure the stability of the specimen. Moreover, the results of biological examinations obtained by various investigators are difficult to compare. Simple physico-chemical methods suitable for estimating macroscopically the biocompatibility of the implant surface are scarce. They primarily include corrosion examinations and tracing the presence of the markers of selected bio-chemical processes that proceed in blood.

M.J. Jones et al. [2], who examined the haemocompatibility



of Ti, TiC, TiN and DLC, combined a macroscopic physical measurement (surface tension in respect to water) and a chemical measurement (haemoglobine release into plasma) with microscopic biological examinations (platelets attachment). These three methods yielded similar results as to the ordering of the biocompatibilities of the materials examined. The measurement of the surface tension was the simplest and absolutely 'non-invasive'. Similar attempts at relating the surface tension with the haemocompatibility were made by J.A. McLaughlin et al. [3], X. Wang et al [4], and B.J. Hunt et al [5]. The relation between the hardness and the surface biocompatibility was studied by L.A. Thomson et al. [6].

In our previous work [1] we made an attempt to relate the electric potential of an electrode immersed in water ( $\epsilon_{\text{water}}$ ) with its electron work function ( $\Phi_M$ ). The preliminary results showed a reasonable agreement between  $\epsilon_{\text{water}}$  and  $\Phi_M$ , although the spread of the values was quite wide.

The present study was concerned with an attempt at utilizing the electric potential of an electrode made of the biomaterial examined as the indicator of the interaction between the components of a given biological medium and the electrode surface. Contrary to the common electrochemical corrosion investigation we only considered the effects of the electron transfer from the electrode into molecules of the surrounding medium. The materials whose ions passed into water were not examined, chiefly because they may be toxic for a living body. Therefore we did not used the equilibrium equation between a metal and its ion expressed as

$$\varphi_M - \varphi_R = \frac{\mu_M^\square - \mu_M^\ominus}{zF} + \frac{RT}{zF} \ln a$$

where  $\mu$  - electrochemical potential, F - Faraday number, a - activity

but we solely measured the contact potential V (Volta voltage) related to the electron work function ( $\Phi_M$ ) of the biomaterial and to the charge neutrality level (CNL) of the molecule, given by

$$\begin{aligned} \Phi_M &= E_F + \text{electron surface states} \\ V &= \Phi_M - \text{CNL} \end{aligned}$$

The contact potential between solids has been described for electronic purposes using the band model theory (7). The same theory was used for describing the solid-molecule contact [8]. Although the band structure of a molecule differs from the band structure of a solid, it has been proved that the effects that occur at the solid-molecule contact are analogous to those that take place between two different solids. When examining the Au-perylenetetra-carboxylicdianhydride molecule contact, these authors observed a broadening of molecular bands at the contact with the metal and ascribed this to the electron hopping interaction  $\Phi_{\text{Au6S}} - \Phi_{\text{mol}}$ . The mechanism associated with the formation of Me-Molecule interface barrier involves the charge transfer between the two materials due to a weak chemical interaction. As a result an electrostatic interface dipole is formed, which tends to align the metal Fermi level and the molecule charge neutrality level.

For example, J.Ristein et al [9] described the contact potential of an H-terminated diamond surface with H<sub>2</sub>O at pH6 to be a result of the electro-chemical potentials of the two bodies becoming equilibrated. Since, under these conditions, C-H shows a negative electron affinity, diamond functions as an electro-donor in this contact.

Investigated biomaterial	$\Phi_M$ [eV]	References
Platinum	5,32-6,35	[15]
Graphite	4,0-4,7	[15]
AlSi316L	Fe-4,31	[15]
Ti6Al4V	Ti-3,9	[15]
Fe <sub>2</sub> O <sub>3</sub>	3,8	[15]
TiN	3,75	[17]
NCD/DLC	3,0	[16]
Investigated fluid		
H <sub>2</sub> O		
Srserum		

TABLE 1.

## Experiments

### Measuring method

The potential of the electrode in the liquid examined was determined by measuring the voltage established between the reference electrode, which was an EK602 calomel minielectrode of a potential of +223 ±5 mV, with respect to the potential of the saturated chinhydron electrode considered to be equal to zero according to the Geneva Convention.

The voltage was measured using a MERAU722A electronic voltmeter with the inner resistance  $R_w=10^9\Omega$  and a sensitivity of 10mV.]

### Materials

The liquids examined were de-ionized water and a fresh human blood serum obtained from drug-free volunteers, at pH=7.2 and a temperature of 300K.

The examinations included biomaterials whose significance seemed prospective for the applications where the implants were to be in contact with blood. Polymer materials were omitted, chiefly because their effectiveness depends on the 'micro-architecture' of the implant made of them [10]. The electrode materials used in the experiments are given in TABLE 1.

TiN was formed on a Ti6Al4V alloy substrate by subjecting it to glow discharge assisted d.c. nitriding in nitrogen at a temperature of 1123K, as described in [13]. Diamond-like carbon (DLC) was produced on a Ti6Al4V alloy substrate by the pyrolysis of methane in an r.f.-frequency plasma at a temperature of 573K. The nanocrystalline diamond (NCD) layer was produced on a Ti6Al4V alloy substrate using the pyrolysis of methane in an r.f.-frequency plasma at a temperature of 873K as described in [14]. The AlSi316L steel was oxidized by heating at 728K in air as described [11].

## Results and discussion

FIG. 1 shows the results of measurements of the electrode potentials in H<sub>2</sub>O ( $\epsilon_{\text{water}}$ ) and the values of the electron work function ( $\Phi$ ) of the non-coated materials. The results classify the materials according to growing  $\epsilon_{\text{water}}$  as follows: Pt>graphite>oxidized steel>TiN. The same sequence is true when ordering according to increasing  $\Phi$ .

The Ti6Al4V alloy and AlSi316L steel differed from the other materials. The value of their  $\epsilon_{\text{water}}$  depended strongly on the time for which the electrode was immersed in water (FIG. 2). This observation seems to suggest that the metallic ions have passed to the water and confirms that electrochemical corrosion occurs in both materials [11,12].

$\epsilon_{\text{water}}$  of oxidized steel remained constant, which confirms the results obtained by Chun-Che Shih et al. [11]. The measurement of  $\epsilon_{\text{water}}$  permitted us to reveal, quickly and immedi-

ately, any metal dissolution, an effect very undesirable when dealing with biomaterials.

The values of non-coated electrode potentials in serum,  $\epsilon_{\text{serum}}$ , are shown in FIG. 3. When immersed in serum, the electrodes behaved in a similar way as in water. Although the electric potentials  $\epsilon_{\text{serum}}$  of the individual electrode mate-

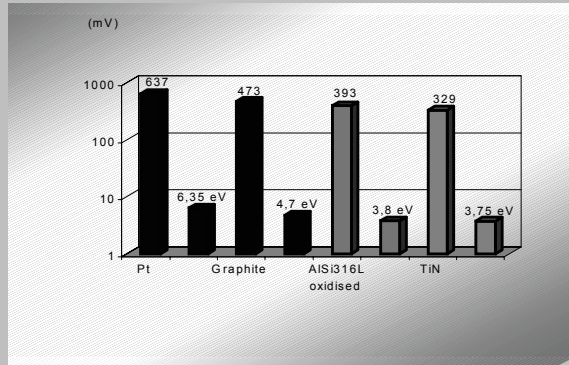


FIG. 1. Electrode potentials in water  $\epsilon_{\text{water}}$  and electron work function  $\Phi$  of noncoated materials.

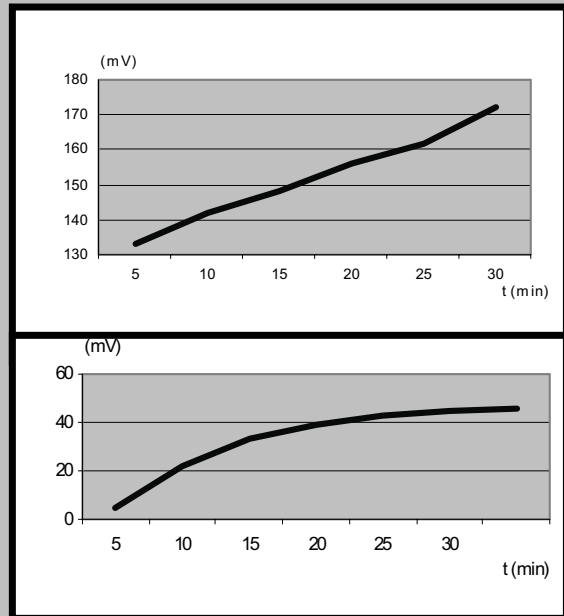


FIG. 2. Electrode potentials in water  $\epsilon_{\text{water}}$  of: a) Ti6Al4V, b) AISI316L.

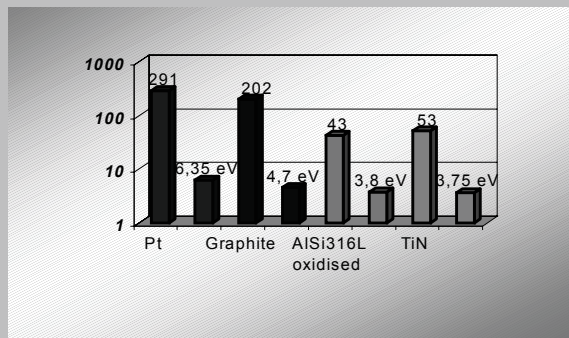


FIG. 3. Electrode potentials in serum  $\epsilon_{\text{serum}}$  of noncoated materials.

rials were changed, the sequence according to growing  $\epsilon_{\text{serum}}$  followed the increase of  $\Phi$  and  $\epsilon_{\text{water}}$  values.

The potential difference  $\epsilon_{\text{serum}} - \epsilon_{\text{water}}$  should be an expression of the phenomena that occur at the biomaterial-serum components boundary. As shown in FIG.4, the electrodes made of various materials differed in their  $\epsilon_{\text{serum}} - \epsilon_{\text{water}}$  value roughly in accordance with the increase of their  $\epsilon_{\text{water}}$ . The difference ( $\epsilon_{\text{serum}} - \epsilon_{\text{water}}$ ) of Pt was the largest. The ( $\epsilon_{\text{serum}} - \epsilon_{\text{water}}$ ) of graphite and TiN were smaller, but almost the same, and did not follow the  $\epsilon_{\text{water}}$  sequence. Therefore, TiN appeared to be an exceptionally surface-active biomaterial.

The results may be described in terms of the existence of the contact potential at a solid-protein junction and the space charge built of negatively charged ions similar to the

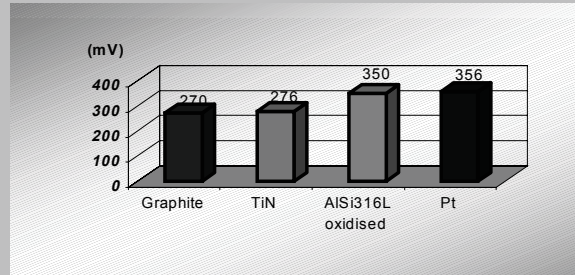


FIG. 4.  $\epsilon_{\text{serum}} - \epsilon_{\text{water}}$  of noncoated materials.

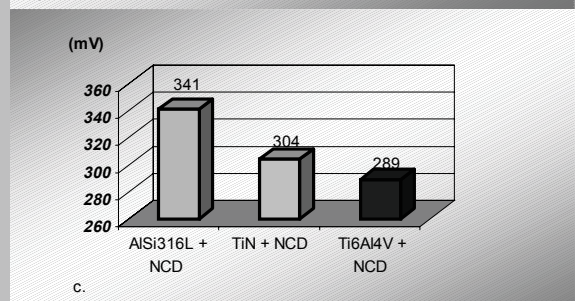
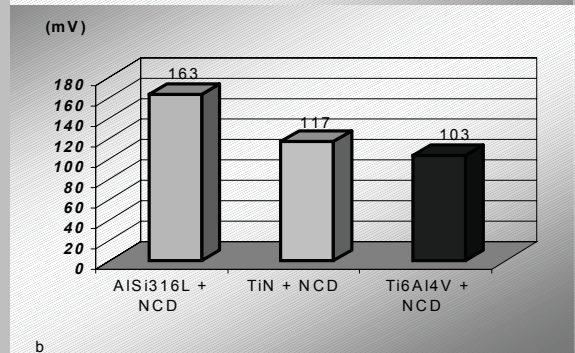
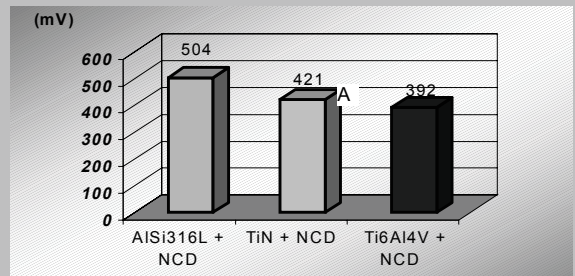


FIG. 5. Electrode potentials of carbon NCD layer coated materials: a)  $\epsilon_{\text{water}}$  of NCD, b)  $\epsilon_{\text{serum}}$  of NCD, c)  $\epsilon_{\text{water}} - \epsilon_{\text{serum}}$  of NCD.



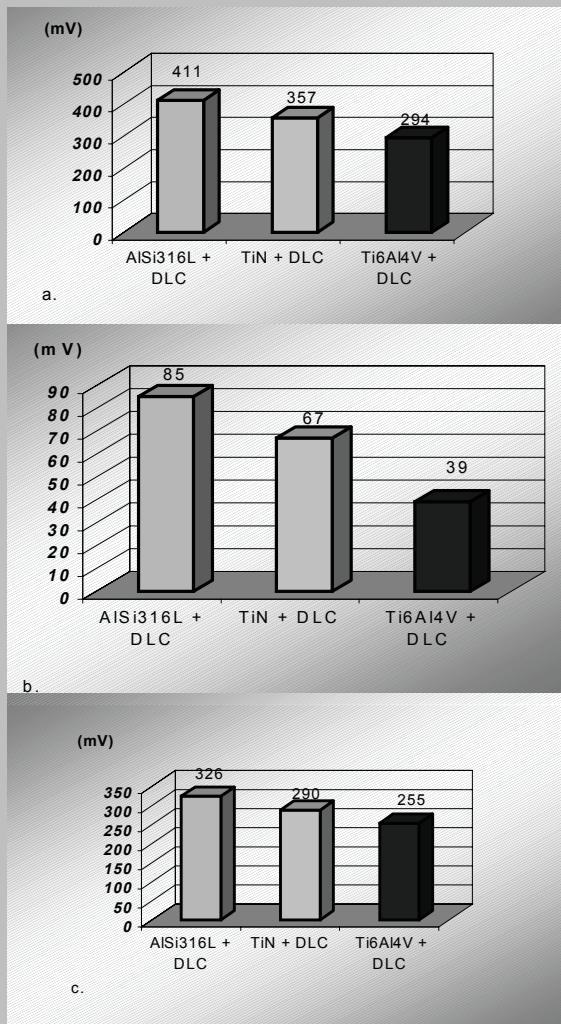


FIG. 6. Electrode potentials of carbon DLC layer coated materials: a)  $\epsilon_{\text{water}}$  of DLC, b)  $\epsilon_{\text{serum}}$  of DLC, c)  $\epsilon_{\text{water}} - \epsilon_{\text{serum}}$  of DLC.

Helmholtz-Stern layer.

The electrodes made of the metals coated with thin dielectric layers (NCD, DLC) behaved in different way as the non-coated electrodes (FIG. 5, 6). Their  $\epsilon$  depended first of all on the kind of the substrate materials in particular on its  $\Phi$  and not on the  $\Phi$  value of NCD, DLC. So it appeared, that a selection of a substrate metal permits changing the interaction between NCD, DLC layer surface and serum components.

## Conclusion

The measurements of the electric potential  $\epsilon$  of various electrodes immersed in water and human serum show that this parameter ( $\epsilon$ ) is sensitive to the dissolution of the metal and to the electron energy structure of the solid-molecule contact. Therefore, the value of  $\epsilon$  seems to be a quick and simple preliminary indicator of the biocompatibility of a material.

The measurements of  $\epsilon$  of thin dielectric carbon layers (DLC, NCD) deposited on various conducting materials show, that the surface biocompatibility of NCD, DLC coatings can be affected by electron properties of their substrates.

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## CARBON FIBRE-BASED POSTS WITH CEMENTIT UNIVERSAL RESIN CEMENTATION SYSTEM AS A MATERIAL FOR RESTORATION OF ENDODONTICALLY COMPROMISED TEETH - SEM EVALUATION OF SEALING

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## Introduction

Dental caries or mechanical injuries can result in substantial loss of hard tissues of the tooth crown. Teeth with partially or completely destroyed coronary structure can still function in the oral cavity provided they undergo root canal treatment and prosthodontic reconstruction with posts and