BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LXII No. 1/2010	25 - 30	Seria Tehnică

Electrochemical Surface Characterization of Diamond-like Carbon Deposited on Biomedical 316L Stainless Steel

Mihai Iordoc*, Elena Petrache*, Gheorghe Ioniţă**,
Elena Valentina Stoian**

* Institutul Naţional de Cercetare Dezvoltare pentru Inginerie Electrică, INCDIE ICPE,
Splaiul Unirii, 313, 030138, Bucureşti
e-mail: mihai_iordoc@icpe-ca.ro

****** Universitatea Valahia din Târgovişte, Bd. Unirii, nr.18-20, Târgovişte

Abstract

Diamond-like carbon (DLC) films were deposited by D.C. magnetron sputtering using a graphite target and argon as the discharge gas. DLC films possess many diamond-like properties including low friction, high hardness, and chemical inertness. This highly biocompatible material can be used as corrosion-resistant coatings for implantable devices. The electrochemical behavior of coated and uncoated biomedical 316L Stainless Steel in simulated body fluid is studied in this paper. DLC coatings were investigated by electrochemical techniques (open circuit potential, variation of polarization resistance in time, potentiodynamic polarization and electrochemical impedance spectroscopy). The electrolyte used in this test was a Hank solution with pH 7.4 at 37 ^{0}C. Electrochemical measurements pointed out that DLC coating could improve corrosion resistance in the simulated corrosive environment of the human body. This could be attributed to the formation of a dense and low-porosity coating, which impedes the penetration of water and ions.

Key words: *diamond-like carbon, 316 L stainless steel, corrosion, biomaterial.*

Introduction

The implantation of biomaterials into the human body allows it to increase the quality of life. Biomaterials should have biological and chemical stability to improve functions of the human body. Also, biocompatibility of biomaterials is probably their most important property because biomaterials are used directly or indirectly in contact with the human body. Among the implanted metals used as biomaterials, Ti alloy (Ti-6Al 4V) compared to Stainless Steel 316L and Co–Cr alloy is extremely similar to bone of the human body. Moreover, Ti alloy has several advantages such as superior biocompatibility and corrosion resistance [1, 2].

The highly corrosive environment of the human body restricts the materials to be used for implants [3]. High corrosion resistance is required for the material to use in this corrosive environment [4]. Moreover, wear debris produced from movement of joints can lead to wear corrosion causing biodegradation [5]. Recently, many researchers have focused on the development of advanced biomaterials to complement these drawbacks [6].

These materials suffer from drawbacks in case of sustained and long-term use like cytotoxicity, release of metal ions, corrosion, and wear. For example, though stainless steel has been successfully used in many biomedical applications, it can become corroded and releases Cr, Ni, Mn, and Mo ions when the metal is placed in coronary vessels [7]. Because the metal ions and other particles released from implants are suspected to trigger allergic reactions, as in the case of Ni, or to cause tumors [8], there is growing interest searching for less corrosive and inert biomaterials for their wide use in clinical applications. Previously, medical devices were selected based on its material and bulk properties. However, it is now recognized that the surface properties of the device mainly govern its biomedical applications. In most cases, a surface modification is considered to be a prerequisite for better biocompatibility. Ion beam processing or coating the medical devices with inert, corrosion resistant, adhesive, and biocompatible materials have been gaining importance from last decade [9].

DLC films for biomedical applications were a great interest to researchers in recent years because of their excellent properties such as electric insulation, low friction, high wear resistance, high hardness, corrosion resistance and biocompatibility. The superior mechanical performance and corrosion resistance make DLC films the preferred candidate for protective films [10].

All these properties match well with the criteria of a good biomaterial for applications in orthopedic, cardiovascular, contact lenses, or dentistry. DLC film comprises a mixture of sp2 and sp3 carbon bonds and is deposited by using high energy carbon species. DLC films are produced by a number of techniques like ion beam deposition, radio frequency plasma enhanced chemical vapor deposition (r.f. PECVD), filtered cathodic vacuum arc (FCVA), ion plating, plasma immersion ion implantation and deposition (PIIID), magnetron sputtering [11], ion beam sputtering, pulsed laser deposition, and mass selected ion beam deposition. The hydrogen content in DLC films varies up to 40%. Because of its amorphous structure, DLC films can be easily doped and alloyed with different elements. This leads to a wide range of properties depending on its sp3, sp2, and hydrogen content together with element incorporation [12].

Many authors have noted the potential of DLC films as a coating for orthopedic implants. However, it is difficult to obtain films that exhibit good adhesion to steel substrates [10].

Experimental

Commercial 316L Stainless Steel (ISO 5832-1) was used as substrate for DLC deposition.

Two identical samples of 316L Stainless Steel were used in this study. One as mark and one covered with DLC.

The DLC deposition process on the 316L Stainless Steel samples was conducted by physical vapor deposition technique in a DC magnetron sputter VUP-5M for one hour at 10^{-2} torr and 600V.

A VoltaLab 40 model electrochemical combine with dynamic EIS (Electrochemical Impedance Spectroscopy) was used for the electrochemical measurements. The electrochemical behavior of these samples was studied in a classical electrolytic cell with three electrodes. A platinum plate electrode and a saturated calomel electrode (SCE) were used as counter and reference electrode respectively. All three electrodes (including working electrode) were placed in a cell which has been connected to an UltraThermostat type U10 with external recirculation of heating water to maintain the temperature inside the cell close to 37 ^{0}C. The working electrode was made from 316L Stainless Steel covered and uncovered with DLC. Samples with 0.25 cm^2 geometric surface area were used. Prior to experiments, all samples were polished with SiC emery paper down to #4000. After polishing, the electrodes were degreased in acetone ultrasonic bath, washed with Millipore water and then one of each sample was introduced 45 minutes into magnetron sputtering for DLC deposition.

The working electrode potential was scanned on the potential range of -1000 mV up to +1000 mV/SCE with scan rate of 0.5 mV/sec. This scan potential range was chosen taking into account that, the potential – pH diagram for physiological conditions generally showed that, the potential value of a metallic biomaterial may vary from -1 to +1 V/SCE in the human body (Black et al). Excellent reproducibility was achieved when a potentiostatic reduction was applied for 10 minutes. The corrosion current density (i_{corr}) was determined by extrapolation of the anodic and cathodic slopes in the Tafel potential range.

Impedance measurements were performed using VoltaLab 40 dynamic EIS with VoltaMaster 4 Software on the frequency range between 100 kHz and 100 mHz with an AC wave of ± 5 mV (peak-to-peak) overlaid on a DC bias potential and the impedance data were obtained at a rate of 10 points per decade change in frequency.

All tests have been performed in Hank solution (Table 1) at 37 ^{0}C under atmospheric oxygen conditions without agitation.

Table 1. Chemical composition of simulated body fluid

Electrolyte	Composition
Hank's solution	NaCl 8 g/l; $CaCl_2$ 0.14 g/l; KCl 0.4 g/l; $MgCl_2{*}6H_2O$ 0.1 g/l; $Na_2HPO_4{*}2H_2O$ 0.06 g/l; KH_2PO_4 0.06 g/l; $MgSO_4{*}7H_2O$ 0.06 g/l; glucose 1 g/l

Results and Discussions

In Figure 1 it is presented the evolution of open circuit potential in time for both 316L Stainless Steel and 316L Stainless Steel coated with diamond-like carbon samples. It can be observed that in the case of biomedical 316L Stainless Steel coated with diamond-like carbon, the stationary potential have and tends to much electropositive values. This evolution of stationary potential pointed out that both samples tends to a noble behavior. In the unfriendly human body environment, this protective layer have a higher stability in time protecting the bulk material from corrosion and blocking the ion release phenomena.

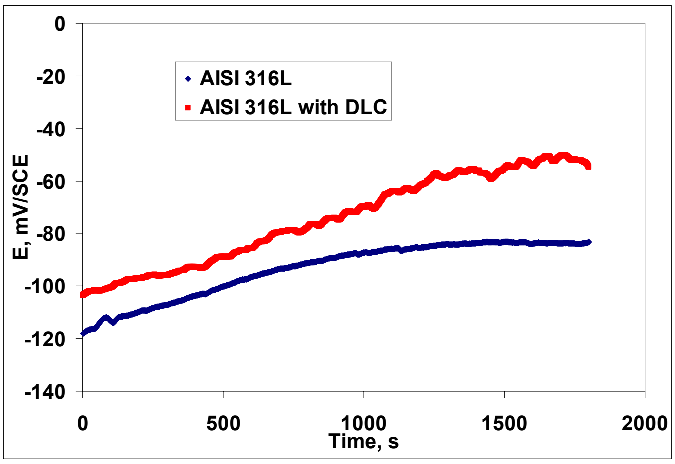

Fig. 1. OCP vs. time curves for studied samples in Hank solution at 37^{0}C

In Figure 2 it can be seen that the polarization resistance increases in time for 316L stainless steel sample covered with diamond-like carbon, while in the case of uncovered proof, polarization resistance remains constant in time, which means that the protective film formed at the interface electrode / electrolyte becomes increasingly stable and prevent the charge transfer.

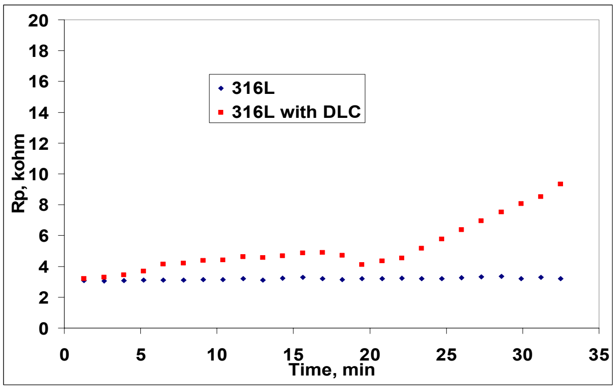

Fig. 2. Rp vs. time curves for studied samples in Hank solution at 37^{0}C

In Figure 3 are given the potentiodynamic polarization curves for studied samples. Analyzing this figure, it can be observed that, for biomedical 316L Stainless Steel covered with diamond-like carbon, the working electrode was directly translated to a stable passive behavior from the Tafel region without exhibiting an active-passive transition.

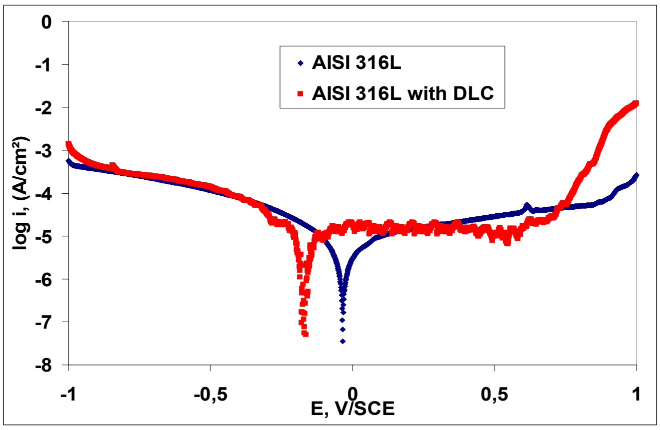

Fig. 3. Polarization curves for studied samples in Hank solution at 37^{0}C

The electrode passivity was observed for a large potential range (almost 700mV). After this passive range at more positive potentials, the current density increased due to both transpassivation and oxygen evolution reaction. If we analyze in comparison the polarization curves from Figure 3, we can see that the uncovered sample translate from the Tafel range into a region in which the process is under diffusion kinetic control when proper formation of an oxide film on the electrode surface takes place, following by a transpasivation domain. As can be seen in Table 1, the corrosion current density value is two times lower in the case of coated sample, while the polarization resistance is two times higher and corrosion rate is about ten times lower. These values are obtained using Evans method.

Analyzing the Nyquist diagram (Figure 4), it can be observed that at higher and medium frequencies there appears a capacitive loop very well defined. This behavior is pointed out by the Bode diagram (Figure 5). As we can see from the Bode diagram on the phase angle versus log frequency curve, there appears a maximum very well defined that corresponds to phase angle of 65^o, which indicates a capacitive behavior with diffusive tendencies of the coated sample in this environment. This behavior of the alloys is due to the DLC deposition on the electrode surface in magnetron sputtering. In the same time, this behavior suggesting that a stable film is formed on the electrode surface. This behavior is due to the adsorption of the aggressive anions from Hank solution on DLC layer followed by the relaxation processes. Values presented in Table 3 are calculated from Nyquist diagram using circular regression method and are consistent with the results obtained from polarization curves.

Table 2. Corrosion parameters of coated and uncoated 316L Stainless Steel in Hank solution at 37^{0}C

Sample	**E_{corr}**, mV/SCE	**i_{corr}**, µA/cm^2	**Corr,** µm/year	**R_P**, kohm·cm^2
316L Stainless Steel	-234.8	1.88	22.03	10.7
316L Stainless Steel coated with DLC	-361.4	0.83	3.52	21.18

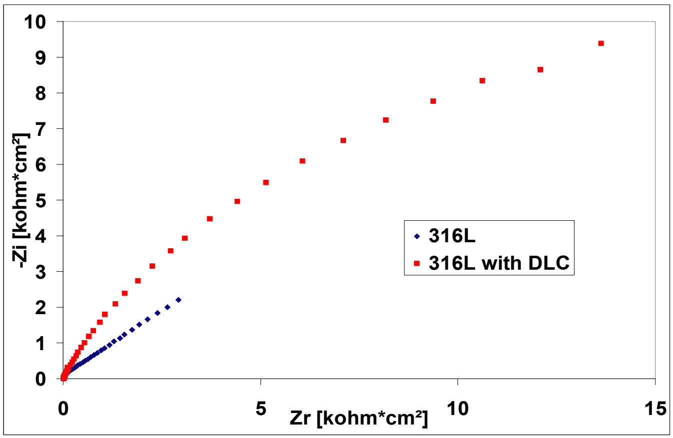

Fig. 4. Nyquist plot for studied samples in Hank solution at 37^{0}C

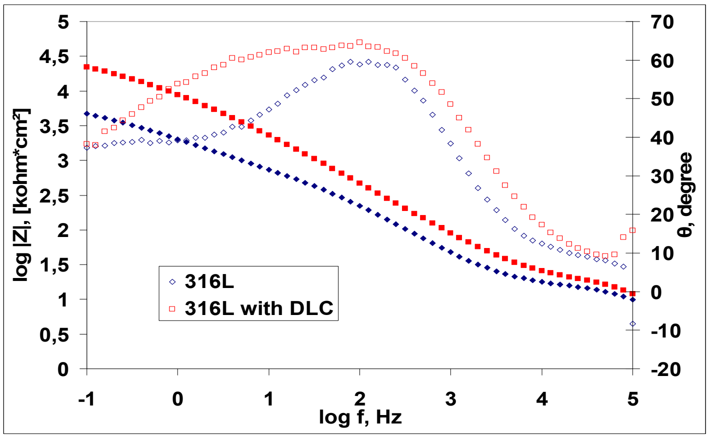

Fig. 5. Bode plot for studied samples in Hank solution at 37^{0}C

Table 3. The electrochemical parameters

Sample	**R_{el}**, ohm*cm^2	**R_P**, kohm*cm^2	**C,** µF/cm^2
316L Stainless Steel	46.88	9.3	171
316L Stainless Steel coated with DLC	54.5	27.09	16.44

Conclusions

Diamond-like carbon coating improves the corrosion resistance and surface Vickers micro-hardness of biomedical 316L Stainless Steel. Values of electrochemical kinetic parameters result from potentiodynamic polarization curves (Table 2) and from electrochemical impedance spectroscopy (Nyquist diagrams) (Table 3) confirm the stability and protection capacity of diamond-like carbon coating. Covering biomedical 316L Stainless Steel with DLC makes that this metallic biomaterial to become safer and more attractive for using in orthopedic surgery for partial / total hip or knee replacement. Increasing the corrosion resistance results in increasing of the life-time period for implants made from this material.

Acknowledgements

The authors acknowledge the European Commission for supporting the present work by the FP7-REGPOT-229906/2009 project.

References

1. Matsuno, H., Yokoyama, A., Watari, F., Uo, M., Kawasaki, T. – *Biomaterials*, **22,** 2001, p. 1253;
2. Kim, H.-G. et al. - *Diamond & Related Materials*, **14**, 2005, pp. 35–41;
3. Hauert, R. - *Diamond Relat. Mater.*, **12**, 2003, p. 583;
4. Hayashi, Y., Nakayama, G. - *Corros. Sci. Technol.*, **1**, 2002, p. 491;
5. Kim, H., Lee, J.J. - *J. Kor. Inst. Met. Mater.*, **16**, 2003, p. 11;
6. Papakonstantinou, P., Zhao, J.F., Lemoine, P., McAdams, E.T., McLaughlin, J.A. - *Diamond Relat. Mater.*, **11**, 2002, p. 1074;
7. Gutensohn, K., Beythien, C., Bau, J., et al. - In vitro analyses of diamondlike carbon coated stents: Reduction of metal ion release, platelet activation and thrombogenicity, *Thromb. Res.*, **99**, 2000, pp. 577–585;
8. Gillespie, W.L., Frampton, C.M.A., Henderson, R.J., Ryan, P.M. - The incidence of cancer following total hip replacement, *J Bone Joint Surg Br*, **70**, 1988, pp. 539–542;
9. Cui, F.Z., Luo, Z.S. - Biomaterials modification by ion beam processing, *Surf. Coat. Technol.*, **112**, 1999, pp. 278–285;
10. Ho-Gun Kima, Seung-Ho Ahna, Jung-Gu Kima, Se Jun Parkb, Kwang-Ryol Lee - Electrochemical behavior of diamond-like carbon films for biomedical applications, *Thin Solid Films,* **475**, 2005, pp. 291–297;
11. Sanchez N.A., Rincon C., Zambrano G., Galindo H., Prieto P. - Characterization of diamond-like carbon (DLC) thin films prepared by r.f. magnetron sputtering, *Thin Solid Films*, **373**, 2000, pp. 247–250;
12. Ritwik Kumar, R., Kwang-Ryeol Lee, J. - *Biomed Mater Res. Part B: Appl. Biomater*, 83B, 2007, pp. 72–84;
13. Black, J. - *Biological Performance of Materials: Fundamentals of Biocompatibility*; Marcel Decker Inc., New York, 1992.

Caracterizarea electrochimică a stratului DLC depus pe oțel inoxidabil 316L biomedical

Rezumat

Filmele de „diamond-like carbon” (DLC) au fost depuse prin tehnica „DC magnetron sputtering” folosind o tinta de grafit si argon ca gaz de descarcare. Filmele de DLC prezinta multe proprietati asemanatoare cu ale diamantului, cum ar fi coeficient de frecare mic, duritate ridicata si stabilitate chimica ridicata. Acest material foarte biocompatibil poate fi folosit la acoperiri rezistente la coroziune pentru protezele implantabile. In aceasta lucrare se studiaza comportamentul electrochimic al probelor de otel inoxidabil biomedical 316L, acoperite cu DLC si neacoperite, in fluid anatomic simulat. Acoperirile DLC au fost investigate prin tehnici electrochimice (potential in circuit deschis, variatia rezistentei la polarizare in timp, polarizare potentiodinamica si spectroscopie de impedanta electrochimica. Electrolitul folosit in aceasta testare a fost o solutie Hank cu pH-ul 7.4 la temperatura de 37 ^{0}C. Masuratorile electrochimice au scos in evidenta faptul ca acoperirea cu DLC imbunatateste rezistenta la coroziune in mediul coroziv simulat al organismului uman. Acest fapt poate fi atribuit formarii unei acoperiri dense cu porozitate scazuta, care impiedica patrunderea apei si a ionilor.