References

[1] Yamac T, The extraction and characterisation of wear particles from tissues around failed orthopaedic implants of different designs PhD Thesis, University of London; 1999.
[2] Kobayashi A, Bonfield W, Kadoya Y, Yamac T, Freeman MAR, Scott G and Revell PA, The size and shape of particulate polyethylene wear debris in total joint replacements. Proc Instn Mech Engrs [H] 211, 11-15; 1997.
[3] Maloney WJ, Smith RL, Schmalzreid TP, Chiba J, Huene D and Rubash H, Isolation and characterisation of wear particles generated in patients who have had failure of hip arthroplasty without cement. J Bone Jt Surg 77A, 1301-1310; 1995.
[4] Revell PA. Tissue reactions to joint prostheses and the products of wear and corrosion. Curr Top Pathol 71, 73-101; 1982
[5] Revell PA, Al-Saffar N and Kobayashi A. Biological reaction to debris in relation to joint prostheses. Proc Instn Mech Engrs 211H, 187-197; 1997.
[6] Al-Saffar N and Revell PA, Pathology of the Bone-Implant Interfaces. J Long-term Effects of Medical Implants 9, 319-347; 1999
[7] Revell PA and Jellie SE. Interleukin 15 production by macrophages in the implant interface membrane of aseptically loosened joint replacements. J Mater Sci; Mater in Med 9, 727-730;1998.
[8] Clarke SA and Revell PA. Expression of ß2 integrins at the bone/biomaterial interface. Proc Soc Biomat, San Diego, California;1998.
[9] Clarke SA. Integrin expression at the bone biomaterial interface. PhD Thesis, University of London, 1999
[10] Al-Saffar N and Revell PA, Pathology of the Bone-Implant Interfaces. J Long-term Effects of Medical Implants 9, 319-347; 1999.
[11] Al-Saffar N and Revell PA. Interleukin-1 production by activated macrophages surrounding loosened orthopaedic implants: a potential role in osteolysis. Br J Rheumatol 33, 309-316: 1994.
[12] Al-Saffar N and Revell PA. Differential expressioin of transforming growth factor-α and macrophage colony-stimulating factor/colony stimulating factor-1R (c-fms) by multinucleated gian cells involved in pathological bone resorption at the site of orthopaedic implants. J Orthop Res 18, 800-807; 2000.
[13] Chiba J, Rhubash HE, Kim KJ and Iwaki Y. The characterization of cytokines in the interface tissue obtained from failed cementless total hip arthroplasty with and without femoral osteolysis. Clin Orthop 300, 304-312; 1994.
[14] Al-Saffar N, Revell PA, Khwaja HA and Bonfield W. Assessment of the role of cytokines in bone resorption in patients with total hip replacement. J Mater Sci; Mater in Med 6, 762-767; 1995.
[15] Al-Saffar N, Revell PA, Khwaja HA and Kadoya Y. Assessment of the role of GM-CSF in the cellular transformation and the development of erosive lesions around orthopaedic implants. Am J Clin Pathol 105, 628-639; 1996.
[16] Xu JW, Kontinnen YT, Li TF, Waris TF, Lassus J, Matucci-Cerinic M, Sorsa T and Snatavirta TS. Production of platelet-derived growth factor in aseptic loosening of total hip replacement. Rheumatol Int 17, 215-221; 1998.
[17] Hercus B, Saeed S and Revell PA. Expression profile of T cell associated molecules in the interfacial tissue of aseptically loosened prosthetic joints. J Mater Sci: Mater Med 13, 1153-1156; 2002.
[18] Lalor PA, Revell PA, Gray AB, Wright S, Railton GT and Freeman MAR. Sensitivity to titanium. A cause for implant failure? J Bone Jt Surg 73B, 25-28; 1991.
[19] Weyand CM, Geisler A, Brack ME, Bolander ME and Goronzy JJ. Oligoclonal T-cell proliferation and interferon-gamma production in periprosthetic inflammation. Lab Invest 78, 677- 685; 1998
[20] Hercus B and Revell PA. Phenotypic characteristics of T lymphocytes in the interfacial tissue of aseptically loosened prosthetic joints. J Mater Sci: Mater Med 12,1063-1067; 2001.
[21] Bainbridge JA, Revell PA and Al-Saffar N. Costimulatory molecule expression following exposure to orthopaedic implants wear debris. J Biomed Mater Res 54, 328-334; 2001.
[22] Al-Saffar N, Revell PA and Kobayashi A. Modulation of the phenotypic and functional properties of phagocytic macrophages by wear particles from orthopaedic implants. J Mater Sci: Mater Med 8, 641-648; 1997.
[23] Altaf H, Saeed S, Bhatt R and Revell PA. The assessment of antigen presenting cells in the bone-implant interface. Biomaterialen 4, 86; 2003.
[24] Altaf H and Revell PA. The characterisation of antigen presenting cells in the bone implant interface & in response to biomaterials. Proc 7th World Biomaterials Congress, Sydney, Australia, 686; 2004.
[25] Bhatt R, Saeed S, Altaf H and Revell PA. In vitro assessment of interactions between T-cells and antigen-presenting cells (Apcs) when challenged with biomaterials: the CD40-CD40L interaction. Proc 7th World Biomaterials Congress, Sydney, Australia, 488; 2004.
[26] Saeed S anad Revell PA. Production and distribution of interleukin 15 and its receptors (IL-15R? and IL-R2ß) in the implant interface tissues obtained during revision of failed total joint replacement. Int J Exp Path 82, 201-209; 2001.
[27] Saeed S, Al-Saffar N and Revell PA. Expression of interleukin-15 (IL-15) and its receptors by U937 cells stimulated by metal wear particles retrieved from periprosthetic tissue. Proc 6th World Biomaterials Congress, Hawaii, 401; 2000.

THE INFLUENCE OF NANOCRYSTALLINE DIAMOND LAYERS OBTAINED BY MW/RF PECVD METHOD ON SURFACE PROPERTIES OF AISI 316 L STEEL

Tadeusz Blaszczyk*, Barbara Burnat*, Henryk Scholl*
Piotr Niedzielski** , Witold Kaczorowski**

*University of Lodz, Faculty of Physics and Chemistry, Department of General and Inorganic Chemistry, 90-136 Lodz, Narutowicza 68, Poland
**Technical University of Lodz, Institute of Materials Science, Department of Biomedical Engineering, 90-924 Lodz, Stefanowskiego 1/15, Poland
e-mail: tebe@chemul.uni.lodz.pl

Abstract

Determination of corrosion parameters of AISI 316 L with nanocrystalline diamond (NCD) layers deposited by means of new Microwave / Radio Frequency Plasma Enhanced Chemical Vapor Deposition (MW/RF PECVD) method in testing solution 0.5 M NaCl was a basic aim of presented work. We measured corrosion potentials, potentiodynamic characteristics, breakdown and repassivation potentials, corrosion resistance and impedance characteristics of AISI 316 L samples with- and without NCD layers. Summarizing obtained results it can be stated that NCD layers improve corrosion features of AISI 316 L and that surface preparation techniques have insignificant influence on these features.

Keywords: biomaterials, austenitic steel AISI 316 L, NCD layers, electrochemistry, corrosion

Introduction

Since 1986 S. Mitura and co-workers from Technical University in Lodz have produced nanocrystalline diamond (NCD) layers on different substrates by means of Radio Frequency Plasma Enhanced Chemical Vapor Deposition Method (RF PECVD) [1-3]. In 2004 a new dual frequency - Microwave and Radio Frequency PECVD method was there applied for NCD layers deposition [4]. Dual frequency

method was in details described by L. Martinu et al. [5] for deposition of P-SiOx films, J. E. Klemberg-Sapieha et.al. [6] for silicon nitride (P-SiN) and amorphous hydrogenerated silicon (a-Si:H) films, and A. Raveh et. al. [7] and P. Reineke et. al. [8] for amorphous diamond-like carbon layers. This method was used also in Technical University of Lodz for NCD layers deposition onto AISI 316 L stainless steel. AISI 316 L has good mechanical properties. That's why it is one of the most frequently used materials as bone-implants placed for short time [9,10]. The improvement both mechanical and corrosion features as result of using NCD layers was mentioned by S. Mitura in earlier publications [11] and in details described by J. Marciniak [9]. Corrosion parameters are different in a lot of publications. The reason lies in preparation processes of samples' surface.

The aim of this work is to presentation of corrosion measurement results of austenitic AISI 316 L prepared by mechanical polishing with abrasive paper SiC and additionally with Al_2O_3, with and without NCD layers. NCD layers were deposited by means of a new MW/RF PECVD method. The following corrosion measurement's results are presented in this work: corrosion potential E_{cor} in open circuit (OCP), polarization resistance R_p using Stern-Geary method, breakdown E_b and repassivation E_{rep} potentials and impedance characteristics (EIS) in 0.5 M NaCl solution.

Experimental methodology

The investigated AISI 316 L samples had cylindrical shapes with 8 mm diameter and ca. 3 mm height. The samples were prepared in two different ways. One part of samples was polished with abrasive paper SiC from 500 to 2000 grit only, rinsed with distilled water and ethanol, and dried with argon (99.999). The other part of samples was additionally polished with Al_2O_3 and next rinsed with distilled water and ethanol, and dried with argon. The surfaces of samples were controlled using optical metallographic microscope.

On such prepared samples' surface NCD layers using MW/RF PECVD method were deposited. Deposition process of NCD layers consisted of two steps: 1) surface etching (power of MW=150 W and RF= 120 W, autopolarization potential V_b=-700V and duration of t=3 min,); 2) NCD layers deposition (MW=150 W and RF=120 W, V_b=-700V, flow of CH_4 50 sccm, and duration of t=2 min). According to above given parameters can estimate a thickness of NCD layers at ca. 1μm.

Electrochemical corrosion measurements were carried out in a glass electrolytic cell (volume ca. 2cm³) in potentiostatic conditions using potentiostat / galvanostat PGSTAT 30 (EcoChemie AUTOLAB). Internal diameter of rubber ring gasket was a 0.6 cm and hence the active surface area (in contact with solution) was ca 0.28cm². During the measurements. temperature was 25⁰±1⁰C and the solution was mechanically stirred and deoxidized with argon. Special miniature calomel electrode in saturated NaCl solution (standard potential E^0=0.243 V) was used as reference electrode - all potentials in this work are given versus this electrode. All measurements were carried out in cycle described in [12]. This cycle consisted of following steps: 1) corrosion potential measurement Ecor in open circuit potential (OCP) method, 2) current - potential characteristic measurement in potential range from E_{cor}-0.020V to E_{cor}+0.020V according to Stern-Geary method with scan rate 0.5 mV•s⁻¹, 3) impedance characteristic measurement at E_{cor} potential in frequency range from 0.04Hz to 10^4 Hz using sinusoidal signal with E_{AC}=5mV, 4) potentiodynamic characteristic measurement with scan rate 1 mV•s⁻¹ from start potential E_{cor} - 0.200V to potential in which the measured current reached to programmed value. Then the scan direction was inversed and the measurement was carried out to the start potential. Steps from 1 to 3 were repeated in post-corrosion and fresh solutions.

Optical metallographic microscope was used for investigation of corroded samples. Scanning electron microscopy HITACHI S-3000N with an X-Ray microprobe analyzer EDX THERMO NORAN was used for structure and elements composition measurements.

Results

Corrosion potentials E_{cor}

For each sample we measured potential E vs time t. A final stable potential was considered as corrosion potential E_{cor}. Average values of E_{cor} and standard deviation are presented in TABLE 1.

It can be stated that E_{cor} values of AISI 316 L without NCD layers are independent from preparation method. A potential E_{cor} of AISI 316 L samples with NCD layers is more anodic in comparison with AISI 316 L samples without NCD layers. This potential depends on preparation technique and can be attributed with changes, which take place in structure of layer's surface during NCD deposition. After anodic polarization (designated "After corrosion") Ecor potentials did not monotonically change. The interpretation of observed E_{cor} changes is difficult. The most significant is a comparison of E_{cor} values in the same conditions i.e. before and after corrosion in fresh solution. Post-corrosion solutions can have different concentrations of corrosion products for each examined sample, which lead to large results dispersion (higher standard deviation). These results can be helpful with analysis of AISI 316 L implant's behavior in contact with human body - products of corrosion can accumulate in tissue nearby implant and cause situations close to second period of presented measurement.

Breakdown potentials E_b and repassivation potentials E_{rep}.

The preparation technique of AISI 316 L surface had a negligible influence on its potentiodynamic characteristics. FIGg.1 present example of potentiodynamic characteristics of samples (prepared with SiC abrasive papers) with and without NCD layers. It is important to notice that breakdown potentials E_b were difficult to detect from these characteristics - increase of measured current was not so sharp as for example in corrosion processes of Ti in KBr solutions [13]. Crevice and pitting corrosion occurred simultaneously near rubber gasket and it is a reason of this current - potential characteristic shape. That's why there is a great possibility to make error by determining the E_b value.

FIG. 2 shows fundamental difference between features of both samples - pits which emerged on surface of AISI 316 L without NCD developed in wide range of polarization potential up to potential close corrosion potential E_{cor}. In con-

Sample	Preparation	Before corrosion		After corrosion		After corrosion (in fresh solution)	
		E_{cor} [V]	ΔE_{cor} [V]	E_{cor} [V]	ΔE_{cor} [V]	E_{cor} [V]	ΔE_{cor} [V]
AISI	SiC	-0.17	0.01	-0.24	0.12	-0.15	0.09
AISI	SiC + Al_2O_3	-0.17	0.05	-0.31	0.12	-0.26	0.07
AISI with NCD	SiC	-0.10	0.05	-0.12	0.04	-0.17	0.06
AISI with NCD	SiC + Al_2O_3	0.01	0.05	0.13	0.16	-0.15	0.10

TABLE 1. Corrosion potentials E_{cor} of investigated samples.

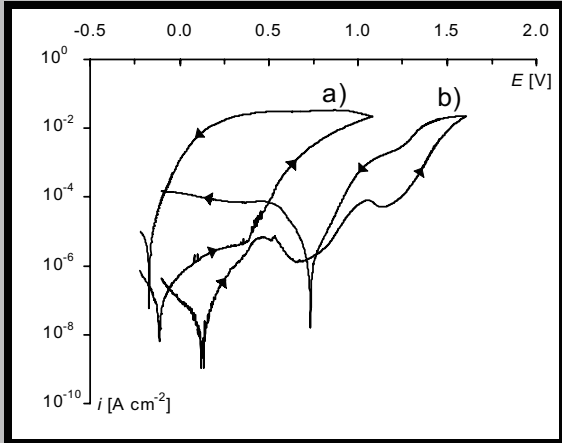**FIG. 1. Potentiodynamic characteristics for a) AISI 316 L and b) AISI 316 L with NCD layers; samples polishing with SiC.**

Sample	Preparation	R_p [Ω cm^2]	ΔR_p [Ω cm^2]	i_{cor} [A cm^{-2}]	Δi_{cor} [A cm^{-2}]
AISI	SiC	$1.28 \cdot 10^5$	$0.43 \cdot 10^5$	$2.22 \cdot 10^{-7}$	$0.72 \cdot 10^{-7}$
AISI	SiC + Al$_2$O$_3$	$1.85 \cdot 10^5$	$0.37 \cdot 10^5$	$1.46 \cdot 10^{-7}$	$0.31 \cdot 10^{-7}$
AISI with NCD	SiC	$1.92 \cdot 10^5$	$0.95 \cdot 10^5$	$1.59 \cdot 10^{-7}$	$0.69 \cdot 10^{-7}$
AISI with NCD	SiC + Al$_2$O$_3$	$3.75 \cdot 10^5$	$1.48 \cdot 10^5$	$7.84 \cdot 10^{-8}$	$3.44 \cdot 10^{-8}$

TABLE 2. Polarization resistance R$_p$ and corrosion current icor before anodic polarization.

sample surface has influence on both values - R$_p$ is higher for samples, which are polished with Al$_2$O$_3$ in comparison with samples, which are polished with SiC. It is connected with surface roughness - after polishing with SiC there are a large quantity of scratches on sample's surface, which enlarge an "electrochemical" surface. This fact has high influence on corrosion processes. Rp resistance of samples with NCD layers decreases drastically after anodic polarization independently of surface preparation technique.

Impedance characteristics

Impedance characteristics of AISI 316 L without and with NCD layers after polishing with abrasive papers SiC and additionally with Al$_2$O$_3$ before anodic polarization as Bode plot shows FIG.3a. Electrical equivalent circuit used for fitting the experimental characteristics is presented in FIG.3b.

All presented characteristics in FIG.3a. are similar and therefore they are not designated. Electrical equivalent cir-

trary - pits which emerged on surface of AISI 316 L with NCD layers repassivated in potential ca. 0.2 V that is more cathodic than breakdown potential E$_{cor}$. The same behavior is observed for AISI 316 L samples after polishing with Al$_2$O$_3$. E$_b$ and E$_{rep}$ potentials are more positive for AISI 316 L with NCD layers in the range from 0.7V to ca. 1V than AISI 316L without NCD. These potentials depend little on preparation technique (FIG.2). It means that possible differences of layers' surface connected with the different preparation technique, which were mentioned with corrosion potential analysis, have no influence on pits creation. Crevice and pitting corrosion were detected by microscopic investigations of samples' surface.
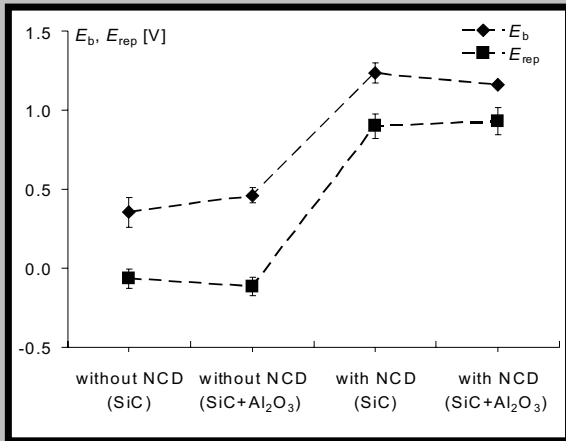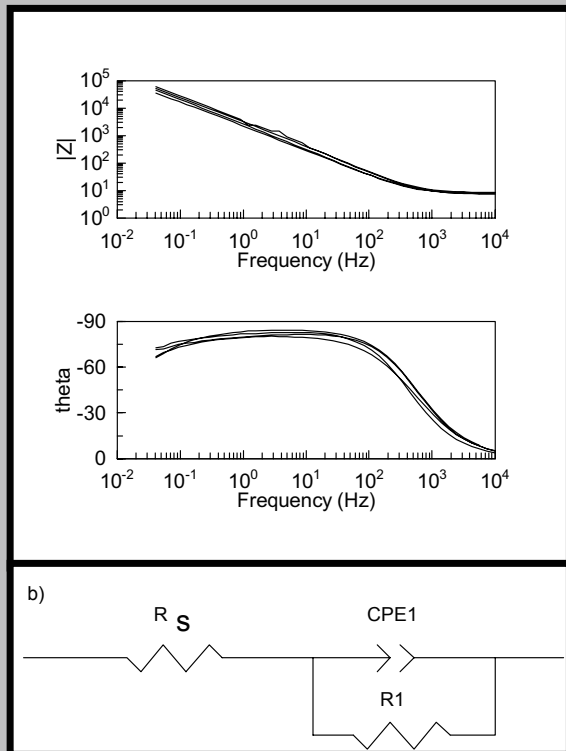

FIG. 2. Breakdown E$_b$ and repassivation E$_{rep}$ potentials vs. samples preparation and NCD layers presence.

Corrosion resistance Rp and corrosion current icor

The R$_p$ resistance and corrosion current icor were calculated from Stern-Geary linear characteristics (see TABLE 2).

Analyzing obtained results it can be stated that before anodic polarization of AISI 316 L with NCD layers the polarization resistance R$_p$ is 1.5÷2.0 times higher than the resistance R$_p$ of the same samples without NCD. A corrosion current icor behaves reversely. A preparation technique of

FIG. 3. Impedance characteristics of AISI 316 L without and with NCD layers;
a) Bode plots (see text), b) electrical equivalent. circuit.

cuit contains uncompensated electrolyte resistance, i.e. the resistance of electrolyte between working electrode and reference one, Rs¨7.4÷8.2 W·cm², constant phase element CPE1-T¨(5.5÷8.8)·10⁻⁵, CPE1-P¨0.89÷0.94 and reaction resistance R1¨(0.4÷1.9)·10⁴ Ω·cm². Constant phase element corresponds to the double layer capacity (CPE1-P is close 1) and includes information about the surface roughness.

Conclusions

Summarizing results presented above it can be stated that NCD layers: 1) shift a corrosion potential E_{cor} in more positive values but surface preparation method has negligible influence on E_{cor} potential; 2) shift breakdown E_b and repassivation E_{rep} potentials in more anodic values and decrease a potential range in which occurs pitting corrosion; 3) increase polarization resistance R_p and decrease corrosion current icor in corrosion potential E_{cor} but R_p and i_{cor} values depend on surface preparation; 4) have no influence on impedance characteristics. In final conclusions it can be stated that NCD layers improve corrosion features of AISI 316 L and that surface preparation techniques have insignificant influence on these features.

Acknowledgements

References

[1] Mitura E., Niedzielska A., Niedzielski P., Mitura S. The properties of carbon layers deposited onto titanium substrates. // Diamond and Related Materials - 1996. -5. - P. 998-1001.
[2] Mitura S. Nanotechnology in Materials Science. - Amsterdam: Pergamon - Elsevier Science Ltd, 2000
[3] Mitura S., Mitura A., Niedzielski P., Couvrat P. Nanocrystalline Diamond Coatings. // Journal of Chaos, Solitons and Fractals (Special Issue) - 1999. - 10(12). - P. 2165-2177.
[4] Kaczorowski W., Niedzielski P., Mitura S. Manufacture of carbon coating for biomedical applications in a new MW/RF reactor. // Eng. of Biomaterials -2005. -43-44. - P. 28-31.
[5] Martinu L., Klemberg-Sapieha J. E., Wertheimer M. R. Dual-mode microwave / radio frequency plasma deposition of dielectric thin films // Appl. Phys. Lett. - 1989. - 54. - P. 2645-2647.
[6] Klemberg-Sapieha J. E., Kuttel O. M., Martinu L., Wertheimer M.R. Dual microwave - R.F. plasma deposition of functional coatings. // Thin Solid Films - 1990. - 193/194. - P. 965-972.
[7] Raveh A., Martinu L., Hawthorne H.M., Wertheimer M.R. Mechanical Properties of Dual-Frequency Plasma Deposited Diamond-like Carbon // Surf. Coat. Technol. - 1993. - 58. - P. 45-55.
[8] Reinke P., Klemberg-Sapieha J.E., Martinu L. Effect of Amorphous Carbon Layers on the Growth of Diamond in Dual-Frequency Plasma // J. Appl. Phys. - 1994. - 76. - P. 5754-5759.
[9] Marciniak J. Biomateriały. - Gliwice: Wydawnictwo Politechniki Śląskiej, 2002 P. 493.
[10] Laskawiec J., Michalik R. Zagadnienia teoretyczne i aplikacyjne w implantach. - Gliwice: Wydawnictwo Politechniki Śląskiej, 2002 P. 170.
[11] Couvrat P., Denis M., Langer M., Mitura S., Niedzielski P., Marciniak J. The corrosion tests of amorphous carbon coatings deposited by r.f. dense plasma onto steel with different chromium contents. // Diamond and Related Materials - 1995. - 4. - P. 1251.
[12] Boguslawski G., Blaszczyk T., Scholl H. Electrochemical corrosion of Ti6Al4V alloy with nanocrystalline diamond coatings. // Eng. of Biomaterials - 2004. - 38-42. - P. 160-163.
[13] Scholl H., Blaszczyk T., Niedzielski P., Gralewski J. Biomaterials in nanoelectrochemistry - corrosion investigations of Titanium and Titanium with NCD layers. // Eng. of Biomaterials - 2004. - 35-36. - P. 45-53.

CORROSIVE FEATURES OF Ti WITH NANOCRYSTALLINE DIAMOND LAYERS OBTAINED BY MEANS RADIO FREQUENCY AND MICROWAVE / RADIO FREQUENCY PLASMA CHEMICAL VAPOR DEPOSITION METHODS

BARBARA BURNAT*, WITOLD KACZOROWSKI**, GRZEGORZ BOGUSLAWSKI**, TADEUSZ BLASZCZYK*, HENRYK SCHOLL*

*UNIVERSITY OF LODZ, FACULTY OF PHYSICS AND CHEMISTRY, DEPARTMENT OF GENERAL AND INORGANIC CHEMISTRY, 90-136 LODZ, NARUTOWICZA 68
**TECHNICAL UNIVERSITY OF LODZ, INSTITUTE OF MATERIALS SCIENCE, DEPARTMENT OF BIOMEDICAL ENGINEERING, 90-924 LODZ, STEFANOWSKIEGO 1/15
E-MAIL: BURNAT@OP.PL

Abstract

A new dual-mode microwave / radio frequency (MW/RF) plasma reactor for deposition of nanocrystalline diamond (NCD) coatings has been developed in Technical University of Lodz. In this work we present the results of investigations concerning influence of NCD layers deposition method on corrosive features of Ti in Tyrode's solution. NCD layers were produced by means of Radio Frequency and Microwave / Radio Frequency Plasma Chemical Vapor Deposition (RF PCVD and MW/RF PCVD). Electrochemical investigations show that both NCD coatings improve some corrosive features of Ti. However obtained results show that pitting corrosion did not occur on Ti/NCD RF samples, but it occur on Ti/ NCD MW/RF despite of thicker NCD layers.

Keywords: Ti; nanocrystalline diamond (NCD); NCD deposition methods; RF PCVD; MW/RF PCVD; electrochemical measurements; corrosion parameters.
[Engineering of Biomaterials, 56-57 ,(2006),34-37

Introduction

Ti and its alloys play an important role in medical applications as implants [1]. Materials used in human body, as medical implants, must be characterized by: good biocompatibility, chemical stability, biostability, good adhesion and excellent mechanical characteristics [2]. In order to enhance mechanical properties, corrosion resistance and biocompatibility of biomaterials a deposition of different carbon coatings is used. Diamond-like carbon (DLC) and nanocrystalline diamond (NCD) are the most often used carbon coatings. DLC films contain 80% sp³-bonded carbon [3,4]. NCD coatings, as Mitura reported in [5], have a thickness of about 0.5-1 μm and are composed of 97% diamond. One of the latest works about Microwave Plasma Chemical Vapor Deposition (MPCVD) technique signalizes a possibility of producing a new form of diamond film called ultrananocrystalline diamond (UNCD) which consist of crystalline grains of 95% sp³-bonded carbon that are 3-5 nm in size [4]. DLC, NCD and UNCD layers are produced in different chemical vapor deposition processes: Radio Fre-