cuit contains uncompensated electrolyte resistance, i.e. the resistance of electrolyte between working electrode and reference one, Rs¨7.4÷8.2 W·cm^2, 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)·10^4 Ω·cm^2. 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

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

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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.

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% sp^3-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% sp^3-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-

Sample	E_{corr} [V]	E_b [V]	E_{rep} [V]
Ti	-0.383±0.026	no exist	no exist
Ti/NCD (RF PCVD)	0.165±0.001	no exist	no exist
Ti/NCD (MW/RF PCVD)	0.065±0.040	3.38±0.33	3.22±0.28

TABLE 2. Corrosion, breakdown and repassivation potentials.

quency Plasma Chemical Vapor Deposition (RF PCVD) [5], Microwave Plasma Chemical Vapor Deposition (MPCVD) [4] and Microwave / Radio Frequency Plasma Chemical Vapor Deposition (MW/RF PCVD) [6-8].

In Technical University of Lodz are available RF PCVD and MW/RF PCVD methods for NCD layers deposition. The aim of this study was to compare an influence of these deposition methods on corrosive features of Ti in Tyrode's solution, especially an oxidation of sp^2-bonded carbon, breakdown potential, repassivation potential, polarization resistance, corrosion rate and type of corrosion. Obtained differences in corrosive features may be joined with changing of surface layers different for used deposition techniques.

Experimental

All measurements were done using cylindrically shaped samples of Ti (99.99 - Aldrich) with a diameter of 6.35 mm. Preparation of Ti electrodes consisted of sequential wet polishing with 1000 and 2000 grit SiC paper, polishing with diamond gel 1 μm and chemical etching in Kroll's solution ($HF:HNO_3:H_2O$ in volume ratio 1:3:5 respectively). Finally, the samples were rinsed with distilled water and dried in argon. The surface appearance was verified using optical metallographic microscope. Such prepared Ti samples were covered by NCD using two different methods: RF PCVD and MW/RF PCVD. RF generator was connected to working electrode with Ti samples. MW power was applied through a quartz tube mounted in opposite to working electrode [8]. The main parameters of NCD deposition processes are shown in TABLE 1.

According to parameters given in TABLE 1 a thickness of NCD layers can be estimated at ca. 0.5 μm for RF PCVD and even four-times higher for MW/RF PCVD.

Electrochemical measurements were carried out in a glass electrolytic cell with a volume of ca. 2 cm^3 [9]. All corrosion measurements were carried out in a typical three-electrode system. Calomel electrode in saturated NaCl solution was used as a reference electrode. Tyrode's solution (0.8 g NaCl, 0.02 g $CaCl_2$, 0.02 g KCl, 0.1 g $NaHCO_3$, 0.1 g D-glucose, 0.1 $MgCl_2$, 0.005 g NaH_2PO_4 and H_2O in 100 cm^3 solution) [10] was prepared from chemical reagents POCh S.A. (Polish Chemical Reagents) and Aldrich - with purity "for analysis" - without additional purification. Following electrochemical methods were used in corrosion measurements according to [11]: open-circuit potential (OCP) for corrosion potential E_{corr} detection, Stern-Geary's method for polarization resistance R_p and corrosion rate CR detection, potentiodynamic curves for breakdown potential E_b and repassivation potential E_{rep} detection and electrochemical impedance spectroscopy (EIS) which allowed to determine properties of phase boundary electrolyte solution / sample [12].

The surface appearance before and after the corrosion process was verified using optical metallographic micro-

scope. Surface structure and elements composition analysis of samples after corrosion process were performed using scanning electron microscopy with X-ray analysis (SEM-EDX) method.

Results and discussion

Electrochemical measurements

Values of open circuit potential E vs. time t were collected for each sample. Time of registration was from 2000s till 6000s. Stabilized electrode potential was established as corrosion potential E_{corr}. Averaged values and standard deviations of E_{corr} are presented in TABLE 2. Potentiodynamic characteristics dependence of current density j=I/A (I - measured current [A], A - sample surface [cm^2]) versus polarization potential E [V] are presented in FIG.1. Breakdown potential E_b and repassivation potential E_{rep} values obtained from these characteristics are also presented in TABLE 2. In case of Ti electrodes with NCD layers deposited by RF PCVD method pitting corrosion did not occur, and therefore E_b and E_{rep} values were impossible to detect.

Analyzing data presented in TABLE 2 it can be stated that NCD layers cause increase of corrosion potential Ecorr form -0.383 V to 0.165 V (ca. 0.45 V) in case of RF PCVD and form -0.383 V to 0.065 V (ca. 0.55 V) in case of MW/RF PCVD deposition methods. In case of Ti without NCD and Ti with NCD layers deposited using plasma vapor deposition method with radio frequency (called Ti/NCD RF) there was no breakdown in Tyrode's solution. Oxidation peak current was observed in potential range 1-3 V on the obtained potentiodynamic characteristics for Ti/NCD RF. This oxidation peak was joined with intensive gas bubbling on sample surface, and it can be attributed to presence of graphitic (sp^2) material on deposited NCD layers [13]. For Ti samples with NCD layers deposited using dual frequency plasma vapor deposition method (called Ti/NCD MW/RF) breakdown potential E_b was close to 3.4 V. Repassivation
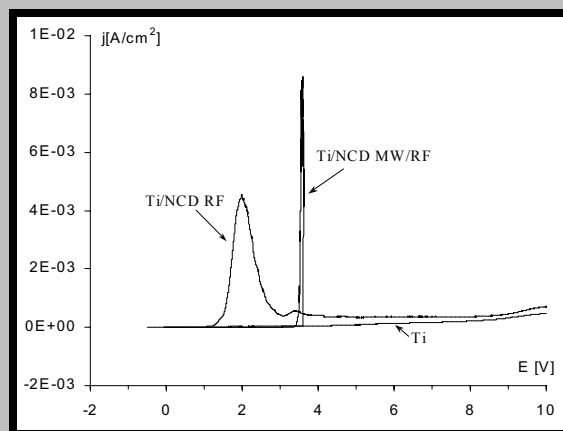
Parameters		RF PCVD	MW/RF PCVD
Ion etching	Gas	Ar	Ar
	Bias voltage	-800 V	-700 V
	RF power	2.5 kW	320 W
	MW power	-	150 W
	Time of etching	2 min	10 min
Deposition of NCD layers	Gas	CH_4	CH_4
	Bias voltage	-800 V	-700 V
	RF power	2.5 kW	500 W
	MW power	-	150 W
	Gas stream velocity	25 sccm	20 sccm
	Time of deposition	10 min	12 min

TABLE 1. The main parameters of NCD deposition processes.

FIG. 1. Potentiodynamic characteristics of investigated electrodes in Tyrode's solution.

Sample	CR [mmPY]	Rp [Mohm·cm²]
Ti	$(5.65\pm0.46)\cdot10^{-5}$	4.0 ± 0.3
Ti/NCD (RF PCVD)	$(3.49\pm0.18)\cdot10^{-6}$	64.7 ± 3.6
Ti/NCD (MW/RF PCVD)	$(4.18\pm0.66)\cdot10^{-6}$	54.6 ± 8.6

TABLE 3. Averaged values of corrosion rate CR and polarization resistance R_p.
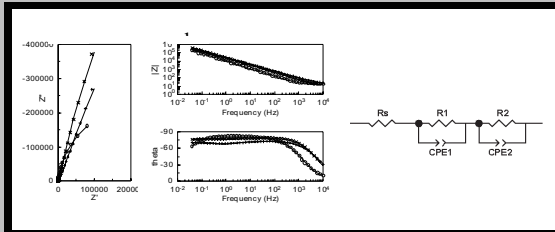

FIG. 2. Nyquist (a) and Bode (b) plots for Ti (o), Ti/NCD RF (´) and Ti/NCD MW/RF (+); electrical equivalent circuit (c).

Sample	Rs [ohm·cm²]	R1 [ohm·cm²]	CPE1-T	CPE1-P	R2 [ohm·cm²]	CPE2-T	CPE2-P
Ti	14.4	64	$8.53\cdot10^{-4}$	0.657	$5.28\cdot10^{5}$	$1.77\cdot10^{-3}$	0.928
Ti/NCD RF	12.1	2498	$5.63\cdot10^{-5}$	0.897	$5.11\cdot10^{6}$	$8.37\cdot10^{-5}$	0.886
Ti/NCD MW/RF	17.3	7246	$2.96\cdot10^{-5}$	0.821	$4.48\cdot10^{6}$	$1.06\cdot10^{-3}$	0.829

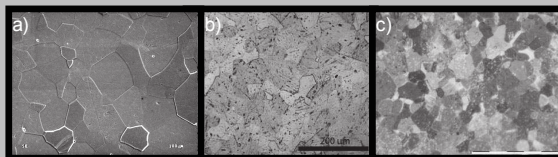**TABLE 4. Elements' values of electrical equivalent circuit.**

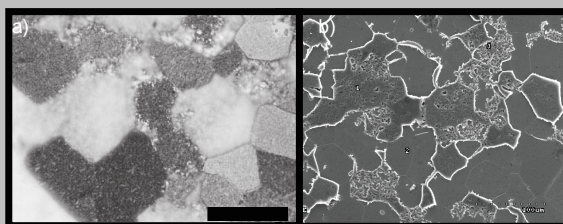**FIG. 3. SEM picture of Ti without NCD (a), optical microscope images of Ti/NCD RF (b) and Ti/NCD MW/RF (c).**

FIG. 4. Pitting corrosion on Ti/NCD MW/RF: optical microscope image (a), SEM picture (b).

	Point 1		Point 2		Point 3	
	Atom %	El. Wt. %	Atom %	El. Wt. %	Atom %	El. Wt. %
Ti	36.88	60.53	87.08	95.50	36.75	60.47
C	5.02	2.06	2.58	0.71	6.46	2.67
O	48.45	26.57	10.34	3.79	46.99	25.82
Na	1.65	1.30	-	-	1.65	1.30
Mg	0.84	0.70	-	-	0.86	0.72
P	0.90	0.95	-	-	1.18	1.25
Cl	4.56	5.54	-	-	4.00	4.87
Ca	1.71	2.34	-	-	2.11	2.91

TABLE 5. SEM-EDX element composition of Ti/NCD MW/RF surface after corrosion.

potential $E_{re}p$ was ca. 3.2 V for these samples. Oxidation peak was not observed on these samples. That's why the presence of graphitic (sp²) material on surface of Ti/NCD MW/RF may be negligible.

Polarization resistance R_p and corrosion rate CR were calculated from Stern-Geary's characteristics using CorrView program. The Stern-Geary's characteristics were registered with scan rate 0.5 mV/s in potential range from E_{corr} -20 mV to E_{corr} +20 mV. Averaged values of these parameters are presented in TABLE 3.

Analyzing data presented in TABLE 3 it can be stated that NCD layers deposition on Ti causes more than ten-times increasing of R_p values. Corrosion rates for Ti with NCD layers, independent of deposition method, are order of magnitude smaller than for Ti without NCD.

Impedance characteristics EIS were registered at Ecorr potential in wide frequency range from 10 kHz to 40 mHz, with a harmonic signal E_{AC} =5 mV. Examples of characteristics for investigated samples and electrical equivalent circuit fitting obtained experimental data are presented in FIG.2.

The circuit was the same for all investigated samples. It contained uncompensated electrolyte resistor Rs, two identical branches CPE1 || R1 and CPE2 || R2 connected in series. The first branch CPE1 || R1 describes impedance characteristics in high frequency range, while the second branch CPE2 || R2 describes them in low frequency range. CPE1-T element corresponds to differential double layer capacity of phase boundary solution / sample, while CPE1-P values corresponds to surface roughness. Resistance R1 describes corrosion processes. R1 value significantly increases after NCD layers deposition, what can be joined with decreasing of corrosion reaction rate. Simultaneously decreases differential double layer capacity (CPE1-T). Physicochemical meaning of CPE2 and R2 is equivocal - these elements may correspond to phase boundary titanium oxide / titanium features [14].

Microscopic measurements - surface structure and elements composition analysis

SEM picture of Ti without NCD and optical microscopes images for Ti with NCD layers are presented in FIG.3. Changes caused by pitting corrosion on Ti/NCD MW/RF are shown in FIG. 4. Elements composition for three points of corroded surface marked on FIG.4b are presented in TABLE 5.

On Ti surface without NCD layers and after NCD layers deposition the crystallites of the substrate are clearly visible (FIG. 3). NCD layers deposited using RF PCVD method change the sample color form metallic-silver to yellow (FIG. 3b), while layers deposited by means MW/RF PCVD method give blue color (FIG. 3c). FIG.4a shows that corrosion processes for Ti/NCD MW/RF take place on whole crystallites surface with preferable orientation (areas out of focus). This effect is confirmed by SEM picture (FIG. 4b). Elements composition data from TABLE 5 show that Ti, O and C are present in any point of this surface. Moreover the presence of other elements such as Na, Mg, P, Cl and Ca was found in points 1 and 3 and it may be joined with corrosion processes in Tyrode's solution. Smooth region with point 2 is a region of crystallites which did not corrode. Making a comparison of C contents in analyzed points it can be found that in points 1 and 3 the contents of C are unexpectedly higher than in point 2. This fact can be explain by the appearance of C from glucose existing in Tyrode's solution.

Summary and conclusions

Electrochemical investigations show that both NCD coatings improve some corrosive features of Ti. In case of Ti

with NCD layers the shift of corrosion potential was observed in more positive values. Moreover the corrosion rates of Ti with both NCD layers are order of magnitude smaller than for Ti without NCD. The both NCD coatings have comparable values of corrosion rate and polarization resistance. Investigated samples with different NCD coatings have similar impedance characteristics and the same equivalent electrical circuit.

Obtained electrochemical results show different corrosive features of NCD layers deposited on Ti using two different techniques - pitting corrosion did not occur on Ti/NCD RF samples, but it occur on Ti/NCD MW/RF despite of thicker NCD layers. Microscopic investigations made for Ti/NCD MW/RF show that localized corrosion process is joined with surface microstructure - pitting corrosion take place on whole crystallites surface with preferable orientation. These differences in corrosive features may be joined with changing of surface layers different for used deposition techniques. In electrochemical aspect the new method MW/RF PCVD (despite of existing breakdown at 3.4V) is better in comparison with RF PCVD, because there is no anodic peak in potential range 1-3V. Therefore it can be supposed that the presence of graphitic (sp2) material on NCD layers deposited by MW/RF PCVD method is smaller.

Summarizing obtained results can be stated that MW/RF PCVD technique requires subsequent improvement of the main parameters of NCD deposition processes on Ti so that the breakdown will be eliminate or the breakdown potential will be shifted to maximum value.

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PROPERTIES OF NiTi - SHAPE MEMORY ALLOY AFTER MODIFICATION BY RF PCVD METHOD

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Abstract

The DLC (diamond-like carbon) and NCD (nanocrystalline diamond) layers coat made implants of medical steel 316 L, titanium and titanium alloys [1]. These layers have excellent properties such as: high hardness, good biocompatibility to various types of cells, good adhesion to implants [2], wheres implants with diamond layer have good corrosion resistance in body fluids. Result received for these materials are encourage to modification other materials for example shape memory alloy NiTi. Nitinol is often used material in interventional cardiology, orthodontics and urology [3]. Shape memory alloy charackterizes of return to designed shape, superelasticity, thermomechanical behavior [3]. This phenomenons are proceeded thanks to the martensite transformation. Modification in high temperature perhaps cause failure martensite transformation which influence on the material properties change.

Key words: nitinol, diamond layer, RF PCVD method

Introduction

Nitinol - equatomic shape memory alloy is often used material to production of vascular stents, filters, implants in orthopedics and orthodontics [3]. NiTi is characterized by an unique combination of properties, superelasticity, thermomechanical behavior, low density and shape memory. These are very favourable phenomenons taking into account the difference of size of blood-vessels where the implants are predicted to be introduced. Phenomenons in NiTi are proceeded thanks to martensitc transformation. The term martensitic phase transformation describes the formation during cooling or during loading with an external stress of the austenite high temperature phase [9]. In this phenomenon occurs atoms re-organise. This transformation dose not change the chemical composition. Results of this transformation are new crystal lattice.

All materials, which are implanted, should fulfill many factors, they could not cause allergic response or inflammatory reaction. They must exhibit biocompatibility - the ability of the human body to endure the implants without destruction of the tissue. They must have a specific system of mechanical properties - good adhesion, good corrosion resistance in body fluids.

Although studies have demonstrated the good corrosion resistance and biocompatibility of Nitinol [4], but the high nickel content at this alloy (54,5 to 57% weight) makes pos-

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