TANTALUM PENTOXIDE CERAMIC COATINGS DEPOSITION ON Ti4Al6V SUBSTRATES FOR BIOMEDICAL APPLICATIONS

N. Donkov, A. Zykova [1], V. Safonov [2], R. Rogowska[3], J. Smolik [3], V. Luk'yanchenko [4]

Institute of Electronics, Bulgarian Academy of Sciences, Sofia, Bulgaria;
[1]Institute of Surface Engineering, Kharkov, Ukraine;
[2]National Science Center „Kharkov Institute of Physics and Technology", Kharkov, Ukraine;
[3]Institute for Sustainable Technologies, National Research Institute, Radom, Poland;
[4]INMASTERS LTD, Kharkov, Ukraine

Tantalum pentoxide ceramic coatings are presented as perspective biomaterials for various biomedical applications. The surface properties and structure of as-deposited, annealed at 450°C and 700°C e-beam evaporated Ta_2O_5 films on Ti alloy substrates (Ti4Al6V) were investigated. The results demonstrated the good cyto compatibility of e-beam evaporated Ta_2O_5 coatings especially in the case of annealed films with strong stoichiometric Ta_2O_5 composition. Replacing the surface bounds with oxygen by either thermal or plasma treatment results in shear at more chemically stable hydrophilic surface region.
PACS: 87.80.Rb

1. INTRODUCTION

Functional coatings based on Ti, Al, Zr, Ta oxides exhibit unique properties: high inductivity, density, bio- and chemically inertness, which are very important for next implant and tissue engineering applications. Tantalum and tantalum based compounds have a high potential in the biomedical field. Ta-based implants show high fracture toughness, corrosion and wear resistance, chemical stability. The results of the animal implantation test of Ta in both soft and hard tissue of rats showed good biocompatibility and osteogenesis of this metal [1]. TaC and TaN materials posses relatively high hardness due to the covalent nature of their bond [2] and demonstrate high thermal stability and superior corrosion resistance [3]. The blood compatibility of TaN films was shown to be better than those of Ta [4].

Cell/biomaterial interaction process and direct cell adhesion to a biological surface creates many important phenomena providing vital functions of a living organism on different levels of its organization. In vitro tests of cell adhesion on material and coating surfaces are the basic tools to determine the material surface/tissue response on a cellular level [5, 6]. The effects of materials composition, surface chemistry and surface topography on cell adhesion and proliferation have been largely studied [7, 8]. The surface energy is also the fundamental material property that can influence on cell behavior [9]. At the present study tantalum pentoxide ceramic coatings are presented as perspective biomaterials for various biomedical applications.

2. MATERIALS AND METHODS

The study of e-beam evaporated Ta_2O_5 film structure and properties effect on cell/material response was performed. The samples were formed on Ti alloy substrates (Ti4Al6V). The main parameters of the process were described in our previous study [10]. The evaporation process was carried out at initial vacuum of 7×10^{-6} Torr, operational-mode vacuum of 3×10^{-5} Torr, anode current of 50 mA and calculated evaporation power of 350 W. The deposition rate under these conditions was 28 nm/min. The layer thickness and the deposition rate were controlled by a digital thin-film deposition monitor MSV-1843/H MIKI-EEV operating at 6 MHz [11].

The surface properties and structure of as-deposited, annealed at 450 and 700°C e-beam evaporated Ta_2O_5 films were investigated by means of XPS and XRD methods. X-ray photoelectron spectroscopy was carried out using ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of $5x10^{-10}$ mbar (during the measurement $1x10^{-8}$mbar), using AlKalpha X-ray source (excitation energy hv=1486.6 eV). The instrumental resolution measured as the full width at a half maximum (FWHM) of the Ag3d5/2, photoelectron peak is 1 eV. The energy scale is corrected to the C1s - peak maximum at 285 eV for electrostatic charging.

The contact angles were measured by means of tensiometric method. Prior to contact angle measurements, samples were ultrasonically cleaned in acetone and deionised water and dried. Advancing contact angle was measured by Wilhelm's method (Kruss K12) at temperature 20°C [12].The standard liquids with well-known values of surface tension, component of dispersion and polar interaction were used. The surface free energy (SFE) and its polar and dispersion components were determined by means of Owens-Wendt-Rabel-Kaelble [13] method. The experiments on study of cytotoxicity and cytocompatibility in vitro – in culture of fibroblasts were carried out. In process of cell cultivation with coated samples the cell cytology, morphology and proliferation activity were determined by means of optical microscopy after 24h and 3, 5 days cultivation. Rat hypodermic cellular tissue was extracted for initial fibroblast culture obtaining. The suspension of extracted cells was centrifuged at 750 orb/min during 15min. Sowing cell area was $3x10^5$ cell/ml density of cultural medium. The fibroblast cultivation at 3 ml of Dulbecco Modified Eagle's Medium (DMEM, Sigma) was made by methods of mono layer culture at thermostat condition (temperature 37 °C during 5 days). After cultivation,

fixation at the acetic acid and methyl alcohol (1:3) solution and azure-eosin coloration the cellular proliferation on the cover glasses was determined by optical microscopy (Micros). The experiments were triplicate. The analysis of cell adhesion on substrates with as-deposited, annealed at 450°C and 700°C e-beam evaporated Ta_2O_5 films after 3,5 days cultivation was made by means AFM methods (Quesant Instrument Corporation,USA).

3. RESULTS AND DISCUSSION

The XPS survey spectra of the e-beam evaporated Ta_2O_5 films (as-deposited sample; sample annealed at 450°C in O_2) were obtained. All spectra consist of well defined XPS lines of Ta 4f, 4d, 4p and 4s; O1s. Fig. 1 shows the high-resolution Ta4f and 4 O1s XPS spectra of the investigated structures. Ta 4f doublets are typical for e-beam evaporated Ta_2O_5 and have two peaks: Ta 4f7/2 at ~ 26.3…26.6 eV and Ta 4f5/2 at the binding energy 1.9 eV higher. The Ta 4f lines of the deposited films agree well with the Ta 4f doublet representative of the Ta-0 bond in Ta_2O_5. The Ta4f7/2 peak is placed at 26.5 and 26.6 eV, and the Ta 4f5/2 one is at 28.4 and 28.5 eV for the annealed and as-deposited films respectively.

The results clearly demonstrate that the annealed films are more stoichiometric Ta_2O_5 composition. The O1s spectra further support this assumption. The O1s peaks of the deposited layers are centered at binding energies of 530.9 and 530.8 eV for the annealed and as- deposited films respectively, which is consistent with reported data for Ta_20_5 [10]. The FWHM of both peaks is 1.9 eV. The O/Ta ratio estimated from the spectra is ~ 3 for all samples. The annealing process varies the Ta_20_5 coatings structure from amorphous one (for as-deposited films) to orthorhombic phase, surface topography from smooth to nano crystalline (up to 20 nm) and improves the crystallinity of Ta_20_5 films. At the same time the dielectric constant of the films increased from 17 to 28 with the increase of annealing temperature due to the improvement in the film crystallinity and packing density [14]. But annealing process after 500°C results in some additional impurities which have been observed at the XPS spectra of e-beam evaporated Ta_20_5 (C1s, Si2p, Na1s).

The calculation of surface free energy of solids from the measurements of contact angle is based on the surface energy balance condition: The values of surface free energy and its polar and dispersion components were calculated by Owens-Wendt-Rabel-Kaeble' method for the liquid system: α-bromonaphthalene- formamide-ethylene glycol-diidomethane-glycerol-water were determined from contact angle measurements at 20°C (see Table).

Replacing the surface bounds with oxygen by either thermal or plasma treatment results in shear at more chemically stable hydrophilic surface region.

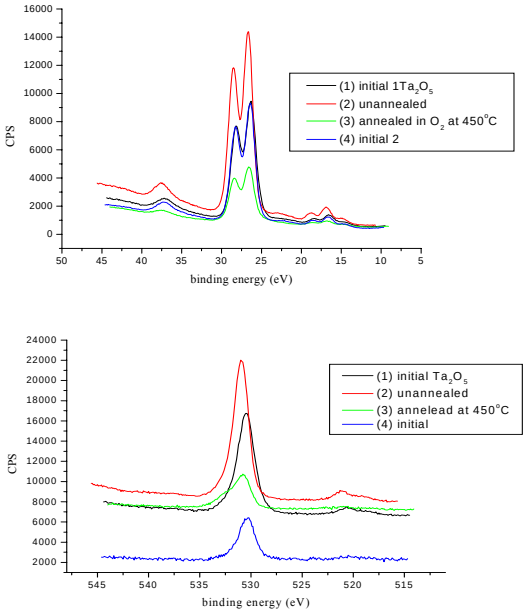

Fig. 1. The XPS high-resolution Ta 4f and 4 O1s spectra of the e-beam evaporated Ta_2O_5 films

After 3 days staying in the culture fibroblast cells were well spread both on the all coated surfaces. The cell morphology was typical for cells on the coated surface. The cell structural organization corresponded to initial fibroblast. After 5 days cultivation the density of cell increased for all samples. The most of cells were ripe fibroblasts with strongly marked phenotype.

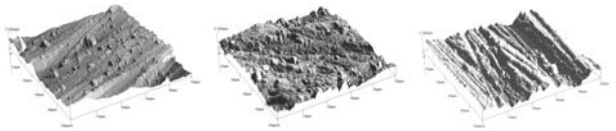

Fig. 2. The characteristic features of fibroblast cell attachment and spreading on the sample surfaces (as-deposited, annealed at 450 and 700°C e-beam evaporated Ta_2O_5 films) after 5 days cultivation observed by means AFM method

Previous studies have examined the effect of surface energy on cell functions such as adhesion, proliferation and differentiation. In some cases cell functions are enhanced on hydrophilic surfaces, in other cases on hydrophobic. In our study the values of SFE are in the range of 41…45 mN/m. The annealing process results in shear at chemically stable hydrophilic surface region.

The values of total surface free energy, dispersion and polar components, fractional polarity (by Owens-Wendt-Rabel-Kaelble's method)

Symbol of coatings	Component of surface free energy [mN/m]			
	Dispers part γ^d	Polar part γ^p	Total γ	Fractional polarity $\gamma^p/(\gamma^d+\gamma^p)$
Ta_2O_5 (as-deposited)	31.52	10.36	41.88	0.247
Ta_2O_5 (annealed at 450 °C)	31.80	12.09	43.89	0.275
Ta_2O_5 (annealed at 700 °C)	32.42	11.54	43.96	0.263

The more detail study of the effect of surface free energy on cell spreading and proliferation requires the account of dispersive and polar components of surface free energy values and fractional polarity [15]. The polar part of SFE changes from 10 for as-deposited to 12 for annealed films and fractional polarity changes from 0.24 to 0.27 correspondently (the Table above). Fibroblast cells were well spread on the all coated surfaces. Differences in cell attachment and spreading on e-beam evaporated Ta_2O_5 coating surfaces have been observed by means AFM method (Fig. 2).

4. CONCLUSIONS

The results demonstrated the good cyto compatibility of e-beam evaporated Ta_2O_5 coatings especially in the case of annealed films with strong stoichiometric Ta_2O_5 composition. Replacing the surface bounds with oxygen by either thermal or plasma treatment results in shear at more chemically stable hydrophilic surface region. But annealing process after 500°C results in some additional impurities which can influence on cell adhesion processes. The best biological response parameters (cell number, proliferation function, morphology) were obtained in the case of annealed at 450°C films with the most parameters of polar part component of SFE and fractional polarity. The results show that the surface properties are strongly influenced by the preliminary treatment. The deposition and treatment conditions effect on the surface parameters of the e-beam evaporated Ta_2O_5 films and the next positive cell response.

ACKNOWLEDGEMENTS

The research project was supported by the Bulgarian-Ukrainian Academies of Science international scientific cooperation program.

REFERENCES

1. H. Matsuno, A. Yokoyama, F. Watari, M. Uo, T. Kawasaki //*Biomaterials.* 2001, v. 22, p.1253.
2. T. Miyazaki, H.-M. Kim, T. Kokubo, C. Ohtsuki, H. Kato, T. Nakamura //*Biomaterials.* 2002, v. 23, p.827.
3. G. Georgeiv, N. Fescheschiev, D. Popov, Z. Uzuuov // *Vacuum.* 1986, v. 36, p. 595.
4. Y.X. Leng, H. Sun, P. Yang, J.Y. Chen, J.Wang, G.J.Wan, N. Huang, X.B. Tian, L.P. Wang, P.K. Chu // *Thin Solid Films*. 2001, v. 398/399, p. 471.
5. U. Meyer, A. Bushter, H.P. Wiesmann, U. Joos, D.B. Jones // *J. Eur. Cells Mater*. 2005, v. 9, p. 39-49.
6. K. Anselme. Osteoblast adhesion on biomaterials// *Biomaterials.* 2000, v. 21, p. 667-681.
7. A. Hunter, C.W. Archer, P.S. Walker, G.W. Blunn// *Biomaterials.* 1995, v. 16, p. 287-295.
8. Marshal Dhayal, Su-In Cho, Jun Young Moon, Su-Jin Cho, Anna Zykova. S180 cell growth on low ion energy plasma treated TiO_2 thin films //*J. Applied Surface Science*. 2008, v. 254, p. 3331-3338.
9. Van der Valk, Van Pelt, H.J. Busscher //*J. Biomed. Mater. Res.* 1983, v. 17, p. 807-817.
10. N. Donkov, E. Mateev, A. Zykova, V. Safonov, V. Luk'yanchenko. Biocompatibility of dielectric Ta_2O_5 coatings in *in vitro* tests// *Journal of Physics: Conference Series.* 2010, v. 223, p. 012030.
11. N. Donkov, A. Zykova, V. Safonov, E. Mateev // *Problems of Atomic Science and Technology. Series „Plasma Physics" (15).* 2009, N 1, p. 153-155.
12. A. Zykova, V. Safonov, V. Luk'yanchenko, J. Walkowicz, R. Rogovska. The influence of surface parameters of coatings deposited by various vacuum plasma methods on the cell / material interection in vitro tests // *Problems of Atomic Science and Technology. Series "Plasma Physics" (13).* 2007, N 1, p. 200-203.
13. D.K. Owens, R.C. Wendtn // *J. Appl. Polym. Sc.* 1969, v. 13, p. 1741.
14. S. Uthanna, Jagadeesh Chandra, et al.// *J. of Physics. Conference Series.* 2008, v. 114, p. 01203.
15. N.J. Hallab, K.J. Bundy, K. O'Connor, et al. // *J. Tissue Engineering.* 2001, v. 7, p. 55-71.

Article received 12.10.10

НАНЕСЕНИЕ КЕРАМИЧЕСКИХ ПОКРЫТИЙ ПЕНТОКСИДА ТАНТАЛА ДЛЯ БИОМЕДИЦИНСКОГО ПРИМЕНЕНИЯ

Н. Донков, А. Зыкова, В. Сафонов, Р. Роговская, Ю. Смолик, В. Лукъянченко

Керамические покрытия пентоксида тантала рассматриваются как перспективный биоматериал для различных биомедицинских целей. Исследованы структура и поверхностные свойства покрытий Ta_2O_5, нанесенных на подложки сплава титана Ti4Al6V электронно-лучевым испарением, и отожженных при температурах 450 и 700°C. Результаты показали хорошую цитосовместимость покрытий Ta_2O_5, особенно в случае отожженных покрытий стехиометрического состава. Замещение поверхностных связей кислородом в процессе термической или плазменной обработки сдвигает поверхностные свойства в более химически-стабильную гидрофильную область.

НАНЕСЕННЯ КЕРАМІЧНИХ ПОКРИТТІВ ПЕНТОКСИДА ТАНТАЛУ ДЛЯ БІОМЕДИЧНОГО ЗАСТОСУВАННЯ

Н. Донков, Г. Зикова, В. Сафонов, Р. Роговська, Ю. Смолік, В. Лук'янченко

Запропоновано керамічні покриття пентоксида танталу як перспективні біоматеріали для різноманітного біомедичного застосування. Було досліджено структуру та поверхневі властивості плівок Ta_2O_5, нанесених на зразки сплаву титана Ti4Al6V електронно-променевим випарюванням та відпалених при температурах 450 та 700°C. Результати довели гарну цитосумісність покриттів Ta_2O_5, особливо у випадку покриттів стехіометричного складу після термічної обробки. Заміщення поверхневих сполук киснем у процесі термічної або плазмової обробки зсуває поверхневі властивості у більш хімічно-стабільну гідрофільну зону.