PLASMA-CHEMICAL DEPOSITION, STRUCTURE, PROPERTIES AND APPLICATION OF NANOCOMPOSITE POLYMER-BASED COATINGS

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The nanocomposite polymer-based thin layers have unique properties that cannot be generally obtained by their individual constituent elements. Particularly, are interesting thin-layer systems containing nanoparticles of noble metals, another polymer or semiconductors. Among the different ways to synthesize these nanocomposites, the vacuum solvent-free methods such as physical, chemical vapor deposition and hybrid plasma chemical techniques are advantageous and provide easy control not only of nanocluster growth but also of its size, shape and distribution into polymer matrix volume. The vacuum-plasma chemical advantages of methods of nanocomposite systems synthesis can be the absence of limitations in the solubility of polymer matrix, for example, sparingly soluble [1].

The works [1–2] suggests a new electron-beam approach to fabricate organosilicon magnesium containing coatings by laser assistive processing. The low-energy electron beam on organosilicon resin, initiates the detachment of methyl substituents. The chemically cross-linked Si-O structures resistant to electron-beam are formed on the target and deposited layers are partially cross-linked. The laser assistive influence is accompanied by decrease in the reactivity of the generated products of resin destruction. The UV (266 nm) laser emission leads to an increase of cross-linked structures in the

coating. The optical emission (532 nm) on the organosilicon resin activates significantly the methyl substituents detachment. The use of magnesium makes it possible to increase the percentage of the organosilicon compound conversion into the coating. Meanwhile, the laser emission influence on the molecular structure of the coating is weakened. Interaction of the metal with organosilicon molecules leads to the formation of magnesium silicide. The UV laser and optical emission lead the formation of magnesium hydroxide $(Mg(OH)_2)$, to magnesium oxide (MgO) respectively. The coatings are potential candidates for deposition on implants aiming at stimulating of osseointegration processes. Highly ordered conductive polyaniline (PANI) coatings containing gold nanoparticles were prepared by low-energy electron beam deposition method, with emeraldine base and chloroauric acid used as target materials. It was found that the emeraldine base layers formed from the products of electron-beam dispersion have extended, non-conductive polymer chains with partially reduced structure, with the ratio of imine and amine groups equal to 0.54. In case of electron-beam dispersion of the emeraldine base and chloroauric acid, a protoemeraldine structure is formed with conductivity 0.1 S/cm. The doping of this structure was carried out due to hydrochloric acid vapor and gold nanoparticles formed by decomposition of chloroauric acid, which have a narrow size distribution, with the most probable diameter about 40 nm. These gold nanoparticles improve the conductivity of the thin layers of PANI+Au composite, promoting intra- and intermolecular charge transfer of the PANI macromolecules aligned along the coating surface both at direct and alternating voltage. The proposed deposition method of highly oriented, conductive nanocomposite PANIbased coatings may be used in the direct formation of functional layers on conductive and non-conductive substrates [3].

Polytetrafluoroethylene (PTFE) composite coatings doped with copper acetate and polyethylene (PE) were fabricated on rubber substrate by electron beam dispersion technique. The effects of dopant nature and glow discharge treatment on morphology, structural and tribological properties of the coatings were investigated. Glow discharge enhances the crystallinity and ordering degree of composite coatings. Friction experiments indicated the significant difference of composite coatings in the nature of their destruction during friction. PE-PTFE coating is characterized of the brittle fracture with clear failure boundaries but Cu-PE-PTFE coating shows a rough surface without cracking and delaminating after friction. Cu doping increases the dynamic coefficient of friction of PE and PE–PTFE composite coatings, but discharge plasma decreases the dynamic coefficient of friction. Cu-PE-PTFE composite coating after discharge treatment has the decreased dynamic coefficient of friction and improved wear resistance [4]. A comprehensive study of the effectiveness of two-layer coatings based on PEG and silver nitrate to combat pathogenic microorganisms - the agents of implant-associated infections was conducted. The paper deals with the features of the structural transformations that occur in the polymer matrix at the stage of deposition and formation of the thin layer, as well as when the thin layer is heat-treated. The PEG matrix was shown to promote thermal stabilization of silver nitrate, which is manifested in the presence of significant amount of oxide (AgO and Ag_2O) and undecomposed salt, in addition to silver nanoparticles, in the annealed organic layer [5]. A new method of forming coatings containing copper nanoparticles and the products of polyethylene thermal destruction is suggested. The method comprises the heat treatment of the two-layer copper acetate-polyethylene system deposited in a vacuum using lowenergy electron flux. The effect of the medium composition and the annealing temperature on the structural and phase state of the copper nanoparticles and the matrix is determined. The high antibacterial activity of the heat-treated surfaces against Escherichia coli ATCC 25922 is shown [6].

The plasma chemical solvent-free method of doped and nanocomposite polyaniline-based conductive coatings deposition was elaborated. The nanocomposite PANI-based coatings were deposited onto interdigital capacitor for ammonia gas sensing applications. The increasing of the sensing performance of the PANI-based coatings with silver nanoparticles was established in particular at the low frequency region of impedance spectra. The high sensitivity and linearity of this sensor response were examined at a direct and alternating voltage with ammonia concentrations up to 10 ppm [7].

The features or chemical composition and molecular structure of polymer silver containing coatings and their changes under the heating were studied. The coatings have been deposited from the gas phase formed by electron-beam dispersion of polymer and silver salt mixture. The impact of polymer matrix and silver salt nature on the parameters of surface plasmon effect occurrence, as well as on the molecular structure of the coatings has been established [8].

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References

1 Micro- and Nanocomposite Polymer Coatings Deposited from Active Gas Phase / M.A. Yarmolenko [et al.] : Edited by A. V. Rogachev. – Moscow: Radiotekhnika, , 2016. – 424 p.

2 Jintao Xiao, A. V. Rogachev, V. A. Yarmolenko, A. A. Rogachev, Xiaohong Jiang, Dongping Sun, M. A. Yarmolenko // Surface & Coatings Technology. – 2018. – 349.– P. 61–70. 3 Surui Wang, A. A. Rogachev, M. A. Yarmolenko, A. V. Rogachev, Xiaohong Jiang, M. S. Gaur, P. A. Luchnikov, O. V. Galtseva, S. A. Chizhik. // Applied Surface Science. – 2018. – 428.– P.1070–1078.

4 B Zhou, Z Liu, B Xu, A. V. Rogachev, M. A. Yarmolenko, A. A. Rgachev // Polymer Engineering & Science – 2018 – Vol. 58, Issue 1 – P. 103–111.

5 Chen Qi, A. V. Rogachev, D. V. Tapal'skii, M. A. Yarmolenko, A.A. Rogachev, Xiaohong Jiang, E. V. Koshanskaya, A. S. Vorontsov // Surface & Coatings Technology – 2017.- Vol. 315. – P. 350-358.

6 Jinguo Sun, A. V. Rogachev, M. A. Yarmolenko, A. A. Rogachev, Xiaohong Jiang, D. V. Tapal'skii, D. L. Gorbachev and A. A. Bespal'ko // RSC Advances. – 2016.–6(35).–P. 29220–29228.

7 A. A. Ragachev, M. A. Yarmolenko, Jiang Xiaohong, Ruiqi Shen, P. A. Luchnikov, A. V. Rogachev // Applied Surface Science 351.–2015.–P. 811–818.

8 A. A. Rogachev, M. A. Yarmolenko, Xiaohong Jiang, A. V. Rogachev, Ruiqi Shen, Zhou Yingjie // Progress in Organic Coatings. -2015. - 81. - P. 80-86.