INVESTIGATION ON THE INFLUENCE OF ZrC COATINGS STRUCTURE ON THEIR RESISTANCE TO CORROSION AND ANTIMICROBIAL PROPERTIES

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Introduction

Coatings deposited on the surface of metallic biomaterials used in orthodontics and jaw implantology should meet special requirements, i.e., in addition to high biocompatibility, should be characterized by good corrosion resistance in mouth environment, good adhesion to the substrate and resistance to brittle fracture, as well as be resistant to microbial growth. Particularly noteworthy in these applications are nanocomposite coatings of the nc-MeC/a-C structure, where Me = Ti, Zr, W, Nb etc. deposited by vacuum-plasma techniques, especially PVD (Physical Vapor Deposition), because they can exhibit particularly advantageous mechanical properties (high hardness, low wear ratio due to friction and good adhesion state to the substrate). These properties depend on the phase composition and structure of the coatings, which are a function of the carbon concentration in the coating and parameters of the deposition process [1,2]. The object of research presented in this article are thin coatings based on ZrC with different concentration of carbon, deposited on substrates made of 304L medical steel. The aim of the research is to determine the optimal composition of the coating due to its mechanical, anti-corrosion and antimicrobial properties in terms of its use for covering biomaterials used in orthodontics and jaw implantology.

Materials and Methods

ZrC coatings were deposited on 304L steel substrates by reactive magnetron sputtering at 400°C and -10 V substrate bias voltage. The coatings were deposited from the metallic Zr target in Ar + C_2H_2 atmosphere at C_2H_2 flow rate of 3.5; 4.5; and 6.5 sccm, thus obtaining coatings with different total carbon concentrations. The evaluation of the corrosion resistance of the systems was carried out using potentiodynamic polarisation tests using the device ATLAS 0531 Electrochemical Unit, in a system of a conventional electrochemical three-electrode cell, where working electrode was a sample with the active area of 0.292 cm^2, reference electrode – saturated calomel electrode (SCE, $Hg/Hg_2Cl_2/KCl$) and counter electrode – platinum sheet. The corrosive medium (electrolyte) was Fusayama-Meyer artificial salvia. The tests were carried out at the temperature 25±1°C with the scan rate of 0.001 V/s. Measurements were repeated until obtaining three similar results – polarisation curves. Corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarisation resistance (R_{pol} – a value inversely proportional to i_{corr}) have been estimated by the Tafel extrapolation method [3]. The static contact angles were measured through the sessile drop method using F4 Gomeiometer by Rame-Hart Instrumental Co. Drops with a volume of approximately 4 µl were deposited onto the investigated surfaces using a microsyringe. Fusayama-Meyer's artificial saliva, was used as a test liquid. The contact angles were measured at 3–5 different points at the surface of each sample. Seven bacterial species representative of the peri-implant and oral cavity environment were used in studies of antimicrobial properties: *Staphylococcus aureus*, *Streptococcus mutans*, *Streptococcus salivarius*, *Streptococcus sanguis*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Candida albicans*. The assessment of antibacterial activity was made using the direct method based on the criteria contained in SN 195920 standard, while the evaluation of antifungal activity was performed based on SN 195921 standard. The susceptibility of the surface to microbial adhesion was assessed using fluorescent staining and observation in a Motic BA410 E fluorescence microscope [4,5]. The assessment of the adhesion of coatings to the substrate and their resistance to cracking was carried out using the Rockwell C test.

Results and Discussion

On the basis of polarization curves, current values and polarization resistance were estimated. The most favorable values of these parameters, from the point of view of corrosion resistance (the highest potential and polarization resistance and the lowest current density among the tested) were observed for the coating with the highest total carbon concentration. Also, based on microbiological tests, it was found that the best bacteriostatic effect and the highest resistance to colonization with microorganisms, characterized ZrC coatings with a higher carbon concentration of 61 and 75% at, obtained at the C_2H_2 flow rate, 4.5 and 6.5 sccm respectively. In turn, on the basis of carried out indentation tests, it was found that as the concentration of carbon in the coating increases, resistance to cracking decreases and the adhesion of the coating to the substrate deteriorates. Additionally, based on the measurements of the contact angle, it was found that the surfaces of all substrate/coating systems exhibited poorer wettability than the steel substrate.

Conclusions

Based on the conducted tests, it was found that all substrate/nc-ZrC/a-C coating systems have significantly better corrosion resistance in the artificial saliva solution than 304L steel substrate (they show several dozen times lower corrosion current and higher polarization resistance in potentiodynamic tests). In the case of the coating with the highest carbon content, in the potentiodynamic studies, no breakdown potential was observed, which may indicate a high resistance of the tested system to pitting corrosion. Coatings with a total carbon concentration above 60% are static for pathogenic microorganisms and have low colonization potential, compared to 304 L medical steel. In summary, the tested ZrC coatings are promising candidates for metal implant coverings, and their use in orthodontics requires the selection of optimal carbon concentration due to the mechanical, antimicrobial and anti-corrosion properties of the substrate/coating system.

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