# INVESTIGATION OF MECHANICAL AND ANTICORROSIVE PROPERTIES OF ZrC COATINGS DEPOSITED BY MAGNETRON SPUTTERING TECHNIQUE

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#### Introduction

One of the key aspects in the field of biomaterials production is the modification of their surface, among others by using vacuum-plasma techniques. In particular, on a large scale are successfully used the PVD (Physical Vapor Deposition) methods for the deposition of protective coatings of various structures and compositions. On the surface of biomaterials using these methods, coatings based on TiN, TaN, ZrN, TiC, TaC, TiO<sub>2</sub>, TaO, TiCN, a-C, ZrCN or ZrCN-Ag are deposited [1-4]. Among them, more and more researchers' attention is focused on coatings based on ZrC and ZrCN. The aim is to optimize the properties of these coatings by selecting the appropriate version of deposition method (among others radio-frequency (RF) magnetron sputtering (MS), pulsed laser deposition (PLD), etc.) and optimization of process parameters for the selected version. Taking into account the potential use of ZrC based coatings, inter alia, in orthodontics, it becomes very important to know the anti-wear and anti-corrosion properties of these coatings deposited on medical steel. Therefore, the analysis of the effect of carbon concentration in ZrC coatings on these properties was adopted as the main goal of the research.

## **Materials and Methods**

The object of research were ZrC coatings 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 C2H2 flow rate of 2.5, 3.5; 4.5; and 6.5 sccm, thus obtaining coatings with different total carbon concentrations. In order to determine the mechanical properties of the coatings, a number of indentation tests were performed using the Berkovich and Rockwell indenters. The tribological properties of coatings were assessed basing on the so-called ball on disk test. On the basis of cross profiles of the wear track, volumetric wear ratio and friction coefficients of the coating with alumina ball were determined. In addition, a detailed analysis of the state of internal stresses in the ZrC/steel substrate and ZrC/Si substrate/coating systems was made using X-ray diffraction and a method based on measuring the radius of curvature of the sample with the deposited coating. Parallel, the analysis of anti-corrosion properties of the tested coatings, in the artificial saliva solution, using potentiodynamic polarisation tests was carried out. The results of corrosion tests were confronted with the results of mechanical and tribological tests.

Basing on the indentation curves (load vs. penetration) and numerical simulations based on FEM (finite element method), one were determined for coatings with different carbon concentrations, among others: Young's modulus, yield point and tangent modulus. In particular, it was shown that for the carbon concentration in the coating C=51 at. % (C<sub>2</sub>H<sub>2</sub> flow rate approx. 2.5 sccm) the hardness and Young's modulus of the tested coatings reach maximum values (respectively H=40 GPa, E=350 GPa), and in case of further carbon concentration increase both values of hardness and Young's modulus decrease. Obtained results of indentation tests were also used in the analysis of the state of adhesion of the coating to the substrate and the assessment of fracture toughness. It was found that the coatings with the highest carbon concentration are characterized by the worst adhesion to the substrate from the tested coatings and posses the low resistance to cracking. Analyzing the results of internal stresses in the coating/substrate system obtained with XRD and based on the measurement of the radius of curvature of the sample with deposited coating, it was found that there was a maximum compressive stresses (about 4.5 GPa) for coatings with a carbon concentration C=56.5 at. % (C<sub>2</sub>H<sub>2</sub> flow rate approx. 3.5 sccm). Increase in carbon concentration to C=84 at.% ( $C_2H_2$  flow rate approx. 6.5 sccm) caused a nearly two times decrease in the value of compressive stresses (about 2.3 GPa).

## Conclusions

On the basis of the conducted research, the evolution of phase composition of the ZrC coating, deposited on the medical steel by the magnetron sputtering method in the C<sub>2</sub>H<sub>2</sub> atmosphere, along with the increase of the carbon concentration was determined. In particular, it has been shown that with increasing carbon concentration the proportion of amorphous carbon surrounding the nanocrystalline ZrC carbides increases. This change in the phase composition of the coating causes a decrease in the coefficient of friction and a decrease in the wear coefficient of the coating in the ball on disk test. Parallel, along with the increase in carbon concentration, a decrease in fracture toughness and deterioration of the adhesion of the coating to the substrate was observed. Independently carried out corrosion tests of the analyzed systems: 304L steel/ZrC coating, confronted with mechanical and tribological tests, allowed to determine the phase structure and coating structure with optimal properties from the point of view of metal implants, including orthodontic wires.

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