

Corrosion resistance of the biocompatible Ti and Zr oxynitride thin films

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INTRODUCTION: In the last few years, thin films of many transition metal oxynitrides such as Ti or Zr oxynitrides have gained increasing importance in various applications due to their excellent combination of high hardness, chemical stability, optical and electrical properties, wear and corrosion resistance [1,2].

The aim of this work is to investigate the microchemical, microstructural, mechanical and anticorrosive characteristics of 316L stainless steel coated with Zr and Ti oxynitride. The choice of these materials for biomedical applications was determined by the fact that they exhibit an optimum combination between the high wear-corrosion resistance of the nitrides and the good biocompatibility of the oxides.

METHODS: The thin films were deposited by pulsed magnetron sputtering [3]. The magnetron cathodes were made of Ti and Zr (both 99.6 % purity) and fed by a pulsed bipolar generator-type ENI RPG5 (positive pulse length 1936 ns, repetition rate 100 kHz). The magnetron current and the negative d.c. substrate bias were of 3 A and 60 V, respectively. The O₂/N₂ mass flow ratios were controlled to be of about 1 and the working pressure was approximately 5x10⁻¹ Pa. The argon pressure was adjusted in order to keep a constant overall pressure. These parameters were kept constant for the deposition of both layers. The overall thickness of all coatings was ~ 1.2 μm.

The experimental work was focused on the corrosion behavior of the coatings in the Ringer solution. Additional information on the thin films properties was obtained by XPS method, XRD analysis, microhardness measurements and adhesion tests. The corrosion resistance was investigated by using a Voltalab 80 apparatus equipped with a saturated calomel electrode (SCE) as the reference electrode. Cyclic potentiodynamic and linear polarisation tests were performed. The following electrochemical parameters were determined: E_{i=0} - corrosion potential (like zero current potential), i_p - passive current density, R_p - the polarization resistance, i_{corr} - corrosion current densities and V_{corr} - corrosion rates.

RESULTS: The XPS analysis showed that the coatings consisted of a mixture of metal (Ti or Zr) oxynitrides and oxides, together with adsorbed

oxygen. The oxynitride compounds had relatively high oxygen content, the O/N ratio being of 2.5 and 1.9 for TiON and ZrON films, respectively. The XRD analysis showed that all deposited coatings were amorphous. Hardness values were in the range 14÷16 GPa – TiON and 18÷22 GPa – ZrON. A good adhesion of all the coatings was found (critical loads of 30 - 35 N were obtained), taken into account the data in the literature for transition metal oxides. In Table 1 are summarized the main electrochemical parameters in the Ringer solution, for uncoated and coated samples.

Table 1. Electrochemical parameters of the uncoated and coated samples in Ringer solution.

Material	E _{i=0} V	i _p μA/cm ²	R _p kohm.cm ²	i _{corr} μA/cm ²	V _{corr} mm/year
316L	-0.33	15	34.7	0.75	5.79x10 ⁻³
TiON	-0.30	8	232.3	0.10	0.78 x10 ⁻³
ZrON	-0.33	6	246.6	0.09	0.72 x10 ⁻³

DISCUSSION & CONCLUSIONS: TiON and ZrON coatings were prepared by pulsed magnetron sputtering on 316L steel. The oxynitride compounds had relatively high oxygen content, the O/N ratio being of 2.5 and 1.9 for TiON and ZrON films, respectively. ZrON layers exhibited hardness values with about 4 GPa higher than that of the TiON films. The experimental results showed the favourable influence of the deposited coatings on the corrosion resistance of the 316L steel in Ringer solution. The main electrochemical parameters were superior to those of the uncoated samples.

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