European Cells and Materials Vol. 16. Suppl. 1, 2008 (page 30) ISSN 1473-2262

Structural, mechanical and anti-corrosive properties of biocompatible Zr/ZrCN coatings

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INTRODUCTION: Multilayer coatings have been shown to outperform single layer films in terms of thermal stability, wear, abrasion and resistance to oxidation [1]. In recent years, nanometer-scale multilayers composed of two different alternating layers have been extensively developed due to their high hardness and excellent wear-corrosion behavior [2].

This work aims to investigate the properties of Zr/ZrCN coatings, with bilayer periods ranging from 4.4 to 190 nm, deposited on 316L stainless steel substrates. ZrCN single layer coatings were also prepared, as reference samples.

METHODS: Zr/ZrCN multilayers were deposited by the cathodic arc technique [3]. The elemental and phase composition, texture, microhardness, adhesion, surface roughness and residual stress were investigated by AES, XRD, Vickers microhardness and scratch adhesion measurements and surface profilometry. The bilayer period values were estimated from the rate and the deposition time of the individual layers. The corrosion resistance of the coated samples was evaluated using electrochemical tests in artificial physiological solution, by measuring the corrosion current and the critical current for passivation.

RESULTS: For the ZrCN monolayers and the ZrCN sub-layer in the multilayer structure, the elemental compositions were: Zr – 34.8 at.%, C – 44.5 at.%, N – 17.3 at.%, O – 3.4 at.%. The C/(C+N) and (C+N)/Zr ratios were found to be of 0.72 and 1.8, respectively. X-ray diffraction patterns revealed that the multilayers with Λ higher than about 20 nm exhibited a (111) orientation (similar to that of the ZrCN monolayers), which gradually changed to no preferred orientation with decreasing Λ. The peaks became broader with the decrease of the bilayer period, indicating a decrease of both the grain size and the stress. The results of the measurements of the main mechanical characteristics (bilayer period Λ, Vickers microhardness HV and critical load L_c, roughness R_a, residual stress σ) of the mono and multilayered coatings are summarized in Table 1.

The decrease of the corrosion current for the coated samples as compared with the uncoated ones indicated that the corrosion resistance of the 316 L steel improved by deposition of both mono and multilayer coatings (Fig. 1). The best corrosion resistance was measured for the multilayer with $\Lambda \approx 6$ nm.

Table 1. Mechanical characteristics of the coatings.

Coating type	Λ (nm)	HV (GPa)	L_c (N)	R_a (nm)	σ (MPa)
ZrCN	-	28.0	44	490	1260
Zr/ZrCN	190	5.2	63	910	1030
Zr/ZrCN	25	15.5	61	780	810
Zr/ZrCN	6.3	28.7	39	510	720
Zr/ZrCN	4.4	17.3	41	350	920

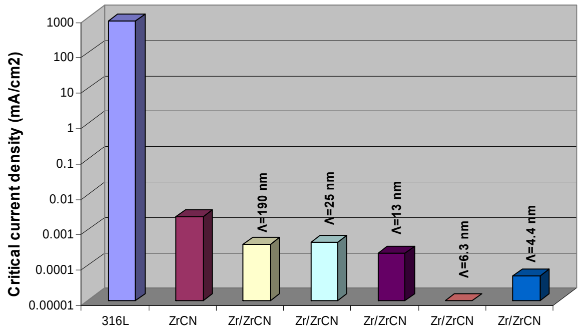

Fig. 1: Critical current densities of the coated and uncoated 316L steel samples

DISCUSSION & CONCLUSIONS: The investigations showed that the coating properties depended both on the values of the modulation period Λ. The mechanical and corrosion properties of the multilayers, for certain deposition parameters, were superior to those of the ZrCN monolayers. The highest microhardnesses of the multilayers, found for Λ = 6.3 nm, was slightly higher than that for the ZrCN monolayers, while a better adhesion was measured for the coatings with relatively large Λ (>13 nm). The corrosion resistance of the multilayers was superior to those of the ZrCN single layer coatings. The multilayers with $\Lambda \approx 6$ nm exhibited the best corrosion behavior.

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ACKNOWLEDGEMENTS: The work was supported under the Project Osteosurf-235/2006.