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Biocompatible coatings of TiNiNb shape memory alloys

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INTRODUCTION: TiNi shape memory alloy (SMA) is extensively used as a material for medical implant devices due to its shape memory effect and biocompatibility. The addition of Nb increases its biocompatibility and conveniently modifies the transition temperatures between austenitic and martensitic phases. However due to its relatively high content in Ni, there are doubts about its use as a biomaterial. Thin film coatings, a transition metal nitride, are widely used for preventing the ions release from the coated substrate, the obtained diffusion barrier films also presenting high protection against corrosion and wear [1], [2].

The paper reports on the results obtained in the corrosion resistance increase of the TiNiNb shape memory alloy (44% at.-Ti, 47% at-Ni, 9% at.-Nb) coated with mono and multilayer films of Ti and Zr nitrides when immersed in an artificial physiological solution (APS).

METHODS: The films (TiN, ZrN, TiN/ZrN) with a thickness of approx. 3.5 μm were prepared by the reactive pulsed magnetron sputtering method [3] and the differential scanning calorimetric tests revealed that the shape memory effect of the alloy were not affected by the coatings. TiN and ZrN monolayer and TiN/ZrN a multilayered structure with 500 layers and a bilayer period of 7 nm were investigated in the present work.

The elemental and phase composition, texture, microhardness and adhesion were investigated by AES, XRD, Vickers micro-hardness and scratch-test. The electro-chemical measurements were carried out at 25^0C using coated and uncoated samples, immersed in an APS with a pH=7.4 and the following composition: NaCl – 8.44 g/l, Na HCO_3 – 0.35 g/l, NaH_2PO_4 – 0.06 g/l, Na $H_2PO_4\cdot H_2O$ – 0.06 g/l. The test consisted in the potentiodynamic polarization of the samples (-1000 ÷ +1500 mV range), using as reference a saturated calomel electrode (SCE). The corrosion current and the critical current for passivation were measured in order to compare the coatings corrosion resistance.

RESULTS: The elemental composition of the coatings, as obtained by AES analysis indicate that the TiN films were slightly overstoichiometric (Ti/N=1.09) and the ZrN films were substoichiometric (Zr/N=0.92). X-ray diffraction analysis revealed that the TiN and ZrN layers exhibit a strong (111) preferred orientation, as already reported [4]. In the case of the TiN/ZrN multilayers the diffraction patterns present typical diffraction patterns of superlattice coatings with a main (111) Bragg peak (similar to that of the TiZrN monolayer), surrounded by satellite peaks. The highest Vickers microhardness $HV_{0.015}$ [GPa] and critical loads L_c [N] values were measured for the multilayer (32 GPa and 46 N), followed by TiN monolayer (23 GPa and 44 N), and ZrN coating (19.2 GPa and 38 N).

The best corrosion resistance was measured for the multilayered coating (Fig.1). The measured decrease of the corrosion currents indicates that the coatings improved the corrosion resistance over the TiNiNb substrates.

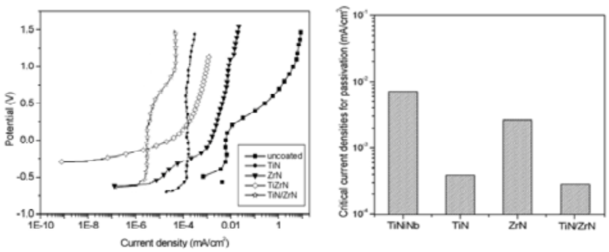

Fig. 1: Current and critical current densities of the coated and uncoated TiNiNb memory shape alloy samples

DISCUSSION & CONCLUSIONS: As compared with the uncoated TiNiNb shape memory alloy samples, all the coated samples exhibited superior corrosion resistance and mechanical characteristics. The TiN/ZrN multilayer coating showed the best corrosion and wear resistance in comparison with the monolayer coatings.

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