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MULTILAYER COATINGS OF TiNiNb SHAPE MEMORY ALLOYS

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Abstract. The paper presents the results related to the improvement of the corrosion protection and wear behavior of the TiNiNb shape memory alloy, when coated with mono and multilayer films of some transition metal nitrides (TiN, ZrN, (Ti,Zr)N, TiN/ZrN), using the cathodic arc deposition method. The corrosion and wear tests were conducted in an artificial physiological solution. Additional information on the film characteristics was obtained by Auger electron spectroscopy (AES) and X-ray diffraction (XRD) analyses, microhardness measurements and adhesion tests. The differential scanning calorimetry test revealed that the shape memory effect of the substrate was not affected by the coating. The obtained results suggest that mono and multilayered coatings based on Ti and Zr nitrides obtained by vacuum arc deposition can improve the performance of TiNiNb alloy, used for biomedical applications, without sacrificing their shape memory effect.

1. INTRODUCTION

TiNiNb shape memory alloy (SMA) has been used extensively as a material for medical implant devices due to its shape memory effect, superelasticity and biocompatibility. However due to its relatively high amounts of nickel, it is not adequate for use in long term implants and prosthesis. As a TiNi based alloy, it exhibits poor resistance to corrosion in chloride containing environments, with low pitting potentials [1]. Also, even if the B2 phase (austenite parent phase in SMA) presents good wear resistance, the B19' martensite phase exhibits poor wear resistance and high coefficient of friction, which restrict its use in medical applications [2,3]. PVD coating methods are widely recognized as a good choice to prevent the ions release from the bulk substrate, the obtained diffusion barrier films also presenting high protection against corrosion and wear [3,4]. Many transition metal nitrides, especially TiN, TiAlN, NbN and ZrN, have been used to protect medical implants or prosthesis against corrosion and wear. Nevertheless, there are few data so far leading to decisive [5-7] conclusions for an adequate choose of the materials to be used as an efficient anticorrosive and wear resistant coating.

The paper reports on the corrosion and wear behavior of monolayered TiN, ZrN, TiZrN and multilayered TiN/ZrN hard coatings deposited on TiNiNb SMA, when immersed in artificial physiological solution. The films were prepared by the cathodic arc method [8] and a differential scanning calorimetry test revealed that the shape memory effect of the substrate was not affected by the coat-

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ing. For the corrosion resistance assessment an electrochemical analysis was conducted. A wear-corrosion test was carried out in order to determine the wear resistance of mobile coated samples immersed in artificial physiological solution. Additional information on the film characteristics was obtained by Auger electron spectroscopy (AES) and X-ray diffraction (XRD) analyses, microhardness measurements and adhesion tests.

2. EXPERIMENTAL PROCEDURES

The experimental set-up has been described in detail elsewhere [8]. The deposition chamber was equipped with Ti and Zr cathodes. Specimens to be coated were ultrasonically cleaned with trichlorethane and ethanol and mounted on a rotating holder. Prior to the deposition, the samples were sputtered in high vacuum by Ti ion bombardment (1200 eV; 5 min).

The TiN/ZrN films were obtained by using two rotating shutters placed in front of each cathode. Various multilayer configurations (with different thicknesses of the individual layers) were prepared, but only a multilayered structure with 1600 bilayers and a bilayer period of 2 nm was investigated in the present work.

AES technique was used to determine the elemental composition of the films by using a PHI Model 3017 AES PC-Based System. The N/Ti ratio was determined from the positive slope of the nitrogen line located at 377 eV and the negative slope of the Ti peak at 418 eV. Phase composition and texture were obtained by XRD analysis using an X-ray DRON diffractometer with Cu K_α radiation. Microhardness (Vickers) measurements were performed with a microhardness tester at 0.15 N load. Scratch tests under standard conditions were undertaken to determine the coating adhesion. The critical load (L_c) values were determined by optical microscopy, L_c being defined as the load where film flaking starts.

To evaluate the corrosion behavior of the coatings, electrochemical measurements were carried out using coated and uncoated samples, immersed in an artificial physiological solution (APS) with 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 of the potentiodynamic polarization of the samples in the range -1000 - +1500 mV, with 20 mV/s scan speed. The corrosion potential and current were measured by an Amel 2049 Potentiostat/Galvanostat. A saturated calomel electrode (SCE) and a platinum electrode were used as a reference and auxiliary electrodes, respectively. The pH and the temperature of the APS were kept constant at 7.4 and 25 °C, respectively. The critical current for passivation was used to compare the corrosion resistance of the coatings.

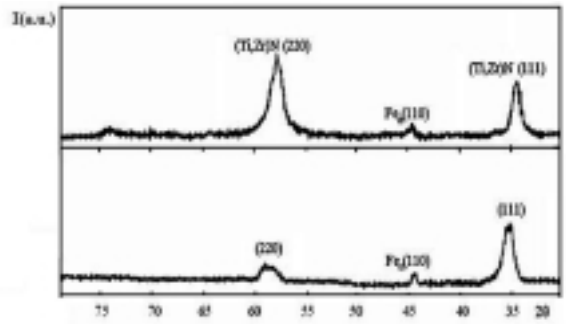

Fig. 1. XRD spectra of a TiN/ZrN multilayer with 2 nm bilayer period (a) and of a (Ti,Zr)N monolayer (b).

Martensitic transformation temperatures of the uncoated and coated TiNiNb samples were determined using a differential scanning calorimeter (DSC) at a heating / cooling rate of 5 K/min, over 100K temperature range (270 - 370K).

The wear resistance of different coatings in APS was determined with a testing apparatus consisting of a coated rotating roller pressed on a flat sample (sliding shoe). Both the roller and the shoe were immersed in APS. The roller (40 mm - diameter and 8 mm – width) and the sliding shoe were made of 316L stainless steel with a Vickers hardness of 2.5 GPa. The testing parameters were: sliding speed – 0.3 m/s, load – 10 N, temperature of the solution – 24 °C. The wear behavior was investigated by measuring the removed volume from the roller. The volume loss V was evaluated by an indentation test on the coated sample, using a Vickers diamond tip at 300 N load. The diagonal of the indent was measured with an optical microscope before and after the wear testing. Geometrical considerations lead to the following expression for the volume loss V:

$$V = \pi u B (D-u),$$

where $u = 0.143(D_0 - D_1)$, D is the roller diameter, B – roller width, D_0 – diagonal of the indent before wear, D_1 – diagonal of the indent after wear.

Table 1. Deposition parameters.

Sample No	Coating	P_{N2} (Pa)	$I_{a\,Ti}$ (A)	$I_{a\,Zr}$ (A)	V_S (U)	T (K)	d (μm)
1	TiN	$1{\cdot}10^{-1}$	90	-	220	323	3.2
2	ZrN	$1{\cdot}10^{-1}$	-	110	220	323	3.0
3	(Ti,Zr)N	$1{\cdot}10^{-1}$	90	110	220	323	3.0
4	TiN/ZrN	$1{\cdot}10^{-1}$	90	110	220	323	3.2

Table 2. Elemental composition of the coatings.

Sample No	Coating	Elemental concentration (at.%) Ti	Zr	N	O	N/M*	Ti/Zr
1	TiN	45.6	-	50.6	3.8	1.11	-
2	ZrN	-	53.1	44.0	2.9	0.83	-
3	(Ti,Zr)N	15.4	33.2	48.7	2.7	1.00	0.46

M* - metal in the compound

Table 3. Microhardness and adhesion of the coatings.

Sample No	Coating type	$HV_{0.015}$ (GPa)	L_c (N)
1	TiN	22.8	44
2	ZrN	19.2	38
3	(Ti,Zr)N	27.2	40
4	TiN/ZrN	29.2	46

3. RESULTS AND DISCUSSION

Deposition parameters are listed in Table 1, where P_{N2} – nitrogen pressure, I_{aTi} and I_{aZr} – arc current at the titanium and zirconium cathodes, respectively, V_s – substrate bias voltage, T – deposition temperature, d - film thickness. The parameters were selected on the base of the results of TiN deposition experiments (presented in a previous paper [9]), to obtain coatings with adequate microstructural and microchemical properties. The deposition duration was chosen to prepare coatings with almost the same thickness: 3.0 – 3.2 μm.

The elemental composition of the coatings, as obtained by AES analysis, is given in Table 2. It can be seen that the TiN films were slightly overstoichiometric, while the ZrN coating was substoichiometric. For the (Ti,Zr)N film, Zr content is higher that Ti content (Ti/Zr = 0.46). The presence of a small amount of oxygen (2.7 - 3.8%) in the films is due both to residual gas in the deposition atmosphere combined with the films contamination during the time elapsed between preparation and the composition analysis.

X-ray diffraction analysis revealed that the TiN and ZrN layers exhibit a strong (111) preferred orientation, as already reported (e.g. [10], [11]). For the (Ti,Zr)N coating (Fig. 1a), the diffraction lines were located nearby the positions of the lines found for the ZrN film, but with a slight shift (0.5 - 0.7°) towards higher Bragg angles. This show that Zr concentration in the film is substantially higher than that of Ti, which is consistent with AES analyses. One may conclude that the investigated layer crystallized in a face centered cubic ZrN lattice with reduced lattice parameters. In the case of the TiN/ZrN multilayers (Fig. 1b), it is interesting to note that the diffraction patterns are similar with those for (Ti,Zr)N monolayer, except for a slight decrease of the (220) peak. This is due to the intermixing of individual layers when the bilayer period has very small values (approx. 2 nm).

Vickers microhardness $HV_{0.015}$ and critical loads L_c are presented in Table 3. The highest microhardness and adhesion values were found for TiN/ZrN multilayer coating. It can also be seen that all the investigated films exhibited a good adhesion ($L_c \geq 38$ N).

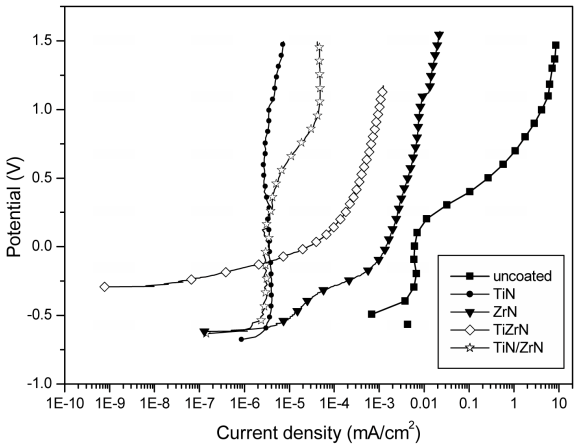

Fig. 2. Polarization curves of the coatings.

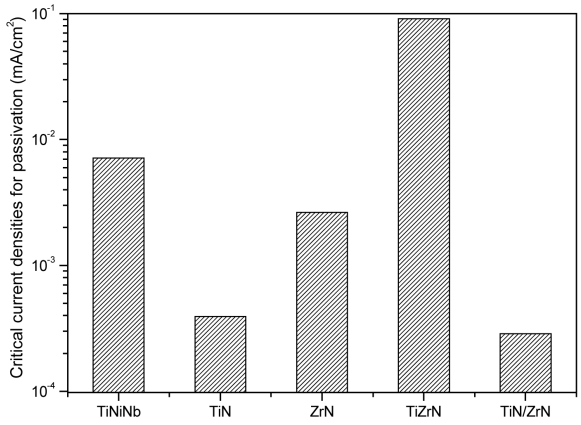

Fig. 3. Critical current densities for passivation of the uncoated TiNiNb alloy and of the different coatings.

Potentiodynamic polarization curves in APS for the coatings deposited on TiNiNb substrates are shown in Fig. 2. From the potentiodynamic curves, the critical current densities for passivation (i_{cr}) were determined (Fig. 3). i_{cr} is defined as the current in the region, before the transpassive domain, where there is little change in current with potential. It can be seen that the coatings improved the corrosion resistance of the uncoated specimens, by decreasing i_{cr} currents, as previously reported for some transition metal nitride coatings [12,13]. As shown in Fig. 3, TiN/ZrN and TiN coatings present the highest corrosion protection, exhibiting the lowest value of the critical current density for passivation, followed by (Ti,Zr)N and ZrN coated samples. It is interesting to note that the best corrosion resistance was found for samples which also proved to exhibit the best adhesion.

The wear resistance of the coatings in APS is illustrated in Figs. 4 and 5. In Fig. 4 is presented

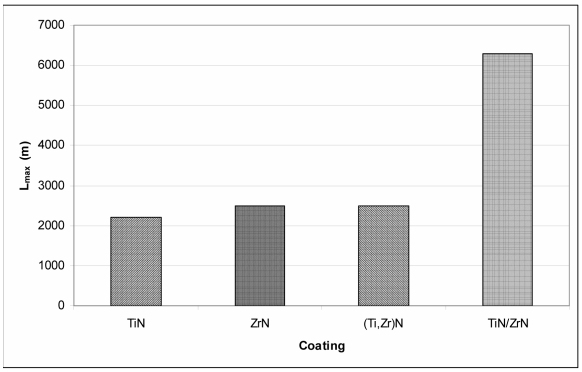

Fig. 4. The maximum sliding distance L_{max} of the coatings.

the maximum sliding distance L_{max} (the distance at which the damage of the coating occurs, commonly associated with a marked increase of the friction coefficient) for the investigated coatings. L_{max} was slightly different for monolayered films (L_{max} = 2200 - 2500 m), while the TiN/ ZrN multilayer had the highest wear life (L_{max} = 6250 m), associated with the highest microhardness (~29.2 GPa) and the highest adhesion value (L_c = 46 N).

The wear behavior of the coatings can also be examined in Fig. 5, where the volume loss from the roller as a function of the sliding distance is shown. The most important result is that all coated rollers exhibited a better wear resistance in comparison with the uncoated roller. Only slight differences in the wear behavior of various coatings were found. However, for a sliding distance up to 2500 m, at which the single layer coatings began to flake, the best wear resistance was found for the multilayer TiN/ZrN, followed by the monolayers (Ti,Zr)N, ZrN and TiN.

The transformation temperatures for the forward (*M*) and reversed (*A*) martensitic transformation, as obtained by DSC, are the same for the uncoated and coated samples (*M* = 305K and *A* = 355K), as the substrate temperature was kept at low temperature during the deposition and the thickness of coated layer was thin compared with the thickness of the TiNiNb substrate.

4. CONCLUSIONS

Protective films of transition metal nitrides (TiN, ZrN, (Ti,Zr)N, TiN/ZrN) were deposited on TiNiNb

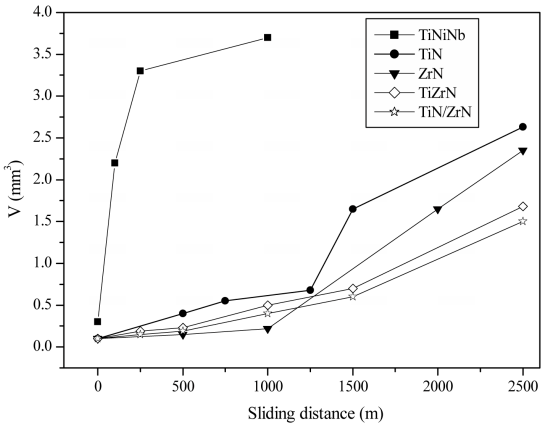

Fig. 5. Wear resistance of the coatings vs. the sliding distance.

SMA substrates in order to enhance their corrosion and wear resistance in artificial physiological solution. Corrosive behavior was evaluated by electrochemical tests, while for the wear resistance experiments a testing apparatus consisting mainly of a coated rotating roller pressed on a flat specimen was used. The coatings were also characterized with respect to elemental and phase composition, texture, microhardness and adhesion.

Chemical composition analysis showed that nitrogen /metal ratio values were in the range 0.83 – 1.11. For the (Ti,Zr)N film, Zr content was higher than that of Ti (Ti/Zr = 0.46). In the case of the TiN/ZrN multilayers, the diffraction patterns are similar with those for (Ti,Zr)N single layer films. Vickers microhardness $HV_{0.015}$ values were in the range 19.2 GPa (for ZrN) - 29.2 GPa (for TiN/ZrN). A good adhesion of the films was found by the scratch tests (critical loads in the range 38 - 46 N were measured).

As the thickness of coated layer was thin compared with the thickness of the substrate and the temperature during deposition was kept low, the DSC test revealed that the coated SMA samples exhibit the same shape memory effect as the uncoated ones.

As compared with the uncoated sample, all the coated samples exhibited a superior corrosion and wear resistance. The TiN/ZrN multilayer coating showed the best corrosion and wear resistance in comparison with the other coatings.

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