CORROSION RESISTANCE OF THE TiN, TiAlN AND TiN/TiAlN NANOSTRUCTURED HARD COATINGS

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Au fost investigate caracteristicile anticorozive ale multistraturilor nanostructurate de TiN/(Ti,Al)N (grosimea straturilor duble în domeniul 4 ÷ 20 nm) depuse prin metoda cu arc catodic. Multistraturile au fost analizate si din punct de vedere al compoziţiei elementale şi fazice, texturii, microdurităţii, grosimii stratului dublu, aderenţei şi rezistenţei la coroziune prin utilizarea tehnicilor EDX, XPS şi XRD, măsuratori ale microdurităţii Vickers, teste de adrenţă şi electrochimice.

The anticorrosive characteristics of nanostructured TiN/(Ti,Al)N multilayers (bilayer periods ranging from 4 to 20 nm) prepared by cathodic arc deposition method have been investigated. Additional coatings properties such as elemental composition, phase composition, texture, microhardness, bilayer period, thickness, adhesion and corrosion resistance were determined by using EDX, XPS and XRD techniques, Vickers microhardness measurements, scratch and electrochemical tests.

Keywords: AES; corrosion resistance; microhardness, multilayer, scratch test; TiN, TiAlN, XRD.

Introduction

Research dedicated to the most adequate biocompatible material for insertion in biological internal environment has led to the development of many alloys, starting with austenitic stainless steels. The implant biocompatibility is directly related with its corrosion resistance in the surrounding environment.

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Austenitic stainless steels such as 316 and 316 L have in general a good corrosion resistance, being widely used for implants. Nevertheless, in strong mechanical stressed or non-oxygenated environments, stainless steels are susceptible to corrosion.

Material properties improvement by coating with suitable thin films represents a modern approach in material processing technologies, being recommendable to enhance qualities required also for biocompatibility.

The recent rapid progress in biomedical requires materials of good mechanical properties and high resistance to wear and corrosion. These requirements can be satisfied by producing surface coatings of specified microstructure and phase composition, using different PVD methods. Many transition metal nitride coatings, especially TiN and TiAlN, have achieved wide application in surface biomedical [1]. This is because these coatings exhibit many interesting properties such as high hardness, good wear and corrosion resistance, low friction and good electrical or thermical conductivity. The clinical advantage of these coatings is due to their biocompatible properties which are dependent upon their composition and structure such as stoichiometry, surface morphology, microhardness, corrosion and wear resistance.

This paper reports the deposition of biocompatible TiN/(Ti,Al)N multilayers on 316L stainless steel substrates using the cathodic arc technique. The influence of the bilayer period on the corrosion resistance of the coatings in artificial physiological solution was analyzed. In order to account for the corrosion behavior of the coatings, some microchemical, microstructural and mechanical properties of the multilayers were also investigated.

1. Experimental

The experimental setup has been described elsewhere [2]. The base pressure in the deposition chamber was of about 10^{-3}Pa. Specimens to be coated were ultrasonically cleaned with trichloroethylene and mounted on a rotating holder inside the deposition chamber. Prior to deposition, the samples were sputtered by Ti ion bombardment (1000 V; 5min).

The main process parameters for the various coatings were as follows: substrate material – 316L stainless steel, cathode material – Ti; Ti+Al, reactive atmosphere - N_2, nitrogen pressure P_{N2} = 7 x 10^{-2}Pa, arc currents I_{Ti} = 100 A, I_{Al} = 90 A, substrate bias U_s = 220V, deposition temperature T = 340^0C, deposition time - 60 min.

The multilayers were obtained by using two adequate shutters which were periodically open and close so that Ti and Ti+Al atoms were alternatively introduced in the chamber for a predetermined time.

To evaluate the corrosion behavior of the coatings, electrochemical measurements were carried out. The test consisted of potentiodynamic polarization from -1100 to +1100 mV with a scan speed of 20 mV/s of the coated samples in artificial physiological solution APS. The chemical composition of the corrosive environment is given in Table 1. 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 temperature and the pH of the solution were kept constant at 25^0C and 7.4, respectively. The corrosion current and the critical current for passivation were used to compare the corrosion resistance of the coatings.

Table 1

Chemical composition of the artificial physiological solution

Compound	Concentration (g/l)
NaCl	8.44
$NaHCO_3$	0.35
NaH_2PO_4	0.06
$NaH_2PO_4 \cdot H_2O$	0.06

The Auger electron spectroscopy (AES) was used to investigate the elemental composition of the films. The samples were analyzed using a PHI Model 3017 AES PC-Based System. The sample was ion sputtered using 3 keV Ar ion beam.

Phase composition and texture were determined by XRD analysis using an X-ray DRON diffractometer with CuK_α radiation.

Microhardness (Vickers) measurements were performed using a microhardness tester at 20 g load. Multilayer thickness was determined by optical microscope examination of the cross section through the coating. The bilayer period was evaluated from the overall thickness of the multilayer and the number of the layers. Scratch tests under standard conditions (indenter – 0.2 mm radius diamond tip, load - continuous increase from 0 to 100 N, scratching speed – 10 mm / min, scratching distance – 10 mm) [3], [4] were undertaken to determine the coating adhesion, using a laboratory apparatus. The critical load (L_C) values were determined by optical microscopy (L_C is defined as the load where film flaking starts). Surface topography of the films was examined by electron microscopy.

2. Results and discussion

2.1. Corrosion behavior

Potentiodynamic polarization curves for the coatings deposited on 316L substrate are shown in Fig.1. From the potentiodynamic curves, corrosion current densities (i_{corr}) and critical current densities for passivation (i_{cr}) (Fig.2) were determined. It can be seen that the coatings improved the corrosion resistance of the uncoated specimens, by decreasing both the i_{corr} and i_{cr} currents, as previously reported for some transition metal nitride coatings [5, 6].

As shown in Fig.2, among all coatings, the TiN/(Ti, Al)N-12 multilayer has shown the highest corrosion protection, exhibiting the lowest value of the critical corrosion current. This coating was followed by the TiN/(Ti,Al)N-360 and TiN/(Ti,Al)N - 720 coated samples.

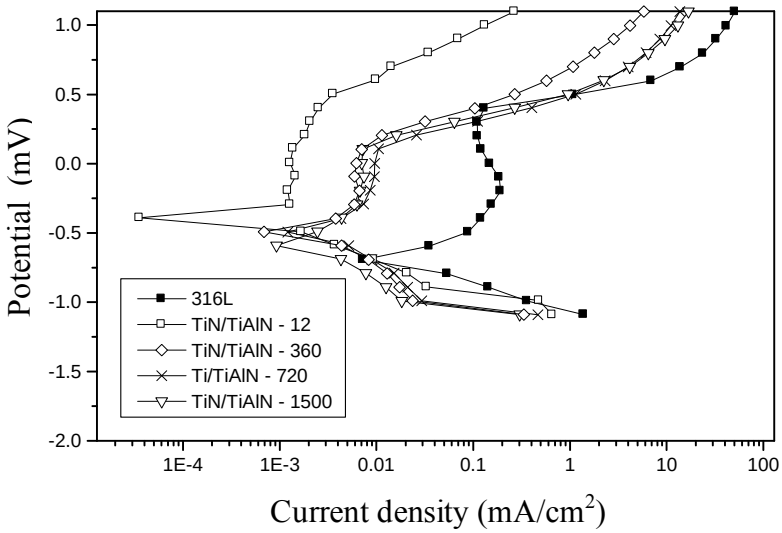

Fig. 1. The potentiodynamic curves of multilayer coatings

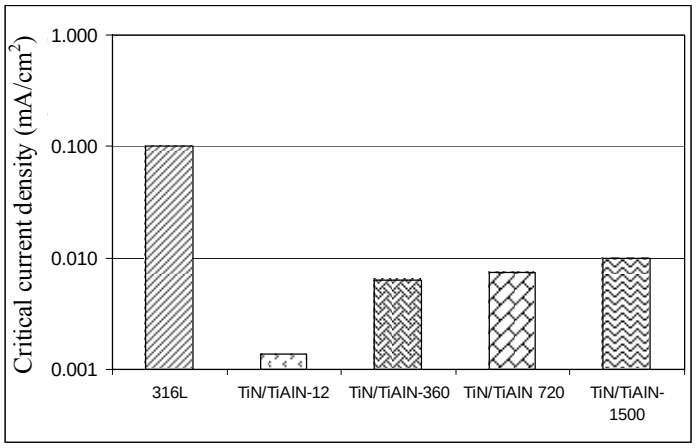

Fig. 2. Critical current densities of the multilayer coatings

3.2 Microchemical, microstructutal and mechanical properties

The elemental composition of the single layer coatings (TiN and TiAlN) was obtained by AES analysis (Table 2). It can be seen that the coatings are almost stoichiometric: N/Ti = 1.07 and N/(Ti+Al) = 1.03. In the case of (Ti,Al)N films, Al/Ti ratio was of about 0.75. The multilayers, irrespective of the bilayer period, consisted of TiN and (Ti,Al)N individual layers with the above mentioned elemental composition. The presence of oxygen is due both to the film contamination during sample handling before the composition analysis and to the purity conditions in the deposition chamber.

Table 2

Elemental composition of the coatings

Coatings	Elemental concentration (at. %)				
	Ti	Al	N	O	Fe
TiN	43.8	-	46.9	8.4	0.9
(Ti,Al)N	25.2	18.9	45.7	9.2	1.0

All coatings exhibited a strong (111) preferred orientation. It is interesting to note that the diffraction patterns from the multilayers with small and large bilayer periods are similar with those for (Ti,Al)N and TiN single layer films, respectively. The X-ray spectrum of TiN/(Ti,Al)N multilayer coatings with 10.6 nm bilayer periods is shown in Fig.3.

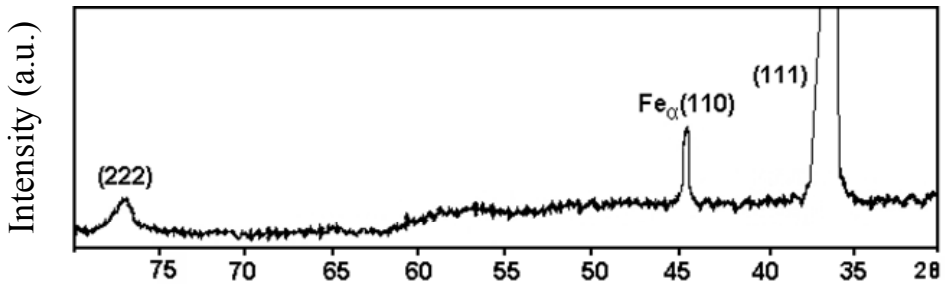

Fig.3 X-ray diffraction patterns from TiN/(Ti,Al)N -720 coating

The Vickers microhardness and the anticipated bilayer period of the coatings are summarized in Table 3. It can be seen that the microhardness of the multilayers was dependent on the bilayer period as follows. Microhardness values first increased (from 24.3 to 31.2 GPa) with the decreasing bilayer period (from 633 to 10.6 nm), followed by a decrease to 27.2 GPa for Λ = 5.1 nm. A similar behavior was reported for other multilayer coatings (TiN/CrN, Nb/TiN, NbN/ZrN, MoN/ZrN) [7, 8].

The scratch tests indicated that all coatings had a good adhesion. Only slight differences (~ 8 N) in the critical load L_c values for different coatings were found. As far as multilayers are concerned, no systematic dependence of the adhesion on the bilayer period was observed. L_c values in the ranges 51 ÷58 N were measured for all the multilayers.

Table 3

Coating microhardness $HV_{0.015}$ and bilayer period Λ

Coating	$HV_{0.015}$ (GPa)	Λ (nm)
TiN/(Ti,Al)N-12	24.3	633
TiN/(Ti,Al)N-200	26.4	38.0
TiN/(Ti,Al)N-720	31.2	10.6
TiN/(Ti,Al)N-1500	27.2	5.1

One may observe that the multilayer coatings had significant influence on the surface topography in comparison to those monolayer coatings, as shown in Fig. 4. The surfaces are smooth and only few defects can be observed.

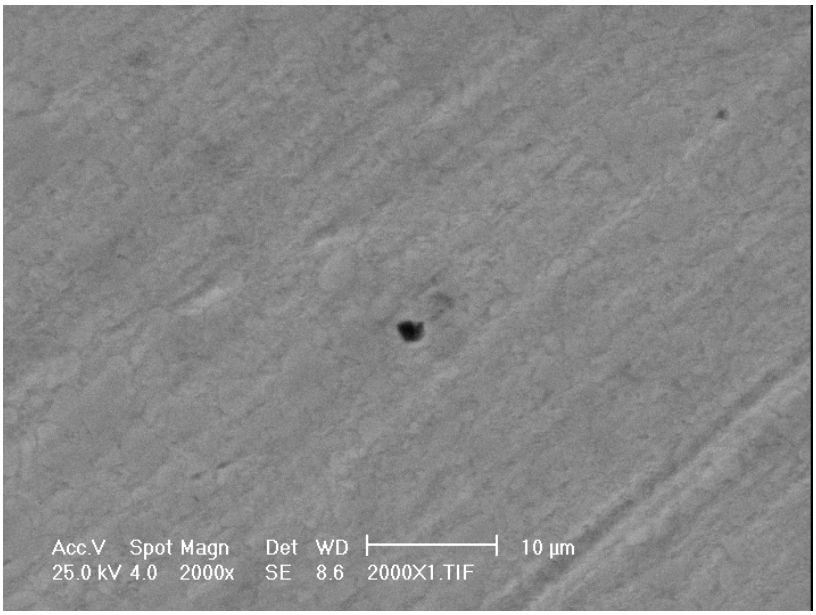

Fig. 4 Surface topography of TiN/(Ti,Al)N - 720 coating (x2000)

Conclusions

Research carried out showed that the corrosion resistance of 316L stainless steel into artificial physiological solution can be improved by multilayers deposition. TiN/(Ti,Al)N multilayered coatings (bilayer periods from 4.5 to 600 nm) were prepared by the cathodic arc deposition method, using Ti and Ti+Al cathodes.

The analysis of the film composition showed that the coatings were almost stoichiometric (N/(Ti+Al) ≈ 1.1), with a relatively low Al content (~ 18 at.%). For the TiN/(Ti,Al)N multilayers, N/(Ti+Al) ratio was close to one and the Al content decreased to 12 – 14 at.%.

The deposition conditions were so chosen in order to obtain stoichiometric films for different biasing conditions, as revealed by quantitative AES analyses. XRD patterns of the all films exhibited a (111) preferred orientation.

Of all the coatings, the highest microhardness values (~30 GPa) were measured for the TiN/(Ti,Al)N multilayers with Λ = 10.6 nm. A good adhesion ($L_c \geq 50$ N) was found for all films. This coating exhibited also the best corrosion resistance (the lowest value of the critical corrosion current).

Since the TiN/(Ti,Al)N – 720 coating was found to have the highest microhardness and adhesion and also a good corrosion behavior, this type of multilayer would be an appropriate solution to enhance the performance of the stainless steel implants.

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