

BIOCOMPATIBLE THIN FILMS DEPOSITED BY CATHODIC ARC METHOD

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Abstract: TiN biocompatible thin films were deposited on 316L stainless steel substrates by cathodic arc evaporation in nitrogen atmosphere under various deposition conditions. The corrosion behavior of TiN films in artificial physiological solution was investigated using an electrochemical test. Microchemical, microstructural and mechanical characteristics of the coatings were also analyzed.

Key words: TiN films, biocompatible materials, corrosion resistance, cathodic arc deposition.

INTRODUCTION

The use of ceramics with specific properties for medical applications has been expanding since the 1970s [1], [2]. It can be said that, with the use of ceramics, a revolution in the ceramic industry began. For decades, TiN coatings have received much attention in the biomaterial engineering because of their ability to properly interact with living tissues. The clinical advantage of these coatings is due to their biocompatibility properties, which are dependent upon their composition and structure such as stoichiometry, surface morphology, microhardness, corrosion and wear resistance. TiN thin films can be deposited on medical implants or prothesis of a large variety of dimensions and shapes.

In this paper the influence of the main deposition parameters on the corrosion resistance of TiN coatings deposited on 316L stainless steel by cathodic arc technique [3] has been discussed. Microchemical, microstructural and mechanical characteristics have also been analyzed.

EXPERIMENTAL

The experimental set-up has been described in details elsewhere [4]. 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; 5 min).

The main process parameters for the various coatings were as follows: substrate material – 316L stainless steel, cathode material - Ti; reactive atmosphere - N_2 , nitrogen pressure $P_{N_2} = 10^{-2}$ Pa, arc current $I_a = 60 - 130$ A, substrate bias $V_s = 0-225$ V; deposition time $t = 15-60$ min.

Chemical composition of TiN films was determined by different methods: X-ray Photoelectron Spectroscopy (XPS), energy dispersive X-ray analysis (EDX), Elastic Recoil Detection (ERD).

The XPS measurements were performed on a SSX-100 spectrometer using monochromated Al $K\alpha$ radiation (1486.6 eV). For ERD experiments an incident 80 MeV Cu^{10+} ion beam was used. The elemental composition of the films was determined by EDX analysis using an XL-30-ESEM TMP scanning electron microscope.

Microhardness (Vickers) measurements were performed by means of a microhardness tester at 20g load. Film thickness was determined by optical microscope examination of the cross section through the coating. Scratch tests under standard conditions were undertaken to determine the coating adhesion.

Corrosion resistance was investigated by an electrochemical test, using a PHOM 4 pH/mV-meter. The electrolyte was artificial physiological solution at room temperature and the test duration was 360 min. Corrosion behavior was appreciated by measuring the changes of the free corrosion potential with time.

RESULTS AND DISCUSSION

CHEMICAL COMPOSITION

Though there were certain differences (within 10%) between the results of the investigation techniques (XPS, EDX and ERD), the measurements revealed the dependence of the chemical composition on the deposition parameters. It is interesting to note that some film characteristics depend on the N_2 pressure and substrate bias in the same manner as the N/Ti ratio does.

An example of XPS spectra for Ti 2p, N 1s and O 1s peaks is shown in Fig. 1, where the peak-fitting procedure, using mixed Gauss/Lorentz (85% G/L) functions, is also presented. From the spectra analysis it resulted that the coatings are composed from a basic TiN compound, cvasistoichiometric ($N/Ti \approx 1$), covered by an oxidized layer, consisting of a mixture of Ti_2O_3 and TiNO, with relative concentrations depending on the deposition parameters.

ERD method was used for the investigation of the TiN films deposited at different N_2 pressures. A typical example of ERDA spectra from a TiN film is shown in Fig. 2, where the computer simulation curve is also plotted (deposition conditions: $p_{N_2} = 10^{-2}$ Pa, $V_s = 220$ V, $I_a = 90$ A). In this case the film composition was: Ti – 44.6%, N – 53.5%, O – 1.3%, C – 0.6%, from which an N/Ti ratio of 1.2 was calculated. The presence of a small amount of oxygen and carbon is due both to residual gas incorporated in the chamber walls and to the contamination during sample handling in open atmosphere before the composition analysis

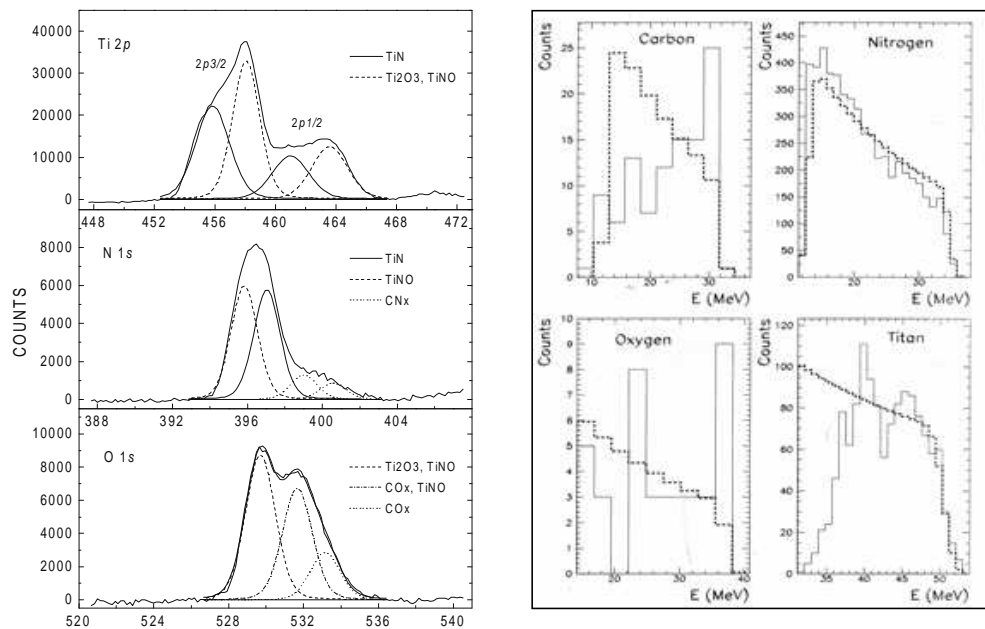


Fig. 1 – XPS spectra for Ti 2p, N 1s and O 1s Fig. 2. – ERD spectra of Ti,O and C for a TiN coating

In the case of the TiN film the elemental composition of the coatings was obtained by EDX analysis. An example of EDX spectrum for a TiN film is given in

figure 3. The deposition conditions for this film were: $p_{N_2} = 10^{-1}$ Pa, $I_a = 90$ A, $V_s = 220$ V.

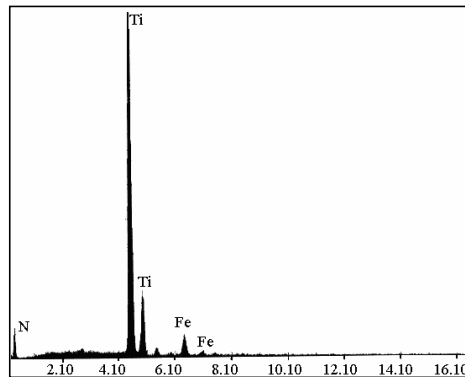


Fig. 3. – EDX spectrum for a TiN coating

MECHANICAL CHARACTERISTICS

The dependence of the Vickers microhardness ($HV_{0.02}$) on the main deposition parameters (N_2 pressure, substrate bias and arc current) revealed that the microhardness reaches its maximum values within a narrow range of the nitrogen pressure, from about 6×10^{-3} to 10^{-2} Pa. For a constant gas pressure, the microhardness increases with the substrate bias, whereas the discharge current variation has only a slight influence on the microhardness. It was also observed that over a large range of the deposition parameters ($p_{N_2} = 2 \times 10^{-2} - 5 \times 10^{-1}$ Pa, $I_a = 60 - 130$ A and $V_s = 50 - 225$ V), the microhardness variation is not important (microhardness values ranging from 2400 to 2700 $HV_{0.02}$ were measured).

Scratch adhesion tests were conducted on coatings prepared with varying gas pressure and substrate bias. The experiments carried out showed that the adhesion mainly depends on the substrate characteristics and on the film properties, as it was already reported (e.g.[5]). The critical load increases with the film microhardness and thickness and with the substrate hardness. For TiN coatings with thickness and microhardness of about 2 μm and 2400 $HV_{0.02}$, respectively, critical loads of 38-42 N were measured.

CORROSION BEHAVIOR

The specimens for the corrosion tests consisted of TiN coated square plates (23x23x4mm) made of 316L stainless steel, carefully polished. Time evolution of the free corrosion potential V_{corr} is shown in figures 4 and 5, where the influence of nitrogen pressure and substrate bias on the film corrosion resistance can be examined. For comparison, the corrosion behavior of an uncoated sample is also illustrated. The deposition conditions are summarized in Table 1.

Table 1

Deposition parameters for TiN coatings:
 P_{N_2} -nitrogen pressure, I_a -arc current, V_s -substrate bias voltage,
 T- substrate temperature, t-deposition duration.

Sample No.	P_{N_2} (Pa)	I_a (A)	V_s (V)	T ($^{\circ}\text{C}$)	t (min)
1	1×10^{-2}	90	220	340	60
2	1×10^{-1}	90	220	340	60
3	1×10^0	90	220	370	60
4	3×10^{-1}	90	0	190	60
5	3×10^{-1}	90	90	280	60
6	3×10^{-1}	90	220	350	60

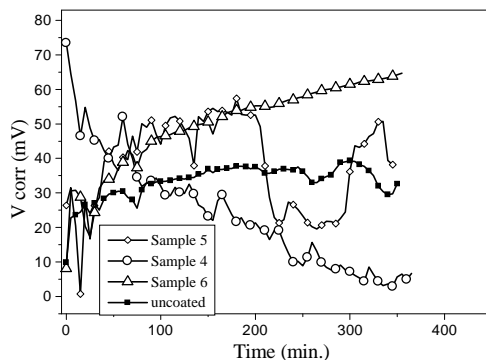


Fig. 4 – Corrosion resistance for TiN coatings deposited at different substrate bias voltages ($p_{\text{N}_2} = 3 \times 10^{-1} \text{ Pa}$)

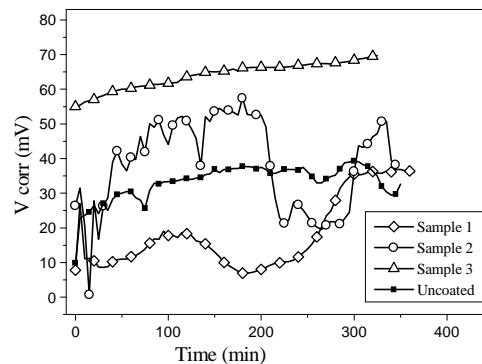


Fig. 5 – Corrosion resistance for TiN coatings deposited at different nitrogen pressures ($V_s = 220 \text{ V}$)

As it comes out from Fig.5, the corrosion resistance increased with N_2 pressure, in the range 10^{-2} - 1 Pa. On one hand, this shows that an increasing film stoichiometry N/Ti leads to an improvement of the film protection against corrosion. On the other hand, as surface topography investigations have brought to light [6], a higher surface

quality (diminution of microdroplets and roughness) was obtained for higher nitrogen pressure. As for the influence of the substrate bias (Fig.4), it can be seen that the corrosion resistance increased with the substrate bias voltage. This can be accounted for by the improvement of the film morphology and structure as a result of the ion bombardment enhancement (e.g. [7]). It is worth mentioning that some of the specimens (6 –Fig.4 and 3-Fig.5) exhibited a better corrosion behavior as compared to the uncoated ones.

In the cases of coatings 5-Fig.4 and 2-Fig.5, one may observe fluctuations of the potential which are attributed to the presence of a significant pitting corrosion process. This can be understood as a consequence of the microdroplets existing on the film surface and/or of a poor adhesion between the coating and the substrate.

CONCLUSIONS

Research carried out showed that the corrosion behavior of 316L stainless steel into artificial physiological solution can be improved by TiN thin film deposition.

The increase of the nitrogen pressure (in the range 10^{-2} – 1 Pa) and of the substrate bias (in the range 50-220 V) resulted in an improvement of the corrosion behavior of the films. Vickers microhardness $HV_{0.02}$ and thickness values of about 2400 $HV_{0.02}$ and 2 μm , respectively, were measured. A good adhesion of the TiN coatings was found (critical loads of 38-42 N were obtained).

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REFERENCES

1. S. BLACK, *Biological performance of materials: fundamental of biocompatibility*, 3rd edition, Ed. Dekker, New York, 1999
2. D.HILL, *Design Engineering of Biomaterials for Medical Devices*, Ed. Wiley, New York, 1998
3. *Handbook of Vacuum Arc Science and Technology*, Ed. R.L.Boxman, D.M.Sanders, P.J.Martin, Noyes Publications, Park Ridge, N.J.U.S.A., 1995
4. M. BALACEANU, M. BRAIC, D.MACOVEI, M.J.GENET, A.MANEA, D.PANTELICA, V. BRAIC, F.NEGOITA, *J.Optoelectron.Adv.Mat.*, **4/1**, 107, 2002
5. F.A STEIMANN, H.E.HINTERMANN, *J.Vac.Sci.Technol.*, **A3 (6)**, 2394, 1995
6. M.BRAIC, S.ZAMFIR, M.BALACEANU, V.BRAIC, G.PAVELESCU, A.ZAMFIR, A.VLADESCU, *J.Optoelectron. Adv. Mat.* **5**, 503-510, 2003
7. K.S. FANCEY, C.A. PORTER, A.MATTHEWS, *J.Vac.Sci. Technol.*, **A13**, 428, 1995