Ti/TiN MULTILAYER COATINGS FOR ORTHOPEDIC IMPLANTS

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Ti/TiN biocompatible multilayers were deposited on 316L stainless steel substrates by reactive magnetron sputtering in nitrogen atmosphere under various deposition conditions. The corrosion behavior of Ti/TiN coatings in artificial physiological solution was investigated using an electrochemical test. Microchemical, microstructural and mechanical characteristics of the coatings were also analyzed.

Key words: multilayer, biomaterials, corrosion resistance, reactive magnetron sputtering.

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 multilayer ceramics, a revolution in the ceramic industry began. For decades, Ti and 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. Ti and TiN thin films can be deposited on medical implants or prosthesis of a large variety of dimensions and shapes.

The objective of this work was to obtain \((\text{Ti/TiN})_n\) multilayers \((n – \text{number of the single layers})\) on 316L stainless steel substrates by reactive magnetron sputtering technique [3].

Coating characterization was performed with respect to chemical composition (RBS, AES), phase composition, texture (XRD), mechanical characteristics (Vickers microhardness, adhesion) and corrosion resistance in artificial physiological solution \((\text{NaCl} – 8.44 \text{ g/l}, \text{Na HCO}_3 – 0.35 \text{ g/l}, \text{Na H}_2\text{PO}_4 – 0.06 \text{ g/l}, \text{Na H}_2\text{PO}_4 \cdot \text{H}_2\text{O 0.06g/l})\).

EXPERIMENTAL

Ti/TiN multilayered coatings (with 4, 16 or 32 single layers) were deposited on 316 L stainless steel and Si samples using an experimental set-up 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:
cathode material – Ti; reactive atmosphere – Ar + N$_2$, nitrogen pressure $p_{N_2} = 5 \times 10^{-1}$ Pa, magnetron current $I_{Ti} = 1–4$ A, substrate bias $-V_s = 0–150$ V; deposition time $t = 60$ min. The multilayered structures were obtained by periodically supplying the working atmosphere with N$_2$ (from 110 to 900 seconds).

Chemical composition of the Ti/TiN films was determined by Rutherford backscattering spectroscopy (RBS) and Auger electron spectroscopy (AES). For the RBS measurements, a Li$^{2+}$ ion beam of 4.5 MeV was used. The elastically scattered particles were analyzed with a silicon detector (energetic resolution – 20 keV). The AES experiments were performed using a PHI Model 3017 AES PC-Based Subsystem. The electron analyzer is model 10-155 single pass Cylindrical Mirror Analyzer (CMA). A PHI Model 04-191 ion gun was used for sputter cleaning of the samples.

Phase composition and texture were determined by XRD analysis using an X-ray DRON diffractometer with Cu K$_\alpha$ radiation.

Microhardness (Vickers) measurements were performed by means of a microhardness tester at 15 g 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 Potentiostat/Galvanostat Model 2049. Corrosion behavior was evaluated from the polarization curves, measuring the changes of the corrosion potential with current density. Electrochemical studies were carried out in simulated body fluids, namely artificial physiological solution. The pH of the solution was maintained at 7.4 and the temperature was 25 ± 1°C. Samples with dimensions $23 \times 23 \times 4$ mm, carefully polished, were immersed in the electrolyte and the potential was monitored as a function of time with respect to Hg/HgSO$_4$, until the potential reached a stable value. Saturated calomel (Hg/HgSO$_4$) and platinum electrodes were used as the reference and auxiliary electrodes, respectively.
RESULTS AND DISCUSSION

MICROCHEMICAL AND MICROSTRUCTURAL CHARACTERISTICS

A typical example of a RBS spectrum obtained from a \((\text{Ti/TiN})_n\) multilayer \((n = 4)\) is shown in Fig. 1 (deposition conditions: \(I_{\text{Ti}} = 2\ A\); \(V_s = 80\ V\)). The simulation of the RBS spectra was performed using a SIMNRA code. The individual layer thickness was calculated to be of about 110 nm, both for the Ti and the TiN films. One may also observe that the multilayer structure exhibits sharp interfaces between the layers.

The composition depth profiles of the TiN single layer coatings were obtained by AES measurements. In Fig. 2 is illustrated an Auger spectrum of a TiN film deposited under the conditions: \(I_{\text{Ti}} = 4\ A\); \(V_s = 50\ V\). The coatings were sputtered with 3 or 5 keV \(\text{Ar}^+\) ion beams for different times (from 0 to 95 minutes). It can be seen that the amounts of carbon and oxygen existing on the as-deposited film surfaces diminished with the increasing sputtering time. Nevertheless, AES spectra confirm the presence of C and O in the film composition even after being sputter etched for 95 minutes.

The AES measurements indicated that almost stoichiometric TiN films were prepared \((N/\text{Ti} = 1)\).

Though there were certain differences (within 10%) between the results of the investigation techniques (RBS and AES), the measurements revealed the same dependence of the chemical composition on the deposition parameters.

A typical X-ray diffraction pattern for a \((\text{Ti/TiN})_{16}\) multilayer is illustrated in Fig. 3. X-ray analysis revealed that the coatings consisted of TiN and Ti layers. One may observe strong \((111)\) and \((002)\) preferred orientations for TiN and Ti films, respectively.
MECHANICAL PROPERTIES

The main mechanical characteristics of the films (microhardness, adhesion, deposition rate) are given in Table 1. It can be seen that the microhardness increases with the number of the individual layers. One may also observe that the microhardness of the Ti/TiN multilayers is much less than that of the TiN monolayer.

Scratch adhesion tests showed that the adhesion does not depend on $n$, but on the substrate characteristics and film properties, as it was already reported. The critical load ($L_c$) increases with the film thickness and with the substrate hardness. For the (Ti/TiN)$_{32}$ coating with thickness and microhardness of about 2100 nm and 1350 HV$_{0.015}$, respectively, critical loads of 35–40 N were measured.
Table 1

Mechanical characteristics of mono- and multilayers

<table>
<thead>
<tr>
<th>Coating</th>
<th>TiN</th>
<th>(Ti/TiN)\textsubscript{16}</th>
<th>(Ti/TiN)\textsubscript{32}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microhardness HV\textsubscript{0.015}</td>
<td>2280</td>
<td>1220</td>
<td>1350</td>
</tr>
<tr>
<td>Adhesion – Lc [N]</td>
<td>25 ÷ 30</td>
<td>28 ÷ 32</td>
<td>35 ÷ 40</td>
</tr>
<tr>
<td>Thickness [nm]</td>
<td>2040</td>
<td>1950</td>
<td>2100</td>
</tr>
<tr>
<td>Deposition rate [nm/min]</td>
<td>34</td>
<td>32.5</td>
<td>35</td>
</tr>
</tbody>
</table>

The total thicknesses of the multilayered structures (Ti/TiN)\textsubscript{16} and (Ti/TiN)\textsubscript{32} were of about 1950 nm and 2100 nm, respectively.

CORROSION BEHAVIOR

Fig. 4 shows cyclic polarization curves, for Ti/TiN coated samples, in comparison with that of the 316L stainless steel. The critical current for passivation, as well as the fluctuation ranges of the corrosion potential, can be observed. As compared with the coatings, the uncoated sample exhibited a larger active zone and a higher critical current. Of the coated samples, the best corrosion behavior was found in the case of the coating with 32 individual layers, for which the lowest critical current and the largest passivation region were measured.

Fig. 4. – Cyclic polarization curves of Ti/TiN multilayers and of 316L stainless steel.
To evaluate the resistance of the Ti/TiN coatings and of the 316L stainless steel to the release of toxic metal ions, the solution was analyzed to determine the concentration of metal ions, namely Al, Ti, Fe, Ni, leached out during the corrosion process. The experiments showed that both the coated samples and the uncoated one exhibited a low corrosion rate (< 0.1 µm/year on a typical 100 cm² area of the sample surface).

CONCLUSIONS

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

The microhardness values of the Ti/TiN multilayers were substantially lower than those of the TiN monolayers. A good adhesion of the Ti/TiN coatings was found (critical loads of 35–40 N were obtained). The Vickers microhardness and the critical load increased with the number of the individual layers.

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REFERENCES