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Corrosion protection of titanium by deposition of niobium thin films

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Abstract

Titanium is a promising material for medical implants, replacing bones and teeth. However, at pH values below 2, which occur in the dental environment, the corrosion resistance is compromised. The deposition of niobium layers onto titanium is a possibility to increase the corrosion resistance, as measured in 5 N HCl solution. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Titanium and titanium based alloys, such as Ti6Al4V, have three important properties: low weight, good mechanical properties and chemical stability [1]. Hence they are increasingly used in different industries, e.g. automotive, aerospace and medical [2]. In the last group they are ubiquitously found as tools, temporal implants (as in osteosynthesis plates) and permanent implants (such as bone and dental replacements) [3]. However, acidity in the mouth can vary greatly from near neutral to strongly acidic, sometimes reaching pH values below 2. At these values titanium shows enhanced corrosion, reducing the lifetime of the implants and releasing titanium into the body.

Deposition of niobium on a titanium surface is one possible way of improving corrosion resistance in this highly acidic region. In this paper we report on investigations concerning niobium layers deposited onto titanium and Ti6Al4V flat samples. Corrosion was measured in 5 N HCl, while the elemental composition of the layers was investigated with Rutherford backscattering spectroscopy (RBS) and Auger Electron spectroscopy (AES). Atomic force microscopy (AFM) was used to obtain information about the surface topology.

2. Experiment

A commercial grade sample of titanium and Ti6Al4V, polished to a mirror-like finish, were used. They were mounted in the Hong Kong PIII system [4] onto a 10 cm diameter copper target stage. A base pressure of better than 10^{-4} Pa was reached. Ar-sputter cleaning was performed on the samples before starting the deposition process. Niobium was deposited onto the samples by sputtering from a pure niobium target in 10 Pa Ar using a d.c. voltage of 1 kV for 2 h. To investigate the influence of energetic ions on the interface properties and to simulate the effect of the planned deposition with niobium ions from a vacuum arc source in a separate experiment plasma immersion ion implantation [5–7] with Ar ions was additionally used. Here the process was stopped after 10 min, and high voltage pulses of −40 kV with a duration of 10 μs and a repetition rate of 100 Hz were applied to a total dose of 10^{17} ions/cm^2. After that the deposition was continued to obtain the same layer thickness as before.

The corrosion properties were tested by carrying out potentiodynamic measurements in 5 N HCl solution to simulate the very acidic environment encountered in the proposed application. The potential was measured against a normal hydrogen electrode (NHE).

The samples were measured with RBS, using a 1.7 MeV He$^+$ beam and a total charge of 20 μC. The scattering angle was 170° in the IBM geometry, at normal incidence.

Sputtering depth profiling was executed with a scanning Auger electron spectrometer MICROLAB 310F

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with field emission electron source and hemispherical sector analyzer. Sputtering was performed while rotating the sample with a 3 keV Ar^+ ion beam at a current density of abut 1 $\mu A/mm^2$.

Surface geometry was investigated with an atomic force microscope, Rasterscope 3000 in the 2-dimensional smooth mode, using a silicon nitride tip covered with gold. The tip was pyramidal with an angle of 70°, tip radius about 30 nm and 3 μm height.

3. Results

The results of the potentiodynamic measurements are shown in Fig. 1. For the deposition process a significant reduction of the corrosion current was obtained compared to the untreated reference materials. In contrast, the combination with the Ar PIII process resulted in no significant change in the corrosion properties from the base materials.

To understand this unexpected result, RBS were obtained for information about the elemental composition. The measured and simulated RBS spectra, using RUMP [8], are shown in Fig. 2. For the simulation, a three layer system, consisting of $Nb/TiO_2/Ti$ and $NbCu_xO_yAr_z/TiO_2/Ti$ was used, corresponding to a titanium sample with native oxide layer and the deposited niobium (with contaminants). The layer thickness and the stoichiometry were used as a fit parameter. For the pure deposition, an area density of 7.3×10^{16} oxygen atoms/cm^2 and 6.4×10^{15} niobium atoms/cm^2 was obtained. For the deposition with the Ar PIII bombardment, the corresponding values are 1.25×10^{17} oxygen atoms/cm^2, 7.1×10^{15} niobium atoms/cm^2, 4.3×10^{15} argon atoms/cm^2.

As the depth sensitivity of RBS for these very shallow niobium layers is not very high, additional AES depth profiles were obtained to gain information about the depth distribution. However, as an absolute concentration and depth calibration is not straightforward, only counts vs. sputter time are presented. A sputter time of 1 s corresponds to a depth of approximately 0.5–1 nm. The resulting spectra are shown in Fig. 3(a) and (b) for niobium deposition and niobium deposition with Ar PIII respectively. A shallow niobium signal on top of a titanium oxide interlayer is found in the first

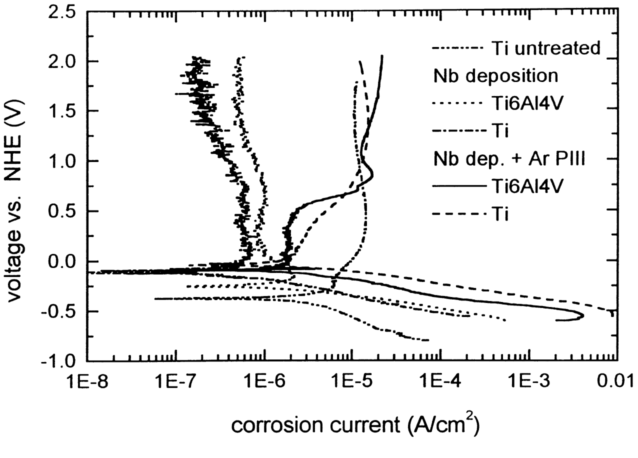

Fig. 1. Potentiodynamic curves measured in 5 N NCl solution against NHE, for untreated and treated titanium and Ti6Al4V samples.

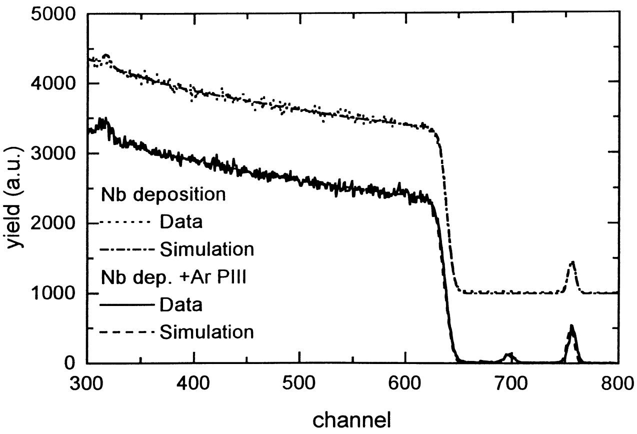

Fig. 2. Measured and simulated RBS data for titanium samples and the two different treatments. The upper two curves are shifted for clarity.

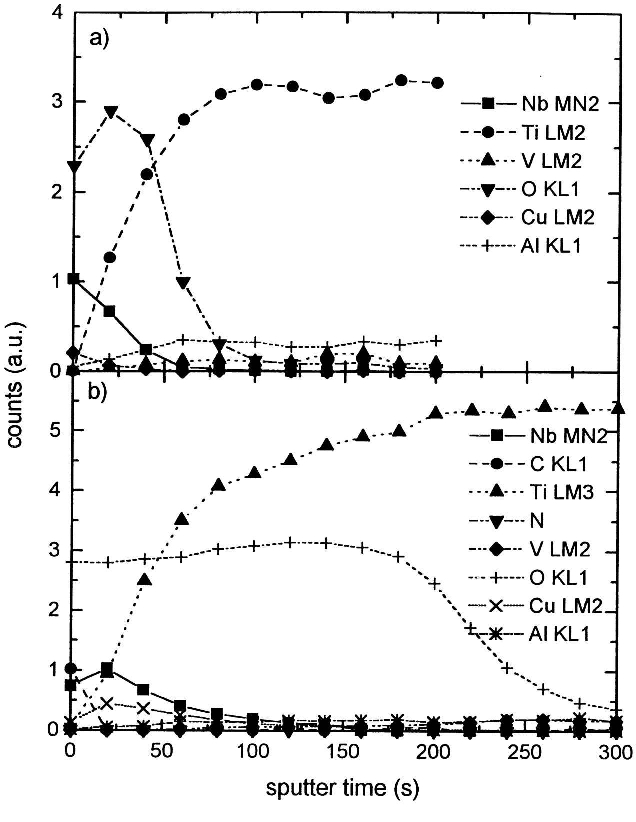

Fig. 3. AES depth profiles as indicated in the legend for Ti6Al4V samples with: (a) niobium deposition; and (b) niobium deposition with Ar PIII treatment.

case before reaching the base material Ti6Al4V, whereas a more complicated picture is obtained from the second case. Here, besides minor carbon contamination at the surface, a considerably larger oxygen contamination, accompanied by copper, is found while the niobium signal is about the same as before.

Finally AFM was used to get information on the surface structure of the deposited layers. In Fig. 4(a) the sample with only niobium deposition shows an island growth with smooth surfaces and a grain size of some 1–2 µm. In contrast, when including an Ar PIII step in the deposition, the resulting structure is very porous and shows dendritic protrusions indicating a completely different growth regime. Here the grain size is approximately 3–5 µm.

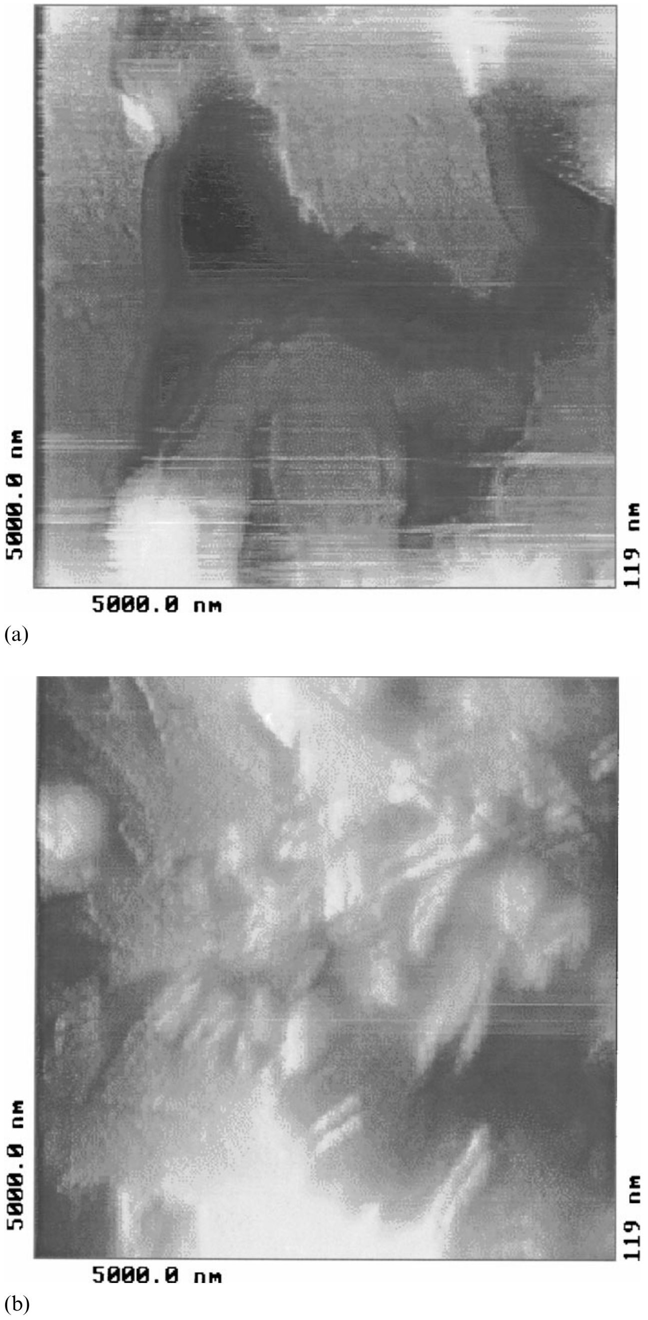

Fig. 4. AFM viewgraphs for titanium samples with: (a) niobium deposition; and (b) niobium deposition with Ar PIII treatment.

4. Discussion

The first thing to notice is the rather low niobium layer thickness after 2 h of d.c. sputter deposition, 6–7 × 10^{15} atoms/cm^2 corresponding to some 10–20 nm. This may be explained by a lowish plasma density as no magnets were used to enhance the sputter current and the plasma density, and a large distance of 15 cm between the sputter target and the titanium samples. In future planned investigations, vacuum arcs will be used to produce niobium ions and this will alleviate this problem.

Nevertheless, excellent corrosion protection of the smooth niobium layers obtained with the pure deposition process, decreasing the corrosion current by two orders of magnitude, were found. The native titanium oxide at the interface between the substrate and the layer apparently does not influence the corrosion properties negatively.

However, the addition of an Ar PIII step in the middle of the deposition process, to increase the adhesion properties, changes the picture dramatically. Due to its high sputter coefficient [9], copper is removed from the target holder, ionised in the plasma and re-implanted into the samples. As the range of 40 keV Ar ions is very low [10] they are stopped within the niobium layer, or no later than the titanium surface, where it can act as a very effective gathering center for residual oxygen from the plasma and the vacuum system. This process is enhanced by the fine-grained and porous structure of the films, as seen in the AFM pictures. This NbCuO alloy, in contrast to pure niobium, has no beneficial effects on the corrosion properties.

Any temperature effect can be excluded as the repetition frequency of 100 Hz is not sufficient to increase the sample temperature beyond 100°C for the given plasma density and voltage [7].

5. Summary and conclusions

Niobium deposition onto titanium for corrosion protection of dental implants is a promising technique, especially when combined with Ar PIII for interface mixing and enhanced adhesion properties. However, the deposition rate using conventional d.c. sputtering is far too low for commercial applications. The use of vacuum arcs, where experiments are in preparation, should result in a far higher deposition rate enabling commercialisation later. One final point — copper with its high sputter coefficient and affinity for oxygen should be avoided as a material in the vacuum chamber altogether to prevent its incorporation in the layers and degradation of the layer properties.

Acknowledgement

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