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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 5N HCl solution.

1. Introduction

Titanium and titanium based alloys, like Ti6Al4V, exhibit three important features:low weight, good mechanical properties, 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 like bone and dental replacements [3].

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However, the 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 human body.

Deposition of niobium onto the titanium surface is one possibility to improve the corrosion resistance in this highly acidic region, and in this report we present investigations on niobium layer deposited onto Ti and Ti6Al4V flat samples. Corrosion was measured in 5N 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

For this experiment commercial grade sample of Ti and Ti6Al4V polished to a mirror-like finish were used. They were mounted in the Hongkong 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 of the samples was performed before starting the deposition process. Nb was deposited onto the samples by sputtering from a pure Nb target in 10 Pa Ar using a d.c. voltage of 1 kV for 2 hours. To investigate the influence of energetic ions on the interface properties and simulate the effect of the planned deposition with Nb ions from a vacuum arc source in a separate experiment plasma immersion ion implantation [5,6,7] with Ar ions was additionally used. Here the process was stopped after 10 minutes and high voltages pulses of – 40 kV with a length 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 5N 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.

Sputter depth profiling was executed with a scanning Auger electron spectrometer MICROLAB 310F 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 about 1 $\mu A/mm^2$.

Surface geometry was investigated with an atomic force microscope, Rasterscope 3000 in the 2-d smooth mode, using a silicon nitride tip, covered with gold. The tip is of pyramidal shape with an angle of 70^0 , tip radius about 30nm and 3μm 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 is obtained compared to the untreated reference materials. In contrast, the combination with the Ar PIII process results in no significant change in the corrosion properties from the base materials.

To understand this unexpected result Rutherford backscattering spectra 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 a native oxide layer and the deposited Nb (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} oxygen atoms/cm^2 and 4×10^{15} argon atoms/cm^2.

As the depth sensitivity of RBS for these very shallow Nb layers is not very high, addi-

tional 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 sec. corresponds to a depth of approximately 0.5 – 1 nm. The resulting spectra are shown in Fig. 3a) and b) for Nb deposition and Nb deposition with Ar PIII respectively. A shallow Nb signal on top of a titanium oxide interlayer is found in the first case before reaching the base material Ti6Al4V, whereas a more complicated picture is obtained from the second case. Here, besides a minor carbon contamination at the surface, a considerably larger oxygen contamination, accompanied by Cu is found while the Nb signal is about the same as before.

Finally atomic force microscopy was used to get information on the surface structure of the deposited layers. In Fig. 4a. the sample with only Nb depositions 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.

4. Discussion

The first thing to notice is the rather low Nb layer thickness after 2 hours of d.c. sputter deposition, $6 - 7 \times 10^{15}$ 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 Ti samples. As planned for the future, employing vacuum arcs to produce Nb ions shall 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 negatively influence the corrosion properties.

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 Nb layer or no later than the Ti surface where it can act as a very effective gettering 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 Nb, has no beneficial effects on the corrosion properties.

Any temperature effect can be excluded as the employed 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

Nb deposition onto Ti for corrosion protection of dental implants is a promising technique, especially when combined with 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 utilisation of vacuum arcs, where experiments are in preparation, should result in a far higher deposition rate, allowing a later commercialisation. One final point, Cu with its high sputter coefficient and affinity to 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.

5. Acknowledgements

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Figure Captions

Fig. 1: Potentiodynamic curves measured in 5N HCl solution against NHE for untreated and treated Ti and Ti6Al4V samples..

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

Fig. 3: Auger electron spectroscopy depth profiles as indicated in the legend for Ti6Al4V samples with a) Nb deposited onto it and b) Nb deposition with Ar PIII treatment.

Fig. 4: AFM viewgraphs for Ti samples with a) Nb deposited onto it and b) Nb deposition with Ar PIII treatment.