Diffusion Mechanisms in Biocompatible Titania Surface Layers

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The biocompatibility and the bioactivity are of foremost importance for osteosynthesis plates used in jaw and skull surgery. Mostly, pure titanium (grade 2) is used, whereas adverse reactions were observed for stainless steel implants. Albeit, a failure rate of about 5% during healing is even observed for titanium implants. The rather good biocompatibility of pure titanium is caused by a thin native oxide layer, which can be partially destroyed by relative movements between the implant and the body tissue, leading to an increased wear. Here, biocompatible titania surface layers were investigated within a Bavarian cluster project encompassing the accelerator laboratory, physics department of the university of Augsburg, clinic for jaw and bone surgery, Munich and the institute for material in mechanical engineering, technical university of Munich. The layers were produced with plasma immersion ion implantation (PIII), where positive ions are accelerated from a plasma by applying negative high voltage pulses on the substrate, suitable for fast and cost-effective treatments and yielding dense surface layers without any adhesion problems. The ERDA measurements were performed with the position sensitive ionization chamber in the ERDA beam line using 200 or 210 MeV Au ions [1].

Pure titanium samples (99.5%) were polished to a mirror-like finish and treated in a HV system at a base pressure of $2 \cdot 10^{-6}$ mbar and a working pressure of $3 \cdot 10^{-3}$ mbar with oxygen PIII. High voltage pulses of - 30 kV were applied at a constant repetition rate of 1 kHz until the process temperature between 265 and 550°C was reached. After this, the frequency was lowered and adjusted via a computerized control loop to maintain this temperature. At an implanted dose of $6 \cdot 10^{11}$ O atoms/cm^2 per pulse, the pulse numbers between 0.5 and $4 \cdot 10^6$ correspond to a total fluence of $3 - 24 \cdot 10^{17}$ cm^2.

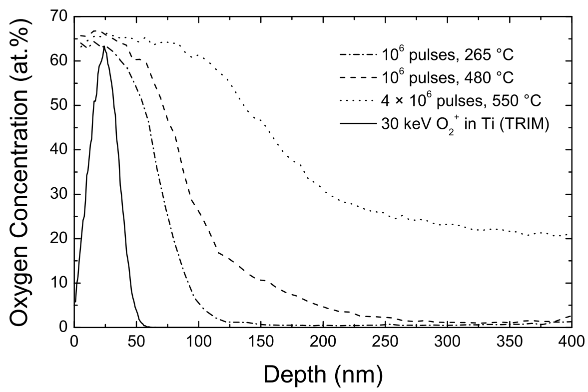

Fig. 1: Oxygen depth profiles for different parameters in comparison to the implantation profile predicted by TRIM.

Raman spectroscopy showed that only the high temperature phase rutile was present at all investigated temperatures [2]. A close examination of the oxygen depth profiles reveals two competing processes. At lower temperatures, an inverse parabolic growth of the closed rutile TiO_2 layer was observed (see Fig. 1). At higher temperatures, additional oxygen diffusion tails into the bulk Ti were measured. Fig. 2 presents the diffusion constant for both processes. An activation energy of 0.5 - 0.6 eV was calculated for the growth of the rutile layer, whereas a higher value of 0.85 eV was obtained for the second process.

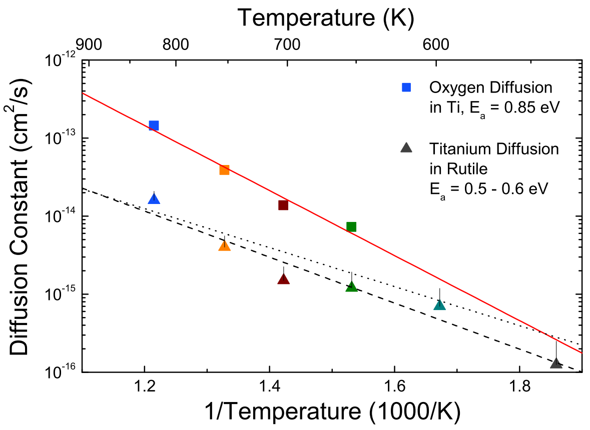

Fig. 2: Thermally activated diffusion constants for the two different processes.

These experimental results allowing the distinction of two different diffusion mechanisms are in good agreement with literature data. A very strong tendency to form TiO_2, skipping the intermediate oxidation states, is found at all temperatures, due to a very large formation enthalpy. At higher temperatures the diffusion of oxygen in titanium becomes the predominant mechanism. This is confirmed by the observation that above 450°C no surface oxygen is detectable during vacuum oxidation of titanium. The osseointegration of rod shaped implants was biomechanically evaluated by pull-out tests using a rat model. Additionally, investigations by histological and fluorescence microscopy examination were performed [3,4]. For evaluation the true pull-out energy, the area of contact between implant and bone and the sliding forces were measured. The treatment of titanium based medical implants by oxygen PIII considerably improved the biocompatibility, as shown with biomechanical pull-out tests and histological examinations for rods implanted in rat femurs. Further investigations on the correlation of the oxygen profiles and the osseointegration are in progress.

References

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