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Effect of Hydrogen Peroxide on the Native Oxide at a Titanium Surface

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Introduction: Titanium alloys have long been used as orthopedic implants, due to their biocompatibility and the fact that they are somewhat conducive to bone regrowth. Yet the failure rate of such implants is still high, and there are many basic unanswered questions about the chemical effects on titanium and titanium oxides in a wound environment [1]. We have studied the surface structure of the titanium/oxide interface in the presence of hydrogen peroxide, which is secreted by cells to combat foreign particles, but which may be reduced to less reactive species in the presence of TiO_2 .

Methods and Materials: A titanium single crystal with nominal (001) orientation was hand polished with colloidal silica, cleaned with water, inserted into a fluid cell with either water or hydrogen peroxide in contact with the surface, and covered with a thin plastic film for reflectivity measurements at an x-ray wavelength of 1.155 Å, with helium atmosphere outside the fluid cell.

Results: Hand polishing produced a surface that was microscopically smooth, but wavy on long length scales: at low reflection angles, rocking curves observed within the reflection plane had long, asymmetric tails. In some alignments it was even possible to obtain a “doubled” peak if the detector was scanned in reflection angle. The resulting difficulties in alignment, absolute normalization and background subtraction limit the interpretation of the data. Nevertheless, clear oscillations are observed in the reflectivity, and these can be related to the thickness and density of the titanium oxide surface layer. Reflectivity data are shown in Figure 1a for Ti in contact with water (circles), and after exposure to 3% hydrogen peroxide (triangles) for 2 and 4.5 hours. The oscillation spacing indicates that the x-rays reflect from interfaces 4.8 nm apart. However, they are much more pronounced than would be expected for a complete coverage of rutile-type TiO_2 . Rutile has an electron density 97% that of Ti metal, and the slight contrast would produce very small oscillations, as shown by the calculated reflectivity curve in Figure 1a and the ideal real-space profile in Figure 1b (dashed lines). A layer of 80% relative density, perhaps due to porosity of the oxide, would produce an oscillation amplitude closer to that observed (dotted lines in figure). However, the oscillations in the data are also shifted by one-half period relative to the calculations from the simplest model profile. Considering coherent models in which x-ray amplitudes (not intensities) of reflecting rays are added together, the only model we obtained to fit this data involved a density-depleted region between the 4.8 nm film and the substrate, and a decrease of the film density to 40-60% that of the substrate. To us this model seems unphysical, and alternative analyses are underway. The same remarks apply to the data obtained after exposure to H_2O_2 . After 2 hours, the film in peroxide is somewhat rougher and appears from the fits to decrease in density; for longer exposures the film is rougher still, but the basic 4.8 nm spacing remains unchanged, until the film becomes so rough that no oscillations are observable at all. Our results suggest that the roughening by H_2O_2 occurs not by dissolving the rutile phase, but at regions of off-stoichiometry that contribute to the porosity of the film. Measurements of a high quality rutile single crystal, in which H_2O_2 did not effect the surface structure, support this conclusion.

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References:

[1] J. L. Gilbert, J. Biomed. Mat. Res. **40** (1998) 233.

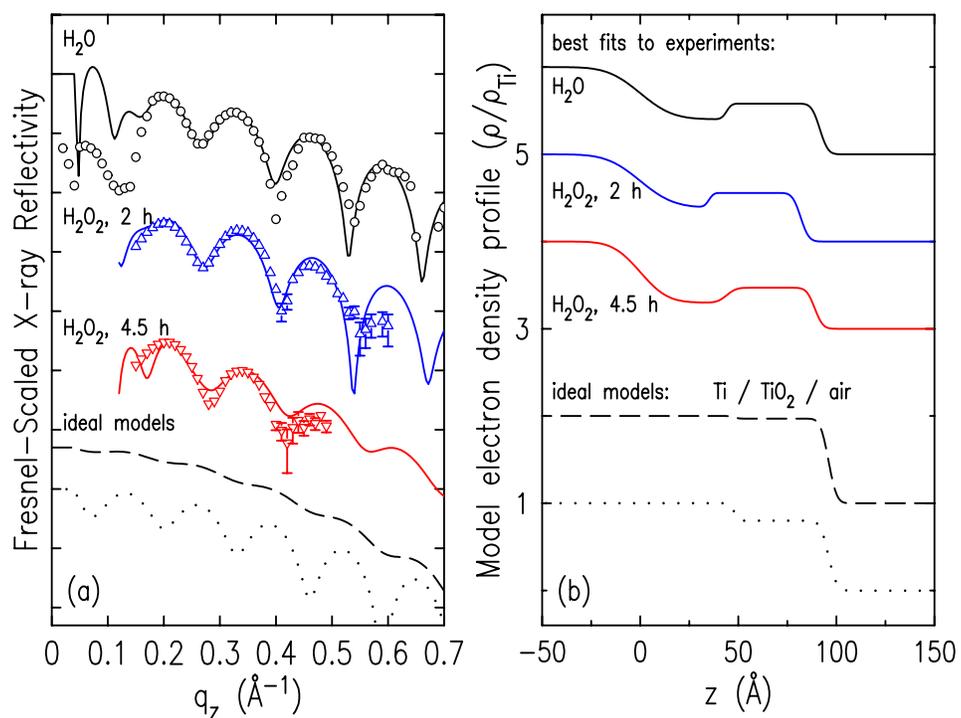


Figure 1. (a) Reflectivity data obtained for a Ti/Ti oxide surface in contact with water (black circles), and with 3% hydrogen peroxide for 2 hours (blue triangles) and 4.5 hours (red triangles). Solid lines are fits to the data. Dashed line: calculated reflectivity for a 100% rutile film of 4.8 nm thickness on Ti. Dotted line: 80% rutile density on Ti, 4.8 nm thick. (b) Model real-space electron density profiles corresponding to the calculations in (a), as labeled. Curves in (a) and (b) are shifted along the vertical axes for clarity.