

STABILITY AND REPASSIVATION OF METALLIC IMPLANTS IN SERUM BOVINE

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INTRODUCTION

Metallic implants show an outstanding corrosion resistance due to the spontaneous formation of a thin protective oxide film (the passive film) [1]. Nevertheless, clinical experience reports that a small percentage of prosthetic devices produce inflammatory response due to corrosion after insertion in the body. Fretting corrosion is regarded as the principle cause of implant failure [2, 4]. Under fretting condition, metal oxidation causes a decrease in the local pH and a rise of metal ion concentration as well as the accumulation of small metal particles. This may affect the existing balance of ions in the tissue as well as the conduction of stimuli by nerve cells. Thus, changes in the conformation and /or structure of molecules that are responsible for the cell attachment to the implants surface, like calcium-binding proteins [5], are to be envisaged. It is therefore of critical importance to get a better understanding of the electrochemical behaviour of metallic implants both after mechanical disruption of the passive film and of the stability of the protecting oxide film when exposed to physiological solutions.

This work describes the results concerning the stability of the passive film on cp titanium, Ti6Al4V, Ti6Al7Nb and CoCrMo implant alloys in serum bovine as well as the repassivation rate after mechanical disruption of the passive film (fretting). The influence of the surface treatment (mechanically polished or sandblasted) is also addressed.

EXPERIMENTAL

Commercial pure (cp) titanium, Ti6Al4V, Ti6Al7Nb and CoCrMo (67% Co, 28% Cr, 6% Mo) both mechanically polished to 1 μm diamond paste and sandblasted (200 – 500 μm alumina particles) were used for the electrochemical tests. Electrolytes used were calf serum bovine at pH 7.0 and 4.0 and 0.1M sodium sulphate; pH 4.0 was reached by adding hydrochloric acid. The stability of the passive

films over time (expressed by the polarization resistance) was determined using electrochemical impedance spectroscopy (EIS).

The repassivation behaviour [6] was studied measuring the open circuit potential before, during and after mechanical disruption of the passive film in serum.

RESULTS AND DISCUSSION

Stability of the passive film

The polarization resistance R_p and thus the stability of the passive film of TiAlV is highest both when sandblasted (fig. 1b) and mechanically polished (fig. 1a). The stability of the passive film is found to be higher in serum bovine compared to 0.1M sodium sulphate solutions, hence, the interaction with biological molecules leads to a general increase in the stability of the sample. This might be due to the formation of an organic adsorption layer which covers part of the electrodes or hinders ion transport.

From the comparison between fig. 1a and 1b it ensues that the sandblasting process improves the stability of the oxide films both in sodium sulphate and in serum. In contrast to mechanically polished samples which have a thin, freshly formed oxide film, sandblasted electrodes are already covered by a stable oxide film originated during the surface treatment and aged through long exposure to air. Thus, changes after immersion are less pronounced.

Fretting and Repassivation

The corrosion currents of the implant materials tested during fretting (in the active state) in serum bovine at pH 4 and 7 are very high, indicating that, under fretting condition, the change in the chemical composition of the electrolyte might be significant. The CoCrMo alloy shows – especially at pH 7 – the lowest dissolution currents.

It is crucial that, when passive films are mechanically damaged, the current produced as a consequence of the repassivation processes and the time requested to rebuild a stable passive film are as low as possible. The repassivation rate after fretting was determined by observing the increase in the open circuit potential of the electrodes. The values of the percentage given in fig. 2b is calculated from the potential measured 30 seconds after the end of fretting and referred to the potential reached after 1 hour of repassivation. As can be observed, the two titanium implants behave similarly at pH 7 whereas the CoCrMo alloy shows a very slow repassivation at pH 4.

CONCLUSIONS

The interaction with serum leads to an increased stability against general corrosion of both mechanically polished and sandblasted samples compared to sodium sulfate solutions.

On mechanically polished samples the thickness of the oxide film increases after exposure to the electrolytes. Hence, the resulting passive film is slightly less stable compared to sandblasted samples of the same composition.

Titanium and Ti6Al4V repassivate with the same velocity and develop the same current in the active state.

CoCrMo alloy at pH 7.0 shows the lowest corrosion current and the highest repassivation rate. However, a decrease of the pH down to 4.0, due to local acidification, renders the cobalt-based alloy worse than titanium and titanium-alloy.

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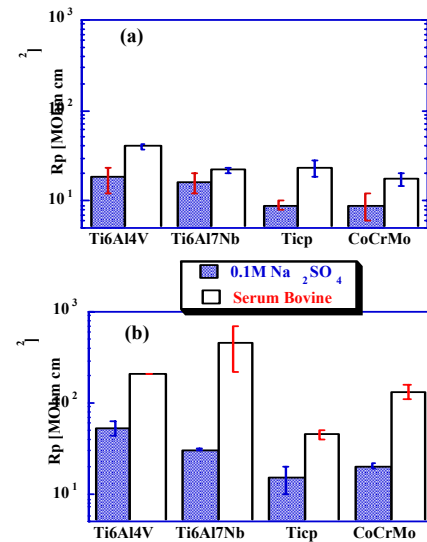


Figure 1: Effect of the electrolyte and sample composition on the steady state polarization resistance of mechanically polished (a) and sandblasted samples (b).

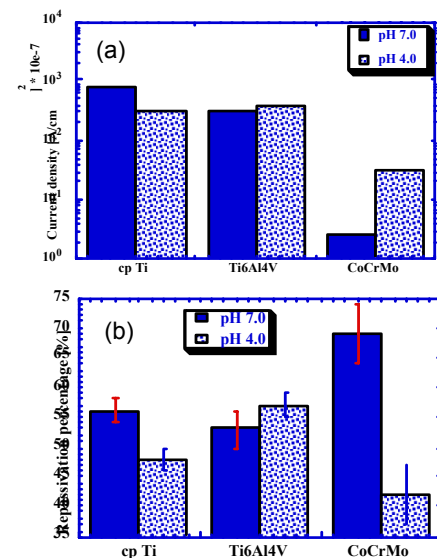


Figure 2: Effect of pH and sample composition on the corrosion current in the active state in serum. (a) and on the repassivation rate in serum (b).