

CORROSION CHARACTERISATION OF PASSIVE FILMS ON CoCrMo WITH ELECTROCHEMICAL TECHNIQUES IN SALINE AND SIMULATED BIOLOGICAL SOLUTIONS

S. Kurz¹, A.W.E Hodgson¹, S. Virtanen¹, V. Fervel² & S. Mischler²

¹ Institute for Materials Chemistry and Corrosion & Department of Materials, Swiss Federal Institute of Technology Zurich, 8093 Zurich, CH, ² Laboratory of Metallurgical Chemistry, Department of Materials, Swiss Federal Institute of Technology Lausanne, University of Geneva, 1015 Lausanne, CH

INTRODUCTION: CoCrMo alloy is regarded as a highly biocompatible material and has been employed in the fabrication of hip prostheses since the 1940's. Its biocompatibility is linked to the spontaneous formation of a stable oxide film. Nonetheless, the release of metal into the body takes place, which can be the result of uniform passive dissolution, of local breakdown of passivity as a consequence of localized forms of corrosion, or of mechanical events such as fretting corrosion. However, the exact chemical, electrochemical and triboelectrochemical mechanisms that lead to the release of metal from CoCrMo prostheses are not known. In this work an electrochemical characterisation of CoCrMo alloy under simulated biological conditions was sought. In particular, the effects of specific ions present in the electrolyte solution and of time on the properties of the passive film were investigated.

METHODS: CoCrMo disc-shaped samples (Protasul-20, Sulzer Winterthur) of 1 cm² area and 5 mm thickness were employed throughout the study. Experiments were performed in simulated body fluid (SBF) and in 0.14 M NaCl solution buffered to pH 7.4 via the use of tris(hydroxyaminomethane) buffer, or to pH 2 and pH 10 by the addition of concentrated HCl and 1 M NaOH. (Table1) The solutions were thermostatted via the use of a water bath to 37 °C, unless otherwise stated. Potentiodynamic measurements and electrochemical impedance spectroscopy (EIS) were carried out to characterise the alloy and to monitor changes in the passive film as a result of exposure to different environments with time.

Table 1: Electrolyte solutions employed in the study. All solutions were adjusted to the desired pH by the addition of HCl (37%) or NaOH (1 M).

Background Electrolyte	Added ions
0.14 M NaCl	—
0.14 M NaCl	1 mM KH ₂ PO ₄ , 2.5 mM CaCl ₂ , 3 mM KCl, 1.5 mM MgCl ₂ , 4.2 mM NaHCO ₃ , 0.5 mM Na ₂ SO ₄ -
Simulated body fluid -	

RESULTS: In Figure 1, potentiodynamic curves acquired after exposure times of 6 min, 90 min, 18 h, 24 h and 7 d to simulated body fluid adjusted to pH 7.4 at 37 °C are shown. It is evident from the curves that the time of exposure to the solution plays an important role, both on the cathodic and the anodic currents recorded. During the first 18 h the cathodic currents are very similar and the open circuit potentials fall close to one another. In the anodic potential range, the currents are passive, but once again, after 18 h the passive current appears to be much smaller indicating that the passive film has become more protective (e.g. by thickening, by becoming more compact or by changing in composition). At potentials positive to + 0.5 V vs. SCE the peak superimposed upon H₂O oxidation, is due to the transpassive dissolution of Cr. It is important to note that the increase with immediate decrease in current observed at potentials positive to the open circuit potential is not necessarily to be attributed to an active-passive transition but possibly to the discharge of hydrogen ions adsorbed onto the surface under cathodic potentials.

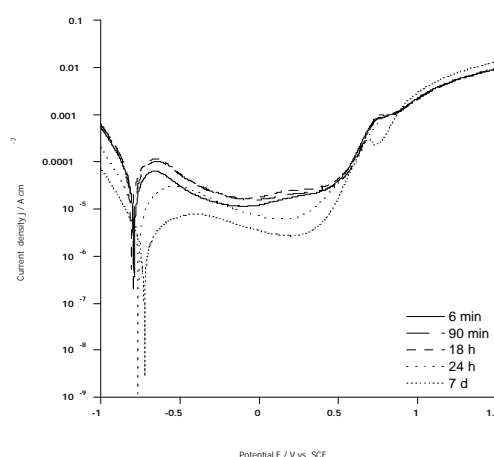


Fig. 1: Current-potential curve recorded at CoCrMo sample at different times of exposure to simulated body fluid adjusted to pH 7.4 at 37 °C. Sweep rate 5 mVs⁻¹.

Electrochemical impedance spectra acquired under the same solution conditions at different times of exposure ranging from 10 minutes to 7 days, clearly showed an increase in the protectiveness of the passive film with time, which could be observed in the increase in impedance values at low frequency with time and in broadening of the capacitive behaviour of the phase angle to lower frequencies with time.

The effects of ions on the passive film properties were also studied. More specifically, the effects of ions present in simulated body fluid, such as Ca^{2+} , PO_4^{3-} , K^+ , Mg^{2+} , were investigated by comparing electrochemical impedance spectra and potentiodynamic measurements with those obtained in 0.14 M NaCl solution also adjusted to pH 7.4 via the use of the same buffer and at 37 °C. The results clearly showed that, unlike Ti and its alloys¹ which selectively adsorbed Ca^{2+} and PO_4^{3-} ions, CoCrMo does not interact with the ions in the electrolyte and the evolution of the spectra with time obtained in the two solutions are very similar.

Experiments were also performed to investigate the effects of exposure of the CoCrMo sample to air prior to immersion into the electrolyte solution. It was found that the passive films formed in air were different to those formed in solution, but that once the sample had been placed in solution a reconstruction of the passive film takes place.

DISCUSSION & CONCLUSIONS: The electrochemical study showed that the passive film formation on CoCrMo is very sensitive to the conditions under which it takes place, therefore affecting the properties of the films, such as protectiveness and degree of metal ion release. Although the passive film is mainly composed of Cr_2O_3 , oxides of Co and Mo can also be present depending on the environment conditions. However the ions present in simulated body fluid do not appear to adsorb or interact with the oxide film. Further studies to investigate the composition of the passive film are currently underway².

REFERENCES: ¹ A.W.E Hodgson, Y. Mueller, D. Forster, S. Virtanen, (2001) Electrochemical characterisation of passive films on Ti alloys under simulated biological conditions. *Electrochim. Acta* in print. ² A.W.E. Hodgson, S. Kurz, V. Fervel, S. Virtanen, S. Mischler, (2002) Electrochemical and surface characterization of passive films on CoCrMo in saline and simulated biological solutions, in preparation.

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