Passivity and Corrosion Behavior of Co-28Cr-6Mo Implant Alloy

S. Virtanen, S. Kurz-Hochstrasser, A. Hodgson
Swiss Federal Institute of Technology, Department of Materials
and
Institute of Materials Chemistry and Corrosion
ETH-Hoenggerberg, 8093 Zurich, Switzerland

Introduction

CoCrMo alloys are regarded as highly biocompatible materials and have been employed in the fabrication of prostheses since the 1940's. The biocompatibility is closely linked to the high resistance towards corrosion due to the spontaneous formation of a passive oxide film, the integrity of which has been strongly correlated to the chemical and mechanical stability of implants. Nonetheless, the release of metal into the body is a well-documented fact. Uniform passive dissolution resulting from the slow diffusion of metal ions through the passive film, transpassive dissolution under highly oxidizing conditions, the local breakdown of passivity as a consequence of localised forms of corrosion such as pitting or crevice corrosion, or as a consequence of mechanical events such as fretting corrosion are all possible mechanisms. However, the exact chemical, electrochemical and tribo-electrochemical mechanisms that lead to the release of metal from CoCrMo prostheses are not known.

With this work, the electrochemical properties of CoCrMo were investigated under simulated biological conditions. In particular, the effects of ions in the electrolyte solution, of pH, temperature, and of time of exposure to the biofluids as well as of specific polarization conditions on the passive behavior were studied. Furthermore, the electrolyte solution was collected for analysis by inductively coupled plasma mass spectroscopy (ICP-MS) to study metal ion release under *in vitro* conditions.

Major results

Electrochemical behavior

In simulated body fluid (sbf), the electrochemical behavior of the alloy is almost identical at room temperature and at 37°C. Also a variation of the pH value between pH 2 and 10 shows only a very minor effect on the corrosion behavior. Further, the electrochemical behavior is basically identical in sbf and NaCl solutions; hence, the specific ions present in sbf (e.g., Ca^{2+} and PO_4^{3-}) do not strongly interact with the surface of the CoCrMo alloy.

Aging in air leads to a slow increase in the protectiveness of the passive film; however the films formed in air are slowly modified at open-circuit potential in sbf and finally all show an identical behavior. The kinetics of passivation (aging of the passive film) is relatively slow .

Measurements of pure Co, Cr and Mo showed that Co is highly active at low applied potentials, whilst Cr could be seen to retrace the current potential response of the alloy in the passive region, indicating an increasing influence of Cr in the electrochemical behaviour of the alloy at these potentials. In particular, Cr was found to dominate the electrochemical properties of the alloy in the passive and transpassive states.

In the transpassive region, an additional current peak corresponding to oxidation of the Cr(III) oxide film into Cr(VI) species was observed. The Cr oxidation reaction is mass transport dependent, which indicates that Cr(VI) species are dissolved in the solution.

Chemical analysis of the electrolyte

For samples exposed to open-circuit potential or polarized in the passive region, only Co can be detected in the electrolyte - the concentration of Cr and Mo is below the detection limit.

Polarization in the transpassive region leads to a very strong increase in the metal ion concentration in the electrolyte - in this case all elements can be detected. It is noteworthy that the ratio of the metal ion concentration very nearly corresponds to the composition of the alloy; hence oxidizing conditions in the region of transpassivity of the alloy lead to a nearly stoichiometric dissolution of the alloy.

In order to simulate passive film destruction (electrochemical; without wear) / repassivation cycles, as could be encountered under mild rubbing conditions, samples were cyclically polarized between potentials in the cathodic and anodic (passive) region. This type of polarization treatment leads to a similarly strong enrichment of Co in the electrolyte as polarization in the transpassive region. However, cyclic polarization leads to a selective dissolution of Co out of the alloy.

Tissue analysis from in vivo experiments

Tissue samples retrieved from experimental sheep with cemented CrCrMo implants were analysed for evidence of Co, Cr and Mo, as a result of wear and or corrosion reactions at the surface of the metal implant. In all cases, a release of metal from the prosthesis has taken place. In addition, the concentrations of all three metal elements measured in the tissue increase with increasing instability of the implant. In all samples analysed, the concentration of Co always largely exceeded that of Cr and Mo. The ratio of the metal ions analysed in the tissue does not reflect the composition of the alloy; instead, a strong selective dissolution of cobalt was observed.

As described above, a similar selective dissolution mode could be observed *in vitro*, when the alloy was exposed to cyclic reduction/oxidation cycles. A comparison of the *in vitro* metal ion release modes with results from the *in vivo* studies will be carried out.