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Influence of alloying elements on the corrosion stability of CoCrMo implant alloy in Hank's solution

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Abstract

The behavior of a CoCrMo alloy and its components was studied in simulated physiological solution (Hank's solution) using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The passivation of all samples occurred spontaneously at the open circuit potential. The composition of the oxide films as a function of the solution components and the applied potential is discussed. The electrochemical properties of the spontaneously passivated electrodes at the open circuit potential were studied by EIS. The polarization resistance (R_p) and the electrode capacitance (C_{dl}) were determined. The higher R_p of the alloy than of the chromium pointed to the stabilizing effect of the other alloy components. The concentration of the metallic ions in a simulated physiological solution, measured by inductively coupled plasma-mass spectrometry, was in accordance with the values of both the R_p determined from EIS data and current densities measured with CV.

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1. Introduction

Metallic materials play an essential role in assisting with the repair or replacement of bone tissue that has become diseased or damaged. Metals are more suitable for load-bearing applications compared with ceramics or polymeric materials because they combine high mechanical strength and fracture toughness [1]. However, the main limitation of these metallic materials is the release of the toxic metallic ions that can lead to various adverse tissue reactions and/or hypersensitivity reactions [2]. The currently approved and commonly used metallic biomaterials include Co-based alloys, titanium and stainless steels. Each material has its own advantage. One of the main applications of CoCrMo alloys is in dental skeletal structures and orthopedic implants such as screws, pins and plates [3]. Their biocompatibility is closely linked to their high resistance towards corrosion which is attributed to the spontaneous formation of a passive oxide film. The integrity of the oxide film has been strongly correlated with the chemical and mechanical stability of implants. In spite of the chemical stability of the alloys, the release of metallic ions into the body tissue is well established [4–6]. It occurs by various mechanisms, including: (a) uniform passive dissolution resulting from the slow diffusion of metal ions through the passive film; and (b) the local breakdown of the passivity as a consequence of the various types of localized corrosion, or various mechanical events such a fretting corrosion. Since the oxide layer on the CoCrMo alloys determines the properties of the implant surface, its characteristics are very important. Yet, electrochemically oriented studies on the passivity of CoCrMo alloys are scarce [3,7–11].

Herein we aimed to study the corrosion stability of the CoCrMo alloy and the properties of the surface oxide layer

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in a simulated physiological solution (Hank's solution). As controls, the individual components, *i.e.* cobalt, chromium and molybdenum were also studied. The corrosion stability was estimated by determining both the polarization resistance and the concentration of the dissolved metallic ions in the solution. The study was performed using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). During the last three decades, EIS has proved to be advantageous for the characterization of the various oxide films on the metal surfaces. This technique requires minimal invasive procedures; *i.e.* neither the oxidation nor the reduction was forced to take place in the open circuit mode. From the EIS data we can obtain information about the passive film dissolution (the rate and type of the control) and the passive film characteristics (film thickness, passive film dielectric constant, diffusion coefficient of the diffusing species, etc.).

2. Experimental

The study was performed with spectroscopically pure cobalt, chromium and molybdenum and CoCrMo alloy (Good Fellow). The alloy was composed of 30 wt.% Cr, 6 wt.% Mo, and the remainder Co. The samples of Cr and alloy were cylindrical. The lateral surfaces of the cylinders were coated with polyester, exposing only the plane of the cylinder bases to the solution. The surface areas of the Cr and alloy samples were 0.385 cm^2 and 0.196 cm^2, respectively. The rectangular shaped samples of Co and Mo were embedded in the Teflon holders; their surface area was 1 cm^2. The electrodes were polished with SiC paper (600 grit) followed with diamond paste (30, 15, 6 and 1.5 μm), degreased in ethanol in an ultrasonic bath and rinsed with distilled water. Prior to each measurement, electrodes were polarized at −1.50 V *vs.* a saturated calomel electrode (SCE) to remove oxides that were air-formed at the surface.

Measurements were performed in Hank's solution, pH 6.8. Its composition was 8.00 g/L NaCl, 0.40 g/L KCl, 0.35 g/L $NaHCO_3$, 0.25 g/L $NaH_2PO_4 \times H_2O$, 0.06 g/L $Na_2HPO_4 \times 2\,H_2O$, 0.19 g/L $CaCl_2 \times 2H_2O$, 0.19 g/L $MgCl_2$, 0.06 g/L $MgSO_4 \times 7H_2O$ and 1.00 g/L glucose. All chemicals were of *p.a.* purity.

The experiments were performed in a two-compartmental glass cell at 298 K. The counter electrode was a large Pt-plate, and the reference electrode was a SCE. All potential values are reported *vs.* SCE. Measurements were carried out using an Solatron SI 1287 Electrochemical Interface and a Solatron SI 1255 HF Frequency Response Analyser.

The concentrations of the metallic ions released into solution were determined in ppb (μg/L) by high resolution inductively coupled plasma-mass spectrometry (HR ICP-MS, Element 2, Thermo Finnigan, Germany). The instrument settings were as follows. Resolutions ($m/\Delta m$): LR = 300, MR = 4000, HR = 10,000; Torch: Fasel typemm i.d.; Nebulizer: Micro Mist, AR40-1-F02, 0.2 mL/min; Spray Chamber: Jacketed Twister, 20 mL, quartz; Cones: Sample and skimmer – nickel, 1.1 and 0.8 mm; Sample uptake: ASX 510, CETAC autosampler; Internal standard: In (1 μg/L). The isotopic mass numbers used were Co 59, Cr 52, Mo 95 or 98.

All specimens with the known surface area (those of Co, Mo and CoCrMo alloy were about 4 cm^2, while Cr samples were about 10 cm^2) were surface-finished with waterproof emery paper of 400 and 1000 grit and then ultrasonically cleaned and placed in the high density polyethylene (HDPE) bottles containing 0.5 L Hank's solution both at pH = 6.8 and pH = 2. The HDPE bottles used for the immersion tests were carefully cleaned with 10 vol.% concentrated HNO_3 solution and thoroughly rinsed with ultra pure deionised water to remove impurities. All bottles were placed at room temperature 23 ± 2 °C. Every day the bottles were agitated in order to homogenize the solution. The concentrations of released metal ions in solutions were determined after 30 days of specimens' immersion. The calibration curves were created with six points obtained by increasing concentrations of standard. A test solution without a metal specimen was used to estimate the blank. From each separate solution, the aliquot of 5 mL was transferred to the sample bottle and acidified with concentrated HNO_3 (50 μL). Prior to ICP-MS analysis the indium standard was added to the sample. The quantity of metal released (μg/cm^2) was calculated using the following formula: (0.5 L)/[(metal concentration) − (blank)]/(surface area of the specimen).

3. Results and discussion

3.1. Cyclic voltammetry

Both CoCrMo alloy and its individual components (Co, Cr and Mo) were investigated in Hank's solution (pH 6.8) using cyclic voltammetry. The Co cyclic voltammogram recorded from −1.5 to 0.0 V is shown in Fig. 1. During the anodic sweep, the oxidation of the metal surface starts at around −0.9 V. The current increases up to −0.7 V, then slightly decreases up to −0.2 V showing a plateau after which a slight increase is observed. At $E > 0.0$ V the cobalt electrode undergoes pitting corrosion. Within the cathodic

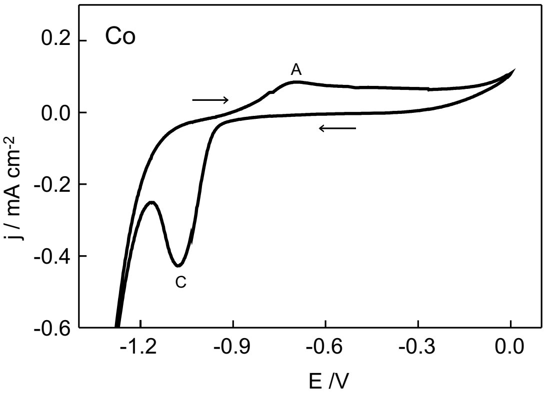

Fig. 1. Cyclic voltammogram of Co in Hank's solution, $v = 20\ mV\ s^{-1}$.

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