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# Study of overall and local electrochemical responses of oxide films grown on CoCr alloy under biological environments

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ABSTRACT

The interaction of the physiological medium and living tissues with the implant surfaces in biological environments is regulated by biopotentials that induce changes in the chemical composition, structure and thickness of the oxide film. In this work, oxide films grown on CoCr alloys at 0.5 V vs Ag/AgCl and 0.7 V vs Ag/AgCl have been characterized through overall and localized electrochemical techniques in a phosphate buffer solution and 0.3% hyaluronic acid. Nanopores of 10–50 nm diameter are homogeneously distributed along the surface in the oxide film formed at 0.7 V vs Ag/AgCl. The distribution of the Constant Phase Element studied by local electrochemical impedance spectroscopy showed a three-dimensional (3D) model on the oxide films grown at 0.5 V vs Ag/AgCl and 0.7 V vs Ag/AgCl. This behaviour is especially noticeable in oxide films grown at 0.7 V vs Ag/AgCl, probably due to surface inhomogeneities, and resistive properties generated by the potentiostatic growth of the oxide film.

## 1. Introduction

The kinetics of the dissolution and formation of the passive film on CoCr alloys in the physiological fluids are mainly influenced by factors such as the type and chemical composition of the alloy [1], long-term exposure to aggressive ions [2–6], pH changes and temperature of the biological environment. However, this is not only inherent to the interaction of physiological medium with the surface but also to the electrical interactions induced by the living tissues, known as biopotentials. In vivo biopotentials control the normal growth and development of cells and tissues inducing a continuous stimulation of the metallic surface.

The insertion of permanent joint replacements activates injury potentials that alter the stable potential patterns of intact tissue after trauma and during healing. At this period, currents of about 1–100 $\mu A/cm^2$ can be measured in injured tissues that imply, considering the resistivity of soft tissues as 100 $\Omega$, electric fields of 1–10 mV/cm [7]. Bone tissue has a piezoelectric behaviour (i.e., electric potential in response to applied forces) that can modify the electrochemical potential of the metallic implants. The physiological environment in combination with constant cyclic loading on the implants, such as wear-corrosion phenomena and micromotion or fretting-corrosion, favours the activation of the passive film as a consequence of the continuous activation/repassivation cycles [8]. These continuous and dynamic processes not only weaken the surface performance but also lead to an increase in the debris around the implant. To date debris produced in in vivo wear-corrosion from articulating surfaces has been identified as one of the most important phenomenon causing the failure of the implant. It is interesting not to forget that the electrical implications of corrosion and its effect on the surrounding tissue can be strongly important on the bone healing. Bone cells are sensitive to electrical signals, stimulating or inhibiting the activity of osteoblast or osteoclast cells and, consequently, breaking the balance between both [9]. Therefore, from the point of view of the implant, a wide potential range is imposed on the surface not only created by the physiological medium (pH, nature and concentration of ion, etc.) but also by that generated by the live tissue.

All these biochemical factors favour several processes on the surface of the metallic implants: slow diffusion of metal ions through the passive film; dissolution and/or growing of the oxide film under high oxidizing conditions, caused by the debris products from cell metabolism and/or the polarization arising from living tissues; and, local breakdown of passivity, due to pitting or crevice corrosion enhanced by the changing pH values and nature of aggressive ions. All of them offer a wide electrochemical potential range occurring in the implantation site on the metallic biomaterial.

In this work, overall and localized electrochemical techniques have been used to characterize the oxide films grown on the CoCr alloy under potentials whose current densities are similar to those reported

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for injured tissues (1–100 μA/cm$^2$). In an attempt to simulate as closely as possible, the real situation of healthy joints [10], the authors have chosen a phosphate buffer solution with 0.3% hyaluronic acid as an electrolyte for the tests. In the literature many solutions have been used to simulate in vivo conditions and identify their tribological roles on artificial joints. The major difference between synovial fluid (SF) and other body fluids derived from plasma is its high content of protein and the presence of hyaluronic acid, which is the main component of SF and is a known joint lubricant.

## 2. Materials and methods

### 2.1. Material

The CoCr alloy with high carbon content supplied by BIOMET Spain Orthopaedics (Valencia), following standard ASTM F75 (Table 1), was used. This alloy was supplied as a disk 38 mm diameter and 4 mm thick, as “double heat-treated” samples, i.e. solution treatment (ST) followed by hot isostatically pressing (HIP). The sample preparation consisted of grinding on SiC paper from mesh 400 to mesh 1200, followed by mechanical polishing with 3 μm diamond paste, ultrasonic cleaning in alcohol and deionized water successively and then air dried.

### 2.2. Corrosive media

The aqueous medium used as electrolyte was based on the Phosphate Buffer Solution: 0.2 g/L KCl, 0.2 g/L $KH_2PO_4$, 8 g/L NaCl and 1.150 g/L $Na_2HPO_4$ (anhydrous) (PBS) adding 0.3% hyaluronic acid (hereafter PBS-HA). The concentration of hyaluronic acid for the overall electrochemical measurements (DC and AC techniques) was 0.3%, in agreement with the range reported for healthy joints [10] simulating the synovial fluid. This solution was diluted 10 times for local impedance measurements. The motivation for using a reduced concentration for the local impedance measurements was the decrease of the current resolution at high conductivity values of the electrolyte.

### 2.3. Overall electrochemical techniques

All electrochemical experiments such as the measurement of the corrosion potential ($E_{corr}$), Electrochemical Impedance Spectroscopy (EIS), chronoamperometry and anodic polarization curves were conducted in a three-electrode cell connected to a Gamry Instrument Potentiostat/Galvanostat/FRA (Reference 600). An Ag/AgCl (NaCl 3 M) electrode was used as the reference electrode, a platinum wire as the counter electrode and the CoCr alloy (0.78 cm$^2$) as the working electrode. Electrochemical tests were performed in triplicate and the $E_{corr}$ was previously measured for 1 h to obtain the stabilization before the application of potentials far from the stationary state.

Single sweep potentiodynamic polarization curves were performed at 10 mV/min scanning rate from the $E_{corr}$ up reaching a potential of 1 V in the noble direction, which is considered approximately as the maximum potential that a metallic biomaterial can reach in the human body [11]. Then, a reverse scan was applied until reaching the protection potential. The passivation currents, $I_p$, and breakdown potentials, $E_{bd}$, were obtained.

The chronoamperometric test was performed by applying potentials for 3600 s. Two different potentials (0.5 V vs Ag/AgCl and 0.7 V vs Ag/AgCl) from the anodic polarization curves were chosen.

The EIS tests were performed on the previously polarized samples at the $E_{corr}$ by applying a sinusoidal wave of 10 mV amplitude at a frequency range from $10^5$ Hz–$10^{-1}$ Hz, spaced logarithmically (five per decade). The EIS results were analysed by fitting the experimental impedance data with the properly electrical equivalent circuit. The parameters of the electrical equivalent circuit were calculated by fitting the impedance function to the measured spectra using a non-linear least-squares program (NLLS program) with Z-plot/Z-view software. The criteria used to estimate the quality of the fitting were the lowest chi-square value ($\chi^2$) and estimative errors (in %) for all the components.

**Table 1**
Chemical composition of high carbon CoCr alloy.

| | C | Co | Cr | Mo | Ni | S | P | Al | W | Mn | Fe | Si | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| HC | 0.22 | 62 | 29.4 | 6.4 | 0.1 | 0.004 | 0.001 | 0.01 | 0.03 | 0.7 | 0.16 | 0.7 | 0.16 |

### 2.4. Characterization of grown-oxide films

The morphology of the grown-oxide films was evaluated with a Scanning Electron Microscope equipped with a Field Emission cathode (FE/SEM), Hitachi 6500FEG. The images were taken at 7 kV acceleration voltage.

Photoelectron spectra were recorded using a Fisons MT500 spectrometer equipped with a hemispherical electron analyser (CLAM2) and a non-monochromatic Mg Kα X-Ray source operated at 300 W. The samples were fixed on small flat discs supported on an XYZ manipulator placed in the analysis chamber. The residual pressure in this ion-pumped analysis chamber was maintained below $10^{-9}$ Torr during data acquisition. The spectra were collected at a pass energy of 20 eV, which is typical of high-resolution conditions. Spectra were analysed using CasaXPS software. The intensities were estimated by calculating the area under each peak after subtraction of the S-shaped background and fitting the experimental curve to a combination of Lorentzian and Gaussian lines of variable proportions. Although specimen charging was observed, it was possible to determine accurate binding energies (BEs) by referencing to the adventitious C 1s peak at 285.0 eV. The maximum allowed variation of the binding energy was ±0.2 eV relative to the value specified for peak centre. The atomic ratios were computed from the peak intensity ratios and the reported atomic sensitivity factors [12].

### 2.5. Localized techniques

#### 2.5.1. Scanning Kelvin probe

Corrosion potential maps of the CoCr surfaces were acquired by means of scanning Kelvin probe (SKP). The measurement system of SKP was developed by GS Frankel, M Stratmann et al. [13]. The equipment consists of a needle that oscillates at a fixed frequency, an AC backing potential, and software analysis and control schemes. This technique can also control the distance between the tip and sample, thereby tracking the topography of the sample. The technical specifications of the SKP used are reported in [13]. SKP tests were performed at 20 °C and 99.8% relative humidity. The samples were placed in a stainless steel chamber, which was purged continuously with humidified air to maintain the relative humidity (RH) at about 99.8%, resulting in a final thin film of water on the metallic surface. After the thin layer was formed, a plane-ended cylindrical Ni-Cr probe with a diameter of 50 μm was used as needle, and was moved over the samples with three stepping motors for x, y and z directions. All areas were performed stepwise and fully automated, while the sample/needle distance was maintained along the scan. Measurements were performed over a scanned area of 9000 × 9000 μm$^2$. Before measuring, the Kelvin probe was calibrated by using a standard Cu/$CuSO_4$ solution to establish a relation between the work function and corrosion potential. SKP potentials are given relative to the potential of the Standard Hydrogen Electrode (SHE).

#### 2.5.2. Localized Electrochemical Impedance Spectroscopy

This technique is based on the pioneering work of Isaac's group [14,15]. Fundamentals of Localized Electrochemical Impedance Spectroscopy (LEIS) measurements are detailed in Refs. [16–18]. LEIS measurements were performed with a PAR Model 370 Scanning Electrochemical Workstation that consisted of a 370 scanning control