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Corrosion behaviour of a novel hybrid Co/UHMWPE composite biocoating with potential application as a biomaterial

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Abstract. In the present paper we report the acquisition of a composite coating based on cobalt and ultra high molecular weight polyethylene (Co/UHMWPE) as a novel hybrid biocoating with potential application as a biomaterial, using the electrochemical deposition technique at room temperature. Three different concentrations of UHMWPE, namely 20 gL^{-1}, 30 gL^{-1} and 50 gL^{-1}, were used in a cobalt sulphate bath. The corrosion behaviour of the Co/UHMWPE hybrid biocoating was studied in comparison with pure cobalt coating at different exposure times in Hanks' solution as simulated body fluid (SBF), using the electrochemical impedance spectroscopy method. The polarisation resistance of the Co/UHMWPE hybrid biocoating increased during immersion time in the SBF medium in comparison to the pure cobalt coating. An easy way to prepare Co/UHMWPE hybrid biocoatings was identified: namely, by properly incorporating UHMWPE microparticles into a Co matrix using electrocodeposition from a cobalt electrolyte plating bath with increasing corrosion resistance in a solution simulating body fluid.

Introduction

The codeposition of various types of non-metallic particles with a metal during electrolysis has been developed for various applications. These metal matrix hybrid coatings are widely used as functional materials due to their improved properties compared to the plain metal. Most research has focussed on nickel matrix composites [1–4], though other metals have been explored, to a lesser extent, as matrices. Cobalt-based coatings can offer properties (hardness and corrosion resistance) comparable with those of nickel composites [5–7]. The data in the literature shows that little research on the codeposition of ceramic particles with electrolytic cobalt, such as SiC [7], ZrO_2 [8], lanthanide oxides [9] and CeO_2 [10], has been performed. Moreover, no research treating the synthesis and properties of Co hybrid coatings containing polymers as dispersed particles, including in codeposition with cobalt, could be found in the literature.

In the present investigation, tests to obtain and characterise surface-modified cobalt with ultra high molecular weight polyethylene (UHMWPE) microparticles (mean diameter: 10 μm) were conducted in order to improve corrosion resistance in simulated body fluid solutions. The characterisation of the Co/UHMWPE hybrid biocoatings thus obtained was done in terms of surface morphology, structure, thickness and corrosion resistance. The novelty of this study consists of the design of a hybrid Co/UHMWPE composite biocoating using the electrocodeposition method in order to obtain a synergy of the performances of cobalt and UHMWPE as biocoatings applied as biomaterials.

Experimental

Preparation of pure Co and Co/UHMWPE hybrid composite coatings. Co/UHMWPE hybrid composite coatings were electrolytically deposited from a cobalt sulphate-chloride plating bath

(with a cobalt sulphate concentration of 300 gL^{-1}) to which UHMWPE microparticles were added in various concentrations. The mean diameter of the UHMWPE particles, supplied by Ticona (Germany), was 10 μm. The concentrations of the UHMWPE dispersed phase added to the electrolyte were 20 gL^{-1}, 30 gL^{-1} and 50 gL^{-1}. The suspension was stirred for 24 hours prior to codeposition.

Electrocodeposition was carried out in a typical three-electrode cell, where 304L stainless steel plates were used as working electrodes, a pure cobalt foil (99.9% purity) as the auxiliary electrode, and a mercury/mercury sulphate (Hg/Hg_2SO_4) with K_2SO_4 saturated solution as the reference electrode (E= + 650 mV vs normal hydrogen electrode – NHE). During the codeposition process, the electrolytic bath was stirred, using a magnetic stirrer at a rate of 600 rpm (determined in preliminary tests to be optimum for this electrochemical setup), in order to keep the UHMWPE microparticles in suspension. The applied current density and the codeposition time were calculated to obtain layer thicknesses of about 30 μm.

Electrodeposition of the coatings in the absence and presence of the dispersed phase was carried out galvanostatically with a VoltaLab PGZ 100potentiostat/galvanostat. The following hybrid composite coating systems were comparatively characterised: Co/UHMWPE (0 gL^{-1}), Co/UHMWPE (20 gL^{-1}), Co/UHMWPE (30 gL^{-1}) and Co/UHMWPE (50 gL^{-1}).

Characterisation of the coatings. The surface morphology and the chemical composition of the pure Co coating and electrochemically-obtained Co/UHMWPE hybrid biocomposite coatings were analysed using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The coating thicknesses were analysed by SEM using a cross section of the samples.

The corrosion tests were performed using a VoltaLab PGZ 100 potentiostat/galvanostat. The corrosion behaviour of the Co/UHMWPE hybrid biocoatings was compared with that of the pure cobalt coating at different exposure times in simulated body fluid (SBF) using the electrochemical impedance spectroscopy (EIS) method. EIS studies were carried out at open circuit potential after 0.5 hour and 168 hours of immersion, respectively, and the impedance spectra were acquired in a frequency range of 10^5–10^{-2} Hz, with an AC perturbation amplitude of 10 mV. The corrosion experiments were performed in a conventional three-electrode cell consisting of a working electrode (WE) made of pure Co coating and Co/UHMWPE hybrid biocomposite coatings (20 gL^{-1}, 30 gL^{-1} and 50 gL^{-1}), a Ag/AgCl reference electrode with KCl saturated solution (E = +200 mV vs. NHE), and a Pt-Rh grid as auxiliary electrode. In this study, Hanks' solution (8.8 gL^{-1} NaCl, 0.4 gL^{-1} KCl, 0.14 gL^{-1} $CaCl_2$, 0.35 gL^{-1} $NaHCO_3$, 1 gL^{-1} $C_6H_6O_6$, 0.2 gL^{-1} $MgSO_4 \times 7H_2O$, 0.1 gL^{-1} $KH_2PO4 \times H_2O$, 0.06 gL^{-1} $Na_2HPO_4 \times 7H_2O$) with a pH of 7.4 was used as a simulated body fluid (SBF).

Results and discussion

The surface morphology of the coatings was studied using SEM. The SEM micrograph of the pure Co coating represented in Fig. 1a is characterised by a needle-like microcrystalline structure typical of cobalt electrolytic deposits with hexagonal crystallographical system; the grains are characterised by clear borders. The punctual SEM-EDX analysis of the Co/UHMWPE (20 gL^{-1}) hybrid coating on stainless steel (Fig. 1b) shows the presence of UHMWPE dispersed phase in the cobalt matrix as well as differences in the surface morphologies of the hybrid coatings compared with those of the pure cobalt coatings obtained under the same conditions. With the addition of UHMWPE microparticles (20 gL^{-1}) in the electrolytic bath, the borders of the grains became lightly blurred and the mean grain size was reduced compared to the pure Co coating under the same preparation conditions.

In order to confirm that the current density and codeposition time were effectively applied for obtaining coating thicknesses of about 30 μm, the actual thicknesses were analysed, using SEM, on a cross section of the samples (Fig. 2a and b).

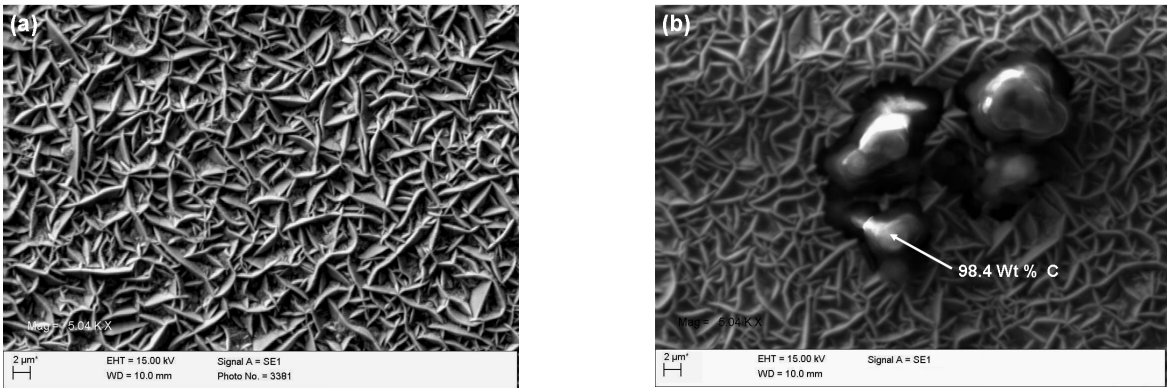

Fig. 1. (a) SEM morphology of Co/UHMWPE (0 gL^{-1}) and (b) SEM+EDX analysis of Co/UHMWPE (20 gL^{-1}) hybrid composite coating; both were prepared under the same conditions.

The coating thicknesses determined using SEM on cross sections are in full accordance with those calculated theoretically. The cross-sectional scanning electron micrographs of electroplated surfaces confirm strong adhesion of the coatings to the stainless steel support. Also, Fig. 2b confirms the presence of UHMWPE particles deep within the coating, not only on the surface.

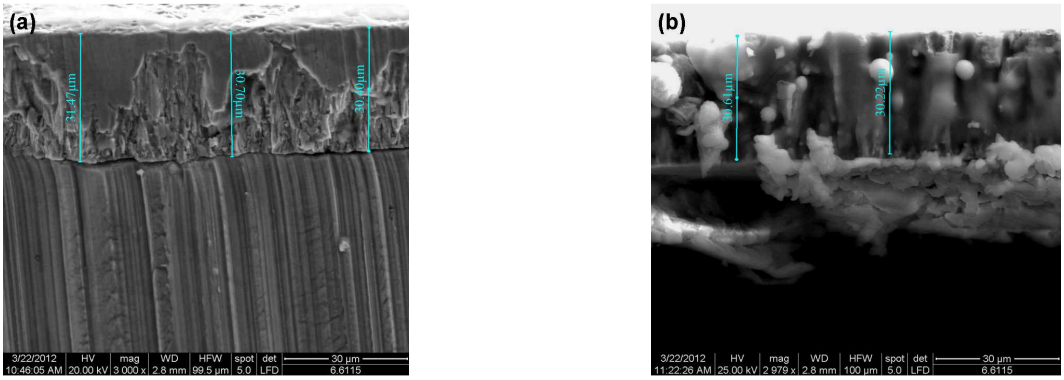

Fig. 2. Cross-section SEM image of the Co/UHMWPE electrodeposited biohybrid coatings: (a) Co/UHMWPE (0 gL^{-1}) and (b) Co/UHMWPE (50 gL^{-1}), both prepared under the same conditions.

The Nyquist representations of impedance diagrams obtained for all electrodeposited coatings are presented in Fig. 3a (after 0.5 hour of immersion) and in Fig. 3b (after 168 hours of immersion).

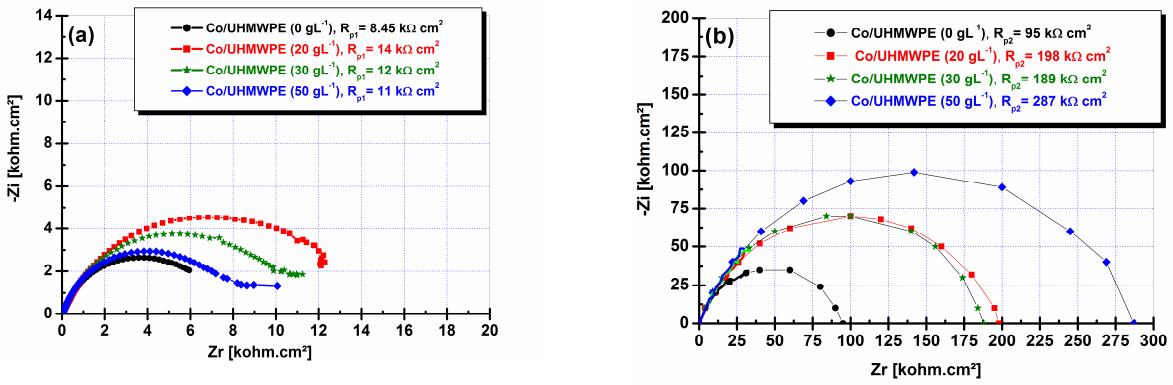

Fig. 3. Nyquist representation of impedance diagrams of tested surfaces in Hanks' solution: (a) 0.5 hour and (b) 168 hours following immersion. The symbols represent experimental data for: (●) Co/UHMWPE (0 gL^{-1}), (■) Co/UHMWPE (20 gL^{-1}), (*) Co/UHMWPE (30 gL^{-1}) and (♦) Co/UHMWPE (50 gL^{-1}). The broken lines represent the corresponding fitted diagrams.

From Fig. 3a and b it can be clearly seen that the polarisation resistance (Rp) of all of the Co/UHMWPE hybrid composite coatings studied increases during immersion time in Hanks' solution to a greater extent than that of pure Co coating. For example, the value of the polarisation resistance of Co/UHMWPE (50 gL^{-1}) is about three times higher than that of pure cobalt.

Conclusions

The incorporation of UHMWPE microparticles modifies the surface morphology of a Co matrix, as demonstrated by SEM/EDX analysis. Cross-sectional scanning electron micrographs of electroplated surfaces confirm the strong adhesion of the coatings to the stainless steel support and also confirm the presence of UHMWPE particles deep within the coating. The corrosion resistance, and therefore the functionality, of Co/UHMWPE electrodeposited biohybrid coatings in SBF solution is three times greater than that of pure cobalt coating.

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