Corrosion of Au–Pd–In alloy in simulated physiological solutions

K. LEINARTAS¹, P. MIEČINSKAS¹, A. SUDAVIČIUS¹, D. JELINSKIENĖ¹, R. JUŠKĖNAS¹, V. LISAUKAS², B. VENGALIS² and E. JUZELIŪNAS¹*

¹Institute of Chemistry, A. Goštauto 9, 2600 Vilnius, Lithuania
²Semiconductor Physics Institute, A. Goštauto 12, 2600 Vilnius, Lithuania,
(*author for correspondence, fax: (3702) 617018, e-mail: ejuzel@ktl.mii.lt)

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Abstract

The corrosion of Au–Pd–In alloy, which is of great importance in dentistry, has been studied using an electrochemical quartz crystal microbalance (EQCM) in simulated physiological solutions. The alloy was deposited on quartz substrates by means of magnetron sputtering (MS). Analysis performed using X-ray photoelectron spectroscopy showed that the chemical composition of the sputtered deposit was similar to that of the MS target made of conventional casting alloy. Investigations by X-ray diffraction indicated a crystalline structure of the MS alloy. The electrochemical and corrosion behaviour of the Au–Pd–In alloy was studied in three simulated physiological solutions: 0.9 M NaCl, 0.1 M NaCl + 0.1 M lactic acid and artificial saliva. Determination of break down potential was complicated by the anodic gold dissolution due to formation of a chloride complex. The onset of anodic currents, therefore, indicated not the potential at which the passive layer starts to be destroyed, but the exceeding of the Au/AuCl₄⁻ equilibrium potential, which does not directly reflect corrosion resistance. The EQCM measurements under open circuit conditions indicated corrosion as an increase in mass, caused by the accumulation of corrosion products on the alloy surface. The increase in mass in acidic solution (pH 2.2) was similar to that in neutral solution (pH 6.5), which implies dissolution of corrosion products to be insignificant.

1. Introduction

Au–Pd–In alloys are widely used in medical practice, especially in dentistry. Due to good biocompatibility, high corrosion resistance and ease of casting and soldering the gold-based alloys are used to produce artificial joints, crowns, bridges and fillings in dentistry. In pathologic states, body fluids can be slightly acidic (pH 5.3–5.6), and so represent a corrosive environment [1]. Moreover, various components of body fluids, such as chloride ions, proteins, amino acids, dissolved oxygen and microorganisms may affect the metal surface state and reduce the corrosion resistance of implants. Due to in vivo corrosion, the functionality of implants may decrease and, furthermore, the release of metal ions into the organism may cause allergic reactions, tissue irritation etc.

To predict material resistance to in vivo corrosion, these materials are usually studied in artificial physiological solutions by using electrochemical methods. Thus, the corrosion potential, the breakdown potential, the rest potential and the polarization resistance have been used to assess the corrosion resistance of gold-based alloys [2–4].

The selection of electrochemical criteria for metallic biomaterials testing is often complicated. It has been shown that the impedance spectra in a low frequency domain did not always exhibit a clear resistive behaviour from which the polarization resistance could be derived and the corrosion current calculated [5–7]. Moreover, biomaterials in simulated physiological solutions often failed to exhibit clear Tafel regions, from which the corrosion current could be obtained. Another commonly used method is the determination of breakdown potentials [2–4]; however, as will be shown, application of this method to gold alloys in physiological solutions is complicated by anodic gold dissolution due to formation of a complex with chloride.

An effective alternative in corrosion testing of gold-based alloys is electrochemical quartz crystal microgravimetry (EQCM). Advantages of the method include the nanogram resolution for mass changes, the continuous information (i.e., the rate of mass change at any practical time interval) and the possibility to perform experiments in both gaseous and liquid environments. In this work an attempt has been made to apply EQCM to corrosion studies of Au–Pd–In alloy in artificial physiological solutions. The greatest difficulty in the use of EQCM as a corrosion sensor arises from coating the quartz with an alloy film, whose physical-chemical properties and, consequently, corrosive behaviour does
not differ greatly from the cast specimen. This problem has been solved in this work by using magnetron-sputtering (MS) technique.

2. Experimental details

The target for magnetron sputtering was made from commercially available Au–Pd–In casting alloy (BegoCer®G), whose exact composition is given in Table 1. The vacuum in the magnetron-sputtering chamber was maintained at 10⁻⁶ mm Hg. Working gas was Ar and its pressure was maintained at 0.1-0.2 Pa. The temperature in the chamber was about 100 °C. The Ar ionization current was 60 mA and the voltage was 600 V. The sputtering duration was 6-8 min, which corresponded to a coating thickness of about 0.15 μm. The set up of magnetron-sputtering apparatus and more details about the MS procedure used are given elsewhere [7, 8].

The coating composition was analysed by X-ray photoelectron spectroscopy (XPS) using surface etching by ionised argon. The spectra were recorded by an Escalab MK spectrometer (Great Britain) using X-radiation of MgKα (1253.6 eV, pass energy of 20 eV). The samples were etched in the preparation chamber by ionized argon at a vacuum of 5 × 10⁻³ Pa. An accelerating voltage of about 15 kV and a beam current of 20 μA cm⁻² were used. Etching was performed at a current of 100 μA, which corresponded to an etching rate of about 20 nm min⁻¹. The data on binding energies were from [9, 10].

The EQCM experimental device was analogous to that described in [11]. Quartz discs (AT plane) were used, their fundamental frequency being f₀ = 5 MHz and radius r = 15 mm (produced by KVG Quartz Crystal Technology GmbH, Germany). Both quartz sides were plated with the same alloy; the coatings acted as excitation electrodes in the oscillation circuit. The crystals were mounted in a special window of a Teflon cell, with one of the sides being exposed to the solution compartment and the other one facing air. The actual electrode area, which contacted the solution, was 0.78 cm². The EQCM measurements were started several seconds after the cell had been filled with solution.

Experiments were performed in the solutions recommended for metallic biomaterials testing by standards DIN 50905, DIN EN ISO 1562 and AFNOR S 90-701, respectively: (i) 0.9 M NaCl, (ii) 0.1 M NaCl + 0.1 M lactic acid, and (iii) artificial saliva (g l⁻¹): Na₂HPO₄ – 0.26; NaCl – 0.67; KSCN – 0.33; KH₂PO₄ – 0.2; NaHCO₃ – 1.5; KCl – 1.2. These solutions were prepared using reagents of analytical grade purity and triply distilled water.

In some experiments the BegoCer®G alloy disc was used as the working electrode (the chemical composition is given in Table 1). The electrode surface was polished by an abrasive SiC paper (grade 1000), rinsed with alcohol and water, dried under ambient conditions and mounted in the window of the cell for EQCM measurements described above. The actual area of the electrode was 0.78 cm².

A saturated Ag/AgCl electrode was used as the reference electrode, and all potentials in this paper were referred to that electrode. A platinum foil served as a counter electrode. The solutions were deoxygenated by using Ar (99.99%)

Voltammetric measurements were conducted by a PS-305 potentiostat (Elchena, USA) and a IM6 apparatus (Zahner, Germany).

3. Results and discussion

3.1. Voltammetric investigations

Figure 1 shows the cyclic voltammogram for Au–Pd–In in the solution containing 0.1 M NaCl + 0.1 M lactic acid (pH 2.3). When sweeping the potential in the positive direction, the electrode exhibits a passive behaviour in the region E = 0-0.8 V. At higher potentials, the anodic current appears with a peak at about 1.4 V. The peak height increased both with the chloride concentration and with the potential sweep rate (the

![Cyclic voltammogram recorded for Au-Pd-In alloy in the solution 0.1 M NaCl + 0.1 M lactic acid (pH 2.3). Potential sweep rate 10 mV s⁻¹.](image-url)

<table>
<thead>
<tr>
<th>Depth/nm</th>
<th>Au (Target) (%)</th>
<th>Pd</th>
<th>In</th>
<th>Ru</th>
<th>Ga</th>
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<tr>
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<td>52</td>
<td>39.7</td>
<td>6.8</td>
<td>0.3</td>
<td>1.2</td>
</tr>
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<td>62.0</td>
<td>26.4</td>
<td>10.0</td>
<td>0.17</td>
<td>1.47</td>
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<tr>
<td>10</td>
<td>53.2</td>
<td>39.1</td>
<td>6.7</td>
<td>0.14</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Table 1. Compositions (in wt %) of the Au–Pd–In target and the alloy deposited on quartz crystal by magnetron sputtering. (Samples were analysed by XPS after surfact sputtering by ionized argon)