Internal stress in multilayer silver–bismuth coatings

I. KRASTEV1*, T. VALKOVA1 and A. ZIELONKA2
1Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
2Forschungsinstitut für Edelmetalle und Metallchemie, 73525 Schwäbisch Gmünd, Germany
(*author for correspondence, e-mail: krastev@ipchp.ipc.bas.bg)

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Abstract

An investigation was carried out on the influence of electrodeposition conditions on internal stress of cyclically modulated Ag–Bi alloys. Pulse currents of different duration and height were used, leading to different composition and thickness of the deposited sublayers, and the resulting changes in the internal stress were measured in situ. The investigated multilayer coatings with Bi contents up to 20 wt.% reveal a positive (tensile) internal stress, and at Bi contents higher than 20 wt.% the internal stress is negative (compressive). The possibility of deposition of stress-free coatings is shown.

1. Introduction

In an effort to reduce some of the disadvantages of electrodeposited silver coatings, e.g. poor hardness and wear resistance, susceptibility to tarnishing and relatively high friction coefficient, silver is alloyed with different metals. In most of the cases alloys containing small amounts of the alloying element are used, leading to improvement in the mechanical parameters of the coating, mainly when solid solutions and intermetallic compounds of silver with the respective metals are formed. In the latter case internal stress in the electrodeposited coating originating from the differences in the size of various metal atoms may result in an increase in hardness and wear resistance in coatings [1]. Similar conclusions have been derived during the investigation of the Ag–Sb system [2, 3].

The Ag–Bi alloy is used in the field of electronics, communication equipment production and for coating subjected to operation under hard conditions [4, 5]. The alloy is deposited mainly in alkaline electrolytes. In previous work we have studied the electrochemical relationships during the electrodeposition of silver [6], bismuth [7] and Ag–Bi alloy [8, 9].

According to the phase diagram bismuth displays a very low solubility (up to 3 wt.%) in solid-state silver [10]. The maximum solubility of bismuth in silver in the electrodeposited alloy reaches approximately 2.5 wt.% [11] and higher concentrations should lead to the appearance of a second phase in the electroplated coating.

In many cases when investigating cross-section cuts of alloy coatings (e.g. Ag–Sb, Ag–Pb, etc.) it is established that they display a lamellar, layered structure. In similar cases the coatings are composed of darker and lighter lamellas containing larger or smaller amounts of the alloying element. The Ag–Bi alloy coatings are heterogeneous, two-phase and are composed of regions containing almost pure silver or pure bismuth [12]. The spatial separation of the two phases leads to the formation of a columnar structure, onto which in some cases a superpositioned lamellar structure is observed. Some of the properties of the alloy coatings electrodeposited under various conditions are described in a previous paper [12]. For example, when the percentage of bismuth in the coating increases, negative internal stress is produced as a result of both the stretching of the silver lattice at low bismuth concentration and the stress of the pure bismuth phase of the heterogeneous alloy coatings [12]. The formulation of the electrolyte is optimised in such a way that offers a possibility to electrodeposit Ag–Bi alloy coatings with random percentage composition; i.e. coatings containing bismuth within the range 0–100% may be plated [9].

The present paper is aimed at the electrodeposition of multilayer cyclically modulated Ag–Bi alloy coatings and investigation of the internal stress as a function of the composition and thickness of the separate sublayers.

2. Experimental

The composition of the electrolyte is presented in Table 1. The method for the preparation of the electrolyte is described in a previous paper [9].
The multilayer coatings were electrodeposited in a single bath by galvanostatically changing the current between two different levels, corresponding to the electrodeposition of alloys with higher or lower bismuth content. The current pulses were applied using a programmable pulse generator Pragmatic Instruments 2411A through a bipolar operational amplifier (Kepco, BOP 20–10 m).

The internal stress of the coatings was measured with the Stalzer instrument [13] based on the bent cathode method. The experimental equipment and the equation for calculating internal stress are described in a previous paper [14]. The signal obtained by the sensor of the instrument is connected via a suitable interface to a PC for further processing and storage. The figures concerning internal stress in the present paper show this signal, which provides more information than the stress value itself [3].

In some cases, parallel to these measurements the potential of the working electrode resulting from the applied current pulses was determined. Registration of the alterations of the potential was carried out with a potentiosstat–galvanostat model M270 made by the PAR Company using a SCE reference electrode. The latter was fixed in a separate cell containing 3 m KCl aqueous solution and the connection with the Haber–Luggin capillary in the electrodeposition and stress measurement cell was by a 3 m KCl filled electrolytic bridge. The working electrodes were copper plates 10.5 × 1 × 0.03 cm onto which the alloy coating was electrodeposited on the front face upon an area of 7 × 1 cm. The rear face of the plate was insulated with a suitable varnish.

The composition and thickness of the electrodeposited coatings were determined by X-ray fluorescent analysis with a Fischerscope XDVM-WW instrument. Pure silver anodes were used. All experiments were carried out at room temperature.

### 3. Results

Figures 1 and 2 show the changes of the sensor signal related to the internal stress during the electrodeposition of both monolayer and multilayer coatings. The individual sublayers of the multilayer coatings were plated at current densities identical to the values used for the electrodeposition of the corresponding monolayer coatings.

The internal stress of the coatings electrodeposited at 0.2 A dm⁻² have low positive values, typical for pure silver plates deposited using similar electrolytes [3, 15].

At higher current densities (0.8 A dm⁻²) negative internal stress is registered, also in accordance with relationships established during other investigations [12]. When multilayer coatings 18 μm thick are deposited at the stated current densities (1:1:2=0.8:0.2 A dm⁻²; t₁:t₂=1:4) characteristic regions on the curves showing the changes of the sensor signal vs. time are registered, corresponding to the internal stress in the coating electrodeposited at one of the two current densities (Figure 1). The internal stress of this multilayer system at

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**Table 1. Electrolyte composition**

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration /g dm⁻³</th>
<th>Concentration /mol dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag as KAg(CN)₂</td>
<td>8</td>
<td>0.074</td>
</tr>
<tr>
<td>Bi as BiONO₃</td>
<td>18</td>
<td>0.086</td>
</tr>
<tr>
<td>NaOH</td>
<td>26</td>
<td>0.64</td>
</tr>
<tr>
<td>KNaC₆H₅O₇·4H₂O</td>
<td>60</td>
<td>0.213</td>
</tr>
</tbody>
</table>

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**Fig. 1.** Change of the sensor signal with time. Cₐg=8 g dm⁻³, Cₕp=18 g dm⁻³; J₁:J₂=0.8:0.2 A dm⁻²; t₁:t₂=1:4 (A) monolayer, 0.2 A dm⁻², 0.7 wt.% Bi, 12.5 μm, (U–Uₚₙₗ) + 0.02 V (B) monolayer, 0.8 A dm⁻², 50 wt.% Bi, 26.3 μm (a) 4 sublayer, 14.0 wt.% Bi, 18.1 μm, (U–Uₚₙₗ) + 0.005 V (b) 8 sublayer, 18.3 wt.% Bi, 18.2 μm, (U–Uₚₙₗ) + 0.01 V (c) 16 sublayer, 20.2 wt.% Bi, 18.9 μm, (U–Uₚₙₗ) + 0.01 V (d) 40 sublayer, 22.2 wt.% Bi, 18.3 μm, (U–Uₚₙₗ) + 0.01 V (e) 160 sublayer, 26.2 wt.% Bi, 18.5 μm, (U–Uₚₙₗ) + 0.02 V.

**Fig. 2.** Change of the sensor signal with time. Cₐg=8 g dm⁻³, Cₕp=18 g dm⁻³; J₁:J₂=0.8:0.2 A dm⁻²; t₁:t₂=1:4 (A) monolayer, 0.2 A dm⁻², 0.7 wt.% Bi, 12.5 μm (B) monolayer, 0.8 A dm⁻², 50 wt.% Bi, 26.3 μm (a) 160 sublayer, 26.2 wt.% Bi, 18.5 μm (b) 400 sublayer, 28.2 wt.% Bi, 20.4 μm (c) 800 sublayer, 26.4 wt.% Bi, 18.9 μm (d) 8000 sublayer, 24.5 wt.% Bi, 19.0 μm (e) 16000 sublayer, 25.8 wt.% Bi, 20.6 μm (f) 40000 sublayer, 33.4 wt.% Bi, 22.0 μm.