In situ stress measurements during electrodeposition of Ag-Sb and Pt-Co alloy multilayers

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Abstract. Internal stresses in multilayer coatings from Ag–Sb and Pt–Co alloys with different alloying element contents in the individual sublayers are measured during the process of deposition. The results are compared with the stresses in thick alloy coatings of a content corresponding to the content of the individual sublayers in the multilayer system. Stresses in the first sublayers of a multilayer Ag–Sb coating correspond to those in a one-layer thick coating. Stresses in the subsequent sublayers are changed under the influence of previous sublayers. Changes in the internal stresses are related to the change in the element and phase content of the coatings. Strong relaxation effects are detected in multilayer alloy Pt–Co coatings, caused by the desorption of the codeposited hydrogen and the layer cracking.

1. Introduction

The materials produced by multilayer deposition could exhibit different electrical, physicomechanical, magnetic, anticorrosion etc properties compared to conventional layers of individual metals or alloys. When the sublayer thickness of a multilayer system is in the order of hundreds of nanometres, the range of new properties acquired could increase dramatically. On one hand this can be attributed to the large number of phase boundaries between the sublayers and on the other to the possible interaction between the layers themselves.

Multilayer coatings can be obtained either from a single or a dual bath. In the dual-plating process, the sublayers of the different metals are deposited alternatively in two different electrolytes. This process requires intermediate steps like rinsing or activation. In a dual bath the deposition produces sublayers of high-purity individual metals and no alloy is formed. Conventional electrolytes can be successfully used for this purpose, due to the considerable stability of the processes. However, the deposition is labour consuming and involves large equipment costs.

In the single-plating process, the metals are deposited from one electrolyte. This requires a suitable electrolyte containing the corresponding metal salts complexes. In order to deposit single layers of different composition, the deposition potential of the two components must have different values. This can be achieved by varying the metal ion concentrations or by using different metal complexes. If the deposition potentials of the two components differ sufficiently, the deposition of multilayers becomes possible by varying the process parameters—for instance potential, current density or hydrodynamic conditions at the cathode surface. Under such conditions no individual metal layers can be produced but alloy layers of various ratios of both elements are formed.

The alteration of electrolysis conditions (concentration of the electrolyte components, pH, current density, temperature, agitation of the electrolyte) leads to change in the element and phase content of the layers deposited, resulting in changes of the respective properties of the deposit. For example, the change in the internal stresses of multilayer systems during electrolytic deposition has been measured by a number of authors [1–3].

The present work aims at *in situ* monitoring of the stress changes occurring in multilayer coatings from two different alloy systems: Ag–Sb and Pt–Co. The systems selected are very different in properties and behaviour. The Ag–Sb system possesses interesting electrical characteristics: antimony alloying results in reduction of the electrical conductivity and increase in the coating wear resistance [4]. They exhibit an anomalous electrical conductivity at low temperatures [5] and at relatively low changes in the plating conditions, different phases of the alloy systems can be produced [6] and multilayer (layered) coatings can spontaneously be formed [7].

The interest in the Pt–Co system originates from its magnetic properties [8]. The deposition process can be performed within a large range of current density and is accompanied by hydrogen discharge. Part of it diffuses in the coating and can lead to significant stress changes in the coating.

2. Experiment

The multilayer compositionally modulated alloy coatings were obtained from a single bath from electrolytes, shown in table 1.

Table 1. Electrolyte content used for deposition of alloy and multilayer coatings.

Component	Ag–Sb (mol)	Pt-Co (mol) [9]
Ag as $AgNO_3$	0.15	
$K_4Fe(CN)_6.3H_2O$	0.17	
K_2CO_3	0.15	
KSCN	1.5	
$KNaC_4H_4O_6.4H_2O$	0.21	
Sb as $K(SbO)C_4H_4O_6.1/2H_2O$	0.06	
Pt as $Pt(NH_3)_2(NO_2)_2$		0.03
Co as $Co(SO_3NH_2)_2$		0.01
$C_6H_5Na_3O_7.2H_2O$		0.1
NH_2CH_2COOH		0.1
$NaPH_2O_2.H_2O$		0.1
Temperature ($^\circ$C)	20	40
pH	9.5	8.0

The internal stresses of first order (macroscopically observed compressive or tensile stresses) were monitored according to the method of Hoar and Arrowsmith [10] with an apparatus constructed by Stalzer and further developed at FEM Schwäbisch Gmünd [11]. The coatings were deposited on the front side of copper electrodes of 9 cm length, 1 cm width and 0.3 mm thickness, back side isolated. After electrochemical decreasing, activation in diluted sulphuric acid solution and rinsing with distilled water the electrode was fixed at the lower end of the holder of the apparatus. The deposition of the Ag and Ag–Sb coatings was carried out on thin silver plated copper substrates to avoid the electrodeless deposition of silver on copper. The anodes were made of silver for the Ag–Sb system and of platinized titanium for the Pt–Co system. The electrolyte volumes were 400 cm^3 for Ag–Sb and 800 cm^3

for the Pt–Co electrodeposition, which were large enough to keep the concentrations of the components nearly constant during the deposition. The bending moment emerging in the galvanized electrode due to the developed internal stresses in the coating was measured and automatically compensated. Thus, in the substrate, respectively in the coating, there were no deformations occurring during the measurement. The signal from the sensor was transferred to a PC through a suitable interface for further monitoring and processing. This electric signal is depicted on the ordinate axis in the figures below.

The internal stress values can be calculated from the values of the signal obtained and the parameters of the substrate, using the following formula [12]:

$$S = \frac{4(U - U_0)KL}{3btd}$$

where S is the internal stresses [N mm^{-2}]; $F = K(U - U_0)$ is the force on the sensor [mN]; K is a calibration coefficient, 161 mN V^{-1}; L is the cathode length [mm]; b is the cathode width [mm]; t is the cathode thickness [mm]; d is the coating thickness [mm]; U_0 [V] is the signal at the beginning of the deposition and U [V] is the signal at the end of the deposition.

The deposition was done with the aid of a program generator Pragmatic 2411A supplied by Pragmatic Instruments and bipolar operation amplifier BOP 20-10M from KEPCO. The one-layer coatings were deposited galvanostatically at different current densities. The multilayer coatings were obtained by alternating changes of the current density between appropriate values with durations, selected to produce sublayers of equal thickness.
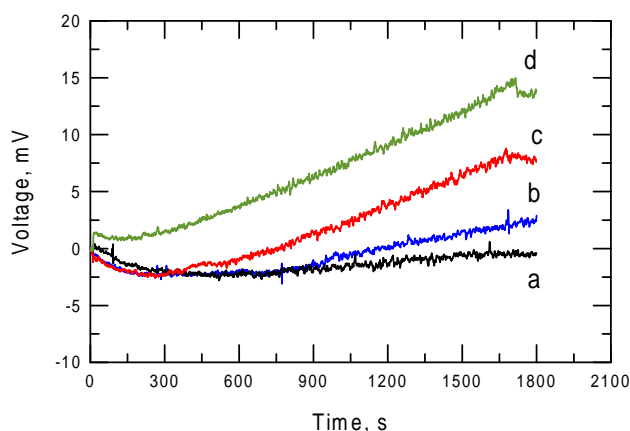

Figure 1. Sensor signal during electrodeposition of silver at different c.d.s: a—0.25 A dm^{-2}, b—0.375 A dm^{-2}, c—0.5 A dm^{-2}, d—0.675 A dm^{-2}.

3. Results

3.1. Multilayer coatings from Ag–Sb alloy

Figure 1 illustrates the sensor signal corresponding to the internal stresses of one-layer silver coatings depending on the time at different cathodic current densities. The increase in the current density leads to a transition from negative (compressive) to positive (tensile) stresses of the silver deposit.

The behaviour of the systems for antimony codeposition is depicted in figure 2. At low current density the antimony deposition is negligible and the curve corresponds to the respective
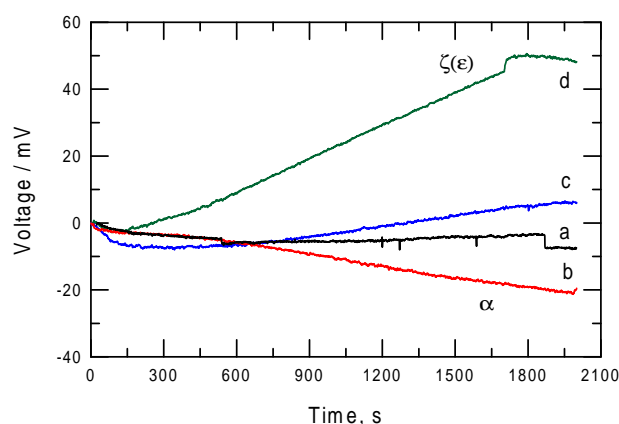
Figure 2. Sensor signal during electrodeposition of silver–antimony alloys at different c.d.s: a—0.25 A dm^{-2}, b—0.5 A dm^{-2}, c—0.75 A dm^{-2}, d—1.0 A dm^{-2}.
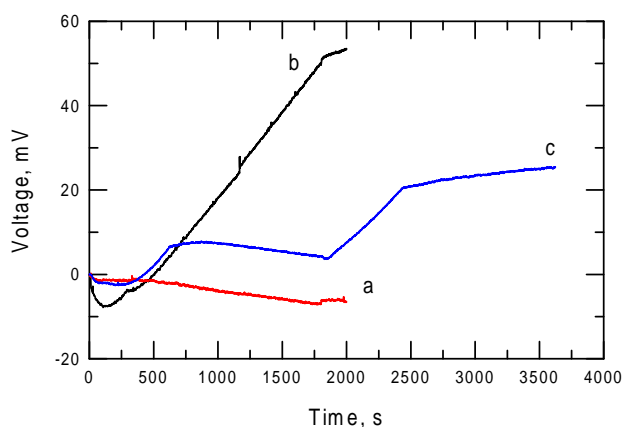

Figure 3. Sensor signal during electrodeposition of silver–antimony alloys at different c.d.s: a—monolayer—0.5 A dm^{-2}, b—monolayer—1.0 A dm^{-2}, c—multilayer with four sublayers—10 min–1.0 A dm^{-2}/20 min–0.5 A dm^{-2}.

curve for pure silver coating. When current density is increased the coating's internal stresses are initially shifted towards the negative direction. In the forming α-phase the antimony atoms are incorporated in the silver lattice, strain it and cause compressive stresses in it. When the silver lattice cannot take any more antimony, the codeposition of the latter leads to a new, richer in antimony phase—ζ- or ε-phase [6]—and the stresses change in sign and become positive.

The current densities in the electrodeposition of the multilayers are selected to obtain sublayers with different composition, with the expectation that the opposite signed stresses could compensate each other markedly.

When multilayer coatings of the Ag–Sb system composed of phases with different content of antimony were deposited, the stresses in the first sublayers follow the course of the stresses in the thick one-layer coatings while the stresses in the next layers are influenced by those of the previous sublayers (figure 3).

The thinner the individual sublayers become, the larger are the observed stress deviations from the course of the stresses in the respective alloy coatings. Under these deposition
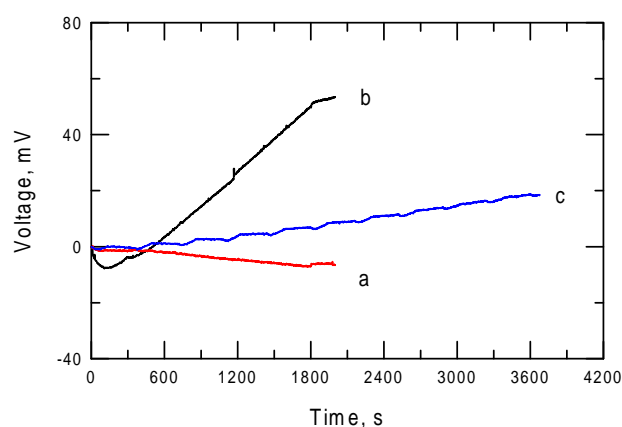
Figure 4. Sensor signal during electrodeposition of silver–antimony alloys at different c.d.s: a—monolayer—0.5 A dm^{-2}, b—monolayer—1.0 A dm^{-2}, c—multilayer with 20 sublayers—2 min–1.0 A dm^{-2}/4 min–0.5 A dm^{-2}.
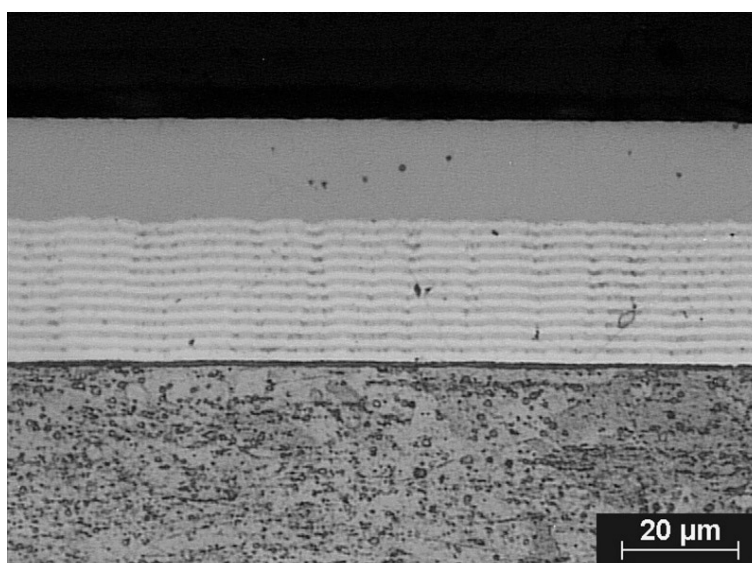

Figure 5. Cross-section of multilayer deposit with 20 sublayers, corresponding to figure 4.

conditions the stresses are positive and their values lie between the stress values of the individual thick layers (figure 4). Figure 5 shows a cross-section of such a coating. At appropriate combinations of the current densities and the sublayer deposition times i.e. sublayer thicknesses it could be expected to obtain coatings with negligible stresses.

3.2. Multilayer coatings from Pt–Co alloy

A transition from compressive to tensile stresses was also observed during deposition of alloy Pt–Co coatings with increased current density (figure 6). In this case the increase in current density leads to a rise in the Pt content of the coatings. The anomalous codeposition of both metals is contributed by the complex character of the electrolyte, its lower cobalt content and
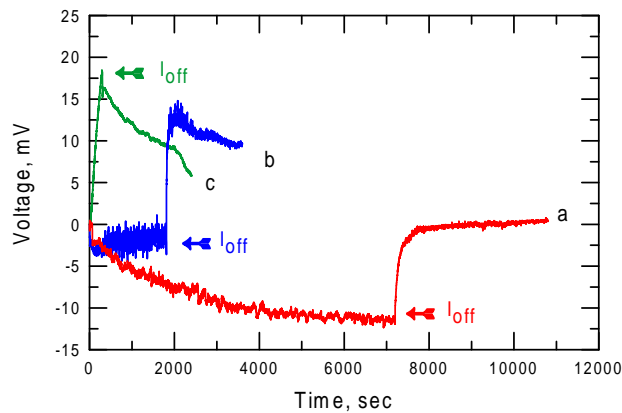
Figure 6. Sensor signal during electrodeposition of platinum–cobalt alloys at different c.d.s: a—0.5 A dm^{-2}, b—5.0 A dm^{-2}, c—50.0 A dm^{-2}.
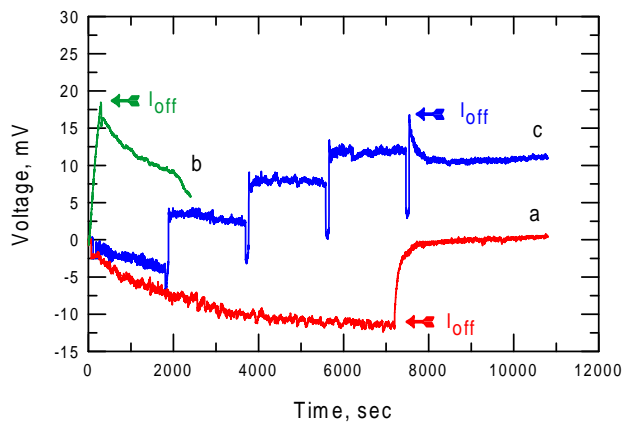

Figure 7. Sensor signal during electrodeposition of platinum–cobalt alloys at different c.d.s: a—monolayer—0.5 A dm^{-2}, b—monolayer—50.0 A dm^{-2}, c—multilayer with eight sublayers— 30 min–0.5 A dm^{-2}/1.25 min–50.0 A dm^{-2}.

the hydrogen codeposition. There are strong relaxation effects observed in this system after the current is turned off (I_{off}) which are due to the desorption of the hydrogen diffused in the coating during the deposition process and crack formation. In the coatings deposited at low current densities (0.5 A dm^{-2}) there are no cracks observed. Thus the post-electrolysis changes of the internal stresses could be connected with the desorption of the codeposited hydrogen. At higher current densities (50 A dm^{-2}) we observe cracks in the coatings after the experiment. In that case the post-electrolysis changes of the stresses are possibly due to the superposition of both effects—desorption of the codeposited hydrogen and formation of cracks in the deposit.

When the current was switched from low to high values during the deposition of multilayer coatings, characteristic changes (jumps to negative direction) in the curves were observed (figure 7 and 8). On one hand they could be attributed to the strong effect of hydrogenation of the coatings at high current density and on the other, to the possible hydrodynamic effects caused by the vigorous electrochemical process undergoing under such conditions. The total
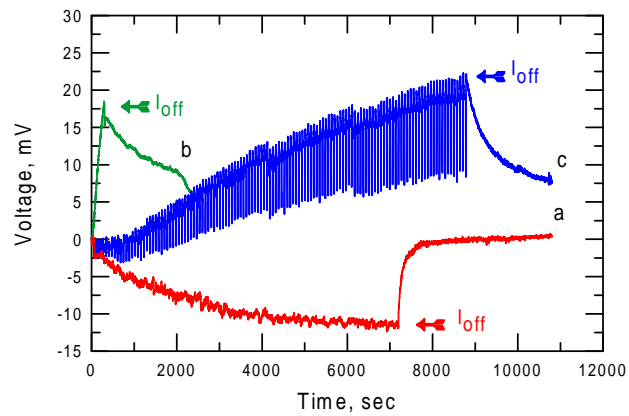
Figure 8. Sensor signal during electrodeposition of platinum–cobalt alloys at different c.d.s: a—monolayer—0.5 A dm^{-2}, b—monolayer—50.0 A dm^{-2}, c—multilayer with 256 sublayers—0.94 min–0.5 A dm^{-2}/0.04 min–50.0 A dm^{-2}.
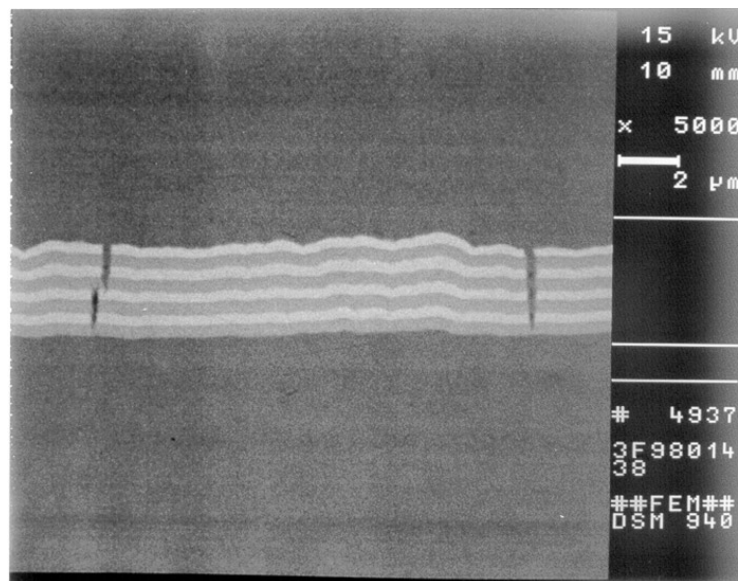

Figure 9. Cross-section of multilayer deposit with eight sublayers, corresponding to figure 7.

stresses in the multilayer coatings remained positive for this system at the deposition conditions used. The relaxation effects occurring during the post-electrolysis period were due to the lowering of these stresses when hydrogen was desorbed and to the subsequent cracking of the multilayer coatings (figure 9).

4. Conclusion

Phase changes in the Ag–Sb alloy system lead to changes not only in the value but in the sign of the internal stresses as well.

The internal stresses of both Ag–Sb and Pt–Co multilayer alloy coatings acquire values lying between the values of the individual alloys composing the system.

The thinner are the individual sublayers, the stronger is the interaction between them.

Desorption of codeposited hydrogen and cracking of strongly stressed one-layer and multilayer Pt–Co systems lead to relaxation effects in the post-electrolysis period.

Acknowledgments

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