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Scientific paper

# SELF-STRUCTURED SILVER ALLOY COATINGS AND THEIR PROPERTIES

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***Abstract***

*The co-deposition of silver with less noble metals results at low current densities in pure silver coatings or solid solutions of these metals in silver. At high current densities, after saturation of the silver lattice with the alloying metal a new richer in this element phase is formed and heterogeneous coatings are obtained.*

*The spontaneous deposition of different phases is sometimes connected with electrochemical instabilities and oscillation phenomena leading to formation of periodically ordered spatio-temporal structures on the surface of the electrode. The spreading of waves of different metal composition over the electrode could result in the spontaneous formation of multilayered coatings, which combine the properties of the phases of the different sublayer. The possibility of spontaneous formation of heterogeneous periodic self-structured coatings in micro- and nano-scale, based on silver alloys with antimony, bismuth, indium, tin, cadmium and other metals without applying external pulses is shown. The effect of electrolysis conditions on the morphology, internal stress, microhardness, electrical contact resistance, wear resistance, roughness and friction properties of the obtained alloy coatings is studied and some properties of the deposited layers are compared and discussed.*

***Key words:*** *Coatings, Silver alloys, Structure.*

## 1. INTRODUCTION

Silver is a noble metal with excellent properties like the best electrical conductivity among the metals, best thermal conductivity, best reflectance of the visible light, some bactericidal properties, chemical resistance etc. To correct some disadvantages of the metal, such as its low hardness and wear resistance, as well as the tarnishing in the atmosphere with even small amount of sulphur, silver is alloyed with small amounts of other metals like antimony, bismuth, indium, tin, lead, cadmium and etc. The mechanical properties of the electrodeposited alloys are enhanced in case small amounts of the alloying element are co-deposited and solid solution of this element with silver is formed. There is always some compromise between the enhancement of the mechanical properties of silver and the worsening of its electrical or thermal conductivity. In most cases the silver lattice is expanded due to the co-deposited metal atoms incorporated therein and this causes an increase in the micro-hardness, abrasion resistance and internal stress of the deposits depending on the amount of the alloying element in the coating. Otherwise the composition of the electrodeposited alloy can be influenced by the electrolysis conditions, like metal ion concentrations in the electrolyte, temperature, current density, agitation and especially by different complex forming agents for both metals. So, under appropriate conditions, for example at high current densities or deposition potentials, it is possible to co-deposit larger amounts of the alloying element than needed for the saturation of the silver lattice. This leads to spontaneous formation of other phases on silver basis richer on the alloying element. The simultaneous appearance of two or more phases in the electrodeposited heterogeneous alloy is connected with their distribution in the coating as well as on its surface. The electrolytic cell is an open system where materials and energy are exchanged with the surroundings and at strong deviation from the equilibrium state, like deposition under limiting current density, it is possible to observe self-organization phenomena and formation of ordered structures with broken symmetry not only in space, but also both in space and time. Such structures were observed for the first time about 70 years ago in 1938 by E. Raub and A. Schall [2] in Germany during electrodeposition of silver-indium alloys (Figure 1).

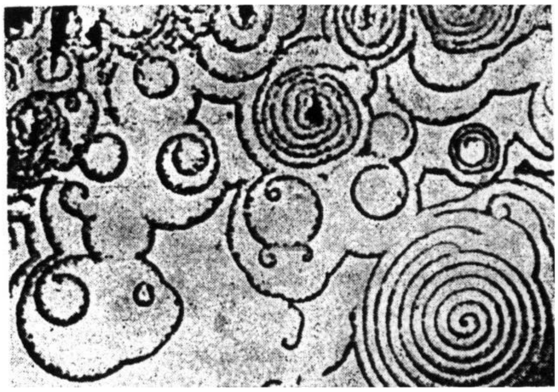


*Fig.1. Spiral structures in electrodeposited* ***Ag-In*** *alloy observed by E. Raub et.al. [2].*

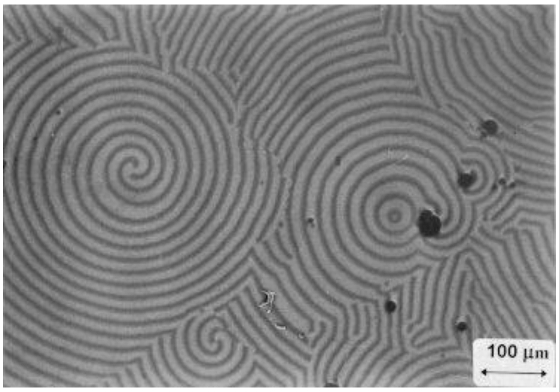



*Fig.2. Spiral and target structures in electrodeposited* ***Ag-Sb*** *alloy coating*

About 50 years later similar dynamical periodic structures in the form of stripes, spirals with different topological charge (number of arms up to 5 and more) and target patterns were observed on the surface of the electrode during electrodeposition of silver-antimony alloys [3] (Fig. 2). Several years later similar phenomena were registered during deposition of other silver alloy systems, such as silver-bismuth [4, 5] (Fig. 3), silver-indium [6, 7] (Fig. 4), silver-tin [8] (Fig. 5) and silver cadmium [9] (Fig. 6).

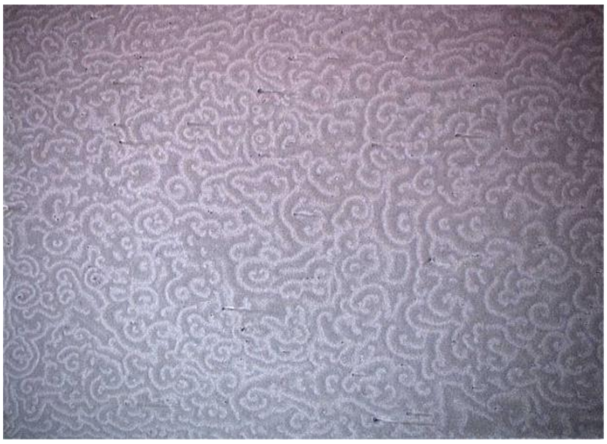


*Fig.3. Spatio-temporal structures in electrodeposited **Ag-Bi** alloy coating*

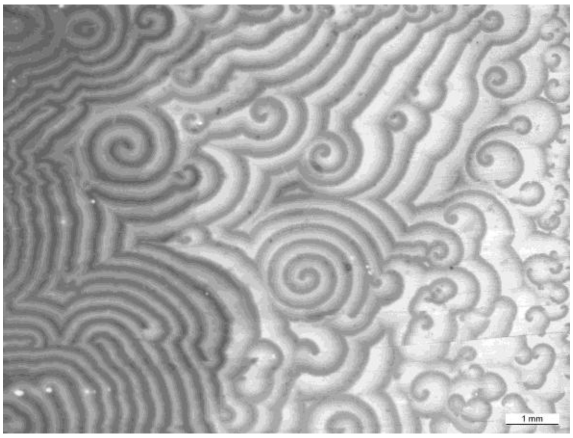


*Fig.4. Spiral and target structures in electrodeposited **Ag-In** alloy coating*

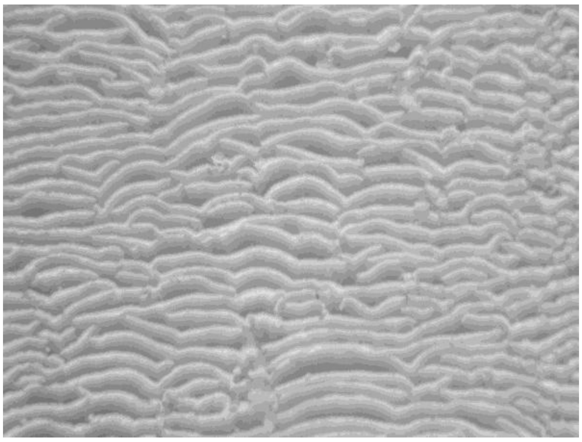


*Fig.5. Spatio-temporal structures in electrodeposited **Ag-Sn** alloy coating*

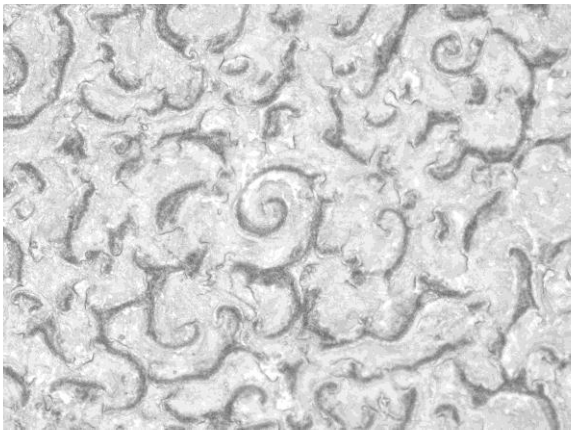


*Fig.6. Spatio-temporal structures in electrodeposited **Ag-Cd** alloy coating*

## 2. RESULTS AND DISCUSSION

Investigations in a strong magnetic field during electrodeposition of Ag-Sb alloy coatings confirmed the suggestion, that the natural convection in the electrolyte plays an important role in the formation of the spatio-temporal structures [10]. All investigated systems are of regular type according to Brenner [1], i.e. an increase in the current density results in an increase of the amount of the alloying element in the coating. An exception was observed during deposition of silver-bismuth alloys, where depending on the amount of free cyanide ions in the electrolyte the deposition potential of silver can be shifted so far in negative direction that bismuth starts to deposit at more positive potential than silver.

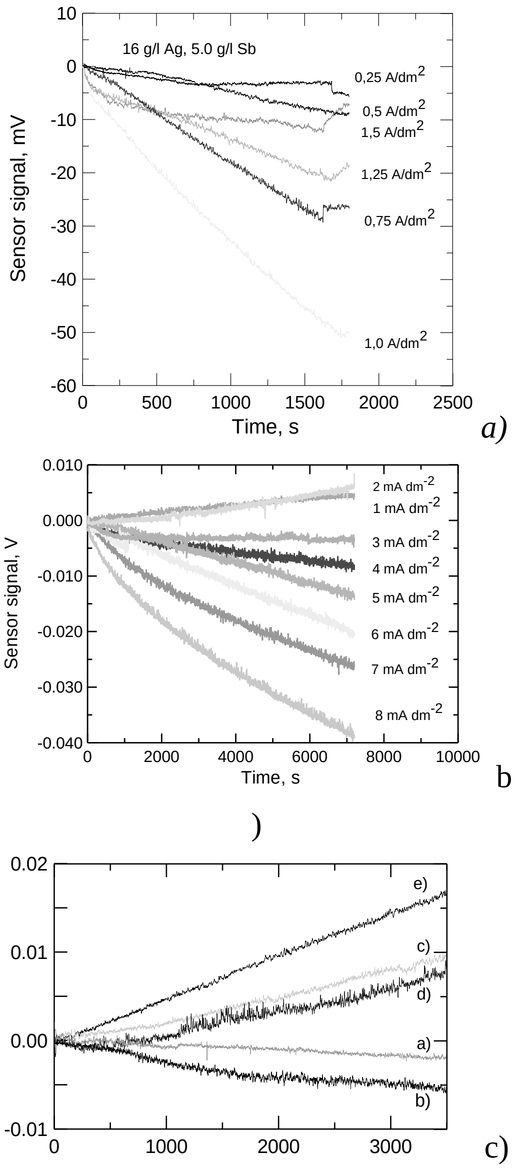
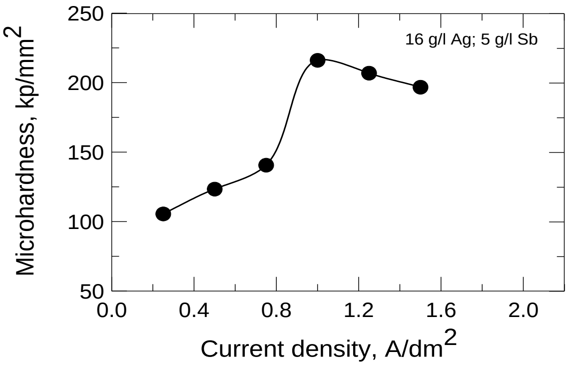



*Fig. 7. Internal stress of different silver alloy coatings:*
*a)* ***Ag-Sb****; b)* ***Ag-Bi****; c)* ***Ag-In***

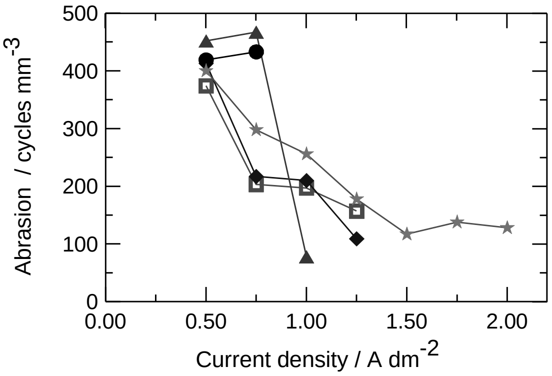
Solid solutions of the alloying elements in silver are formed at low current densities which results in changes of the physico-mechanical and electrical properties of silver. The micro-hardness, the abrasion resistance, the internal stress and the electrical contact resistance as well as the lubricating properties of the coatings increase compared to pure silver (Fig. 7-9), some of them reaching a maximum at highest amount of the alloying element in the solid solution phases of the respective alloys (Fig. 8).

When the current density becomes sufficiently high and the co-deposited amount of the alloying element becomes higher than necessary for the saturation of the silver lattice with its atoms, the surplus amount of this element forms a new phase of the alloy system and the coatings become heterogeneous. This transition results in changes in the properties of the alloy coating, like decrease in the IS, microhardness, abrasion resistance etc. Silver coatings from cyanide electrolytes show positive internal stress, while the stress in antimony, bismuth and indium coatings is negative. The formation of solid solutions of antimony (Fig. 7a) and bismuth (Fig. 7b) in silver leads to an increased compressive stress with increasing current density (i.e. increasing amount of the alloying element in the coating). The low negative stress of pure indium is insufficient to change the positive stress of the pure silver, when alloying (Fig. 7c).

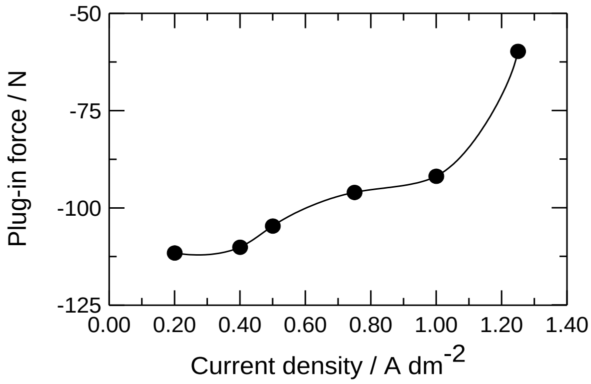
The abrasion resistance and the plug-in forces, the latter considered as a indication for the lubricating properties of the alloys, decrease in the heterogeneous coatings richer in the alloying element (Fig. 8b, c and Fig. 9). At higher bismuth content in the deposits the abrasion resistance reaches the values of pure bismuth coatings (Fig. 9a). As a measure of the lubricating properties of the deposits the plug-in forces of electrical contact pins into silver plated jacks pro length of insertion was proposed [11] (Fig. 9c).




a)

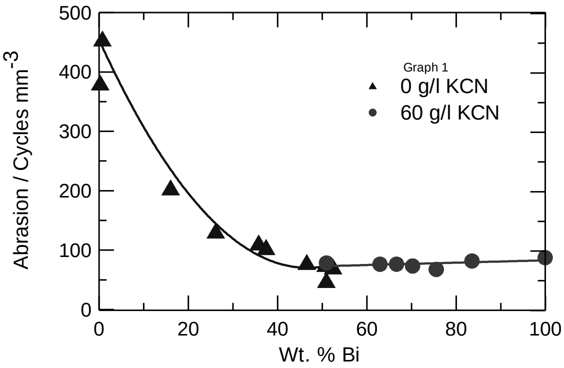



b)

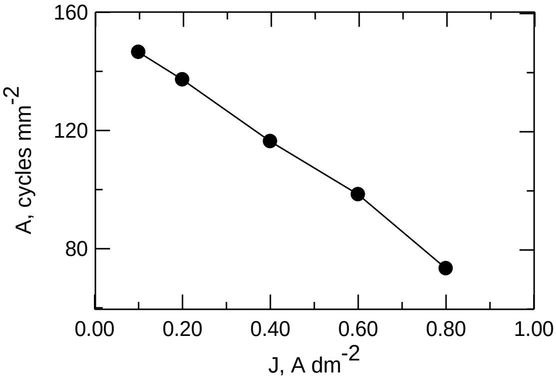



c)

*Fig. 8. Properties of **Ag-Sb** electrodeposits depending on the current density (percentage of the alloy); a) microhardness, b) abrasion resistance and c) plug-in forces.*




a)

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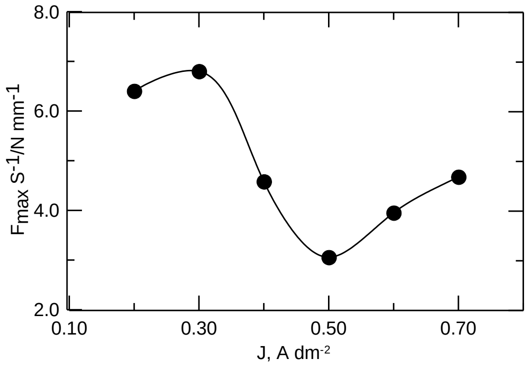



c)

*Fig. 9. Tribological and lubricationg properties of electrodeposited silver alloys. Abrasion resistance: a) **Ag-Bi**; b) **Ag-In**; Plug-in forces: c) **Ag-In**.*

Independently of the changed properties of silver by alloying with other metals, its electrical parameters are always worsened. The electrical contact resistance of the alloy coatings increases with the current density, i.e. with increased amount of the alloying element in the deposits (Fig. 10).

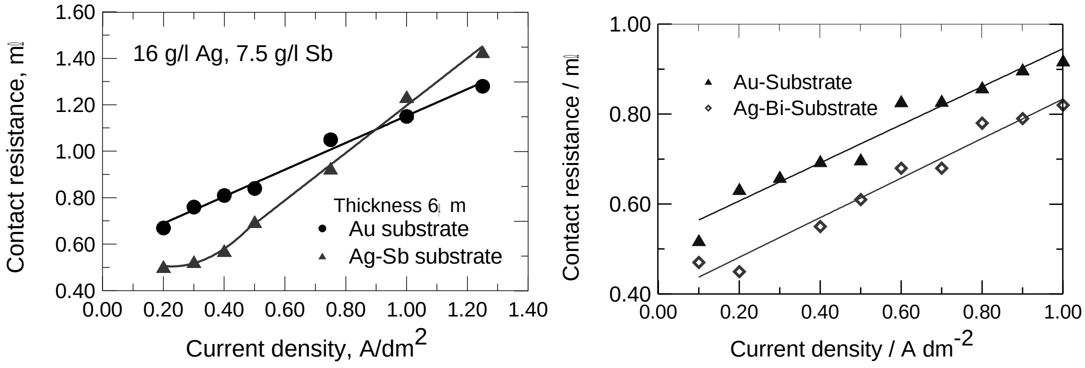
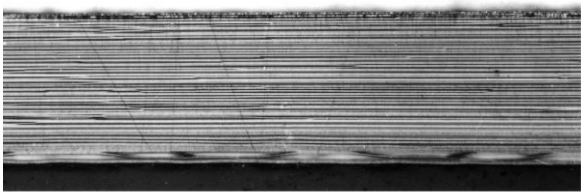
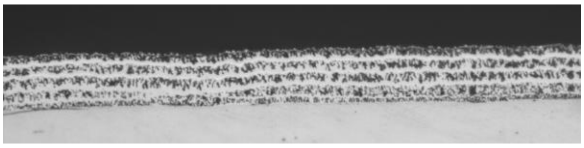



*Fig.10. Electrical contact resistance of **Ag-Sb** and **Ag-Bi** coatings*

At higher current densities, i.e. higher deviation from the equilibrium state, the phase heterogeneity of the coatings becomes ordered and the formation of spatio-temporal structures is observed (see Figs. 2-6). The electrochemical processes during electrodeposition of several alloys show instabilities (region with negative slopes in the polarization curves) and oscillatory behavior of the current or potential. These oscillations are connected with the formation and movement of waves of different phase composition on the surface of the heterogeneous electrode, which results in deposition of multilayered coatings in absence of any external pulses. Fig. 11).



a)



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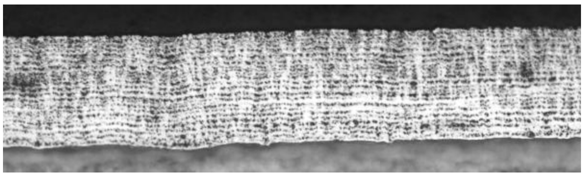

*c)*

*Fig. 11. Oscillatory electrodeposition and spontaneously formed lamellar coatings without external pulses; a) **Ag-Sb**, b)**Ag-In**, c) **Ag-Sn***

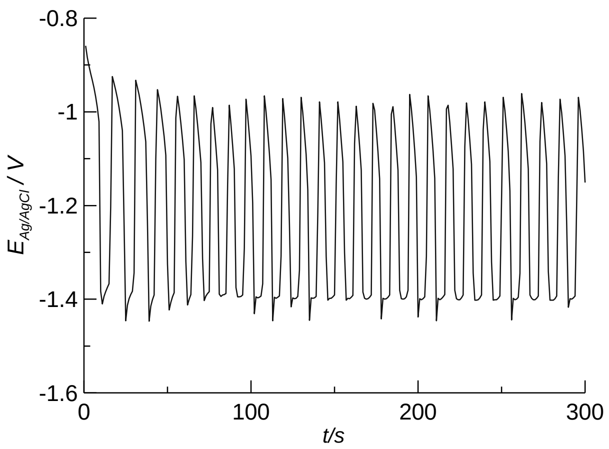


*Fig. 12. Potential oscillation during deposition of **Sn-Ag** alloy*

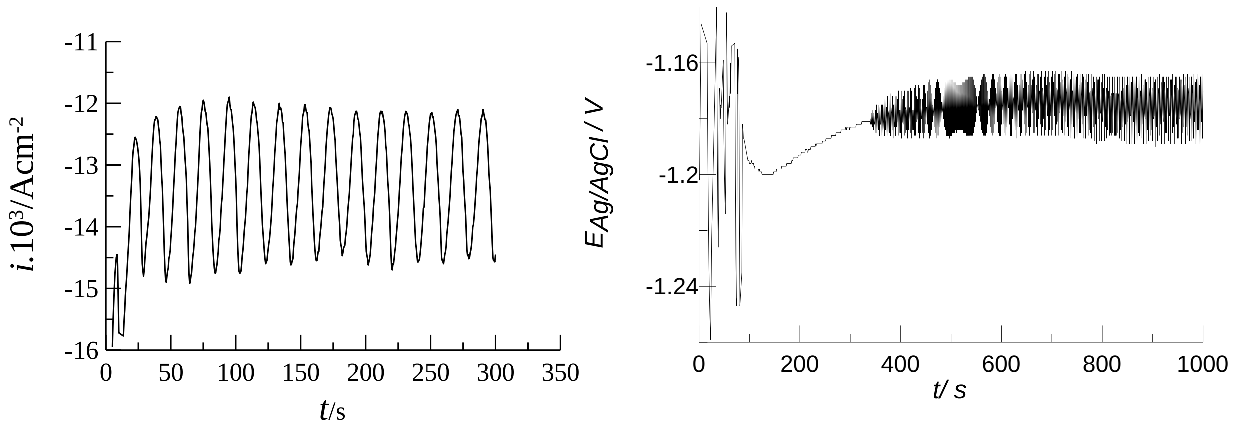


*Fig.13. Current and potential oscillations during alloy deposition; a) **Ag-Sb** [12] and b) **Ag-In***

Depending on the velocity of wave spreading and the preferred deposition of some metals on their own or on foreign substrate, structures in different scale (see Fig. 2-6) or columnar coatings (Fig. 12) can be formed. If pulsed current is applied, multilayered cyclic modulated silver alloy coatings can be deposited which combine the properties of the phases of the different sublayer. Antimony is more easily deposited on its own substrate than on silver and it results in a well formed multilayer (Fig. 15) of different composition formed not only spontaneously, but also by pulse technique. The Ag-Bi cyclic modulated alloy multilayers are discontinuous because of the island structure of bismuth on silver substrate (Fig. 14b and Fig. 16)

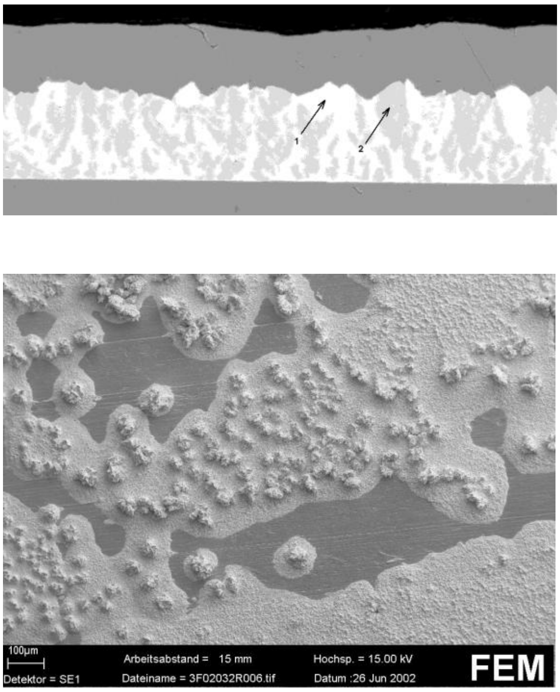


*Fig. 14. Columnar **Ag-Bi** alloy coating; a) cross section and b) preferential deposition of each metal on its own substrate*

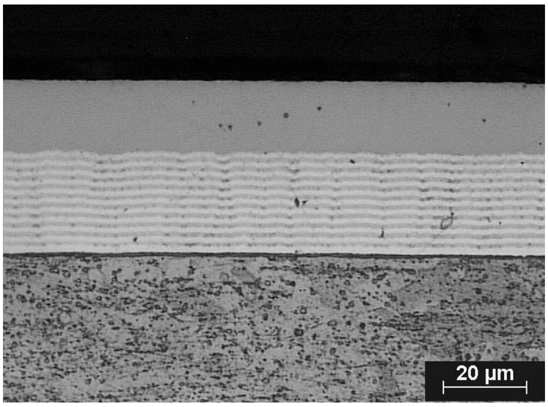


*Fig.15. **Ag-Sb** pulse plated alloy multilayer*

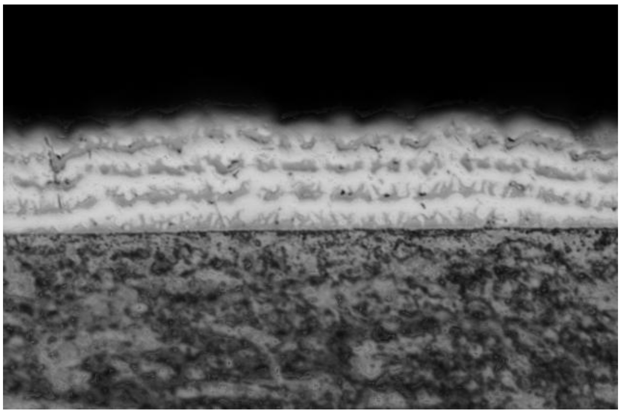

*Fig.16 **Ag-Bi** pulse plated alloy multilayer*

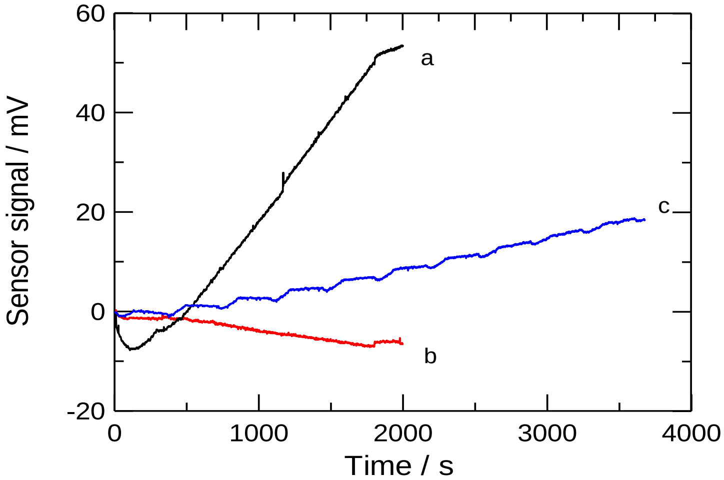


*Fig.17. Internal stress during deposition of Ag-Sb multilayer; a) monolayer corresponding to the white lamellae of Fig. 15; b) monolayer corresponding to the dark lamellae of Fig. 15; c) multilayer of Fig. 15*

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The properties of the multilayered silver alloys with antimony and bismuth are thoroughly investigated and described in some previous papers [13, 14]. Through combination of the pulse parameters, which affect the thickness and the elemental, as well as the phase composition of the alloy sublayer, it is possible to control the properties of the deposited multilayer. An excellent example is the internal stress in the Ag-Sb multilayer coatings, where the positive stress of the silver-rich sublayer is compensated by the negative stress of the antimony-richer sublayer. The deposition of stress-free coatings with well conducting silver-richer lamellae in combination with antimony-richer lamellae with increased wear resistance or better lubricating properties (depending on the antimony content) is possible.

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