FORMATION OF PERIODIC SPATIO-TEMPORAL STRUCTURES OF SILVER-INDIUM ALLOY COATINGS ELECTRODEPOSITED FROM CYANIDE ELECTROLYTES

Ts. Dobrovolska*, z, L. Veleva , I. Krasteva*, A. Zielonka*****

* Institute of Physical Chemistry, Bulg. Acad. Sci, 1113 Sofia, Bulgaria

**CINVESTAV-IPN, Unidad Mérida, Appl. Physics. Dept, Mexico

***Forschungsinstitut für Edelmetalle und Metallchemie, 73525 Schwäbisch Gmünd

The first attempts of Ag alloying with In have been aimed at the increase in the tarnish resistance of silver. [1-4] Due to the difficult preparation and the instability of the alkaline cyanide electrolytes used, the properties of the electrodeposited alloy are not studied extensively. The the presence of KOH the cyanide electrolytes are stable, with higher cathodic current yield, and a possibility for obtaining uniform compact coatings. The interest in these electrolytes originates by possibility of formation of periodic spatio-temporal structures on the surface of the deposited coatings. Similar structures have been observed also in Ag-Sb[5-8] and Ag-Bi[9] alloy systems.

The present study is aimed at the effect of electrolyte conditions on the composition and structure of the Ag-In alloy coatings from stable cyanide electrolyte. The surface morphology and composition of the coatings, deposited under galvanostatic conditions changes depending the current density (Figs.1) and with increasing current density heterogeneous indium richer alloy coatings were deposited, containing different phases, such as Ag, Ag_3In, In_4Ag_9 and $AgIn_2$. The resulting coatings were characterized by, SEM, EDAX , X-Ray fluorescence and X-Ray diffraction. The simultaneous deposition of several phases of different composition leads to the formation of *periodic spatio-temporal* structures on the electrode surface (Figs.2). Depending on the conditions of the electrolysis, it is possible to obtain large (visible with naked eye) structures of lower thickness and equal morphology on the surface or small structures of a substantial depth in the coating with considerably different surface morphology. A relationship between Ag and In metal ratio in the electrolyte and the current density of electrodepositing has been established (Fig.3). Following this relation, the reproducible formation and observation of the self-organization phenomenon is possible without any preliminary treatment of the electrolyte.

References

1. D. Gray, U.S. Pat. 1,935,630 (1933).

2. D. Gray, *Trans. Electrochem. Soc.*, **65,** 377 (1934).

3. E. Raub and A. Schall, *Mitt. Forsch. Inst. Probieramts Edelmetalle staatl. Höheren Fachschule Schwäb.Gmünd*, **12,** 55 (1938).

4. A. Brenner, in *Electrodeposition of Alloys*, Vol.2, p.165, Academic Press, New York (1963).

5I. Kristev and M. Nikolova, *J. Appl. Electrochem.*, **16,** 875 (1986).

6. I. Kristev, M. Nikolova, and I. Nakada, E*lectrochim. Acta*, **34,** 8 1219 (1989).

7. I.Krastev and M.T.M. Koper, *Physica A*, **213,** 199 (1995).

8. S. Nakabayashi, K. Inokuma, A. Nakao, and I. Krastev, *Chem. Lett. (Japan)*, **88,** (2000).

9. I. Krastev, T. Valkova, and A. Zielonka, *J. Appl. Electrochem.*, **34,** 79 (2004).

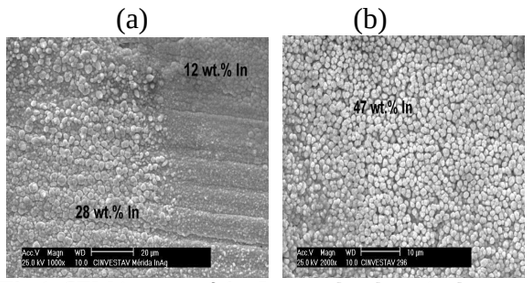

Fig 1. SEM images of Ag-In samples deposited at (a) 0.6 A.dm^{-2}, 26 min ; b) 0.8 A.dm^{-2}, 19 min ; (CD+-Glucose = 0.1mol dm^{-3} ; CKCN = 1mol dm^{-3} ; CAg = 0.08 mol dm^{-3}; CIn =0.2 mol dm^{-3})

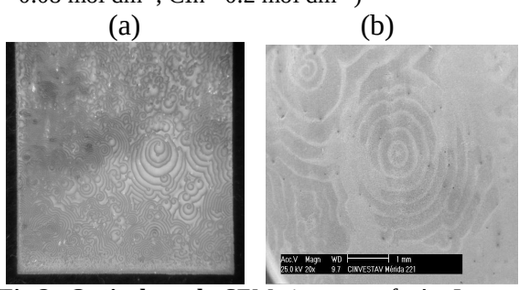

Fig.2 Optical and SEM images of Ag-In samples deposited at 0.1 A dm$^{-2;}$ deposition time 156 min

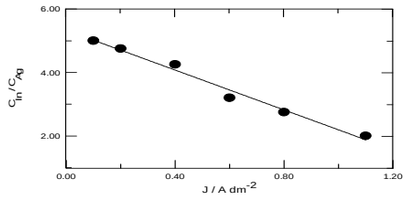

Fig3. Relation between Ag and In metal concentration ratio in the electrolyte and current density of electrodepositing, necessary for observing spatio-temporal structures in fresh electrolytes.