07 - 10 September 2009

PROCEEDINGS

54. IWK

Internationales Wissenschaftliches Kolloquium
International Scientific Colloquium

Information Technology and Electrical Engineering - Devices and Systems, Materials and Technologies for the Future

Faculty of Electrical Engineering and Information Technology

Startseite / Index:
http://www.db-thueringen.de/servlets/DocumentServlet?id=14089

TECHNISCHE UNIVERSITÄT
ILMENAU

Impressum

Herausgeber: Der Rektor der Technischen Universität Ilmenau
Univ.-Prof. Dr. rer. nat. habil. Dr. h. c. Prof. h. c.
Peter Scharff

Redaktion: Referat Marketing
Andrea Schneider

Fakultät für Elektrotechnik und Informationstechnik
Univ.-Prof. Dr.-Ing. Frank Berger

Redaktionsschluss: 17. August 2009

Technische Realisierung (USB-Flash-Ausgabe):
Institut für Medientechnik an der TU Ilmenau
Dipl.-Ing. Christian Weigel
Dipl.-Ing. Helge Drumm

Technische Realisierung (Online-Ausgabe):
Universitätsbibliothek Ilmenau
ilmedia
Postfach 10 05 65
98684 Ilmenau

Verlag:
Verlag ISLE, Betriebsstätte des ISLE e.V.
Werner-von-Siemens-Str. 16
98693 Ilmenau

ISBN (USB-Flash-Ausgabe): 978-3-938843-45-1
ISBN (Druckausgabe der Kurzfassungen): 978-3-938843-44-4

Startseite / Index:
http://www.db-thueringen.de/servlets/DocumentServlet?id=14089

PATTERN FORMATION IN ELECTRODEPOSITED SILVER-CADMIUM ALLOYS

Ts. Dobrovolska, I. Krastev*, A. Zielonka***

* Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
** Institute of Precious Metals and Metal Chemistry, 73525 Schwäbisch Gmünd, Germany

ABSTRACT

The effect of electrolysis conditions on the composition and structure of silver-cadmium alloys from cyanide electrolytes is investigated. Homogeneous coatings are deposited at low current densities, while at higher current densities after saturation of the silver lattice with cadmium heterogeneous coatings consisting of phases of different cadmium content are obtained. The different phases established by XRD measurements form pattern, which under certain conditions can organize themselves in periodic spatio-temporal structures. The influence of the natural convection on the shape and position of the pattern is shown. Oscillatory electrochemical processes are observed under galvanostatic conditions. The dependence of the potential oscillations on the electrolysis conditions is shown and discussed.

Some properties of the deposits like hardness, roughness, internal stress, electrical contact resistance, abrasion resistance etc. are established depending on the electrolysis conditions. The observed correlations between composition, structure and properties of the deposits are discussed.

Index Terms - Alloys, electrodeposition, self-organization, silver-cadmium

1. INTRODUCTION

Alloying of silver with other metals was motivated in the past mainly by the idea to improve its tarnish resistance [1, 2]. Cadmium and indium were regarded as appropriate metals for such purposes, because they do not tarnish and are light colored. The alloying of silver with indium improves not markedly its tarnish resistance but pattern formation has been observed on the cathode surface [3]. Later, similar formation of spatio-temporal structures, as a result of the self-organization phenomena in reaction–diffusion systems have been observed and studied during co-electrodeposition of silver with antimony [4], bismuth [5], tin [6] and indium [7, 8].

The silver-indium and silver-cadmium alloy systems have not achieved any special practical importance, but the silver-cadmium system is of considerable academic interest, because of the large variety of formed phases [9-15]. There are not any known reports about formation of spatio-temporal structures on the electrode surface. However, the experience with the electrodeposition of some other silver alloy coatings allows the assumption of the possible existence of similar structures in this system. Examples of structure formation as a result of self-organization phenomena could be observed in different physical, chemical, biological etc. systems [16-20] and the electrochemical methods allow their investigation in well defined and controlled conditions.

The aim of the present investigation is to find out the conditions for self-organized structure formation during electrodeposition of silver-cadmium alloys.

2. EXPERIMENTAL

The composition of the electrolyte for deposition of the alloy coatings is shown in Table1.

Table 1

Electrolyte composition	Concentration	
	g dm^{-3}	mol dm^{-3}
Cd as $3CdSO_4.8H_2O$	34.2	0.3
Ag as $KAg(CN)_2$	4	0.038
KCN	78	1.2

The electrolytes were prepared using chemicals of *pro analisi* purity and distilled water.

The CV experiments were performed in a 100 cm^3 tri-electrode glass cell at room temperature. The working electrode (area 1 cm^2) and the two counter electrodes were made from platinum. An Ag|AgCl reference electrode ($E_{Ag|AgCl}$ = 0.197 V vs. HE) was used. The reference electrode was placed in a separate cell filled with 3 M KCl solution (Merck), connected to the electrolyte cell by a Haber-Luggin capillary through an electrolyte bridge containing also 3 M KCl solution.

The experiments were performed at room temperature by means of a computerized potentiostat/galvanostat (GAMRY Reference 600) using PHE 200, version 5.5 software (Gamry Instruments).

The Hull experiments were performed in a 25 cm^3 Hull cell onto copper substrates (5 x 3.5 cm) with a

platinized Ti anode with a c.d. of 100, 200 or 300 mA for 10 minutes.

The alloy coatings with thickness between 5-7 μm were deposited onto copper cathodes with an area of 2 x 1 cm in the cell for CV experiments. The preliminary preparation of the copper cathodes includes a standard procedure of electrochemical degreasing followed by pickling in a 20% solution of sulphuric acid. In order to avoid the contact deposition of silver, the cathode was immersed into the electrolyte under current. Two platinum counter electrodes (about 4 cm^2 each) were used.

The elemental composition on the coating surface was measured by EDAX.

The X-ray spectra were measured in the 2θ range between 20°-140° with $Cu_{K\alpha}$ irradiation.

The surface morphology was studied by SEM and optical microscopy.

3. RESULTS AND DISCUSSION

Figure 1 shows CV curves of an electrolyte containing both metals separately or together. Deposition of Ag (black curve 1) is characterized by the cathodic maximum at a potential of – 1.0 V. The coating deposited during the cathodic period dissolves in the anodic period and a broad anodic current maximum around -520 mV is observed. This shape of curve is a typical for this concentration of silver and the respective quantity of free cyanide [21]. Silver is supposed to be deposited in this electrolyte from the complex $Ag(CN)_4^{3-}$ with the instability constant of $2{,}1x10^{-21}$ [22].

The deposition of cadmium (curve 2) is characterized by one cathodic maximum at about -960 mV and one anodic peak with maximum at about -212 mV. The higher rates of the reactions of reduction and oxidation compared to pure silver are due to the higher concentration of the metal ions in the solution.

Two cyanide complexes of cadmium are possible in this electrolyte – $Cd(CN)_3^-$ and $Cd(CN)_4^{2-}$ with instability constants of $5x10^{-16}$ and $1.41x10^{-19}$, respectively [22]. The molar ratio of the cyanide ions to the cadmium ones is 4:1 (this is a minimum molar ratio, ensuring the clearness of the cyanide cadmium electrolyte) and therefore it could be supposed, that the deposition of cadmium is realized from a complex with four cyanide ligands.

The first cathodic maximum in the alloy electrolyte appears at about -600 mV (curve 3) and corresponds to the deposition of silver at more positive potentials than in the absence of cadmium probably because of using of all the free cyanide in the electrolyte in the formation of the cadmium complex. This would correspond to the deposition of silver from the dicyanoargentate complex [21].

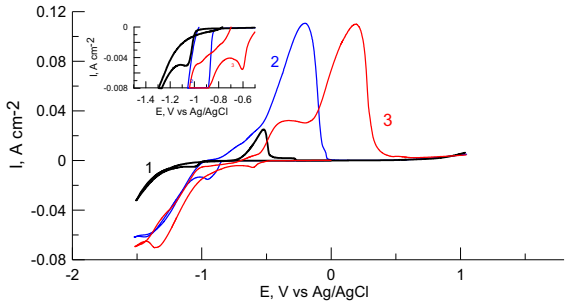

Figure 1. Cyclic voltammetric curves of the single metals and the alloy. Curves: 1 – Ag; 2 – Cd; 3 – AgCd

The deposition of the alloy from this electrolyte is of regular type according to Brenner and the cadmium content in the coatings increases with an increase in the current density.

The concentration of the metal ions in the solution was chosen similar to the electrolytes for deposition of silver-indium alloys where a structure formation is observed according to a linear relationship between the concentration ratio of both metals in the electrolyte and the applied current density [7, 8].

Current densities of 100, 200 and 300 mA were applied in a 25 cm^3 Hull-cell. Deposition of structured heterogeneous coatings was observed on the surface of the electrode in the current density region between 1.0 and 2.5 $A.dm^{-2}$ (Figures 2 and 3).

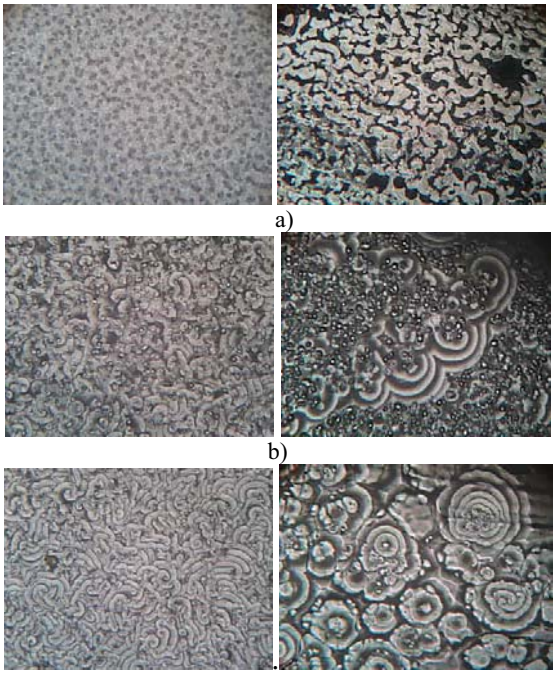

Figure 2 and 3. Optical images of the coatings in the c.d. interval between 1 and 2 Adm^{-2}; deposition time - 10 min.

——— 100 μm.

Fig. 2. 100 mA cell current; *Fig. 3. 200 mA cell current*

At low current density (about 1 Adm^{-2}) dark spots are observed on the surface (Figure 2a, 3a). At increased current density the spots organize they (Figure 2b, 3b) to develop into waves and spiral structures at higher current densities (Figures 2c, 3c).

Figure 4a shows the SEM image of the coating, presented in Figure 2c in different magnifications. The different morphology and the considerable difference in the contrast of the different zones of the structures are visible in Figures 4 b and 4c.

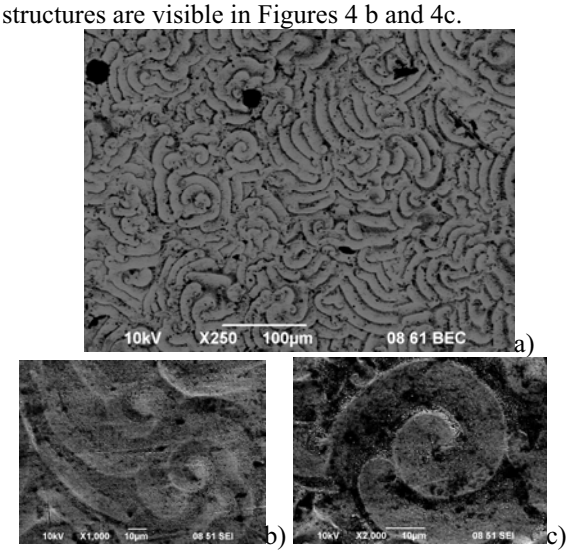

Figure 4. SEM images of the part of the coating, presented in Figure 2c, at different magnification

Figure 5 shows the SEM image of a coating, deposited at 1.5 Adm^{-2} on copper substrate. The coating is compact, dark-gray and bright. The left part of the image in Figure 5a corresponds to the bottom of the electrode. There is an effect of the hydrodynamic flow on the development of the structures similar to the effect observed during electrodeposition of silver–antimony [4] and silver-indium [7,23] alloy coatings.

EDS analysis show, that the upper part of the coating is cadmium–richer and contain about 64 wt. % cadmium in the light areas and about 71 wt. % cadmium the dark areas (Figure 5b).

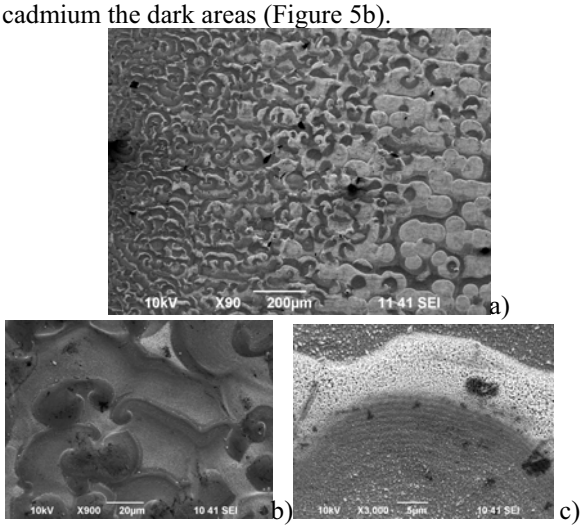

Figure 5. SEM images of the surface of an Ag-Cd coating, obtained at 1.5 Adm-2; deposition time – 20 minutes.

The existence of structures and waves of different scale was also observed as a part of the structures on the surface of the coating (Figure 5c).

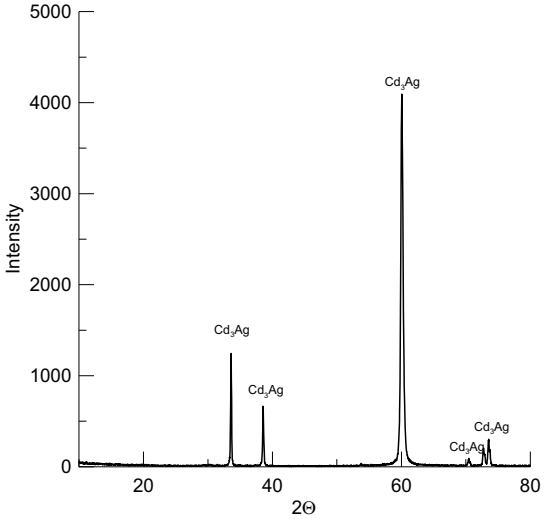

Figure 6. XRD spectrum of the sample of Figure 5.

The XRD-spectrum of the sample of Figure 5 is presented in Figure 6. Surprisingly only reflexes of the Cd_3Ag phase were observed in spite of the believed multiphase heterogeneity of the coatings. Possibly there is a very strong preferred orientation of the crystallites of the hexagonal Cd_3Ag phase leading to this result.

4. CONCLUSION

Silver is deposited predominantly from the investigated electrolyte in which a molar ratio of cyanide to cadmium ions of at least 4:1 should be kept in order to ensure its clearness.

Depending on the electrolysis conditions it is possible to obtain structures on the electrode surface with considerably different morphology.

The reproducible formation and observation of the self-organization phenomenon is possible without any preliminary treatment of the electrolyte.

Acknowledgments

The authors express their gratitude to Deutsche Forschungsgemeinschaft (DFG) for the support of project 436 BUL 113/97/(0)–4.

5. REFERENCES

[1] A. Brenner, Electrodeposition of Alloys. Principles and Practice, Academic Press, New York, pp. 158, London, 1963.

[2] K. M. Gorbunova and Yu. Polukarov, Elektroosazhdenie metallov i splavov, Itogi nauki, Moskva, , pp. 59,1966.

[3] E. Raub and A. Schall, Zeitschrift für Metallkunde, 30, 149, 1938.

[4] I. Krastev and M. T. M. Koper, Pattern formation during the electrodeposition of a silver-antimony alloy, Physica A: Statistical Mechanics and its Applications, 213, 199, 1995.

[5] I. Krastev, T. Valkova, and A. Zielonka, Effect of electrolysis conditions on the deposition of silver-bismuth alloys, 33, 1199, 2003.
[6] A. Hrussanova and I. Krastev, Electrodeposition of silver-tin alloys from pyrophosphate-cyanide electrolytes, Journal of Applied Electrochemistry,39, 989, 2009.
[7] Ts. Dobrovolska, L. Veleva, I. Krastev, and A. Zielonka, Composition and structure of silver-indium alloy coatings electrodeposited from cyanide electrolytes, Journal of the Electrochemical Society, 152, C137-C142, 2005.
[8] Ts. Dobrovolska, I. Krastev, and A. Zielonka, Electrodeposition of silver-indium alloy from cyanide-hydroxide electrolytes, Russian Journal of Electrochemistry, 44, 676, 2008.
[9] C. W. Stillwell, The crystal structures of electrodeposited alloys. Silver-cadmium, Journal of the American Chemical Society, 53**,** 2416, 1931.
[10] C. W. Stillwell and L. E. Stout, The crystal structures of electrodeposited alloys. An x-ray diffraction study of silver-cadmium deposits, The Journal of the American Chemical Society, 54, 2583,1932.
[11] C. W. Stillwell and H. I. Feinberg, The structure of electrodeposited alloys. II. The effect of current density and temperature of deposition on the structure of silver-cadmium deposits, Journal of the American Chemical Society, 55, 1864, 1933.
[12] I. Nambissan and A. J. Allmand, The electrodeposition of silver-cadmium alloys, Transactions of the Faraday Society, 47, 303, 1951.
[13] L. N. Rastorguev, I. D. Kudryavtseva, E. A. Kislitsyn, S. A. Barinov, and V. M. Momotova, Phase composition of electrodeposited alloys in the silver-cadmium system with reference to varoious technological properties, Sov. Electrochem, 11, 1696, 1975.
[14] L. W. Flott, Silver-cadmium alloy plating, Metal Finishing, 83, 11, 1985.
[15] S. Jayakrishnan, Electrodeposition of silver-cadmium alloys from cyanide electrolytes, Transactions of the Institute of Metal Finishing, 78, 124, 2000.
[16] I. R. Epstein, Nonlinear oscillations in chemical and biological systems, Physica D: Nonlinear Phenomena, 51, 152, 1991.
[17] A. M. Turing, The chemical basis of morphogenesis, Philos. Trans. R. Soc. London, Ser. B, 237, 37 1952.
[18]I. Prigogine, Time, structure, and fluctuations, Science, 201, 777, 1978.
[19] M. C. Cross and P. C. Hohenberg, Pattern formation outside of equilibrium, Reviews of Modern Physics, 65, 851, 1993.
[20] A. S. Mikhailov and G. Ertl, Nonequilibrium microstructures in reactive monolayers as soft matter systems, ChemPhysChem, 10, 86, 2009.
[21]Ts. Dobrovolska - PhD Thesis, Electrodeposition, structure and properties of silver-indium alloys, Insitute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria, 2006.
[22] Spravochnik khimika, Moskva, Leningrad, 1965, p. 143.
[23] Ts. Dobrovolska, G. Beck, I. Krastev, and A. Zielonka, Phase composition of electrodeposited silver-indium alloys, Journal of Solid State Electrochemistry, 12, 1461, 2008.