1	Electrochemical deposition and characterization of AgPd alloy layers
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14	Abstract: The AgPd alloys were electrodeposited onto Au and glassy carbon (GC) disc
15	electrodes from the solution containing 0.001 mol $dm^{-3} PdCl_2 + 0.04$ mol $dm^{-3} AgCl + 0.1$
16	mol dm ⁻³ HCl + 12 mol dm ⁻³ LiCl under the conditions of non-stationary $M = 0$ and
17	convective diffusion (RPM = 1000), to the different amounts of charge and at different
18	current densities. Electrodeposited alloy layers were characterized by the anodic linear sweep
19	voltammetry (ALSV), scanning electron microscopy (SEM), energy dispersive X-ray
20	spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). Compositions of the AgPd
21	alloys determined by the EDS were almost identical to the theoretically predicted ones, while
<mark>22</mark>	the compositions obtained by XPS and ALSV analysis (they were very similar) were
23	different. Deviation from the theoretically predicted values (determined by the ratio
24	$j_{\rm L}({\rm Pd})/j({\rm Ag})$) was more pronounced at lower current densities and lower charges of AgPd
25	alloys electrodeposition, due to lower current efficiencies for alloys electrodeposition. The
26	ALSV analysis indicated the presence of , Pd, expressed by two ALSV peaks, and in some
27	cases the presence of additional peak (UP), which was found to correspond to the dissolution
28	of large AgPd crystals formed at thicker electrodeposits (higher electrodeposition charge),
29	indicating, for the first time, that one of the phase structure, the morphology of alloy
<mark>30</mark>	electrodeposit could also influence the shape of the ALSV response. The XPS analysis,
31	among the Ag and Pd, confirmed the presence of AgCl at the surface of samples
32	electrodeposited to low thicknesses (amounts of charge).
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34	Keywords: AgPd alloys electrodeposition, ALSV, XPS, EDS, SEM

35 1. INTRODUCTION

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The possibility of AgPd alloys electrodeposition from the solution containing high
concentration of chloride ions (12 mol dm⁻³ LiCl) was first mentioned by Brenner,¹
considering results obtained by Graham et al.^{2,3} for the electrodeposition of AgPt alloys. It
was shown later⁴⁻⁷ that in the excess of chloride ions AgCl could dissolve to the
concentrations sufficient for the electrodeposition of AgPd alloys, with Pd electrodeposition
starting at more positive potentials than Ag.
In our previous work⁷ AgPd alloys were characterized by the ALSV technique,

indicating the possibility of the formation of additional phase in the electrodeposited alloys, as 44 a consequence of the appearance of additional peak on the ALSV responses. These 45 investigations were in accordance with some other work,⁸ where the measurement of 46 47 microhardness and specific electric resistivity indicated the possibility of the formation of ordered structures (or intermetallic compounds) with approximate stoichiometric 48 49 compositions Ag₂Pd₃ and AgPd in the AgPd alloys below 1200 °C, while all of the data found in binary alloys literature⁹ claimed that the AgPd alloy consists of a homogeneous solid 50 51 solution phase over the entire composition range.

Müller et al.¹⁰ conducted an unbiased search of fcc-based Ag_{1-x}Pd_x structures consisting of up to many thousand atoms by using a mixed-space cluster expansion (MSCE). They found an unsuspected ground state at 50%-50% composition - the *L*1₁ structure, currently known in binary metallurgy only for the Cu_{0.5}Pt_{0.5} alloy system. They also provided predicted shortrange-order profiles and mixing enthalpies for the high temperature, disordered alloy. Using MSCE they predicted the existence of following ordered structures in the system AgPd: Ag₃Pd, Ag₂Pd, AgPd, Ag₂Pd₂, Ag₃Pd₃, AgPd₂ and AgPd₃.

In this work an attempt was made to characterize AgPd alloy layers electrodeposited
from high concentration chloride solutions by different techniques and compare their results,
with the intention to define the appearance of additional peak on the ALSV responses.

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63 **2. EXPERIMENTAL**

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All experiments of AgPd alloys electrodeposition and ALSV analysis were performed in a standard electrochemical cells at the temperature of 333 ± 1 K using rotating Au and GC disc electrodes (d = 5 mm) and CTV 101 Speed Control Unit (Radiometer Analytical, S.A.). The AgPd alloys were electrodeposited onto Au and GC disc electrodes from the solution

containing 0.001 mol dm⁻³ PdCl₂ + 0.04 mol dm⁻³ AgCl + 0.1 mol dm⁻³ HCl + 12 mol dm⁻³ 69 LiCl under the conditions of non-stationary (RPM = 0) and convective diffusion (RPM = 0) \bigcirc (1000), to the different amounts of charge (-0.05 C cm⁻² to -3.0 C cm⁻²) at a constant current 71 density and at different current densities (-0.178 mA cm⁻² to -0.415 mA cm⁻²) to the constant 72 amount of charge (-0.2 C cm⁻²). Pure Pd and Ag samples were electrodeposited onto Au disc 73 electrode from the solutions 0.04 mol dm⁻³ PdCl₂ + 0.1 mol dm⁻³ HCl + 12 mol dm⁻³ LiCl and 74 $0.04 \text{ mol dm}^{-3} \text{ AgCl} + 0.1 \text{ mol dm}^{-3} \text{ HCl} + 12 \text{ mol dm}^{-3} \text{ LiCl}$, respectively, under the 75 conditions of non-stationary and convective diffusion. The dissolution of all coatings by the 76 ALSV technique was performed in another cell containing 0.1 mol dm⁻³ HCl + 12 mol dm⁻³ 77 LiCl under the conditions of convective diffusion $\bigcirc M = 1000$) at the same temperature of 78 333±1 K. The alloy samples for the ALSV analysis were electrodeposited onto Au disc 79 80 electrode, while those for EDS and XPS analysis were electrodeposited onto GC electrode. All solutions were made from extra pure UV water (18.2 M Ω), Smart2PureUV, 81 TKA, and p.a. chemicals (PdCl₂, AgCl, LiCl, HCl), SIGMA-ALDRICH. 82 Saturated calomel electrode (SCE), Radiometer Analytical, was used as the reference 83

electrode in all measurements, while Pt mesh, placed parallel to the working electrode, was
used as a counter electrode in both cells.

The *j*-*E* curves for Ag, Pd, and AgPd alloys electrodeposition and ALSV responses for their dissolution were recorded using potentiostat Reference 600 and software PHE 200 and DC 105 (Gamry Instruments). Before each experiment all solutions were purged with 5.0 N_2 for 30 min. Rotating disc electrodes were polished with emery papers 1200 - 4000 and polishing alumina (1 µm, 0.3 µm, 0.05 µm) before the electrodeposition of each sample.

91 The SEM-EDS characterization of all coatings was performed with FEI Versa 3D field
92 emission gun (FEG)-SEM equipped with energy dispersive spectrometer (EDS).

93 The XPS analysis of samples was carried out in the ultrahigh vacuum system $(3 \cdot 10^{-10})$ mbar) equipped with hemispherical analyzer (SES R4000, Gammadata Scienta). The Mg Ka 94 source of incident energy of 1256.6 eV was applied to generate core excitation. The 95 spectrometer was calibrated according to ISO 15472:2001. The energy resolution of the system, 96 measured at full width at half maximum for Ag $3d_{5/2}$ excitation line, was 0.9 eV. The analysis 97 area of prepared sample was about 3 mm². No gas release and no changes in the sample 98 99 composition were observed during the measurements. The CasaXPS 2.3.12 software was applied for analysis of the XPS spectra. No charging was observed for the studied sample, 100 therefore no additional calibration of the spectra energy scale was applied. In the spectra, the 101 102 background was approximated by a Shirley profile. The spectra deconvolution into a minimum 103 number of components was done by application of the Voigt-type line shapes (70:30 104 Gaussian/Lorentzian product). The analytic depth of the XPS method was estimated as 10.2 105 nm. The calculations were performed with QUASES-IMFP-TPP2M Ver 2.2 software according 106 to an algorithm proposed by Tanuma et al.¹¹ This estimation takes into account 95% of 107 photoelectrons escaping from the surface. The experimental error of the XPS analysis was \pm 108 3%.

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110 **3. RESULTS AND DISCUSSION**

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112 **3.1. Electrodeposition of samples for the ALSV, XPS and EDS analysis**

113 3.1.1. AgPd alloys electrodeposited under the conditions of non-stationary diffusion

Polarization, *j* - *E* curves, for the electrodeposition of pure Ag, pure Pd and AgPd alloys 114 onto Au disc electrode, recorded at a sweep rate of 1 mV s⁻¹ and RPM = 0 are presented in 115 Fig. 1. Electrodeposition of Pd is characterized with well-defined diffusion limiting current 116 density ($i_{\rm L}$ (Pd)) in the solution containing only PdCl₂ (PdCl₄²⁻ ions), as well as in the solution 117 containing $PdCl_2$ and $AgCl \bigcirc Cl_4^{3-}$, with that recorded in the presence of AgCl being 118 slightly higher ($j_L(Pd) = -59.18 \ \mu A \ cm^{-2}$). In the absence of AgCl sharp peak corresponding to 119 the formation of Pd-H^{6,12,13} is detected at -0.10 V, while in the presence of AgCl such peak 120 doesn't exist, indicating that Pd-H cannot be formed during the AgPd alloy electrodeposition. 121 Electrodeposition of Ag is seen to commence at about -0.11 V being characterized with the 122 sharp increase of current density until the peak at about -0.15 V has been reached. The j - E123 curve for AgPd alloy electrodeposition practically represents the sum of those for Pd and Ag. 124 125 The current density values for AgPd alloy electrodeposition are marked in the figure as i(1) = $3i_L(Pd)$, $i(2) = 5i_L(Pd)$ and $i(3) = 7i_L(Pd)$. 126

127The composition of the AgPd alloy could be calculated from the parameters of each128metal electrodeposition. Masses of the electrodeposited Pd (G_{Pd}) and Ag (G_{Ag}) are given as

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$$G_{\rm Pd} = \frac{j_{\rm L}({\rm Pd})tM_{\rm Pd}S}{zF}$$
(1)

$$130 \qquad G_{\rm Ag} = \frac{f({\rm Ag})tM_{\rm Ag}s}{zF}$$
(2)

(131) where: $j_{\rm L}({\rm Pd})$ – diffusion limiting current density for Pd electrodeposition; t – time of

- (132) electrodeposition; M_{Pd} molecular weight of Pd; S electrode surface area; z number of
- (133) exchanged electrons; F Faradays' constant; j_d current density for AgPd alloy
- (134) electrodeposition; j(Ag) current density for Ag electrodeposition ($j(Ag) = j_d j_L(Pd)$); M_{Ag} –
- 135 molecular weight of Ag.







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Fig. 2. Composition of the AgPd alloys calculated from Eqns. (1-4): (□) at.% Pd; (●) at.% 191 Ag. Composition of AgPd alloys obtained by different techniques: (Δ) at.% Pd and (∇) at.% 192 Ag obtained from the ALSV; (\diamond) at.% Pd and (\diamond) at.% Ag obtained from the XPS; (\ddagger) at.% 193 Pd and (\bigstar) at.% Ag obtained from the EDS (see Tables I – III). 194

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3.1.2. AgPd alloys electrodeposited under the conditions of convective diffusion 196

In the case of pure Pd electrodeposition from the solution containing 0.001 mol dm⁻³ 197 $PdCl_2 + 0.1 mol dm^{-3} HCl + 12 mol dm^{-3} LiCl under the conditions of convective diffusion$ 198 the diffusion limiting current density for Pd cannot be precisely defined, as shown in Fig. 3a. 199 200 Although the commencement of Pd electrodeposition is moved to slightly more cathodic potentials in comparison with that at non-stationary diffusion (Fig. 1), a well-defined plateau 201 202 of the $j_{L}(Pd)$ does not exist at any applied rotation rate. A sharp peak of Pd-H formation appears at the same potential (about -0.10 V), as in the case of non-stationary diffusion. The 203 reason for such behavior might be that the sweep rate of 1 mV s⁻¹ is faster than necessary for 204 Pd electrodeposition. An attempt was made to apply sweep rate of 0.1 mV s⁻¹, but with that 205 206 sweep rate the plateau of the diffusion limiting current density could be obtained only with the **RPM=400**, while at higher values of **RPM** such plateau could not be detected. Taking into 207 account that at M=900 the diffusion limiting current density for Pd electrodeposition is 10 208

times higher than that for non-stationary diffusion (see Figs. 1 and 3a) the amount of 209 210 electrodeposited Pd is 10 times higher and in the region of the plateau of the diffusion limiting current density electrodeposit becomes rougher with increasing cathodic potential producing 211 212 increase of the $i_{\rm L}$ (Pd) due to increase of the real surface area. This increase is more pronounced than in the case of non-stationary diffusion and $j_{L}(Pd)$ cannot be well-defined. 213 For AgPd allov electrodeposition in the solution 0.001 mol dm⁻³ PdCl₂ + 0.04 mol dm⁻³ 214 $AgCl + 0.1 mol dm^{-3} HCl + 12 mol dm^{-3} LiCl the situation is even worse. The current density$ 215 for Pd electrodeposition increases in the potential range where a plateau is expected, as seen 216 in Fig. 3b (black solid line). As in the case of non-stationary diffusion, electrodeposition of 217 Ag commences at the same potential, characterized with the sharp increase of current density. 218 219 Hence, the calculation of alloy composition using Eqns. (1-4) is impossible and the

- composition must be determined by other techniques, such as ALSV, XPS or EDS.
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Fig. 3. (a) The *j* - *E* curves for electrodeposition of pure Pd recorded at a sweep rate of 1 mV 238 s⁻¹ and different RPM's (given in the figure) form the solution 0.001 mol dm⁻³ PdCl₂ + 0.1 239 mol dm⁻³ HCl + 12 mol dm⁻³ LiCl. (b) The *j* - *E* curves for electrodeposition of pure Ag 240 (green dashed line), pure Pd (red dotted line) and AgPd alloy (black solid line), recorded at 241 the sweep rate of 1 mV s⁻¹ at the RPM=1000 form the following solutions: (Ag) - 0.04 mol 242 dm⁻³ AgCl + 0.1 mol dm⁻³ HCl + 12 mol dm⁻³ LiCl; (Pd) - 0.001 mol dm⁻³ PdCl₂ + 0.1 mol 243 dm⁻³ HCl + 12 mol dm⁻³ LiCl; (AgPd) - 0.001 mol dm⁻³ PdCl₂ + 0.04 mol dm⁻³ AgCl + 0.1 244 mol dm⁻³ HCl + 12 mol dm⁻³ LiCl. 245

247 3.2. Characterization of electrodeposited AgPd alloys by the ALSV technique

The samples for the ALSV analysis were electrodeposited onto Au disc electrode, due
to reasons explained in our previous work.⁷

250 3.2.1. Characterization of AgPd alloys electrodeposited under the conditions of non-

251 *stationary diffusion*

Typical ALSV responses¹⁴ for dissolution of AgPd alloys electrodeposited under the conditions of non-stationary diffusion (Fig. 1) are shown in Fig. 4a for samples electrodeposited at different j_d ($Q_d = -0.2 \text{ C cm}^{-2}$) and in Fig. 4b for samples electrodeposited to different Q_d ($j_d = -178 \ \mu\text{A cm}^{-2}$).



Fig. 4. ALSV responses for dissolution of AgPd alloys recorded at RPM = 1000 and a sweep rate of 1 mV s⁻¹ in the solution containing 0.1 mol dm⁻³ HCl + 12 mol dm⁻³ LiCl. (a) Alloys electrodeposited to the charge $Q_d = -0.2 \text{ C cm}^{-2}$ at different current densities: (1) - $j_d(1) =$ $3j_L(Pd) = -178 \ \mu\text{A cm}^{-2}$; (2) - $j_d(2) = 5j_L(Pd) = -296 \ \mu\text{A cm}^{-2}$; (3) - $j_d(3) = 7j_L(Pd) = -415 \ \mu\text{A}$ cm⁻²; (4) - $j_d(4) = 5j_L(Pd) = -296 \ \mu\text{A cm}^{-2}$; Q_d = -1.0 C cm⁻². (b) Alloys electrodeposited to different charges (given in the figure) at a constant current density $j_d = -178 \ \mu\text{A cm}^{-2}$.

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Considering these ALSV responses it seems that all of them are characterized with two dissolution peaks, one corresponding to the dissolution of Ag and one corresponding to the dissolution of Pd. With the increase of the amount of charge for AgPd alloy electrodeposition (thickness of the alloy layer) the peak current densities on the ALSV responses become higher. In order to determine approximate composition of the AgPd alloys (taking into

account high values of current efficiencies for alloy electrodeposition, see Tables I - III), the 280 ALSV responses were analyzed as schematically presented in Fig. 4a for sample 4, as well as 281 in Fig. 4b for sample corresponding to the dissolution of AgPd alloy electrodeposited to Q_d = 282 - 0.6 C cm⁻² (see also Fig. 5b). The ALSV responses were divided in two parts, one 283 corresponding to the dissolution of Ag ($Q(Ag)_{ALSV}$) and another one corresponding to the 284 dissolution of Pd ($Q(Pd)_{ALSV}$). The at.% of Pd and Ag, calculated from their charges on the 285 286 ALSV responses, are presented in Fig. 2 (points (Δ) and (∇) respectively), while calculated percentages are presented with (\Box) for Pd and (\bigcirc) for Ag. The percentages of Pd and Ag. 287 obtained from the XPS analysis are presented with (\diamondsuit) for Pd and (\diamondsuit) for Ag, while those 288 obtained from the EDS analysis are presented with (\ddagger) for Pd and (\bigstar) for Ag, respectively. It 289 290 should be stated here that only two samples presented in the Fig. 2 were analyzed by the XPS and EDS (see Table I). Results of the composition analysis with all three techniques were 291 292 different (Tables I – III). Relatively good agreement was obtained for those obtained from the XPS and ALSV analysis, where the at.% Pd was the lowest for sample AgPd2. The difference 293 294 between the calculated percentages of Pd (\Box) and Ag (\bigcirc) and those determined from their charges on the ALSV responses (Pd (Δ), Ag (∇)), as well as those determined by XPS 295 296 $(Pd(\diamond), Ag(\diamond))$, is seen to increase with the decrease of electrodeposition current density. Actually, for the ALSV and XPS analysis, the increase in the at.% Pd is equal to the decrease 297 in the at.% Ag. Taking into account that the results of XPS and ALSV analysis are in 298 relatively good agreement, the difference between theoretically predicted and experimentally 299 detected alloy compositions could be the consequence of lower current efficiency for alloy 300 electrodeposition at lower current densities (j_d) and lower amounts of charge for alloy 301 302 electrodeposition (Q_d) (see Tables I and II). At higher current densities (> 400 μ A cm⁻²) and higher values of Q_d the current efficiency η_i for alloy electrodeposition is very high (> 97 %) 303 causing identical theoretical and experimentally determined compositions of AgPd alloys (see 304 Fig. 2 and Tables I and II). Due to low current densities for AgPd alloys electrodeposition, the 305 highest amount of charge was $Q_d = -1.5 \text{ C cm}^{-2}$ (see Table I, sample (5)). 306 3.2.2. Characterization of AgPd alloys electrodeposited under the conditions of convective 307

308 *diffusion*

ALSV responses for dissolution of AgPd alloys electrodeposited under the conditions of convective diffusion are shown in Fig. 5a for samples electrodeposited at different j_d ($Q_d = -$ 0.2 C cm⁻²) and in Fig. 5b for sample electrodeposited at $j_d = -7.0$ mA cm⁻² to the $Q_d = -3.0$ C

- cm^{-2} . For dissolution of these samples the same comments and conclusions as those for
- samples electrodeposited under the conditions of non-stationary diffusion are valid.

With the increase of j_d the peak of Ag dissolution increases, while that for Pd 314 dissolution decreases (Fig. 5a), as in the case of samples electrodeposited under the conditions 315 of non-stationary diffusion. For samples electrodeposited under the conditions of convective 316 diffusion the peak potential of Pd dissolution is seen to become more negative with the 317 increase of *i*_d (Fig. 5a), while that for samples electrodeposited under the conditions of non-318 stationary diffusion remains practically the same (Fig. 4a). Such behavior could be the result 319 of different morphology of AgPd samples electrodeposited by these two procedures (see Figs. 320 9-11). For sample electrodeposited to the highest charge ($Q_d = -3.0 \text{ C cm}^{-2}$), the separation of 321 Ag and Pd peaks is not as well-defined as for samples electrodeposited to the lower charges. 322 323 Table I. Electrodeposition of the AgPd alloys to $Q_d = -0.2$, -1.0 and -1.5 C cm⁻² at M=0 and different 324

325 current densities (j_d) from the solution: 0.001 M PdCl₂ + 0.04 M AgCl + 0.1 M HCl + 12 M LiCl.

326 Dissolution (ALSV) in the solution 0.1 M HCl + 12 M LiCl at M=1000 with a sweep rate of 1 mV s⁻¹.

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	$j_{\rm d}$ (µA cm ⁻²)	$Q(Pd)_{ALSV}$ (C cm ⁻²)	$Q(Ag)_{ALSV}$ (C cm ⁻²)	(0/)	ALSV		XPS		EDS		O(IIII)
Sample				$Q_{ m ALSV}/Q_{ m d}$	at.%	at.%	at.%	at.%	at.%	at.%	$Q(OP)_{ALSV}$
					Pd	Ag	Pd	Ag	Pd	Ag	(%)
				$Q_{\rm d} = -0.2$ C	C cm ⁻²						
(1)AgPd1	178	0.088	0.093	90	24	76	27.4	72.6	16.2	83.8	0
(2)	296	0.059	0.139	96	12	88					15.7
(3)AgPd2	415	0.042	0.154	98	8	92	13.4	86.6	9.8	90.2	10.2
				$Q_{\rm d} = -1.0$ C	C cm ⁻²						
(4)	296	0.290	0.700	99	12	88					17.2
				$Q_{\rm d} = -1.5$ C	C cm ⁻²						
(5)	296	0.469	1.018	99	13	87					27.6

328 $j_{\rm L}({\rm Pd}) = -59.18 \ \mu{\rm A \ cm^{-2}}$

Table II. Electrodeposition of the AgPd alloys to the different amounts of charge (Q_d) at $j_d = -178 \ \mu A \ cm^{-2}$

331 $(j_d = 3j_L(Pd))$ and RPM = 0 from the solution: 0.001 M PdCl₂ + 0.04 M AgCl + 0.1 M HCl + 12 M LiCl.

332 Dissolution (ALSV) in the solution 0.1 M HCl + 12 M LiCl at M = 1000 with a sweep rate of 1 mV s⁻¹.

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$Q_{\rm d}$ (C cm ⁻²)	$Q(Pd)_{ALSV}$ (C cm ⁻²)	$Q(Ag)_{ALSV}$ (C cm ⁻²)	$\eta_{ m j}(\%) \ Q_{ m ALSV}\!/Q_{ m d}$	at.% Pd	at.% Ag	$Q(\text{UP})_{\text{ALSV}}(\%)$
-0.05	0.0243	0.0191	73	38	62	0
-0.1	0.043	0.043	86	33	67	0
-0.2	0.097	0.088	93	35	65	0
-0.4	0.176	0.206	96	30	70	16
-0.6	0.312	0.267	97	37	63	23

at.% of Pd and Ag, as well as Q(UP), are obtained from the ALSV responses.

Only one sample (ALSV presented in Fig. 5b) was analyzed by the XPS and EDS.
Results of conditions for AgPd alloy electrodeposition and their compositions are shown in
Table III.



Fig. 5. ALSV responses for dissolution of AgPd alloys recorded at RPM = 1000 and a sweep rate of 1 mV s⁻¹ in the solution 0.1 mol dm⁻³ HCl + 12 mol dm⁻³ LiCl. (a) Alloys electrodeposited to the charge $Q_d = -0.2$ C cm⁻² at different current densities (marked in the

figure). (b) Alloy electrodeposited to the highest amount of charge.

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357Table III. Electrodeposition of AgPd alloys to the different amounts of charge (Q_d) at different current358densities and M = 1000 from the solution: 0.001 M PdCl₂ + 0.04 M AgCl + 0.1 M HCl + 12 M LiCl.359Dissolution (ALSV) in the solution 0.1 M HCl + 12 M LiCl at M = 1000 with a sweep rate of 1 mV s⁻¹.360

	0.	$O(\mathbf{Pd})_{\rm Mark}$	$O(\Delta \sigma)_{\rm MSW}$	n(0)	ALSV		XPS		EDS		O(IIP)
Sample	\mathcal{L}^{α}	$\mathcal{Q}(\mathbf{I} \mathbf{u}) \mathbf{ALSV}$	$\mathcal{Q}(\mathbf{r} \mathbf{g}) \mathbf{ALSV}$	$\eta_{\rm J}(10)$	at.%	at.%	at.%	at.%	at.%	at.%	(%)
	(C chi)	(0 011)	(0 0 1 1)	QALSV/Qd	Pd	Ag	Pd	Ag	Pd	Ag	(70)
			<i>j</i> d =	= -5 mA cm ⁻¹	² ; RPM	= 1000)				
(1)	-1.0	0.195	0.796	99	11	89					4
(2)	-2.0	0.214	1.512	86	7	93					40
			<i>j</i> d =	= -7 mA cm ⁻²	² ; RPM	= 1000)				
(3)AgPd3	-3.0	0.649	2.065	90	13.4	86.6	15.2	84.8	3.4	96.6	55

363 *3.2.3. Procedure of fitting ALSV responses*

According to the theoretical predictions for the ALSV technique,¹⁴ ALSV responses of 364 solid solution type alloys should be characterized with two separate peaks only 365 (corresponding to the dissolution of each metal), since in the case of alloys with intermediate 366 phases (intermetallic compounds) each phase should be characterized with a separate peak on 367 the ALSV. The shape of the ALSV responses of AgPd alloys is seen to change from ALSV 368 369 responses with two peaks only to the ALSV responses with more than two peaks, depending on the value of j_d and Q_d (see Figs. 4 and 5). The procedure of fitting ALSV responses with 370 two peaks (using multi-peaks Lorentzian function) was possible only for samples 371 electrodeposited at smaller current densities (< 200 µA cm⁻²) and samples electrodeposited to 372 the cathodic charges lower than 0.4 C cm⁻². In Fig. 6 are presented results of fitting ALSV 373 responses of the AgPd alloys dissolution electrodeposited at different values of j_d to a 374 different Q_d under the conditions of non-stationary diffusion. Fitting lines (black solid lines) 375 are in a good agreement with the experimental ones (magenta dash-dot-dot lines), with the Ag 376 peak being labeled with red dash lines, Pd peak with green dotted lines and a third, unknown 377 peak, UP, whose origin was undefined, labeled with a blue dash-dot lines. It should be 378 379 emphasized that fit of the most positive peak, Pd peak, cannot follow the shape of the Lorentzian peak after the peak maximum has been reached, since the peak current density 380 sharply decreases due to removal of the traces of the electrodeposit and certain discrepancy 381 between the fitting and experimental lines must exist, as it could be seen in Figs. 6 and 7. As 382 already stated only sample electrodeposited at $j_d = 3j_L(Pd)$ could be fitted with two peaks, Fig. 383 6a and b, while the appearance of a third peak (UP) could already be observed for the sample 384 385 electrodeposited at $j_d = 7j_L(Pd)$.

For the AgPd alloys electrodeposited at a constant current density $j_d = -178 \ \mu A \ cm^{-2} \ (j_d = 3j_L(Pd))$ and RPM = 0 to the different amounts of charge (Fig. 4b, Table II), the appearance of a third peak (UP) was detected at cathodic charges higher than -0.2 C cm⁻².

389 $Q(Pd)_{ALSV}$ and $Q(Ag)_{ALSV}$ in Tables I - III are presented results obtained by 390 the analysis of the charge under the third peak, $Q(UP)_{ALSV}$, and the whole ALSV responses 391 (Q_{ALSV}) . The peak appears to be more pronounced, its charge, expressed in percentages of 392 the total charge under the ALSV (Q_{ALSV}) , increases with the increase of cathodic current 393 density and cathodic charge. It should be stated that such approach is rough approximation, 394 since all three peaks obtained by fitting procedure overlap and it is practically not possible to 395 determine exact amount of charge for the UP peak.



Fig. 6. Results of fitting ALSV responses of the AgPd alloys electrodeposited at $j_d = 3j_L(Pd)$, $Q_d = -0.1 \text{ C cm}^{-2}$ (a), $j_d = 3j_L(Pd)$, $Q_d = -0.2 \text{ C cm}^{-2}$ (b) and $j_d = 7j_L(Pd)$, $Q_d = -0.2 \text{ C cm}^{-2}$ (c). Fitting (black solid lines), experimental (magenta dash-dot-dot lines), Ag (red dashed lines), Pd (green dotted lines), unknown peak (UP) (blue dash-dot lines).

In Fig. 7 are presented ALSV responses of AgPd alloy layers electrodeposited at different current densities and different amounts of charge under the conditions of convective diffusion M=1000. Since the cathodic charges are higher than -0.4 C cm⁻² all ALSV responses had to be fitted with three peaks. The UP peak is seen to increase with the increase of Q_d .

426 Results presented in Table III are obtained by the analysis of ALSV responses shown in 427 Fig. 7. As can be seen the charge for UP reaches high values in samples electrodeposited to 428 higher cathodic charges ($Q_d = -2.0 \text{ C cm}^{-2}$ and $Q_d = -3.0 \text{ C cm}^{-2}$). The composition of only one 429 sample (AgPd3, $Q_d = -3.0 \text{ C cm}^{-2}$) was analyzed by the XPS and EDS techniques.

Hence, considering the results of the ALSV analysis it appears that all electrodeposited
AgPd alloy layers do not represent solid solution type alloy, being characterized with the
presence of two peaks only (corresponding to the dissolution of Ag and Pd). The appearance
of a UP peak could be either the consequence of the formation of additional phase, or the
properties of the AgPd electrodeposit. Theoretically, there is a possibility for the formation of

different ordered structures in the AgPd system,¹⁰ but the question arises is it possible to
detect these ordered structures by the application of the ALSV technique. In order to define
the appearance of UP peak on the ALSV responses, additional analysis, using XPS and SEMEDS techniques was performed.





Fig. 7. Results of fitting ALSV responses of the AgPd alloys electrodeposited at M=1000: (a) $j_d = -5 \text{ mA cm}^2$, $Q_d = -1.0 \text{ C cm}^2$; (b) $j_d = -5 \text{ mA cm}^2$, $Q_d = -2.0 \text{ C cm}^2$; (c) $j_d = -7 \text{ mA}$ cm⁻², $Q_d = -3.0 \text{ C cm}^2$. Fitting (black solid lines), experimental (magenta dash-dot-dot lines), Ag (red dashed lines), Pd (green dotted lines), unknown phase (UP) (blue dash-dot lines).

461 3.3. Characterization of the AgPd alloys by the XPS analysis

462 Five peaks, namely O1s, Ag3d, Pd3d, C1s and Cl2p were detected on the surface of AgPd1, AgPd2 and AgPd3 samples. For the composition analysis the most important peaks 463 are Ag3d and Pd3d and their percentages were taken from the complete XPS spectra. The 464 XPS results for these two elements are shown in Fig. 8. By their deconvolution it was 465 discovered that certain amount of AgCl could be detected on Ag3d spectra. The amount of 466 AgCl is seen to decrease from AgPd1 to AgPd3 samples, being 19.3 % for AgPd1, 16.4 % for 467 AgPd2 and 5.3 % for AgPd3. Certain amount (smaller in percentages than AgCl) of PdO was 468 detected under the Pd3d spectra, also decreasing from AgPd1 to AgPd3. 469 470



498 Fig. 6. Results of the XPS analysis for Ag3d (a,b,c) and Pd3d (d,e,f) in samples AgPd1,
499 AgPd2 and AgPd3 respectively.

501 3.4. Characterization of the AgPd alloys by the EDS analysis

Result of the EDS analysis for sample AgPd1 is presented in Fig. 9a, while SEM 502 micrograph of that sample is shown in Fig. 9b. The surface is heterogeneous and rough, with 503 the presence of white and gray parts and the substrate is not completely covered with 504 electrodeposit (a,b). White parts on the EDS (a) contain approximately 12.6 at.% Cl, while the 505 EDS of gray parts shows only 0.6 at.% Cl, indicating that white parts of the electrodeposit 506 could be AgCl with excess of chloride since the ratio Ag/Cl is higher than 1. The AgCl was 507 detected on much bigger surface area (3 mm²) and much lower depth (10.2 nm) by the XPS 508 analysis. Hence, for the EDS analysis only gray parts of the electrodeposit were considered 509

and corresponding results are given in Tables I - III. As can be seen in Fig. 9a, AgPd crystals
are characterized by rounded shape with the dimensions of about 200 nm.



Fig. 9. (a) EDS analysis at two positions of the surface of AgPd1 sample. Average
composition is given in Table I. (b) SEM micrograph of the surface of AgPd1 sample: inset –
SEM recorded at higher magnification.

Result of the EDS analysis for sample AgPd2 is presented in Fig. 10c, while SEM micrograph of that sample is shown in Fig. 10d. Again, the surface is heterogeneous and rough, with the presence of white and gray parts and the substrate is not completely covered with electrodeposit (c,d), but the non-covered substrate surface is smaller in comparison with that for sample AgPd1. White parts on the EDS (c) contain approximately 13.1 at.% Cl, while the EDS of gray parts shows only 0.9 at.% Cl. Concerning the presence of AgCl (XPS) on the surface of sample AgPd2, the same conclusion, as that for sample AgPd1, is valid. AgPd crystals (Fig. 10c) are characterized by rounded shape with the dimensions of about 300 nm.







Fig. 10. (c) EDS analysis at two positions of the surface of AgPd2 sample. Average
composition is given in Table I. (d) SEM micrograph of the surface of AgPd2 sample: inset –
SEM recorded at higher magnification.

Result of the EDS analysis for sample AgPd3 is presented in Fig. 11e, while SEM 547 micrograph of that sample is shown in Fig. 11f. The surface is rough, composed of much 548 larger crystals than those of samples AgPd1 and AgPd2. No presence of white parts was 549 550 detected on the sample surface, indicating the absence of AgCl. Since this electrodeposit is much thicker, the substrate is completely covered with electrodeposit (e,f). At some positions 551 552 large AgPd crystals, of about 10-20 µm high (marked with arrows in Fig. 11f), growing normally to the electrode surface are detected (f), which is typical for metals with fast 553 nucleation rate, as are Ag and Pd.¹⁵⁻¹⁷ 554



Fig. 11. EDS analysis at two positions of the surface of AgPd3 sample. Average
composition is given in Table I. SEM micrograph of the surface of AgPd3 sample: inset –
SEM recorded at higher magnification.

568
Considering the results of ALSV, XPS and EDS analysis for samples electrodeposited
570 under the conditions of non-stationary diffusion (Fig. 2), it could be stated that similar

under the conditions of non-stationary diffusion (Fig. 2), it could be stated that similar 571 compositions obtained by the ALSV and XPS are the result of high surface area analysis (in the case of ALSV the whole sample, in the case of XPS 3mm²), taking into account the 572 **573** presence of AgCl on their surfaces. For the EDS analysis only gray parts of the surfaces were analyzed, giving higher percentages of Ag in the electrodeposit (Tables I – III). The 574 appearance of UP on the ALSV responses, recorded for samples obtained at higher 575 electrodeposition current densities and higher charges, is most probably the consequence of 576 577 different morphologies. Actually, with the increase of j_d and Q_d the morphology becomes similar to that presented in Fig. 11f and the Ag from large AgPd crystals, particularly those of 578 higher heights (marked with arrows in Fig. 11f), dissolves easier and faster than from the rest 579 of the surface (the dissolution is a pure inversion of deposition).¹⁸ When the whole amount of 580 Ag from the large AgPd crystals is dissolved, the current density on the ALSVs starts to 581

decrease until the Ag begins to dissolve from the rest of the surface, causing the appearance of 582 an additional peak on the ALSV responses. Hence, the appearance of an additional peak could 583 be the consequence of this phenomenon.¹⁵⁻¹⁸ The ALSV response for thin AgPd alloy layer 584 (Fig. 6a,b – low j_d and Q_d) shows no additional peaks and could be fitted with two peaks using 585 Origin multi-peaks Lorentzian function. Hence, it appears that additional peak on the ALSV 586 responses is the result of faster dissolution of large crystals of higher heights. This means that 587 $Q(UP)_{ALSV}$, given in Tables I - III, roughly represents the percentage of total surface area 588 containing large AgPd crystals of higher heights. 589

590

591 4. CONCLUSIONS

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The AgPd alloys electrodeposited from the solution containing 0.001 mol dm⁻³ PdCl₂ + 593 $0.04 \text{ mol dm}^{-3} \text{ AgCl} + 0.1 \text{ mol dm}^{-3} \text{ HCl} + 12 \text{ mol dm}^{-3} \text{ LiCl}$ under the conditions of non-594 stationary $\mathbb{M} = 0$ and convective diffusion $\mathbb{M} = 1000$, to the different amounts of 595 charge and at different current densities, were characterized by the ALSV, SEM, EDS and 596 XPS techniques. Compositions of the AgPd alloys determined by the EDS were almost 597 598 identical to the theoretically predicted ones, while the compositions obtained by XPS and ALSV analysis (they were almost identical) were different. Deviation from the theoretically 599 predicted values (determined by the ratio $j_{\rm L}({\rm Pd})/j({\rm Ag})$) was more pronounced at lower current 600 densities and lower charges of AgPd alloys electrodeposition, due to lower current 601 efficiencies for alloys electrodeposition. The ALSV analysis indicated the presence of Ag, Pd, 602 expressed by two ALSV peaks, and additional peak, which was found to correspond to the 603 dissolution of large AgPd crystals formed at electrodeposits with higher charge and larger 604 cathodic current densities. The XPS analysis, among the Ag and Pd, confirmed the presence 605 of AgCl at the surface of samples electrodeposited to low amounts of charge. 606 607

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616	ИЗВОД
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618	Карактеризација електрохемијски исталожених слојева сребро-паладијум ле 😥
619	различитим техникама
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632	
633	Апстракт: Танки слојеви сребро-паладијум легура исталожени су електрохемијским
634	поступком на дисковима од злата и стакластог угљеника из раствора01 дм ⁻³
635	PdCl ₂ + 4 4 4 4 4 5 4 5 4 5 4 5 6 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7
636	нестационарне ($\omega = 0$ o min ⁻¹) и конвективне ($\omega = 1000$ o min ⁻¹) дифузије, при
637	различитим вредностима густине струје таложења и количине наелектрисања.
638	Електрохемијски исталожени слојеви окарактерисани су анодном линеарном
639	волтаметријом (ALSV), скенирајућом електронском микроскопијом (SEM), енергетски
640	диспергованом рендгенском спектроскопијом (EDS) и рендгенском фотоелектронском
641	спектроскопијом (XPS). Састав сребро-паладијум легура одређен EDS техником био је
642	скоро идентичан теоријски предвиђеном, док су састави одређени XPS и ALSV
643	техникама (који су били скори идентични) одступали од теоријски предвиђеног, при
644	чему је то одступање било израженије код узорака исталожених мањим густинама
645	струје и узорака исталожених до мањих количина наелектрисања. ALSV анализа је
646	показала присуство сребра и паладијума, изражено као два струјна врха, као и
647	присуство још једног струјног врха, за који је установљено SEM и EDS анализама да је
648	последица растварања великих сребро-паладијум кристала који се формирају код
649	дебљих превлака, исталожених до већих количина наелектрисања. На тај начин је по

- 650 први пут показано да поред фазног састава и морфологија талога легура може утицати
- 651 на облик ALSV одговора. XPS анализом је на површини тањих узорака (исталожених
- 652 до мањих количина наелектрисања у условима нестационарне дифузије) потврђено
- 653 присуство сребро хлорида, поред сребра и паладијума.
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