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MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF
CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

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ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE*

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Zn/Au alloys formation by Zn electrodeposition from a deep eutectic system

Formiranje Zn/Au legura elektrohemijским taloženjem Zn iz dubokog eutektikuma

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Abstract

The electrochemical deposition of Zn onto Au from a choline chloride/ethylene glycol deep eutectic system containing different ZnCl₂ concentrations has been investigated. The voltammetric results demonstrated that Zn electrodeposition commences in the zinc underpotential deposition (UPD) and proceeds through to the zinc overpotential deposition (OPD) region. The results of X-ray diffraction analysis revealed that the deposit prepared at a relatively low Zn overpotential of – 0.050 V vs. Zn was composed of cubic AuZn alloy. The morphology of the deposit has been characterized by means of a scanning electron microscope and displays a relatively compact and dendrite-free Zn/Au alloy deposit formed.

Keywords: zinc electrodeposition; deep eutectic solvent; zinc/gold alloys; morphology

Izvod

U radu je ispitivano elektrohemijško taloženje Zn na Au iz dubokog eutektikuma koji se sastojao od holin hlorida/etilen glikola i sadržavao je različite koncentracije ZnCl₂. Na osnovu voltametrijskih rezultata ustanovljeno je da elektrohemijško taloženje Zn započinje u oblasti potpotencijala Zn i nastavlja se u oblasti natpotencijala. Rezultati rengenske difrakcione tehnike su pokazali da se talog dobijen elektrohemijškim taloženjem Zn u oblasti natpotencijala Zn, na potencijalu od – 0.050 V vs. Zn sastoji od kubne AuZn legure. Skenirajuća elektronska mikroskopija je pokazala da je dobijeni AuZn talog relativno kompaktan i bez dendrita.

Ključne reči: elektrohemijško taloženje cinka; duboki eutektikum; cink/zlato legure; morfologija

Introduction

The electrodeposition of metals from ionic liquids, particularly those employing deep eutectic solvents, (DESs), has gained significant attention recently [1,2]. Deep eutectic electrolytes have been suggested as alternatives to classical room temperature ionic liquids and nowadays are used on an industrial scale for the electrodeposition processes to produce protective metal coatings [2]. As it is well known, zinc is an important industrial metal, particularly in anticorrosion protection [3]. However, the electrodeposition of zinc coatings for anticorrosion protection from the aqueous electrolytes is accompanied by massive hydrogen evolution. Zinc deep eutectic solvents (DESs) have become an alternative choice of electrolytes for hydrogen-free industrial plating of zinc coatings. Several studies on the electrodeposition of Zn, Co, Ni, Pd, Ag, Cu, Sn, or Ru, from DESs have been reported. It has been shown that DES not only combines the advantages of the system's wide electrochemical window in low-temperature operation but can also provide metals and alloys that are

otherwise electrodeposited usually from high-temperature molten salts [4]. Several groups have studied the electrodeposition of Zn from deep eutectic systems mainly composed of choline chloride (ChCl):ethylene glycol (EG) or ChCl:Urea containing ZnCl_2 [1,4–6]. Abbot et al. studied the electrodeposition of Zn from ChCl:EG and ChCl:Urea DESs onto a platinum disc working electrode [1]. Whitehead et al. investigated the Zn electrodeposition process by cyclic voltammetry and potential step techniques from ChCl:EG containing ZnCl_2 using static and rotating glassy carbon (GC) disc cathodes at 30°C [7]. The voltammetric behavior of the Zn in ChCl:EG with 0.3 M ZnCl_2 by employing glassy carbon, stainless steel, Au, Pt, Cu, and Zn working electrodes was investigated by Vieira et al. [6]. In the literature, a number of studies reported the usage of additives, in order to improve deposit morphology and physical characteristics [1,5].

In this work, we have investigated zinc electrodeposition onto polycrystalline gold electrode from choline chloride (ChCl):ethylene glycol 1:2 (ChCl:EG) electrolyte at 60°C. The main task was to achieve a dendrite-free Zn coating onto polycrystalline gold electrodes without using additives. Cyclic voltammetry and chronoamperometry have been used to attain a better understanding of the nature of the electrode reaction involved in Zn electrodeposition.

Experimental

The electrolyte was prepared by mixing choline chloride ($\geq 98\%$, $\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$) and ethylene glycol (99.8%, ethane-1,2-diol) at a 1:2 molar ratio. The mixture was then placed onto a hot plate for 2.5 hours at 40°C, and slowly mixed under an argon atmosphere until a colorless liquid phase was formed. The electrolytes containing ZnCl_2 (0.01 M, 0.1 M and 0.5 M) were prepared similarly by adding zinc chloride (99.999% ZnCl_2), to the based electrolyte. The electrolyte was stirred again until all of the zinc salt had been completely dissolved. A three electrode electrochemical cell configuration was employed, in which gold (Au, 99.999%, wires or plates) was used as a working electrode, reference electrode was made from a Zn rod (Zn, $\phi = 3\text{mm}$, 99.99%) and the counter electrode was a zinc plate (active surface area in the electrolyte 7.5 cm^2 , Zn 99.99%). The details of the electrochemical cell set up and procedure of the electrodes preparation have already been reported elsewhere [8,9]. All experiments were performed at 60 °C. The electrochemical measurements: cyclic voltammetry (CV, using various scan rates in the range of 2–20 mV/s), chronoamperometry, potentiodynamic and open-circuit potential chronopotentiometry, were controlled by an potentiostat/galvanostat Interface 1010 E (Gamry Instruments, Warminster, PA, US). Zn electrodeposition was performed by applying constant potentials to the Au cathode in the electrolytes containing Zn^{2+} ions. The structure analysis of the deposit was revealed by X-ray diffraction (XRD), employing a SmartLab® X-ray diffractometer (Rigaku Co., Tokyo, Japan). The morphology and composition of Zn deposits were explored using a scanning electron microscope (JOEL JSM-IT300LV), equipped with an energy-dispersive X-ray spectroscopy (EDS) Oxford Instruments X-MAX^N and AZtec version 3.1 software.

Results and Discussion

Figure 1. shows the CVs recorded on a polycrystalline Au electrode immersed in ChCl:EG with different ZnCl_2 concentrations at 60 °C. One reduction (C_1) current wave with peak potentials at ≈ 0.170 V vs. Zn was observed in the Zn underpotential region (UPD) region, Fig. 1a) and b). In Zn overpotential region (OPD), at potentials negative to ≈ -0.050 V vs. Zn, classical nucleation loops indicating the deposition of the Zn bulk metal were recorded. These nucleation and electrocrystallization loops have been often reported for Zn deposited on a foreign substrate from ionic liquid electrolyte media [5]. When the concentration of Zn^{2+} ions was increased in the electrolyte, the beginning of the current loops was shifted to less negative electrode potentials. In the 0.01 M ZnCl_2 electrolyte, the start of the nucleation loop was observed at potential of ≈ -0.150 V, (Fig. 1a), in 0.1 M ZnCl_2 at ≈ -0.100 V vs. Zn, (Fig. 1b). The cyclic voltammetry of zinc deposition/dissolution on

gold electrodes shows multiple stripping peaks in the anodic potential range which could be attributed to the dissolution of bulk zinc (A_3) and the dissolution of Zn/Au alloys at more positive potentials (A_2 and A_1). Diffusion controlled Zn bulk deposition in the voltammograms becomes obvious only at the cathodic end potentials applied above -0.200 V vs. Zn.

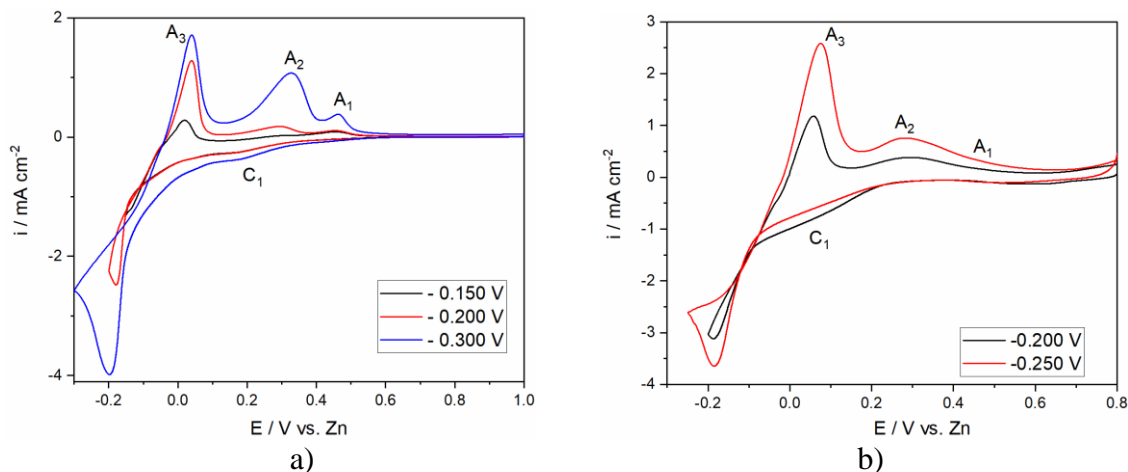


Figure 1. Cyclic voltammograms of Au cathodes in choline chloride:ethylene glycol (1:2 molar ratio) electrolyte containing different concentrations of $ZnCl_2$: a) 0.01 M $ZnCl_2$; b) 0.1 M $ZnCl_2$. The CVs started from initial potential E_i towards different cathodic end potential E_c with a scan rate of 5 mV/s.

To get further inside into Zn electrodeposition the system was investigated by the open-circuit potentiometry. The open-circuit measurements were recorded after Zn deposition in the electrolytes containing different concentration of Zn(II). Open circuit measurements registered the start of dissolution of a solid phase at around 0.000 V vs. Zn in both systems, followed by a plateau I, Fig. 2a) and b). According to the open-circuit measurements in Fig. 2a) the plateau II at the potential of ≈ 0.300 V and the plateaux II and III at ≈ 0.280 and 0.400 V, Fig. 2b) were recorded. This dissolution current plateau after Zn deposition at $E_{dep} = -0.100$ V on Au cathode for only 3 min, suggests dissolution of zinc from deposited metal zinc and Zn/Au alloys formed during Zn deposition.

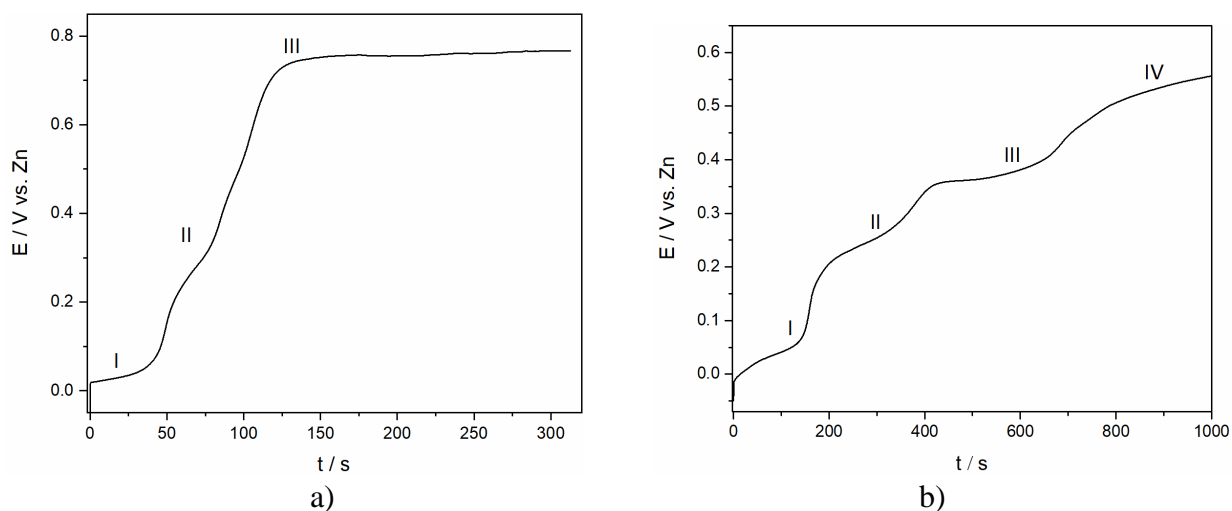


Figure 2. Open-circuit potential transient curves obtained after short polarization ($t = 3$ min), at -0.100 V vs. Zn in choline chloride:ethylene glycol (1:2 molar ratio) electrolyte containing different concentrations of $ZnCl_2$: a) 0.01M $ZnCl_2$; b) 0.1 M $ZnCl_2$.

Figure 3. shows surface morphology obtained by electrodeposition from 0.1 M Zn(II) at an overpotential of -0.050 V vs. Zn (Fig. 3a)), and XRD analysis of the same sample in Fig. 3b). It is apparent that the Zn deposition under these electrodeposition conditions resulted in the formation of the compact, hard adherent and dendrite-free electrodeposit.

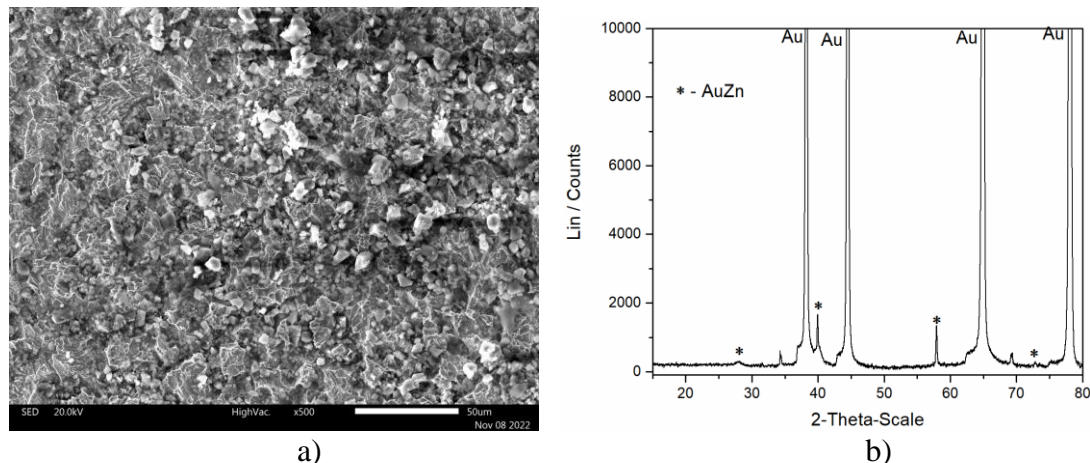


Figure 3. a) The SEM micrograph of deposit obtained by electrodeposition from 0.1 M Zn(II) in: an overpotential region (-0.050 V vs. Zn) and b) X-ray diffraction analysis of the deposit obtained by Zn electrodeposition in potentiostatic mode (deposition potential -0.050 V vs. Zn) from choline chloride:ethylene glycol (1:2 molar ratio), deposition time 30 min.

X-ray diffraction analysis of the samples formed by Zn potentiostatic deposition from 0.1 M ZnCl₂ electrolyte onto the Au polycrystalline substrate at -0.050 V vs. Zn revealed that AuZn phase was formed. The XRD results were in agreement with those reported in the literature which name the cubic AuZn₃ and AuZn phases, as well as the hexagonal Au_{1.2}Zn_{8.8} phase, as the main alloys of gold and zinc [10]. However, recently it was suggested that the transition in AuZn phase at low temperature can be trigonal or rhombohedral with a very small distortion [11].

Conclusions

The electrochemical deposition of Zn from an ionic liquid based on a eutectic solvent of choline chloride and ethylene glycol (1:2) containing Zn(II) as a source of metal components was studied on the Au electrode. Cyclic voltammetry results indicated that electrodeposition of Zn commences in zinc underpotential deposition (UPD) and proceeds through to the zinc overpotential deposition (OPD) region. Applying relatively low Zn electrodeposition overpotential of -0.050 V vs. Zn, resulted in a dendrite-free deposit consisting of cubic AuZn intermetallic.

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References

1. A. P. Abbott, J. C. Barron, G. Frisch, K. S. Ryder, A. F. Silva, The effect of additives on zinc electrodeposition from deep eutectic solvents, *Electrochim. Acta.*, **56**, 5272–5279, 2011. <https://doi.org/10.1016/j.electacta.2011.02.095>.
2. K. K. Maniam, S. Paul, Progress in electrodeposition of zinc and zinc nickel alloys using ionic liquids, *Appl. Sci.*, **10**, 1–20, 2020. <https://doi.org/10.3390/AP10155321>.
3. Y.-S. Wang, H.-W. Yeh, Y.-H. Tang, C.-L. Kao, P.-Y. Chen, Voltammetric Study and Electrodeposition of Zinc in Hydrophobic Room-Temperature Ionic Liquid 1-Butyl-1-methylpyrrolidinium

- Bis((trifluoromethyl)sulfonyl)imide ([BMP][TFSI]): A Comparison between Chloride and TFSI Salts of Zinc, *J. Electrochem. Soc.*, **164**, D39–D47, 2017. <https://doi.org/10.1149/2.0451702jes>.
4. H. Qian, X. Fu, Y. Chi, R. Zhang, C. Zhan, H. Sun, X. Zhou, J. Sun, Study on electrodeposition and corrosion resistance of Cu-Sn alloy prepared in ChCl-EG deep eutectic solvent, *J. Solid State Electrochem.*, **26**, 469–479, 2022. <https://doi.org/10.1007/s10008-021-05086-7>.
 5. H. K. Ismail, Electrodeposition of a mirror zinc coating from a choline chloride-ethylene glycol-based deep eutectic solvent modified with methyl nicotinate, *J. Electroanal. Chem.*, **876**, 114737, 2020. <https://doi.org/10.1016/j.jelechem.2020.114737>.
 6. L. Vieira, R. Schennach, B. Gollas, The effect of the electrode material on the electrodeposition of zinc from deep eutectic solvents, *Electrochim. Acta.*, **197**, 344–352, 2016. <https://doi.org/10.1016/j.electacta.2015.11.030>.
 7. M. Pölzer, A. H. Whitehead, B. Gollas, A Study of Zinc Electrodeposition from Zinc Chloride: Choline Chloride: Ethylene Glycol, *ECS Trans.*, **25**, 43-55, 2010. DOI 10.1149/1.3378972.
 8. N. Jovičević, V. S. Cvetković, Ž. J. Kamberović, J. N. Jovičević, Al-Zn alloy formation by aluminium underpotential deposition from AlCl₃+NaCl melts on zinc substrate, *Int. J. Electrochem. Sci.*, **7**, 10380–10393, 2012.
 9. V. S. Cvetković, N. Jovičević, J. S. Stevanović, M. G. Pavlović, N. M. Vukičević, Z. Stevanović, J. N. Jovičević, Magnesium-Gold alloy formation by underpotential deposition of magnesium onto gold from nitrate melts, *Metals*, **7**, 95, 2017. <https://doi.org/10.3390/met7030095>.
 10. F. M. Schuett, M. K. Heubach, J. Mayer, M. U. Cebelin, L. A. Kibler, T. Jacob, Electrodeposition of Zinc onto Au(111) and Au(100) from the Ionic Liquid [MPPip][TFSI], *Angew. Chemie - Int. Ed.*, **60**, 20461–20468, 2021. <https://doi.org/10.1002/anie.202107195>.
 11. B. Winn, S. M. Shapiro, J. C. Lashley, C. Opeil, W. Ratcliff, Structural phase transition in AuZn alloys, *J. Phys. Conf. Ser.*, **251**, 012027, 2010. <http://dx.doi.org/10.1088/1742-6596/251/1/012027>