UDC 621.357

F.I. Danilov, V.S. Protsenko

ELECTRODEPOSITION OF COMPOSITE COATINGS USING ELECTROLYTES BASED ON DEEP EUTECTIC SOLVENTS: A MINI-REVIEW

Ukrainian State University of Chemical Technology, Dnipro

The literature data on composite coatings electrodeposition from electrolytes based on deep eutectic solvents (DESs) are summarized in this mini-review. DESs are now considered as a promising kind of ionic liquid analogues, they can be successfully used to create new type different electrochemical systems, especially in metal electroplating. Electrodeposition of ceramic, polymer and metal colloidal particles distributed within metal matrix is known to produce composite coatings with attractive physicochemical and service properties. DES-based electrochemical systems afford new opportunity to fabricate composite electrodeposited coatings with enhanced properties. The main characteristic features of composites electrodeposition from DES-containing electroplating plating baths are overviewed. The application of DES-based electrolyte contributes to a considerable improvement in aggregative stability of colloidal systems from which composite films can be electrodeposited. In addition, DESs strongly affect the kinetics of electrochemical reaction proceeding on the electrode, especially, the nucleation/growth steps. The literature data concerning the electrodeposition of composites with silver, copper, nickel, cobalt and chromium matrices fabricated using DES-based systems are not numerous to date, they are systematically reviewed. Some ways of further improving the processes of composite coatings electrodeposition from DES-based electrolytes are surveyed.

Keywords: electrodeposition, composite, coatings, deep eutectic solvent, ionic liquids.

Introduction

Deep eutectic solvents (DESs) are nowadays considered as a novel and highly promising kind of room temperature ionic liquids analogues [1]. DESs are fluids which consist of a eutectic mixture of organic and inorganic components. The melting point of a DES is lower than those of individual constituents due to hydrogen bond interaction between molecules and ions in the liquid mixture. DESs have an ionic character regarding their transport properties [2–5]. Thus, the physicochemical properties of DESs are similar to those typical of «traditional» room temperature ionic liquids, while DESs are much cheaper, more available and environmentally friendlier [1].

Owing to these important advantages, deep eutectic solvents attract considerable attention in many fields of research and industry, especially, in electrochemistry and electroplating [6–8]. The application of DESs in metal electroplating processes provides a number of significant advantages, such as wide potential windows, high solubility of metals salts, negligible vapor pressure, non-toxicity, biodegradability and high conductivity compared to non-aqueous solvents [1,6–8].

To date, a great number of papers have been published in which different aspects of electrodeposition of various metals and alloys were reported [9–29].

At the same time, only a limited number of published works were devoted to composite electrodeposition from DESs-based plating baths [30–39]. It is well-known that the electrodeposition of composites, i.e. embedding of dispersed «inert» particles suspended in electrolyte in a growing metallic matrix, allows imparting a complex of useful and important physicochemical and service properties to the coatings [40,41]. The goal of this mini-review is to summarize literature data regarding the main features of composites electrodeposition from electrolyte based on deep eutectic solvents and characterize the content, structure and properties of obtained coatings.

Characteristic features of composites electrodeposition from DES-containing plating baths

In pioneer work [30], Abbott et al. showed that

---

a key advantage of DESs for their usage in composite electroplating processes is that the particulate suspensions are stable over a prolonged period of time as compared with both aqueous baths and those based on traditional organic solvents. This advantage is presumably due to a combination of the increased viscosity (of the neat liquid), compared to water and coulombic screening of surface charge by the ionic liquid (high ionic strength).

The application of DESs-based electrolyte allows improving the aggregative stability of colloidal systems from which composite films are electrodeposited. For instance, whereas Ni–PTFE (polytetrafluoroethylene) composites can be fabricated from aqueous plating bath only in the presence of some nonionic or cationic wetting agents, these coatings have been easily obtained in a DES-containing bath without stabilizing additives as the PTFE particles were well dispersed in the electrolyte without any wetting agents [37]. The measurements of the contact angles (CAs) of the water and choline chloride/ethylene glycol based DES droplets placed on a PTFE plate surface showed that the CA value of water droplet was about 112^0 while the value of DES droplet was 73^0; this result definitely indicated that a better dispersion of the PTFE particles would be obtained in DES system than in water [37].

Since deep eutectic solvents can effectively reduce the agglomeration of nanoparticles in the electroplating bath, they allow increasing the content of nanoparticles in the metal matrix compared with aqueous solution [32]. This phenomenon was attributed to a decrease in hydration force between SiO_2 particles and non-aqueous electrolyte [33].

Thus, the introduction of nano- and micro-sized particles into DESs significantly affects colloid-chemical and rheological properties of these fluids. In some cases, unexpected phenomena are observed that have not yet received a clear and unambiguous theoretical explanation. For instance, the incorporation of micron-sized particles (SiC) into ionic liquids containing copper salt has resulted, in one case (for a certain concentration), in a decrease in viscosity [30]. This observation was both unusual and surprising; the authors tried to explain this phenomenon in terms of an increase in the free volume of the fluid and local solvent perturbation (that is, particles act as microstirrers in the liquid).

As concerns the mechanism of composite co-deposition, many theories have been developed [40,41]. Evidently, these theories can be adopted to interpret the experimental data on composites fabrication from DESs. However, different concepts take into consideration different aspects of complex process of composite electrodeposition; thus, there is no universal model and the reliability of each to describe the behavior of a wide range of metallic coatings and particle types requires validation [40].

Abbott et al. noted that gravitational settlement should be excluded as the main mechanism for particulate inclusion into the electrolytic deposits [30] and the main mechanism of composite co-deposition is thought to be through dragging material onto the electrode surface [31].

It should be also observed that each particle suspended in electroplating bath based on DESs is covered by a thin layer of viscous electrolyte which must be shed to be embedded into the growing metal deposit. In much the same way, a thin layer of electrolyte should be removed from the electrode surface during the entrapment of particles into the depositing matrix. Since DESs containing electrolytes differ from aqueous ones by considerably higher viscosity and density, they require appreciably more time and energy to destroy dense and viscous films forming on the surfaces of both particles and growing metal matrix. That may decelerate the rate of particles inclusion into deposits and, in some cases, results in reducing the content of inert dispersed phase in the synthesized composite coatings as compared with aqueous electrolytes.

The introduction of dispersed phase particles into DESs affects also the kinetics of electrochemical reaction proceeding on the electrode. Cathode current is often attenuated when particulates are added to the solution. One possible cause of this effect is an increase in fluid viscosity [30] which hinders the transport of metal ions to the electrode surface.

The presence of SiO_2 nanoparticles in $NiCl_2$-containing solution based on DES was shown to affect the cyclic voltamograms response [32]. The potential of the peak of Ni (II) electroreduction shifts towards more positive values and the maximum current density grows when SiO_2 nanoparticles are introduced into the DES. The authors of study [32] think that the role of SiO_2 particles in the electrodeposition process can be ascribed to two aspects. On one hand, the active SiO_2 particles can act as effective preferential nucleation sites which facilitate the electrodeposition reaction. On the other hand, the SiO_2 nanoparticles can participate in the electrode process and directly catalyze nickel electrodeposition.

The nucleation/growth process of Ni–SiO_2 composite deposition was investigated by chronoamperometry experiments [33]. The nucleation of pure Ni was demonstrated to fits most closely to a 3D progressive nucleation at more positive potential, and then gradually changes to 3D instantaneous nucleation with shifting the applied potential to more negative values. However, the nucleation in Ni–SiO_2 system agreed well with a 3D instantaneous mechanism. The nucleation mode gradually deviated from the theoretical model with the increment of SiO_2 concentration. The difference of nucleation behavior between the pure Ni deposition and Ni–SiO_2 deposition was attributed to the change of the surface charge of particles and the thickness of electrical double layer due to the presence of SiO_2 nanoparticles. The observed deviations of nucleation in Ni–SiO_2 system were connected with the fact that the growth process exhibited diffusion and partial kinetic control. The partial kinetic control of the growth may be ascribed to chemical reactions between the unsaturated bond of oxygen atoms on SiO_2 particles surface and Ni (II) ions.

A detailed study of the nucleation/growth mechanism during Ni–SiC composites electrodeposition in choline chloride/ethylene glycol based DES in the presence of micro- and nano-sized SiC particles has been conducted in [34]. The nucleation of Ni without added SiC particles well obeyed the three-dimensional progressive mechanism if the applied potential is relatively positive. With negative shift of potential the nucleation mode gradually inclines to a 3D instantaneous mechanism. These findings agree well with the results of study [33]. However, when the micro-particles of SiC (0.3 μm) were added into the DES bath, the nucleation mechanism of nickel initially conformed to the 3D instantaneous nucleation and then deviated somewhat from the theoretical model. The nucleation of nickel in the presence of nano-particles of SiC (40 nm) was shown to fit most closely the 3D instantaneous nucleation mechanism. Hence, the micro- and nano-sized particles demonstrate different effects on metal nucleation/growth mechanism [34].

Case studies

Copper- and silver-based composites

The paper by Abbott et al. [30] was the first in which the electrodeposition of composite from deep eutectic solvents based on choline chloride was reported. The authors investigated the electrodeposition of Cu–Al_2O_3 and Cu–SiC composites using two ionic liquids: the first one contained a eutectic mixture of choline chloride and ethylene glycol (commercially known as Ethaline), the second one contained a eutectic mixture of choline chloride and urea (commercially known as Reline). The particles of alumina (0.05 μm and 1.0 μm) or silicon carbide (1–3 μm) were introduced into the plating baths as inert dispersed phases. The loading of Al_2O_3 and SiC particles in the resulting electroplated films strongly depends on the concentration of particulate in solution but is largely independent of the concentration of copper metal ion or timescale. An increase in the concentration of colloidal particles in solution leads to an increase in their content in deposits.

It is interesting that at low solution loadings the larger particles are incorporated more effectively than the smaller ones but at higher loadings both particle types are partitioned preferentially into the metal deposit [30]. The main mechanism for particles inclusion was stated to be diffusional/convection caused by the concentration gradient.

The electrodeposition of silver-based composite using an ethylene glycol/choline chloride containing DESs has been examined in study [31]. The incorporation of nano-sized SiC particles (50 nm) does not affect the surface morphology of the silver matrix; however, it doubles the microhardness of the deposited films. An increase in the size of the SiC particles from 50 nm to 2 μm does not change the composites microhardness, although it does decrease the wear volume significantly. This was a significant result of the study as it means that the deposition of silver for electrical contacts with improved wear resistance should be possible using DESs based plating baths. The incorporation of Al_2O_3 nano-particles (50 nm) had the highest effect upon microhardness of coatings; however, the wear volume and surface morphology were similar to the coatings with the same sized SiC particles. Thus, the friction coefficient and wear resistance depend on the nature, but not on the size of the added particles [31].

Nickel-based composites

Most of literature data on composite electrodeposition from DESs-based electrolyte are related to materials with nickel matrix [32–37].

The paper [32] reported a novel in-situ synthesis of SiO_2 nanoparticles in DES was developed to electrodeposit a homogeneous Ni matrix composite coating with uniformly distributed SiO_2 nanoparticles. The highly dispersive SiO_2 nanoparticles were in-situ fabricated from the choline chloride/ethylene glycol based DES to obtain homogeneous Ni/SiO_2 composite coatings. To this end, tetraethyl orthosilicate ($Si(OC_2H_5)_4$) was mixed with Ethaline and hydrolyzed by the addition of 10 wt.% HCl. The synthesized SiO_2 nanoparticles have diameters ranging from 40 to 65 nm. The maximum content of incorporated SiO_2 nanoparticles in composite coatings was equal to 5.13 wt.%. The friction and wear tests showed that the uniformly distributed SiO_2 nanoparticles in the nickel matrix significantly improved the tribological properties of the composite coating providing stable friction coefficient and wear resistance.

The nano-sized SiO_2 particles were also successfully codeposited in the Ni matrix from a choline chloride/ethylene glycol based DES by pulse electrodeposition technique in work [33]. It was stated that the presence of embedded SiO_2 nanoparticles has a profound influence on the nucleation/growth processes, microstructure and composition of the composite coatings. A maximum incorporation of 4.69 wt.% was observed in the system without any stabilizing additives. As compared with Ni coating, the Ni–SiO_2 nanocomposite coatings exhibited much better corrosion resistance, the corrosion resistance being increased with increasing SiO_2 nanoparticles content in the coatings [33].

Ni–SiC composite coatings were fabricated by pulsed electrodeposition from choline chloride/ethylene glycol based DES in work [34]. Silicon carbide particles with different sizes (0.3 μm and 40 nm) were used to prepare the plating baths. Both micro- and nano-sized SiC particles were uniformly distributed through the nickel matrix. The effects of particle concentration in the bath, electrolyte stirring rate and cathode current density on the content of SiC particles in composite electrodeposited coatings have been investigated. The maximum contents of micro- and nano-sized silicon carbide dispersed phase in Ni matrix were up to 12.80 wt.% and 5.37 wt.%, respectively. The Ni–SiC composite coatings exhibited good wear resistance and higher hardness than that of pure nickel films. For instance, if the microhardness of pure Ni was about 289 HV, it reaches 716 HV and 895 HV in the cases of the incorporation of micro- and nano-sized SiC particles into metal matrix, respectively [34].

Nickel based composite coatings were electrodeposited using choline chloride/carbamide deep eutectic solvent (Reline) containing dispersed carbon nanotubes (CNTs) [35]. The Ni–CNTs composites are characterized by larger crystalline grain size of Ni than the pure deposited metal. In addition, the introduction of CNTs provides an increase in the surface roughness: it increases from 58 nm to 94 nm after the CNTs incorporation in the deposits. The average friction coefficient (COF) of pure Ni deposited from DES-based plating bath reaches 0.378, while the average COF of the composite coating decreased to 0.12 after the CNTs incorporation. Thus, the composite Ni–CNTs films show super-low friction coefficient and exhibit excellent tribological properties [35].

The electrodeposition of compact nickel-multiwalled carbon nanotube (Ni/MWCNT) composites using choline chloride/urea based DES (Reline) was reported for the first time in study [36]. A highly stable dispersion of pristine as well as oxidized MWCNTs in the system under consideration resulted in a highly uniform distribution of MWCNTs into Ni metallic matrix. Surface morphology, crystallinity, roughness and corrosion electrochemical behavior of the synthesized coatings were stated to depend on the presence of MWCNTs.

Ni–PTFE electrodeposited composite coatings attract close attention due to their good water repellency, solid lubrication and low friction coefficient. The work [37] reported a DES-based electrolyte for the depositing Ni–PTFE composite films without the additive of any wetting agents. The deposits with the content of PTFE of about 3 wt.% have been prepared. CA measurements revealed that the Ni–PTFE composite containing 3.1 wt.% PTFE showed a hydrophobic behavior with CA value of ca. 121^0. The composites had an enhanced wear resistance as compared with the pure Ni coating due to the incorporation of PTFE. Surprisingly, the potentiodynamic polarization investigations indicated that the pure nickel has a better anticorrosion behavior than the Ni–PTFE electrodeposited composite coatings. Moreover, the higher the PTFE content in the Ni–PTFE composite coatings, the more negative was the corrosion potential and the higher corrosion current of the coatings was observed [37].

Cobalt-based composites

The composites based on electrodeposited cobalt matrix with embedded multiwalled carbon nanotubes (MWCNTs) were prepared from a choline chloride-urea based deep eutectic solvent [38]. Smooth and uniform Co and Co-MWCNT composite coatings exhibited a good adherence to the copper substrates. The results of XRD analysis revealed that the presence of nanotubes promoted a preferential orientation of Co crystallites on (220) and showed the grain refining properties of the MWCNTs. Whereas pure Co deposit was formed by sharp edge grains, Co-composites were less compact and formed by relatively spherical particles connected by MWCNTS. It was stated that the presence of MWCNTs contributed to diminishing the deposits roughness. The Co-MWCNT composite coatings demonstrated a comparable or slightly better corrosion performance than that of pure Co, in particular for long term exposure to 0.5 M NaCl solution. This behavior was associated with the presence of the MWCNT that hinders the diffusion of aggressive Cl^- ions.

Chromium-based composites

The authors of work [39] reported the preparation and characterization of chromium–single walled carbon nanotube (Cr–SWCNT) composite coatings on copper substrate by pulse electrodeposition method. An eco-friendly trivalent chromium bath containing $CrCl_3$, choline chloride, ethylene glycol, KCl and SWCNT (typically below 2 nm in diameter and 5–15 μm in length) was used. It is very important that the current efficiency of ca. 70% was achieved for Cr–SWCNT composite electrodeposition compared to common industrial Cr(VI) plating baths where the current efficiency of chromium deposition reaches only ca. 10–20% [42,43].

SEM images of composites obtained [39] showed crack free and uniformly embedded chromium decorated SWCNTs, which form bundles and are incorporated in the chromium metal matrix as aggregates. The synthesized Cr–SWCNT composite had higher hardness (about 540 HV) as compared with pure chromium (only ca. 280 HV). In accordance with the results of polarization studies conducted using 3.5% NaCl solution as a corrosive environment, composite coating showed higher anticorrosive property compared to «pure» chromium.

Prospects and potential trends of composites electrodeposition

Practically all kinds of composites fabricated and described in previous papers [30–39] can be obtained from «common» aqueous electrolyte, although DESs systems allow developing new facilities and properties. In our opinion, a very important task is to electrodeposit novel composite which in principle cannot be prepared in water systems. First of all, this applies to the electrodeposition of matrix of highly electronegative metals. A number of electronegative metals cannot be deposited from aqueous electrolyte or they electrodeposit with low current efficiency and deposition rate. Due to very wide electrochemical windows [1], deep eutectic solvents can give an opportunity to extend the range of the metals used for composites electroplating.

A very interesting problem is to electrodeposit matrices containing metal alloys. Hopefully, the application of DESs will permit to prepare new kinds of alloys that cannot be obtained in water electrolytes, and, hence, to fabricate novel types of composites with unique composition, structure and properties.

The application of DESs based systems not only expands the range of metallic matrices but also enables to broaden the spectrum of dispersed phases and provide an increase of their maximum available concentration in the plating bath and, hence, in composites obtained. For example, the authors of study [38] indicated that the use of different DESs as dispersion media for carbon nanotubes (CNTs) allows preparing suspensions that are more concentrated than in the cases of common aqueous electrolytes or traditional ionic liquids.

It was recently shown [26–29,44,45] that the introduction of extra water into the deep eutectic solvents results in an appreciable improvement in physicochemical properties of liquid mixtures: a decrease in viscosity and an increase in conductivity can be achieved. Changing the extra water content allows the fine tuning of physicochemical properties of the ionic liquids to match the system requirements. In case of composites deposition, the introduction of water can affect various colloid-chemical properties of suspension electrolyte. Especially, it concerns the sedimentation behavior and aggregative stability of the systems. We think that the addition of extra-water to the DESs-based plating bath is a promising way to improve electrodeposition characteristics and properties of the synthesized composite coatings.

The development of new theoretical models and the fitting of known theories to composite coatings electrodeposition still remain an important task. There is a need to elaborate the theoretical concepts which would correctly describe the effects of various parameters (concentration of dispersed phase in the plating bath, particles size, stirring rate, current density, temperature and so on) on composites content, deposition rate and properties. Thus, the accumulation of new experimental data on composite coatings electrodeposition and their generalization are expected to provide more profound understanding of the physicochemical processes underlying the observed results.

REFERENCES

1. *Smith E.L., Abbott A.P., Ryder K.S.* Deep eutectic solvents (DESs) and their applications // Chem. Rev. – 2014. – Vol.114. – P.11060-11082.

2. *Abbott A.P., Harris R.C., Ryder K.S.* Application of hole theory to define ionic liquids by their transport properties // J. Phys. Chem. B. – 2007. – Vol.111. – P.4910-4913.

3. *Novel* solvent properties of choline chloride/urea mixtures / A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah // Chem. Commun. – 2003. – P.70-71.

4. *Ionic* liquids based upon metal halide/substituted

quaternary ammonium salt mixtures / A.P. Abbott, G. Capper, D.L. Davies, R. Rasheed // Inorg. Chem. – 2004. – Vol.43. – P.3447-3452.

5. *Deep* eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids / A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed // J. Am. Chem. Soc.. – 2004. – Vol.126. – P.9142-9147.

6. *Abbott A.P., McKenzie K.J.* Application of ionic liquids to the electrodeposition of metals // Phys. Chem. Chem. Phys. – 2006. – Vol.8. – P.4265-4279.

7. *Abbott A.P., Ryder K.S., König U.* Electrofinishing of metals using eutectic based ionic liquids // Trans. Inst. Met. Finish. – 2008. – Vol.86. – P.196-204.

8. *Abbott A.P., Frisch G., Ryder K.S.* Electroplating using ionic liquids // Annu. Rev. Mater. Res. – 2013. – Vol.43. – P.335-358.

9. *Whitehead A.H., Pölzler M., Gollas B.* Zinc electrodeposition from a deep eutectic system containing choline chloride and ethylene glycol // J. Electrochem. Soc. – 2010. – Vol.157. – P.D328-D334.

10. *Electrochemical* deposition of zinc from deep eutectic solvent on barrier alumina layers / Starykevich M., Salak A.N., Ivanou D.K., Lisenkov A.D., Zheludkevich M.L., Ferreira M.G.S. // Electrochim. Acta. – 2015. – Vol.170. – P.284-291.

11. *Ghosh S., Roy S.* Electrochemical copper deposition from an ethaline-$CuCl_2 \cdot 2H_2O$ DES. // Surf. Coat. Technol. – 2014. – Vol.238. – P.165-173.

12. *Ghosh S., Roy S.* Codeposition of Cu–Sn from ethaline deep eutectic solvent // Electrochim. Acta. – 2015. – Vol.183. – P.27-36.

13. *Speciation,* physical and electrolytic properties of eutectic mixtures based on $CrCl_3 \cdot 6H_2O$ and urea / Abbott A.P., Al-Barzinjy A.A., Abbott P.D., Frish G., Harris R.C., Hartley J., Ryder K.S. // Phys. Chem. Chem. Phys. – 2014. – Vol.16. – P.9047-9055.

14. *Investigation* of Ni-Mo and Co-Mo alloys electrodeposition involving choline chloride based ionic liquids / Costovici S., Manea A.-C., Visan T., Anicai L. // Electrochim. Acta. – 2016. – Vol.207. – P.97-111.

15. *Ferreira E.S.C., Pereira C.M., Silva A.F.* Electrochemical studies of metallic chromium electrodeposition from a Cr(III) bath // J. Electroanal. Chem. – 2013. – Vol.707. – P.52-58.

16. *Electrodeposition* of Ni–Co alloys from a deep eutectic solvent / You Y.H., Gu C.D., Wang X.L., Tu J.P. // Surf. Coat. Technol. – 2012. – Vol.206. – P.3632-3638.

17. *On the electrodeposition* of nickel–zinc alloys from a eutectic-based ionic liquid / Yang H.Y., Guo X.W., Chen X.B., Wang S.H., Wu G.H., Ding W.J., Birbilis N. // Electrochim. Acta. – 2012. – Vol.63. – P.131-138.

18. *Electrodeposition* of nickel using eutectic based ionic liquids / Abbott A.P., El Ttaib K., Ryder K.S., Smith E.L. // Trans. Inst. Met. Finish. – 2008. – Vol.86. – P.234-240.

19. *Bernasconi R., Magagnin L.* Electrodeposition of nickel from DES on aluminium for corrosion protection // Surf. Eng. – 2017. – Vol.33. – P.131-135.

20. *A comparative* study of nickel electrodeposition using deep eutectic solvents and aqueous solutions / Abbott A.P., Ballantyne A., Harris R.C., Juma J.A., Ryder K.S., Forrest G. / / Electrochim. Acta. – 2015. – Vol.176. – P.718-726.

21. *Srivastava M., Yoganandan G., William Grips V.K.* Electrodeposition of Ni and Co coatings from ionic liquid // Surf. Eng. – 2012. – Vol.28. – P.424-429.

22. *Microstructure,* nanoindentation, and electrochemical properties of the nanocrystalline nickel film electrodeposited from choline chloride-ethylene glycol / Gu C.D., You Y.H., Yu Y.L., Qu S.X., Tu J.P. // Surf. Coat. Technol. – 2011. – Vol.205. – P.4928-4933.

23. *Bright* metal coatings from sustainable electrolytes: the effect of molecular additives on electrodeposition of nickel from a deep eutectic solvent / Abbott A.P., Ballantyne A., Harris R.C., Juma J.A., Ryder K.S. // Phys. Chem. Chem. Phys. – 2017. – Vol.19. – P.3219-3231.

24. *Tailoring* nickel coatings via electrodeposition from a eutectic-based ionic liquid doped with nicotinic acid / Yang H., Guo X., Birbilis N., Wu G., Ding W. // Appl. Surf. Sci. – 2011. – Vol.257. – P.9094-9102.

25. *Choline* chloride based ionic liquids containing nickel chloride: Physicochemical properties and kinetics of Ni(II) electroreduction / Kityk A.A., Shaiderov D.A., Vasil'eva E.A., Protsenko V.S., Danilov F.I. // Electrochim. Acta. – 2017. – Vol.245. – P.133-145.

26. *Effect* of water content on physicochemical properties and electrochemical behavior of ionic liquids containing choline chloride, ethylene glycol and hydrated nickel chloride / Protsenko V.S., Kityk A.A., Shaiderov D.A., Danilov F.I. // J. Mol. Liq. – 2015. – Vol.212. – P.716-722.

27. *Bobrova L.S., Danilov F.I., Protsenko V.S.* Effects of temperature and water content on physicochemical properties of ionic liquids containing $CrCl_3 \cdot xH_2O$ and choline chloride // J. Mol. Liq. – 2016. – Vol.223. – P.48-53.

28. *Protsenko V.S., Bobrova L.S., Danilov F.I.* Physicochemical properties of ionic liquid mixtures containing choline chloride, chromium(III) chloride and water: effects of temperature and water content // Ionics. – 2017. – Vol.23. – P.637-643.

29. *Electrodeposition* of nanocrystalline nickel coatings from a deep eutectic solvent with water addition / F.I. Danilov, V.S. Protsenko, A.A. Kityk, D.A. Shaiderov, E.A. Vasil'eva, U. Pramod Kumar, C. Joseph Kennady // Prot. Met. Phys. Chem. Surf. – 2018. – Vol.54 (in press). Available at: http://dx.doi.org/10.1134/S2070205118010203.

30. *Electrodeposition* of copper composites from deep eutectic solvents based on choline chloride / Abbott A.P., El Ttaib K., Frisch G., McKenzie K.J., Ryder K.S. // Phys. Chem. Chem. Phys. – 2009. – Vol.11. – P.4269-4277.

31. *The electrodeposition* of silver composites using deep eutectic solvents / Abbott A.P., El Ttaib K., Frisch G., Ryder K.S., Weston D. // Phys. Chem. Chem. Phys. – 2012. – Vol.14. –

P.2443-2449.

32. *Electrodeposition* of homogenous Ni/SiO$_2$ nanocomposite coatings from deep eutectic solvent with in-situ synthesized SiO$_2$ nanoparticles / Li R., Hou Y., Liu B., Wang D., Liang J. // Electrochim. Acta. – 2016. – Vol.222. – P.1272-1280.

33. *Li R., Hou Y., Liang J.* Electro-codeposition of Ni–SiO$_2$ nanocomposite coatings from deep eutectic solvent with improved corrosion resistance // Appl. Surf. Sci. – 2016. – Vol.367. – P.449-458.

34. *Li R., Chu Q., Liang J.* Electrodeposition and characterization of Ni–SiC composite coatings from deep eutectic solvent // RSC Adv. – 2015. – Vol.5. – P.44933-44942.

35. *Super-low* friction nickel based carbon nanotube composite coating electro-deposited from eutectic solvents / Liu D.G., Sun J., Gui Z.X., Song K.J., Luo L.M., Wu Y.C. // Diamond Relat. Mater. – 2017. – Vol.74. – P.229-232.

36. *Electro-generated* nickel/carbon nanotube composites in ionic liquid / Martis P., Dilimon V.S., Delhalle J., Mekhalif Z. // Electrochim. Acta. – 2010. – Vol.55. – P.5407-5410.

37. *Electrochemical* preparation and characterization of Ni–PTFE composite coatings from a non-aqueous solution without additives / You Y.-H., Gu C.-D., Wang X.-L., Tu J.-P. // Int. J. Electrochem. Sci. – 2012. – Vol.7. – P.12440-12455.

38. *Electrodeposition* of Co and Co composites with carbon nanotubes using choline chloride-based ionic liquids / Pereira N.M., Brincoveanu O., Pantazi A.G., Pereira C.M., Araújo J.P., Silva A.F., Enachescu M., Anicai L. // Surf. Coat. Technol. – 2017. – Vol.324. – P.451-462.

39. *Maharaja J., Raja M., Mohan S.* Pulse electrodeposition of Cr–SWCNT composite from choline chloride based electrolyte // Surf. Eng. – 2014. – Vol.30. – P.722-727.

40. *Low C.T.J., Wills R.G.A., Walsh F.C.* Electrodeposition of composite coatings containing nanoparticles in a metal deposit // Surf. Coat. Technol. – 2006. – Vol.201. – P.371-383.

41. *Walsh F.C., Ponce de Leon C.* A review of the electrodeposition of metal matrix composite coatings by inclusion of particles in a metal layer: an established and diversifying technology // Trans. Inst. Met. Finish. – 2014. – Vol.92. – P.83-98.

42. *Protsenko V.S., Danilov F.I.* Chromium electroplating from trivalent chromium baths as an environmentally friendly alternative to hazardous hexavalent chromium baths: comparative study on advantages and disadvantages // Clean Techn. Environ. Policy. – 2014. – Vol.16. – P.1201-1206.

43. *Danilov F.I., Protsenko V.S.* Electroreduction of hexavalent chromium compounds on the gold electrode // Russ. J. Electrochem. – 1998. – Vol.34. – P.276-281.

44. *Effect* of water presence on choline chloride-2urea ionic liquid and coating platings from the hydrated ionic liquid / Du C., Zhao B., Chen X.-B., Birbilis N., Yang H. // Sci. Rep. – 2016. – Vol.6. – No.29225.

45. *Vykorystann'ya* teorii vakansii dl'ya interpretatsii danykh shchodo elektroprovidnosti ionnykh ridyn, yaki mist'yat' khrom(III) khloryd, kholin khloryd i dobavky vody / Protsenko V.S., Bobrova L.S., Burmistrov K.S., Danilov F.I. // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2017. – No. 1. – P.27-35.

Received 5.01.2018

ЕЛЕКТРООСАДЖЕННЯ КОМПОЗИЦІЙНИХ ПОКРИТТІВ З ВИКОРИСТАННЯМ ЕЛЕКТРОЛІТІВ НА ОСНОВІ НИЗЬКОТЕМПЕРАТУРНИХ ЕВТЕКТИЧНИХ РОЗЧИННИКІВ. МІНІ-ОГЛЯД

Ф.Й. Данилов, В.С. Проценко

Наведено міні-огляд літературних даних стосовно електроосадження композиційних покриттів з електролітів на основі низькотемпературних евтектичних розчинників (НЕР). НЕР наразі розглядаються як перспективний різновид аналогів іонних рідин, вони можуть бути успішно застосовані для створення нових типів різноманітних електрохімічних систем, особливо для електроосадження металів. Відомо, що електроосадження керамічних, полімерних і металевих колоїдних частинок у металевій матриці дозволяє одержувати композиційні покриття з привабливими фізико-хімічними та експлуатаційними властивостями. Електрохімічні системи на основі НЕР відкривають нові можливості для створення композиційних електроосаджених покриттів з покращеними властивостями. Надано огляд основних особливостей електролітів для осадження композитів на основі НЕР. Використання електролітів на основі НЕР сприяє суттєвому підвищенню агрегативної стійкості колоїдних систем, з яких осаджуються композити. Крім того, НЕР помітно впливають на кінетику електрохімічних реакцій, що відбуваються на електроді, особливо на стадії енуклеації та росту зародків. Літературні дані щодо електроосадження композитів з срібною, мідною, нікелевою, кобальтовою і хромовою матрицями, утворених з систем на основі НЕР, є наразі нечисленними, наведено їх систематичний огляд. Охарактеризовано деякі шляхи подальшого удосконалення процесів електроосадження композиційних покриттів з електролітів, що містять НЕР.

Ключові слова: електроосадження, композит, покриття, низькотемпературний евтектичний розчинник, іонні рідини.

ELECTRODEPOSITION OF COMPOSITE COATINGS USING ELECTROLYTES BASED ON DEEP EUTECTIC SOLVENTS: A MINI-REVIEW

F.I. Danilov, V.S. Protsenko

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

The literature data on composite coatings electrodeposition from electrolytes based on deep eutectic solvents (DESs) are summarized in this mini-review. DESs are now considered as a promising kind of ionic liquid analogues, they can be successfully used to create new type different electrochemical systems, especially in metal electroplating. Electrodeposition of ceramic, polymer and metal colloidal particles distributed within metal matrix is known to produce composite coatings with attractive physicochemical and service properties. DES-based electrochemical systems afford new opportunity to fabricate composite electrodeposited coatings with enhanced properties. The main characteristic features of composites electrodeposition from DES-containing electroplating plating baths are overviewed. The application of DES-based electrolyte contributes to a considerable improvement in aggregative stability of colloidal *systems from which composite films can be electrodeposited. In addition, DESs strongly affect the kinetics of electrochemical reaction proceeding on the electrode, especially, the nucleation/growth steps. The literature data concerning the electrodeposition of composites with silver, copper, nickel, cobalt and chromium matrices fabricated using DES-based systems are not numerous to date, they are systematically reviewed. Some ways of further improving the processes of composite coatings electrodeposition from DES-based electrolytes are surveyed.*

Keywords: electrodeposition; composite; coatings; deep eutectic solvent; ionic liquids.

REFERENCES

1. Smith E.L., Abbott A.P., Ryder K.S. Deep eutectic solvents (DESs) and their applications. *Chemical Reviews*, 2014, vol. 114, pp. 11060-11082.

2. Abbott A.P., Harris R.C., Ryder K.S. Application of hole theory to define ionic liquids by their transport properties. *Journal of Physical Chemistry B*, 2007, vol. 111, pp. 4910-4913.

3. Abbott A.P., Capper G., Davies D.L., Rasheed R.K., Tambyrajah V. Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications*, 2003, pp. 70-71.

4. Abbott A.P., Capper G., Davies D.L., Rasheed R. Ionic liquids based upon metal halide/substituted quaternary ammonium salt mixtures. *Inorganic Chemistry*, 2004, vol. 43, pp. 3447-3452.

5. Abbott A.P., Boothby D., Capper G., Davies D.L., Rasheed R.K. Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. *Journal of the American Chemical Society*, 2004, vol. 126, pp. 9142-9147.

6. Abbott A.P., McKenzie K.J. Application of ionic liquids to the electrodeposition of metals. *Physical Chemistry Chemical Physics*, 2006, vol. 84, pp. 265-4279.

7. Abbott A.P., Ryder K.S., König U. Electrofinishing of metals using eutectic based ionic liquids. *Transactions of the Institute of Metal Finishing*, 2008, vol. 86, pp. 196-204.

8. Abbott A.P., Frisch G., Ryder K.S. Electroplating using ionic liquids. *Annual Review of Materials Research*, 2013, vol. 43, pp. 335-358.

9. Whitehead A.H., Pölzler M., Gollas B. Zinc electrodeposition from a deep eutectic system containing choline chloride and ethylene glycol. *Journal of the Electrochemical Society*, 2010, vol. 157, pp. D328-D334.

10. Starykevich M., Salak A.N., Ivanou D.K., Lisenkov A.D., Zheludkevich M.L., Ferreira M.G.S. Electrochemical deposition of zinc from deep eutectic solvent on barrier alumina layers. *Electrochimica Acta*, 2015, vol. 170, pp. 284-291.

11. Ghosh S., Roy S. Electrochemical copper deposition from an ethaline-$CuCl_2{\cdot}2H_2O$ DES. *Surface and Coatings Technology*, 2014, vol. 238, pp. 165-173.

12. Ghosh S., Roy S. Codeposition of Cu-Sn from ethaline deep eutectic solvent. *Electrochimica Acta*, 2015, vol. 183, pp. 27-36.

13. Abbott A.P., Al-Barzinjy A.A., Abbott P.D., Frish G., Harris R.C., Hartley J., Ryder K.S. Speciation, physical and electrolytic properties of eutectic mixtures based on $CrCl_3{\cdot}6H_2O$ and urea. *Physical Chemistry Chemical Physics*, 2014, vol. 16, pp. 9047-9055.

14. Costovici S., Manea A.-C., Visan T., Anicai L. Investigation of Ni-Mo and Co-Mo alloys electrodeposition involving choline chloride based ionic liquids. *Electrochimica Acta*, 2016, vol. 207, pp. 97-111.

15. Ferreira E.S.C., Pereira C.M., Silva A.F. Electrochemical studies of metallic chromium electrodeposition from a Cr(III) bath. *Journal of Electroanalytical Chemistry*, 2013, vol. 707, pp. 52-58.

16. You Y.H., Gu C.D., Wang X.L., Tu J.P. Electrodeposition of Ni–Co alloys from a deep eutectic solvent. *Surface and Coatings Technology*, 2012, vol. 206, pp. 3632-3638.

17. Yang H.Y., Guo X.W., Chen X.B., Wang S.H., Wu G.H., Ding W.J., Birbilis N. On the electrodeposition of nickel–zinc alloys from a eutectic-based ionic liquid. *Electrochimica Acta*, 2012, vol. 63, pp. 131-138.

18. Abbott A.P., El Ttaib K., Ryder K.S., Smith E.L. Electrodeposition of nickel using eutectic based ionic liquids. *Transactions of the Institute of Metal Finishing*, 2008, vol. 86, pp. 234-240.

19. Bernasconi R., Magagnin L. Electrodeposition of nickel from DES on aluminium for corrosion protection. *Surface Engineering*, 2017, vol. 33, pp. 131-135.

20. Abbott A.P., Ballantyne A., Harris R.C., Juma J.A., Ryder K.S., Forrest G. A comparative study of nickel electrodeposition using deep eutectic solvents and aqueous solutions. *Electrochimica Acta*, 2015, vol. 176, pp. 718-726.

21. Srivastava M., Yoganandan G., William Grips V.K. Electrodeposition of Ni and Co coatings from ionic liquid. *Surface Engineering*, 2012, vol. 28, pp. 424-429.

22. Gu C.D., You Y.H., Yu Y.L., Qu S.X., Tu J.P. Microstructure, nanoindentation, and electrochemical properties of the nanocrystalline nickel film electrodeposited from choline chloride-ethylene glycol. *Surface and Coatings Technology*, 2011, vol. 205, pp. 4928-4933.

23. Abbott A.P., Ballantyne A., Harris R.C., Juma J.A., Ryder K.S. Bright metal coatings from sustainable electrolytes: the effect of molecular additives on electrodeposition of nickel from a deep eutectic solvent. *Physical Chemistry Chemical Physics*, 2017, vol. 19, pp. 3219-3231.

24. Yang H., Guo X., Birbilis N., Wu G., Ding W. Tailoring nickel coatings via electrodeposition from a eutectic-based ionic liquid doped with nicotinic acid. *Applied Surface Science*, 2011, vol. 257, pp. 9094-9102.

25. Kityk A.A., Shaiderov D.A., Vasil'eva E.A., Protsenko V.S., Danilov F.I. Choline chloride based ionic liquids containing nickel chloride: Physicochemical properties and kinetics of Ni(II) electroreduction. *Electrochimica Acta*, 2017, vol. 245, pp. 133-145.

26. Protsenko V.S., Kityk A.A., Shaiderov D.A., Danilov F.I. Effect of water content on physicochemical properties and electrochemical behavior of ionic liquids containing choline chloride, ethylene glycol and hydrated nickel chloride. *Journal of Molecular Liquids*, 2015, vol. 212, pp. 716-722.

27. Bobrova L.S., Danilov F.I., Protsenko V.S. Effects of temperature and water content on physicochemical properties of ionic liquids containing $CrCl_3 \cdot xH_2O$ and choline chloride. *Journal of Molecular Liquids*, 2016, vol. 223, pp. 48-53.

28. Protsenko V.S., Bobrova L.S., Danilov F.I. Physicochemical properties of ionic liquid mixtures containing choline chloride, chromium(III) chloride and water: effects of temperature and water content. *Ionics*, 2017, vol. 23, pp. 637-643.

29. Danilov F.I., Protsenko V.S., Kityk A.A., Shaiderov D.A., Vasil'eva E.A., Pramod Kumar U., Joseph Kennady C. Electrodeposition of nanocrystalline nickel coatings from a deep eutectic solvent with water addition. *Protection of Metals and Physical Chemistry of Surfaces*, 2018, vol. 54. Available at: http://dx.doi.org/10.1134/S2070205118010203.

30. Abbott A.P., El Ttaib K., Frisch G., McKenzie K.J., Ryder K.S. Electrodeposition of copper composites from deep eutectic solvents based on choline chloride. *Physical Chemistry Chemical Physics*, 2009, vol. 11, pp. 4269-4277.

31. Abbott A.P., El Ttaib K., Frisch G., Ryder K.S., Weston D. The electrodeposition of silver composites using deep eutectic solvents. *Physical Chemistry Chemical Physics*, 2012, vol. 14, pp. 2443-2449.

32. Li R., Hou Y., Liu B., Wang D., Liang J. Electrodeposition of homogenous Ni/SiO_2 nanocomposite coatings from deep eutectic solvent with in-situ synthesized SiO_2 nanoparticles. *Electrochimica Acta*, 2016, vol. 222, pp. 1272-1280.

33. Li R., Hou Y., Liang J. Electro-codeposition of $Ni-SiO_2$ nanocomposite coatings from deep eutectic solvent with improved corrosion resistance. *Applied Surface Science*, 2016, vol. 367, pp. 449-458.

34. Li R., Chu Q., Liang J. Electrodeposition and characterization of Ni–SiC composite coatings from deep eutectic solvent. *RSC Advances*, 2015, vol. 5, pp. 44933-44942.

35. Liu D.G., Sun J., Gui Z.X., Song K.J., Luo L.M., Wu Y.C. Super-low friction nickel based carbon nanotube composite coating electro-deposited from eutectic solvents. *Diamond and Related Materials*, 2017, vol. 74, pp. 229-232.

36. Martis P., Dilimon V.S., Delhalle J., Mekhalif Z. Electro-generated nickel/carbon nanotube composites in ionic liquid. *Electrochimica Acta*, 2010, vol. 55, pp. 5407-5410.

37. You Y.-H., Gu C.-D., Wang X.-L., Tu J.-P. Electrochemical preparation and characterization of Ni–PTFE composite coatings from a non-aqueous solution without additives. *International Journal of Electrochemical Science*, 2012, vol. 7, pp. 12440-12455.

38. Pereira N.M., Brincoveanu O., Pantazi A.G., Pereira C.M., Araújo J.P., Silva A.F., Enachescu M., Anicai L. Electrodeposition of Co and Co composites with carbon nanotubes using choline chloride-based ionic liquids. *Surface and Coatings Technology*, 2017, vol. 324, pp. 451-462.

39. Maharaja J., Raja M., Mohan S. Pulse electrodeposition of Cr–SWCNT composite from choline chloride based electrolyte. *Surface Engineering*, 2014, vol. 30, pp. 722-727.

40. Low C.T.J., Wills R.G.A., Walsh F.C. Electrodeposition of composite coatings containing nanoparticles in a metal deposit. *Surface and Coatings Technology*, 2006, vol. 201, pp. 371-383.

41. Walsh F.C., Ponce de Leon C. A review of the electrodeposition of metal matrix composite coatings by inclusion of particles in a metal layer: an established and diversifying technology. *Transactions of the Institute of Metal Finishing*, 2014, vol. 92, pp. 83-98.

42. Protsenko V.S., Danilov F.I. Chromium electroplating from trivalent chromium baths as an environmentally friendly alternative to hazardous hexavalent chromium baths: comparative study on advantages and disadvantages. *Clean Technologies and Environmental Policy*, 2014, vol. 16, pp. 1201-1206.

43. Danilov F.I., Protsenko V.S. Electroreduction of hexavalent chromium compounds on the gold electrode. *Russian Journal of Electrochemistry*, 1998, vol. 34, pp. 276-281.

44. Du C., Zhao B., Chen X.-B., Birbilis N., Yang H. Effect of water presence on choline chloride-2urea ionic liquid and coating platings from the hydrated ionic liquid. *Scientific Reports*, 2016, vol. 6, article no. 29225.

45. Protsenko V.S., Bobrova L.S., Burmistrov K.S., Danilov F.I. Vykorystann'ya teorii vakansii dl'ya interpretatsii danykh shchodo elektroprovidnosti ionnykh ridyn, yaki mist'yat' khrom(III) khloryd, kholin khloryd i dobavky vody [The application of hole theory for the interpretation of data on conductivity of ionic liquids containing chromium(III) chloride, choline chloride and water additives]. *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2017, no. 1, pp. 27-35. (*in Ukrainian*).