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\*Corresponding author

Vyacheslav Protsenko, Ukrainian State  
University of Chemical Technology,  
Dnipro, Ukraine

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# Electrodeposition of Composite Ni-TiO<sub>2</sub> Coatings from a Deep Eutectic Solvent, Ethaline

Vyacheslav Protsenko\*, Dmytro Bogdanov, Anna Kityk, Tetyana Butyrina and Felix Danilov

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

## Abstract

The electrodeposition of Ni-TiO<sub>2</sub> composite coatings was carried out from a plating bath based on a deep eutectic solvent, ethaline (a eutectic mixture of ethylene glycol and choline chloride). The effects of electrolyte composition and electrolysis conditions on the content of Titania particles, microstructure and microhardness were investigated. The introduction of TiO<sub>2</sub> nano-particles into Ni-matrix was shown to improve the corrosion stability and electrocatalytic activity of the synthesized composite electrodeposits.

## Introduction

It is known that the electrochemical deposition of composite coatings yields finishing electrodeposited layers with improved physicochemical and service properties, such as increased microhardness, high wear, and corrosion resistances, etc. This work deals with the electrodeposition of composite Ni-TiO<sub>2</sub> coatings using an electrolyte based on the so-called ethaline, a deep eutectic solvent [1]. Deep Eutectic Solvents (DESs) are now considered as a promising kind of room temperature ionic liquids.

## Materials and Methods

Ethaline is composed of the eutectic mixture of choline chloride and ethylene glycol in the molar ratio of 1:2, respectively. The NiCl<sub>2</sub>·6H<sub>2</sub>O salt served as a source of Ni(II) ions in the electrolyte. Titania nano-powder (Degussa P 25, Evonik, the particle size of ca. 25-30 nm) was used as a dispersed phase in colloidal plating electrolyte. The electrodeposition of composite was performed from a plating bath described in detail in our previous studies [2,3] under the condition of continuous agitation at a constant value of current density.

## Results and Discussion

Due to high viscosity and density, the colloidal electrolyte based on DESs provides excellent dispersion stability in comparison with common aqueous plating baths. No visible signs of coagulation and sedimentation were detected during one week of observations. This is one of the most important advantages of colloidal electroplating baths containing DESs. The effects of TiO<sub>2</sub> content in electrolyte, stirring rate and current density were investigated. The highest content of TiO<sub>2</sub> in composite electrodeposited coatings, equal to ca. 2.35 wt.%, was achieved at 500 rpm, 10 mA.cm<sup>-2</sup> and 15 g dm<sup>-3</sup> TiO<sub>2</sub>. It was stated that the electrodeposition of Ni-TiO<sub>2</sub> composites well obeys known concepts on the mechanisms of composites electrochemical synthesis (Guglielmi theory, etc.) [4]. The X-ray analysis of composites revealed the reflections of face centered cubic nickel and anatase TiO<sub>2</sub> planes. The broad half-width values of the XRD spectra of Ni showed the nanocrystalline structure of the metallic matrix. The calculated values of crystalline size varied in a range of ca. 9-14 nm.

An introduction of TiO<sub>2</sub> particles into the nickel matrix results in an increase of coatings' microhardness. This is due to the so-called Orowan mechanism. It is associated with the dispersion of fine colloidal particles, which impedes the motion of dislocations in the metallic matrix and results in an increase in the material hardness. Electrochemical impedance spectroscopy showed that the insertion of Titania nano-particles in Ni matrix leads to an increase in corrosion stability of the coatings. The improvement in corrosion resistance may be caused not only by the formation of a protective physical barrier, which partially blocks the surface and is composed of TiO<sub>2</sub> particles, but also by the formation of corrosion micro-cells in which TiO<sub>2</sub> acts as cathode and nickel as anode. The electrocatalytic properties of Ni-TiO<sub>2</sub> composite electrodeposits were tested in the of hydrogen and oxygen evolution reactions proceeding in an alkaline solution. It was shown that the incorporation of Titania nano-particles into the Ni matrix ensures improvement in electrocatalytic performance of the electrochemically deposited layers [5].

## Conclusion

The main characteristics of Ni-TiO<sub>2</sub> composite electrodeposition from a deep eutectic solvent, ethaline, were reported in this work. Due to higher viscosity and density, the colloidal electrolyte based on DES shows excellent dispersion stability as compared with "usual" aqueous systems. This is one of the most important advantages of colloidal electroplating baths containing deep eutectic solvents. An increase in TiO<sub>2</sub> content in composite coatings enhances microhardness, corrosion stability and electrocatalytic activity.

## References

1. Smith EL, Abbott AP, Ryder KS (2014) Deep eutectic solvents (DESs) and their applications. *Chemical Reviews* 114: 11060-11082.
2. Kityk AA, Shaiderov DA, Vasileva EA, Protsenko VS, Danilov FI (2017) Choline chloride based ionic liquids containing nickel chloride: physicochemical properties and kinetics of Ni(II) electroreduction. *Electrochimica Acta* 245: 133-145.



3. Protsenko VS, Kityk AA, Shaiderov DA, Danilov FI (2015) 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* 212: 716-722.
4. Danilov FI, Kityk AA, Shaiderov DA, Bogdanov DA, Korniy SA, et al. (2019) Electrodeposition of Ni-TiO<sub>2</sub> composite coatings using electrolyte based on a deep eutectic solvent. *Surface Engineering and Applied Electrochemistry* 55: 138-149.
5. Protsenko VS, Bogdanov DA, Korniy SA, Kityk AA, Baskevich AS, et al. (2019) Application of a deep eutectic solvent to prepare nanocrystalline Ni and Ni/TiO<sub>2</sub> coatings as electrocatalysts for the hydrogen evolution reaction. *International Journal of Hydrogen Energy* 44: 24604-24616.