COMPOSITE ZINC COATINGS WITH POLYMERIC MODIFIED CuO NANOPARTICLES AGAINST CORROSION AND BIOFOULING OF STEEL

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Abstract

Biofouling and corrosion are well-known problems in the marine industries. In this study, the role of copper oxide (CuO) nanoparticles on the biofouling and corrosion performance of composite (hybrid) zinc coating on steel is examined. A cationic polyelectrolyte polyethylenimine (PEI) is used to stabilize the CuO suspension before particles electrodeposition on a steel substrate. The size and charge density of the PEI coated CuO nanoparticles are followed using light scattering methods and microelectrophoresis.

The polymeric modified CuO nanoparticles are electrodeposited on the steel (cathode) surface at pH 9.0 aiming to minimize the effect of aggregation in the suspension and dissolution of the CuO nanoparticles. Standard zinc coating is then electrodeposited on the CuO coated steel sample from a zinc sulfate solution at pH 4.5-5.0. Distribution of CuO nanoparticles at the steel surface and morphology of the composite zinc coating are studied by scanning electron microscopy.

The protective properties of this system are investigated in a model corrosive medium of 5% NaCl solution by application of Potentiodynamic polarization (PDP) curves and Polarization resistance (Rp) measurements. The results obtained allow to conclude that the embedded polymeric modified CuO particles ensure better corrosion resistance and protective ability compared to the ordinary zinc.

Key words: *composite coatings, corrosion, CuO nanoparticles, polymeric modification*

1. INTRODUCTION

Biofouling and corrosion are undesirable problems for marine structures since both processes lead to increased fuel consumption of ships, microbiologically and chemically induced corrosion degradation of metals, etc. One effective solution to combat biological fouling is treating the substrate with biocide as a component of an antifouling coating deposited on the metal surface [1-3]. Incorporation of biocide into the matrix of the coating is expected to provide long-term biocorrosion protection due to the controllable release of this compound. Cooper and cooper-containing coatings can be used in antifouling coatings due to the well-known cooper toxicity to marine microorganisms [4-7]. In the seawater, the antifouling performances of the copper-based coatings are realized through the release of cuprous and copper ions, reacting with Cl^- ions [8].

Incorporation of cooper oxide (CuO) nanoparticles into the protective coatings seems to be a promising way to ensure a controlled release of the biocide on demand. In the aquatic systems, the dissolution of CuO nanoparticles depends on several factors such as particle size, shape and surface charge, and characteristics of the media (pH, ionic strength, dissolved organic matter) [9,10]. CuO nanoparticles may dissociate into Cu^{2+} and higher concentrations significantly affect the growth of aquatic microorganisms [11]. Recent studies also reported that CuO was reduced into Cu (0) or Cu_2O during electrophoretic deposition at cathode surface due to release of H_2 gas formed as a result of electrolysis of water [12].

One challenge of using commercial CuO nanopowder for incorporation in protective coatings is to find out suitable stabilizing conditions since CuO nanoparticles sediment in water. A simple method to prepare stable CuO suspension is to adjust the pH to regions with high electrostatic repulsion between the nanoparticles. At acidic conditions, CuO nanoparticles are highly charged and stable, and the aggregation is minimized because of the high repulsive forces dominating the van der Waals forces

between the particles [10,13]. At the isoelectric point, CuO particles have little or no charge, leading to a significant weakening in the repulsive forces between them, which implies that suspension becomes not stable. After the isoelectric point, the repulsive forces between nanoparticles become stronger, decreasing aggregation. However, the CuO dissolves under acidic conditions. Titration to alkaline conditions is also possible, but this is less effective close to the particles isoelectric point. Another method for stabilization of suspension is surface modification of the particles using polyelectrolytes, which can control electrostatic (and steric) forces between the particles [14].

The protection of metals from corrosion is technological problem since the metallic structures are in contact with aggressive corrosive species in the marine environment (e.g. Cl^- ions in the sea water). Steel is widely used due of low cost and its availability in ease for the fabrication of various vessels. One common method to preserve steel against corrosion is the application of metallic or organic coatings, aimed to impede the diffusion of corrosive agents into the depth of the metal. Deposition of zinc or zinc-based coatings is often used for corrosion protection of steel. Zinc provides sacrificial galvanic protection to the steel substrates since it is anodic with respect to iron and dissolves first in a case of corrosion attack.

The corrosion resistance of metals has been substantially enhanced by deposition of nanoparticles or nanocomposite films on metal substrates [15-19]. Among the different techniques used for preparation of such films, electrophoretic deposition is gaining increasing interest as attractive technique that offers high deposition rate and possibility for obtaining of relatively thick films [20]. Electrophoretic deposition is a colloidal processing method that involves the electrophoretic motion and deposition of charged particles onto a conducting substrate. Therefore, to control the colloidal behavior of the nanoparticles is a key point in order to prepare stable suspensions suitable for electrophoretic deposition. The general rule is that the particles have to possess a significant surface charge density to remain well dispersed in the suspension to provide homogeneous and smooth deposition.

In the present work, we describe the results on the preparation of CuO coating on steel by electrophoretic deposition of the oxide particles from a suspension stabilized against aggregation with a cationic polyelectrolyte – poly(ethylenimine) (PEI). Aiming at developing of new system with improved biofouling and corrosion protective properties, the polymeric stabilized CuO nanoparticles are incorporated into zinc coating on mild steel substrate. A two-step procedure is applied for preparation of the composite zinc coating on steel. Electrophoretic deposition of polymeric modified CuO nanoparticles is realized at pH 9.0 in order to minimize the effect of CuO dissolution and aggregation. In a second step, zinc coating is electrodeposited on the CuO covered steel substrate from a zinc sulfate electrolyte at pH 4.5-5.0. The protective characteristics of the newly obtained system are evaluated in a model corrosive medium by application of two electrochemical methods – Potentiodynamic polarization (PDP) and Polarization resistance (Rp) measurements.

2. MATERIALS AND METHODS

2.1. Materials and stock solutions preparation

Commercially available CuO nanopowder (from Sigma-Aldrich) is used without additional purification. According to the supplier, the mean particle diameter is less than 50 nm. The CuO nanoparticles stock suspension of concentration 1 g/l is prepared by sonication in ice for 15 min. The working concentration of nanoparticles is set to 2×10^{-2} g/l to ensure the quality of the results of the electrophoretic and size determination measurements. The suspension pH is varied from 4 to 11 by 0.1 M HCl or 0.1 M NaOH.

Poly(ethyleneimine) (M_w=25 kDa) is also obtained from Sigma-Aldrich. PEI is selected as a cationic polyelectrolyte to improve the stability of CuO suspension against aggregation and to promote the particles cathodic deposition on steel substrate by electrophoresis. The branched PEI is positively charged in neutral and acidic solutions due to protonation of –N–, –NH– or $–NH_2$ groups. In this experiment, the CuO nanopowder (1 g/l) is added to a PEI aqueous solution (1 g/l) and the suspension

is ultrasonicated for 15 min to improve the CuO dispersion. The pH of the suspension is ~ 11, quickly decreasing to ~ 7.5 after dilution with water to the working concentration of 2 x 10^{-2} g/l.

2.2. Characterization of CuO nanoparticles

Suspension dispersion and stability are evaluated in terms of particle size and zeta potential variation by dynamic light scattering (DLS) and electrophoresis measurements. A DLS particle sizer (Zetasizer Nano ZS, Malvern) is used to measure the hydrodynamic diameter of the CuO nanoparticles. A He-Ne laser is used as a light source and the intensity of the scattered light is measured by a detector at 173°. The intensity size distribution and the z-average diameter are obtained from the autocorrelation function.

The electrophoretic mobilities U_e of the CuO nanoparticles are measured with a Mark 2 apparatus (Rank Brothers, Great Britain) using a flat cell at room temperature. The electrokinetic zeta potential ζ is calculated from the electrophoretic mobility by applying Smoluchowski equation $\zeta = 4\pi\eta U_e/\varepsilon$, where ε is the electric permittivity and η is the viscosity of the medium.

Transmission Electron Microscopy (TEM) is applied for size determination of CuO nanoparticles (HR STEM JEOL JEM 2100). The surface morphology of the CuO nanoparticles covered steel surface and of bare and composite zinc coatings is investigated with Scanning Electron Microscopy by using of INCA Energy 350 unit.

2.3. Electrophoretic deposition of CuO nanoparticles and composite zinc coating on steel

The CuO nanoparticles and composite zinc coating are obtained on low carbon steel samples with working area of 3 cm^2 (sizes 3 x 1 x 0.1 cm). At first, a layer of cationic PEI coated CuO nanoparticles with a thickness of about 30 nm (concentration of the suspension – 4 x 10^{-2} g/l) are electrodeposited on steel sample at pH 9.0 (in order to minimize the CuO solubility and aggregation effects) at a cathodic current density of 0.02 A/dm^2 and application of non-soluble (inert) anodes. Second, ordinary zinc coating with a thickness of about ~ 12 μm is formed on the CuO nanoparticles covered steel substrate by electrodeposition from a slightly acidic zinc electrolyte (pH 4.5 - 5.0) at a cathodic current density of 2 A/dm^2 and application of soluble metallurgic zinc anodes to obtain the final bi-layer coating.

2.4. Corrosion characterization

Aiming at characterizing of the protective properties and corrosion behavior of the newly obtained coating system compared to the ordinary zinc coating with the same thickness two selected reliable electrochemical methods are applied - Potentiodynamic (PDP) polarization and Polarization resistance (Rp) measurement. The coatings are tested at ambient room temperature by application of computerized PAR unit "VersaStat 4" in three-electrode glass cell with a volume of 300 mL. Saturated calomel electrode (SCE) serves as a reference electrode and platinum plate - as a counter one. Working electrode is the tested sample (composite bi-layer system or ordinary zinc coating). PDP curves are stopped after visual appearance of the steel substrate checked by "naked eye" and the Rp measurements are carried out for a prolonged interval of 25 days.

2.5. Corrosive medium

Electrochemical corrosion tests are performed at room temperature in a model corrosive medium with pH value of ~ 6.7 - 5% NaCl solution.

2.6. Reproducibility

The results from the investigations are in average of 3 samples per type and per stage, i.e. for each measurement 3 replicates of a Zn and composite (hybrid) coatings are conditioned for initial and follow-up measurements.

3. RESULTS AND DISCUSSION

3.1. Characterization of CuO nanoparticles

A TEM image of CuO nanoparticles obtained from aqueous suspension is presented in Fig. 1. It shows that most of the CuO nanoparticles are spherical in shape having mean diameter of 63.5 ± 12.9 nm. In aqueous media (pH 6.5 - 7.5), the CuO nanoparticles form aggregates with hydrodynamic diameter of about 225 ± 4 nm as obtained by DLS measurements. Similar agglomeration of CuO nanoparticles in water solutions has been previously reported by other researchers [10,13,14,21]. The change in particles size compared to the primary particle size (< 50 nm) may be due to an increase in van der Waals forces among the nanoparticles, which results in the formation of larger aggregates in solution [22].

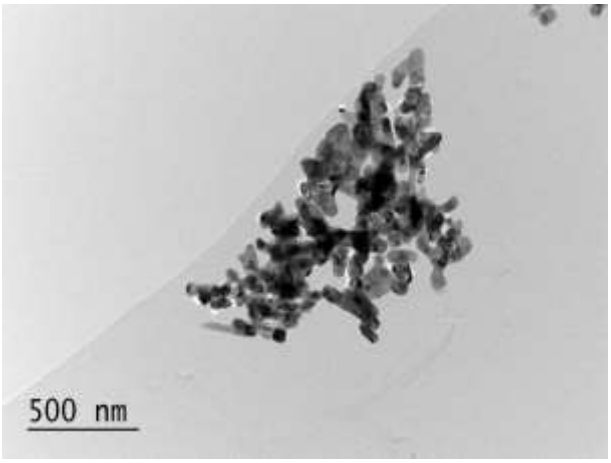


Figure 1. TEM image of CuO nanoparticles obtained in aqueous suspension

The impact of pH on the zeta potential of the CuO suspension (2 x 10^{-2} g/l) is also investigated. As shown in Fig. 2, CuO nanoparticles exhibit stable positive charge (+50 mV) at pH 4.0 - 5.0. Subsequently, the zeta potential strongly decreases to the isoelectric point at a pH ~ 9.5 and charge reversal is observed achieving value of ~ −38 mV at pH 11.0. These results are consistent with previous studies [10,13]. Nanoparticles with zeta potential higher than ± 30 mV are considered stable in the solution which means that aggregation in our suspensions can be observed between pH values 7.5 and 10.5 (most strongly expressed around the isoelectric point pH ~ 9.5). According to Khan et al., dissolution of CuO nanoparticles increases with decreasing pH from 7.0 to 2.0 and this is consistent with previous studies [23,24]. Under acidic conditions, the interaction of H^+ ions with CuO nanoparticles releases a large amount of Cu^{2+} ions [25].

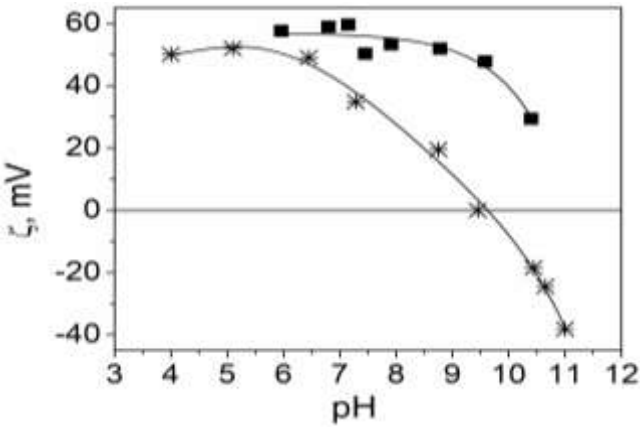


Figure 2. pH dependence of electrokinetic potential of CuO nanoparticles in the absence (∗) and in the presence of PEI (■)

3.2. Stabilization of CuO suspension through PEI addition

Considering the dissolution of CuO nanoparticles in acidic solutions and strong aggregation of the suspension close to the isoelectric point, stabilization of the CuO nanoparticles with PEI is conducted at pH 9.5 aiming minimizing both undesirable effects. As shown in Fig. 2, zeta potential of the CuO nanoparticles increases after the addition of PEI at all investigated pH values. The particles exhibit positive charge: zeta potential increases from +50 mV for bare CuO nanoparticles in acidic conditions to +58 mV in the presence of PEI, slightly decreasing at pH 7.0 - 9.5 and more strongly at pH 11.0. The important result is that zeta potential of the CuO nanoparticles at the isoelectric point (pH 9.5) is high enough after the adsorption of PEI on the particle surface (+48 mV) to minimize the aggregation in the suspension.

The mechanism of PEI adsorption on similarly charged CuO nanoparticles has been discussed in a work focused on electrophoretic deposition of CuO nanoparticles on metallized surfaces using PEI as a dispersing agent [14]. According to zeta potential measurements, CuO nanoparticles have a positive charge at pH values below the isoelectric point and the PEI chains are positively charged as well [14]. The authors founded best stabilization conditions at pH 3 and pH 9. At pH 3, fully protonated amine groups [-$(NH_3)^+$] of the PEI repel each other, while the un-protonated amine groups form weak dative bonds with the surface Cu^{2+}. At pH 9, stronger dative bonds are formed between the surface Cu^{2+} and the un-protonated amine groups. At both pH values, the mechanism of stabilization has been characterized as electro-steric repulsion.

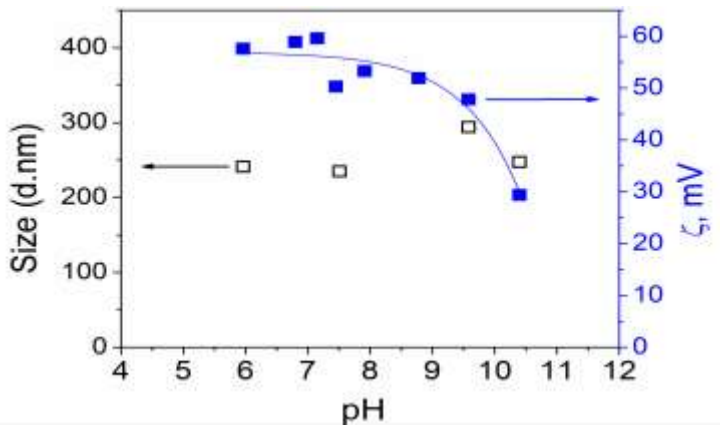


Figure 3. pH dependence of ζ-potential (■) and hydrodynamic diameter (□) of CuO nanoparticles in the presence of PEI

As shown in Fig. 3, the hydrodynamic diameter of the CuO nanoparticles slightly increases (from 225 ± 4 nm to 240 ± 7 nm) due to the adsorption of PEI chains on the particles surface. The suspensions are stable because of the high zeta potentials of bare and polymeric modified CuO nanoparticles. At pH 9.5, the particle diameter increases to about 295 ± 7 nm suggesting some residual aggregation in the suspension at conditions close to the isoelectric point of the starting aqueous suspension (see Fig. 2). Since the suspension in addition of PEI seems stable enough at pH 9.0, this pH value is used as optimal for electrophoretic deposition of the CuO nanoparticles on the steel substrate. Similar conditions for obtaining of homogeneous and bubble free deposits on platinized silicon wafers are recommended by S. Shehayeb et al. for the same CuO nanoparticles [14].

3.3. Surface morphology

Fig. 4A presents SEM image of CuO nanopartices coated with PEI after deposition on steel substrate from a suspension of concentration 4 x 10^{-2} g/l at pH 9.0. The average diameter of some particles (white aggregates) is below 0.5 μm, which means that they are electrodeposited on the steel surface preserving the sizes in the starting suspension. However, most of the electrodeposited particles have size close to that of the primer dry CuO nanoparticles (less than 50 nm). The surface morphology of the bare and the composite zinc coatings with incorporated CuO nanoparticles is demonstrated in Fig. 4B and 4C. Both micrographs show the formation of uniform zinc coatings on the steel substrate consisting of needle-like formations, most probably with metallic character (zinc compounds). There are no visible CuO particles (or CuO agglomerates) on the surface of the composite zinc coating what indicates that the CuO nanoparticles are fully covered by zinc during the electrodeposition process from zinc sulphate electrolyte solution.

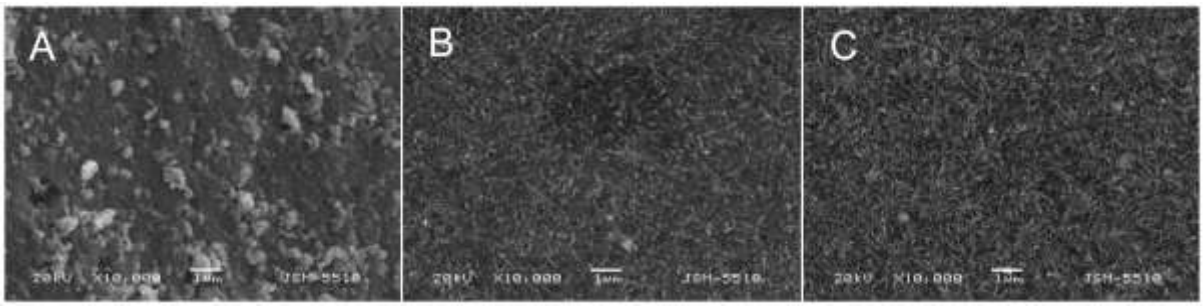


Figure 4. SEM images of CuO nanoparticles stabilized by PEI (A), composite CuO-zinc coating (B), and bare zinc coating (C) on steel samples.

3.4. Potentiodynamic investigations

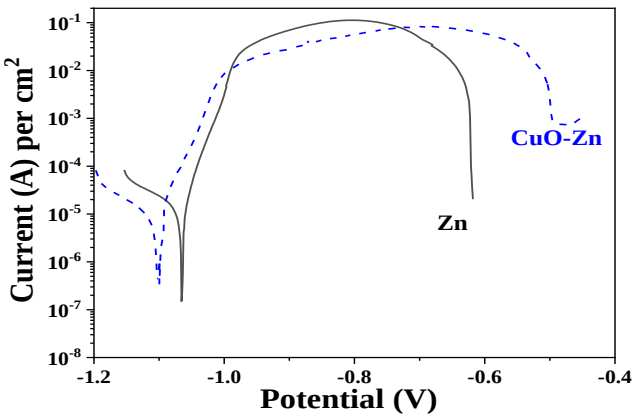


Fig. 5. Potentiodynamic polarization (PDP) curves in 5% NaCl solution of ordinary Zn and the composite CuO/Zn

The potentiodynamic polarization curves of ordinary Zn as well as of the composite system CuO-Zn are demonstrated in Figure 5. It is obvious that the anodic curve of the composite coating system is longer – it begins at ~ -1100 mV and stops at ~ -500 mV – i.e. its length is about 600 mV. For comparison, the length of the anodic curve of the ordinary zinc coating is about 450 mV. The corrosion current density of CuO-Zn composite is ~ 9.5 x 10^{-6} A.cm^{-2}, while the same parameter of the ordinary zinc is 1.4 x 10^{-5} A.cm^{-2} which means more intensive dissolution of the latter. In addition, the composite coating dissolves at lower anodic current density in the potential interval between – 1V and – 0.75 V – i.e. in the area of the maximal anodic dissolution.

These results clearly demonstrate that the CuO-Zn composite lasts longer at conditions of external anodic polarization. In addition, the corrosion potential value of the composite is with about 50 mV more negative compared to this of the zinc which means that the composite system will be more sacrificial ensuring better protection of the steel substrate due to earlier appearance of corrosion products with low product of solubility value.

3.5. Polarization resistance measurements

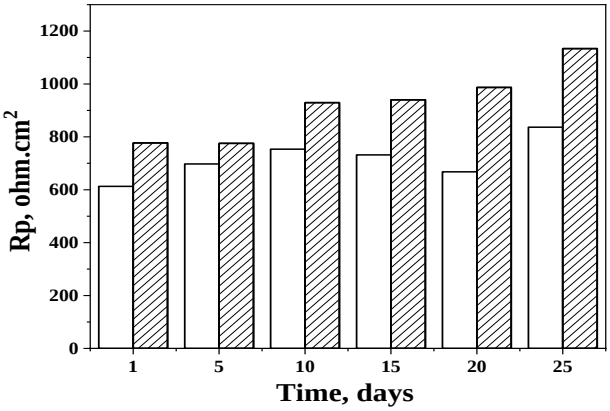


Fig. 6. Polarization resistance measurements in 5% NaCl solution of ordinary Zn and the system CuO/Zn

The data obtained during the polarization resistance measurements for a 25 days period of time is presented in Figure 6. It can be registered that the composite CuO-Zn demonstrates a constantly increasing tendency for this parameter reaching ~ 1100 Ω.cm^2 at the end of the test. The Rp values of the ordinary zinc are varying during the investigating period showing about 800 Ω.cm^2 at the 25-th day. It can be summarized from these results that the newly developed composite coating demonstrates better protective properties against the iron substrate compared to the ordinary zinc in a model medium containing Cl^- ions as corrosion activators.

4. CONCLUSIONS

This study demonstrates that addition of PEI to stabilize the CuO suspension against aggregation near the isoelectric point (pH ~ 9.0) leads to formation of positively charged nanoparticles suitable for electrophoretic deposition on cathode (steel) substrate. The deposition of PEI covered CuO nanoparticles on steel surface at this pH allow also to minimize the CuO dissolution, mainly occurred in acidic solutions. Standard zinc coating is then successfully deposited from a zinc sulphate electrolyte at pH 4.5-5.0. The obtained composite coating shows homogeneous structure with no visible presence of CuO nanoparticles on the coating surface. The result points to CuO incorporation in the composite coating mainly near the interface between the steel and zinc coating.

The investigation of the protective properties of the obtained bi-layer composite coating with the same thickness as the ordinary zinc one show better corrosion resistance and protective ability during a prolonged time interval as well as at conditions of external anodic polarization. Having in mind the

obtained results it could be expected that at real exploitation conditions this system could also protect the substrate against biofouling.

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