ISSN 1995-0780, Nanotechnologies in Russia, 2018, Vol. 13, Nos. 1–2, pp. 61–66. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © M.Yu. Kvasnikov, O.A. Romanova, A.V. Pavlov, A.A. Silaeva, Lwin Ko Ko, 2018, published in Rossiiskie Nanotekhnologii, 2018, Vol. 13, Nos. 1–2.

Nanostructured Metal–Polymer Paint Coatings

M. Yu. Kvasnikov[a]*, **O. A. Romanova**[a], **A. V. Pavlov**[a], **A. A. Silaeva**[a], **and Lwin Ko Ko**[a]
[a] *Mendeleev Russian University of Chemical Technology, Moscow, 125047 Russia*
**e-mail: kvasnikovm@mail.ru*

Received November 26, 2017; in final form, December 2, 2017

Abstract—A new in situ method for the fabrication of nanostructured metal–polymer paint coatings via the electrolytic cathodic deposition of amine-containing oligomeric film-forming electrolytes in combination with the electrolytic deposition of metals such as nickel, copper, zinc, and cadmium is proposed for the first time. The composition, morphology, and properties of these coatings are studied. The metal–polymer coatings are established to have new commercially valuable properties.

DOI: 10.1134/S1995078018010056

INTRODUCTION

Polymeric nanocomposites are a major focus of interest in polymer science. This also concerns metal polymers, whose polymeric matrix is filled with nanosize metal particles, which impart a complex of new interesting properties to such materials [1]. One of the most widely used methods for the fabrication of nanosized metal particles is the reduction of metals from their salts in the presence of polymers or surfactants [2].

In the last 50 years, painting via the electrodeposition of waterborne paint materials based on water-soluble film-forming electrolytes, including their cathodic electrodeposition, has found wide application in industry for the fabrication of ground and one-layer coatings on metals [3, 4]. In connection with this, the idea about the possible fabrication of metal–polymer coatings by combining this method with the galvanic electrodeposition of metals has arisen. In this case, the conditions for the formation of nanosized sols of metals must be created in the near-cathode layer during the simultaneous electrodeposition of polyelectrolytes and metals in the process of their electrolytic cathodic reduction. This may ensure the fabrication of nanostructured metal–polymer coatings with a polymer-based matrix and new properties.

The fabrication of a metal–polymer coating by this method implies a combination of physicochemical processes, such as the electrodeposition of polyelectrolytes and galvanic electrodeposition of metals. These processes are similar to each other from the technological viewpoint, but the mechanisms and parameters of their individual electrodeposition are different.

The formation of coatings in the process of electrodeposition painting is based on the ability of electrolytes, which are film-forming agents in the applied paint materials, to change their solubility depending on the pH of a medium. An amine-containing film-forming oligomer is brought to a water-soluble state via its interaction with an acid (most often, acetic or formic acid). The main electrochemical process of cathode electrodeposition is water electrolysis, as a result of which the near-cathode space is alkalized (pH tends to 14). This results in the regeneration of anime groups, which were primarily neutralized with an acid, and an oligomer loses its solubility in an alkaline medium and precipitates on the cathode. The pigments and fillers of a paint system are electrodeposited in an electrophoretic way. The formation of an electrode precipitate is accompanied by electroosmosis and syneresis, due to which the precipitate is densified and dewatered [4]. The further thermosolidification of this precipitate leads to the formation of a cross-linked three-dimensional polymer coating. Hence, the metal particles reduced from salts simultaneously with the electrodeposition of a polyelectrolyte turn out in a polyelectrolyte medium, which stabilizes them. This is an attractive method of their in situ introduction into a polymeric matrix.

EXPERIMENTAL

This paper deals with paint metal–polymer coatings obtained from compositions based on a polymeric film-forming electrolyte for cathode electrodeposition and acetates of metals such as nickel, zinc, copper, and cadmium. The process of their simultaneous electrodeposition and the composition, properties, morphology, and structure of formed coatings were studied.

The industrial electrodeposition paint material binder representing an epoxyanime adduct, which was modified with blocked isocyanate and brought to a

Table 1. Parameters of the electrolytic deposition of metals and the electrodeposition of polyelectrolytes

Parameters	Electrodeposition of polymeric electrolytes	Electrolytic deposition of metals
Process time, min	2–3	30–90
Voltage, V	240	10–30
Current density, A/dm^2	1–2	10–50
pH	5–5.8	3–8
Temperature, °C	28–32	50–60
Electroconductivity, μS/cm	<2000	>3500
Concentration, g/L	30–34	20–250

water-soluble state via its interaction with acetic acid, was used as a film-forming polyelectrolyte [5]. The concentration of a polyelectrolyte solution was 12–16% on a dry residue basis at pH = 5–5.5 and an electroconductivity of $\mu = 1200–1500$ μS/cm.

Aqueous solutions of nickel, zinc, copper, and cadmium acetates with a concentration of 0.45, 0.93, 0.3, and 0.8 mol/L were used for simultaneous cathodic electrodeposition. It has been preliminarily established that all the systems are aggregatively and kinetically stable within a broad range of component ratios. Simultaneous electrodeposition was performed on a laboratory electrodeposition painting machine in a bath with a volume of 0.5 L. An insoluble 08Kh10N20T2 (AISI 303) stainless steel anode applied for the electrodeposition of polyelectrolyte-based systems was used.

The thickness, adhesion, bending-strength (elasticity) hardness, impact strength of coatings, and the characteristics of accelerated corrosion tests were measured by standard methods adopted in paint and galvanic industries. The characteristics of metal–polymer coatings were compared with the characteristics of coatings fabricated from a pure polyelectrolyte under standard electrodeposition conditions.

The elemental composition of coatings was determined by energy-dispersive X-ray microanalysis on a Quanta 650 instrument with an EDAX module.

The crystal structure of the metal phase of coatings was studied by X-ray diffraction on a DRON-2 automatic diffractometer with a specially collimated diffraction beam in the "by reflection" mode within a range of angles of $2\theta = 1–90°$ (CuK_α radiation, $\lambda = 1.54$ Å).

The morphology of coatings was studied by atomic scanning microscopy on a Bruker Adviserscap microscope in the contact mode using an NSG-10 probe.

The process of solidification was studied by differential scanning calorimetry on a NETZSCHDSC 204 F1 calorimeter.

RESULTS AND DISCUSSION

As was mentioned above, the parameters of the individual electrodeposition of metals and polyelectrolytes are different (Table 1).

It can be seen that the electrodeposition of polyelectrolytes occurs at a high voltage and a low current and, on the contrary, the electrodeposition of metals requires a relatively low voltage and a high current. The time for the formation of an acceptable thickness differs by an order of magnitude. Nevertheless, we have managed to find the conditions of their simultaneous electrodeposition for the formation of high-quality coatings. Since the matrix of a coating is a polymer, we tried to select electrodeposition parameters closer to the level optimal for the electrodeposition of a polyelectrolyte. Electrodeposition was performed in the regime of a constant voltage within 120–240 V at a temperature of 27–35°C and a time of 60–180 s. The cathodes were metal plates of 08KP steel (AISI A 622), which were degreased and prepared according to the requirements of GOST (State Standard) 9.402-2004 (ISO 1513), with a surface area of 0.2 dm^2. The thermosolidification of coatings was performed at 180°C for 20 min. Defectless coatings satisfying GOST R (Russian State Standard) 51691–2008 (ISO 4628) in regards to their appearance were formed under these conditions.

The optimal composition of the working solution in the bath and the content of metal in the formed coatings are given in Table 2.

From the data it follows that the content of metal in a coating depends on its content in the working solution as indicated by the polymeric electrolyte/metal acetate ratio.

Nevertheless, the optimal technological regime allows one to control the simultaneous electrodeposition processes, and this in turn results in defectless coatings (Table 3).

It can be seen that a common feature of all the metal–polymer coatings in comparison with the metal-free coatings is an appreciable increase in hardness with the retention of high elasticity (bending

Table 2. Composition of the working solution in the bath and the content of metal in a coating

Composition of a system	Polyelectrolyte/metal salt component ratio in the working solution of the bath, g/g	Content of metal in a coating, wt %
Polymeric electrolyte + nickel acetate	10/1	3–6
Polymeric electrolyte + copper acetate	29/1	1.4–2.5
Polymeric electrolyte + zinc acetate	22/1	2.1– 2.6
Polymeric electrolyte + cadmium acetate	10/1	2.5–6

Table 3. Properties of coatings

Coating properties	Nickel–polymer	Copper–polymer	Zinc–polymer	Cadmium–polymer	Polymer coating
Thickness, μm	20–22	21–23	17–22	18–21	23–25
Adhesion index, GOST 31149-2014 (ISO 2409)	0	0	0	0	0
Impact strength, cm, GOST R 53007-2008 (ISO 6272)	100	100	100	100	70
Hardness, arb. units, GOST R 54586-2011 (ISO 15184)	8H	8H	8H	8H	4–5H
Bending strength, GOST R 52740-2007 (ISO 1519)	1	1	1	1	1

strength) and impact strength (resistance to fast strain).

The DSC curves recorded when studying the coating thermosolidification processes are shown in Fig. 1.

It can be seen that the thermosolidification of metal–polymer coatings begins 20–40°C earlier than for polymer coatings, thus providing deeper cross linking, and this may be due to the catalytic properties of the considered metals belonging to the group of transition ones. The formed chemosorption bonds also must make their contribution to the formation of a dense network of metal–polymer coatings.

These results agree with the data of thermomechanical studies, which are based on the dependence of specimen elongation under heating and show that the second-order phase transition temperatures of all metal–polymer coatings grow appreciably as befits an increasing degree of cross-linking in coatings [6].

To estimate the degree of cross linking in the network, we determined the molecular weight per cross-link unit. The method of equilibrium swelling with respect to a polymer in a thermodynamically active solvent representing butyl cellosolve, which is just the solvent providing the maximum swelling of polymer

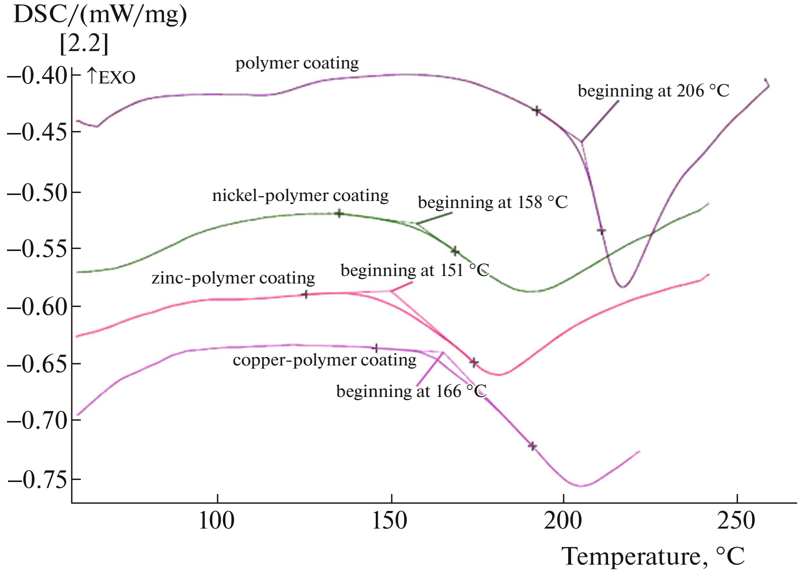

Fig. 1. (Color online) DSC curves of metal–polymer coatings.

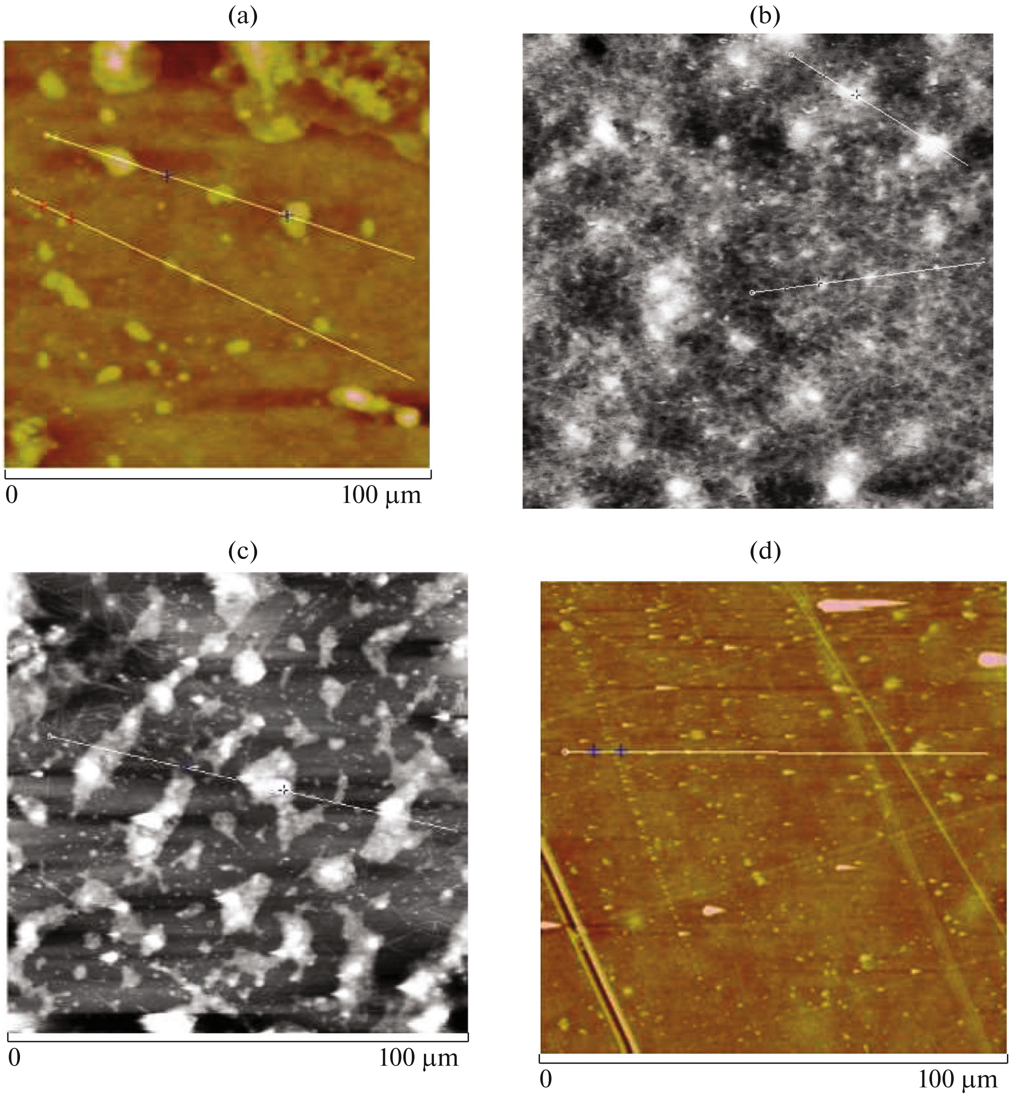

Fig. 2. (Color online) Morphology of metal–polymer coatings: (a) nickel–polymer, (b) copper–polymer, (c) zinc–polymer, and (d) polymer.

coatings at zero mixing heat and system volume change, was applied. The data of this study were used to calculate the number-average molecular weight per cross-link unit (Mc), which reached 970 g/mol for the polymer coating, 390 g/mol for the zinc–polymer coating, 300 g/mol for the nickel–polymer coating, 201 g/mol for the copper–polymer coating, and 290 g/mol for the cadmium–polymer coating. This may argue for a denser polymeric network of metal–polymer coatings.

Such an increase in the degree of cross-linking in the fabricated metal–polymer coatings promotes the growth of their strength and hardness, but this might lead to a decrease in their elasticity, which usually changes inversely with respect to the mentioned parameters. The only possible explanation of this fact may be related with the formation of metal nanoparticles in the polymeric matrix [1]. It is known that similar properties are inherent in polymeric nanocomposites with nanosized fillers

Table 4. Protective and anticorrosion properties of coatings

Coating properties	Nickel–polymer	Copper–polymer	Zinc–polymer	Cadmium–polymer	Polymer coating
Salt resistance, h, GOST 9.905-2007 (ISO 9227)	More than 1500	720	700	1800	700
Water resistance, h, GOST 9.083-78 (ISO 12944)	1850	1700	More than 8000	2000	1000

Fig. 3. (Color online) Photo of the zinc–polymer coating after testing for 6000 h in water (GOST 9.083-78, ISO 12944).

(nanotubes and clusters of nanosized metals). The photos of the morphology of coatings at a magnification of $\times 10^7$ are shown in Fig. 2.

Atomic force microscopic (AFM) studies have shown that associates (clusters) of metal nanoparticles with a primary size from 50 to 400 nm are formed in the polymeric matric, thus confirming our hypothesis.

We expected an appreciable increase in the protective and anticorrosion properties of nickel–polymer, zinc–polymer, and cadmium–polymer coatings (Table 4).

It is known that zinc is an anode with respect to iron and provides its galvanic protection. However, there is no galvanic protection in the case of nanosized zinc particles with a low concentration, probably because the required percolation threshold is not attained. Similar results were obtained in [7] for the example of epoxide coatings fabricated by traditional methods in a composition with a nanosized zinc. An increased strength of specimens at good elastic properties and the absence of galvanic protection were also observed in this case. The photo of the zinc–polymer coating after tests is shown in Fig. 3.

It can be seen that there is no corrosion at all, and the coatings have very high water resistance. This should be hypothesized to result from the formation of insoluble zinc products inside the coating and a high degree of cross linking, which improves the barrier properties.

The protective properties of nickel–polymer coatings have proven to be much more surprising. This is illustrated in Fig. 4, which presents the polymer and nickel–polymer coatings after exposure in a 3% NaCl solution for 1500 h.

It can be seen that the nickel–polymer coating has not demonstrated any corrosion propagation signs for the period of testing, while the polymer coating failed and was taken out of tests.

We expected an increase in the heat conductivity of copper–polymer coatings. However, despite the rather low content of copper in the coating (2%), the heat conductivity of the copper–polymer coatings is two times higher than for the polymer coatings. The heat conductivity of nickel–polymer coatings has also been studied to reveal that nickel in a coating decreases its heat conductivity (Table 5).

The composition of the crystalline phase of metal–polymer coatings was studied by X-ray diffraction. Calculations show that the nickel–polymer coating contains nickel–iron intermetallide instead of pure iron. The formed metal–polymer coating has a cubic symmetry system (symmetry group 1*m*3*mc*) with a unit-cell parameter $a = 0.2868$ nm and has a structure composed of four parallel differently oriented kamac-

Fig. 4. (Color online) Photos of specimens after salt resistance testing by submerging into a 3% NaCl solution: polymer coating (left) and nickel–polymer coating (right).

Table 5. Heat conductivity of metal–polymer coatings

Coating type	Heat conductivity, m^2/(K W)
Polymer coatings	0.929
Copper–polymer coatings	1.835
Nickel–polymer coatings	1.835

ite (α-Ni–Fe) lamellae with taenite (γ-Ni–Fe) interlayers against the background of a fine-grained kamacite–taenite mixture [8]. This fact of a wonderful structure of synthesized intermetallide formed in the lower layer of the coating requires further studies. We can hypothesize that the presence of such intermetallide also makes a contribution to the protective ability of a coating.

In the case of zinc–polymer coatings, zinc–iron intermetallide has also been revealed.

According to X-ray diffraction data, the metal phase of copper–polymer coatings exhibiting high heat conductivity has no crystal structure; this means that copper is present in a coating in a form different from metals.

CONCLUSIONS

Hence, new metal–polymer coatings with a nanosized metal phase have been fabricated via the simultaneous cathodic electrodeposition of film-forming polyelectrolytes of metals such as nickel, zinc, copper, and cadmium. This imparts them with a variety of valuable properties.

The wonderful properties of coatings have attracted the interest of commercial enterprises. The considered metal–polymer film-forming agents were used as a basis to create filled paint systems for special purposes:

(i) nickel–polymer systems for the fabrication of wear-resistant anticorrosion coatings in the military industrial complex;

(ii) copper–polymer systems with an increased heat conductivity for painting household and industrial convectors and radiators; and

(iii) zinc–polymer systems instead of cold galvanizing and as ground coatings for self-healing polymer lacquer coatings.

It should be noted that our work, devoted to a new method for the in situ fabrication of nanostructured metal–polymer coatings, yields opportunities of further studies for electrochemists, material engineers, and specialists in the field of polymer chemistry.

ACKNOWLEDGMENTS

This work was performed within the Federal Target Program “Research and Development in the Priority Fields of the Scientific and Technological Complex of Russia for 2014–2020” (project identifier RFMEFI57417X0133).

REFERENCES

1. A. D. Pomogailo, A. N. Rozenberg, and V. K. Uflyand, *Metal Nanoparticles in Polymers* (Khimiya, Moscow, 2000) [in Russian].
2. V. I. Roldugin, “Quantum-size colloid metal systems,” Russ. Chem. Rev. **69**, 821 (2000).
3. I. A. Krylova, “Painting by electrodeposition on the eve of the 21st century,” Prog. Organic Coat. **42**, 119–131 (2001).
4. M. Yu. Kvasnikov and I. A. Krylova, “Painting by electrodeposition at the turn of the century,” Lakokras. Mater. Primen., No. 4, 10–15 (2001).
5. M. Yu. Kvasnikov, V. S. Tochilkina, L. A. Rudkovskaya, I. A. Krylova, and S. E. Pavlikhin, “Current state and perspectives of the development of the painting method by the electrodeposition of water-dilutable paints and varnishes,” Promyshl. Okraska, No. 4, 6–11 (2008).
6. O. A. Romanova, K. N. Smirnov, I. F. Utkina, M. R. Kiselev, Y. M. Korolev, I. A. Krylova, E. M. Antipov, and A. A. Silaeva, “Obtainment of a metal-polymer coating via the simultaneous combination of electrodeposition on the cathode of oligomeric electrolytes and electrodeposition of metals,” Polym. Sci., Ser. A **57**, 473–479 (2015).
7. P. Vertuest, “Anti-corrosion properties of zinc powder paintings using nano zinc metal powder,” China Coat. J., No. 7, 24–36 (2009).
8. V. V. Busarev, “Study of asteroids by spectrometry methods,” Doctoral (Phys. Math.) Dissertation (Lomonosov Mosc. State Univ., Moscow, 2012).

Translated by E. Glushachenkova