Effect of Current Density on Electrodeposition of Nickel-Organic Microcapsules Composite Coatings

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Abstract

A formation of protective composite coatings based on nickel and organic substance of inert nature, containing a corrosion inhibitor, encapsulated in a polymer shell, was studied. The microcapsules were synthesized in an aqueous-organic emulsion using the method of formation of shell of the modified gelatine on the surface of microdroplets. Composite coatings were obtained by electrochemical codeposition of nickel matrix and microcapsules, suspended in the electrolyte. Changes of surface morphology, microhardness and corrosive properties of coatings with respect to changes of deposition parameters of coatings were investigated.

The distribution of particle sizes in coatings depending on the current density was studied. It was shown that an increase in the mass fraction of the microcapsules in the coating leads to an increase in its corrosion resistance.

Introduction

Composite electrochemical coatings (CEC) are used as coatings of enhanced mechanical durability for tools, chemically and thermally durable coatings in internal combustion engines, corrosion-resistant coatings to protect parts from environmental impacts, etc. [1, 2].

Nickel is one of the common matrix metals and composite coatings on its basis are the most studied presently. Successful implementation of composite additives of both organic [3, 4] and inorganic [5, 6] nature into the nickel matrix is possible. Such nickel features as plasticity, corrosive resistance and low costs make composite electrochemical coatings based on nickel most commonly used in practice [7, 8].

During last period attention of researchers is attracted to development of corrosive resistance coatings with functional properties. Existing protection techniques with application of protective galvanic and varnish and paint coatings have the disadvantage of the necessity in frequent renewal of the protective layers, besides, they retain their properties only in the absence of mechanical damages, i.e. they are absolutely unsuitable for use under mechanical loads. Thus, there is an objective need for development and study of protective coatings that can independently prevent specified environmental influences [9].

An interesting idea is to try to suppress the corrosion of galvanic coatings by administering specific agents therein, which could promote the formation of passive layer for a long time, inhibiting the corrosion process. In this regard, the most effective method of obtaining of such coatings is the electrochemical method that allows to obtain composite coatings with microcapsules, containing substances that inhibit corrosion. During the electrodeposition of the galvanic coating the microcapsules suspended in the electrolyte are captured and overgrown by growing layer of metal. After formation of such a composite material the diffusion of the active component from the capsules protects the metal for a long time. These composites are especially effective under a possible violation of the integrity of the coating when the cracks will lead to the release of the content of the microcapsules.
Proposed by the authors composite electrochemical coatings contain capsules of micron size range, designed to modify the electrochemical properties of nickel coatings.

There is a significant amount of investigations [10-19] devoted to studies of production and application of nickel composite coatings, as well as the corrosion-resistant organic (polymer and epoxy) coatings containing microcapsules, produced by use of different methods [20-26].

However, there are few studies [27-30] concerning composite coatings created by means of electrochemical codeposition of metals with organic microcapsules. And the number of studies covering the research and production of CECs containing microcapsules is extremely small [31-33].

In this paper, the authors investigate an electrochemical method of preparation of composite nickel coatings with microcapsules, containing a functional substance, dissolved in organic liquid, which inhibit the corrosion processes. This article is devoted to studying the effect of current density of the electrodeposition on the composition, properties and morphology of the coatings. This is important because the amount of microcapsules, codeposited in metal matrix determines the properties of CECs such as microhardness, ductility, uniformity, porosity, and corrosion resistance. We believe that the results are supposed to attract attention of scientists interested in developing methods to protect metals against corrosion.

Experimental

To investigate the processes occurring during the electrochemical deposition of CEC the Watts sulphate-chloride electrolyte of matte nickel of the following composition was used (g per L): NiSO₄·7H₂O – 300; NiCl₂·6H₂O – 60; H₃BO₃ – 30 (A.C.S.).

A layer of galvanically deposited nickel served as the matrix of composite coating, the second phase substance was organic microcapsules synthesized by liquid emulsification [34]. This method is based on hard shell formation around the emulsion particles of organic substance in the water.

Basis of the method that is widely used for preparation of microcapsules [35-41] is the formation of emulsions in the system of two immiscible liquids with the subsequent formation of hard shells on the surface of the droplets.

Modern methods of microencapsulation allow enclosing in a sheath the substance practically in any aggregative state. It allows keeping properties of encapsulated substances till the moment of its direct use. Today there are lots of ways for producing microcapsules which can be carried out by various methods: chemical, physical and physico-chemical. In a number of technologies combined methods of sheath formation are used, and the choice of optimum methods of their combinations are defined by properties of encapsulated product, requirements to produced microcapsules and advantages of technological process.

In the present work the method of producing gelatinous microcapsules was advanced by us. At first stage modification of gelatine was carried out by means of addition of 4 g 1%-solution of sodium palmitate C₁₅H₃₁NaO to gelatine aqueous solution (10%). At the second stage emulsification of encapsulated liquid (carbon tetrachloride) into the modified gelatine solution was carried out by intensive mixing to attain a degree of the necessary size fractions. Then the additive (15 mL 20%-solution of sodium sulfate) was injected into produced emulsion (20-25 mL) as the result of which gelatine sedimentation on a surface of emulsion of micro drops took place. Further sheath formation of microcapsules occurred by two ways:

1) by slow decrease of solution temperature up to 50 °C with the subsequent addition of 37%-solution of formaldehyde (2 mL) for solidification of microcapsules.

2) by pouring produced emulsion into a great volume of cooled 7%-solution of sodium sulfate Na₂SO₄. The volume of solution of sodium sulfate has to be 4 times larger than the volume of the emulsion. Solidification of microcapsules was carried out by addition of 37%-solution of formaldehyde (2 mL).

Microcapsules produced by this way have got the size 30-50 micrometers.

For realization of codeposition of microcapsules into a nickel matrix they were administered into the electrolyte bath in the form of an aqueous suspension.

Voltammetric studies were carried out in a temperature controlled three-electrode cell on the potentiostat-galvanostat “Autolab-30” with PC software management. Electrodeposition of CEC was carried out at 25 °C temperature and electrolyte stirring with a magnetic stirrer. The range of operating current densities for deposition of nickel CECs was selected on the basis of the results of voltammetric studies. In particular based on the current densities, corresponding with the areas of the nickel reduction waves on the potentiodynamic curves. Curves were recorded at sweep rate of 20 mV/s.

Previously polished and chemically etched according to the established procedure [42] copper and steel (purity 99.9%) cathodes with 1.5 cm² area of working surface were used for electrodeposition.
of nickel CECs. A pure nickel plate was used as the anode. Silver chloride electrode was used as a reference electrode.

Microhardness of deposited coatings was determined using micro-durometer “PMT-3” with 50 g load. Micrographs of coating surface, microscopic morphology study and calculation of amount of microcapsules encapsulated into the coating were made by means of digital material science microscope “Leica DM 6000” and scanning electron microscope “Quanta 200i 3D” with energy dispersive X-ray analysis (EDXA) system.

Investigation of corrosive resistance was performed in a neutral 3% NaCl solution (pH ≈ 6.3) by means of electrochemical method. Polarization curves were obtained by means of potentiostat-galvanostat “Autolab-30”. Values of corrosive currents, steady-state potentials for each coating and expected protective effects were determined on the basis of obtained data. In particular, a comparison of the corrosion current in the presence of inhibitor ($i_{\text{cor}}$)' and without inhibitor ($i_{\text{cor}}$) allows to calculate the protective effect (Z, %) and protective factor ($\gamma$):

$$Z = 100 \times \frac{i_{\text{cor}} - i_{\text{cor}}}{i_{\text{cor}}}, \quad \gamma = \frac{i_{\text{cor}}}{i_{\text{cor}}}.$$ 

All used chemicals have a highest purity, set by American Chemical Society (A.C.S.).

\section*{Results and Discussion}

\subsection*{The Study of Electrodeposition Processes of Composite Coatings}

To study the processes of nickel electroreduction during the CEC formation the series of potentiodynamic polarization curves on copper and steel electrodes depending on the concentration of the microcapsules in the composition of the electrolyte were recorded.

As it can be seen from Fig. 1, with increase of concentration of microcapsules in the electrolyte the potential of nickel reduction shifted towards the cathode region, it indicates the difficulty of the process of electrochemical reduction associated with the adsorption of the products of partial dissolution of the gelatine shell of the microcapsules in the electrolyte, as it was demonstrated by a series of specific tests. Introduction of gelatine into the electrolyte shifts the potential of nickel reduction towards the negative direction. Difference of shifts of nickel reduction potential between iron and copper characterizes different gelatine adsorption on these metals.

![Polarization curves](image)

**Fig. 1.** Polarization curves of deposition of composite coatings "Ni-organic microcapsules" on copper (a) and steel (b) electrodes at different concentration (pieces per mL) of microcapsules in the electrolyte: 1 – 0; 2 – 7×10⁵; 3 – 1.5×10⁶.

The range of operating current densities for deposition of nickel CECs was selected on the basis of the results of voltammetric studies. Influence of current density at two concentrations of microcapsules in the electrolyte on copper and steel substrates on the composition, properties and corrosive resistance of coatings was investigated. The main characteristics of obtained nickel CECs and electrolysis process are shown in Table 1.

It is not quite normal that at a constant concentration of microcapsules in the electrolyte there is a tendency of increasing the current efficiency (yield with respect to current) with increasing current density of deposition for CECs, deposited both on copper and steel substrates. Most likely, this is due to the desorption of gelatine from the electrode surface at more negative potentials, as indicated by the polarization curves (Fig. 1) which show strong inhibition of process of electrochemical reduction of nickel in the presence of the microcapsules, while the influence of microcapsules on the wave of hydrogen evolution is insignificant.
Table 1
The microhardness of the obtained nickel CECs and the current efficiency of the electrolysis at different concentrations of the microcapsules in the electrolyte and different current densities

| Concentration of microcapsules in the electrolyte, pieces per ml | \( i, \) mA/cm\(^2\) | Current efficiency, \% | HV\(_{30}\), kg-f/mm\(^2\) |
|---------------------------------------------------------------|-----------------|------------------|-----------------|
|                                                               | Copper cathode | Steel cathode    | Copper cathode | Steel cathode |
| 7\times10^5                                                  | 50             | 90              | 95             | 940           | 990           |
|                                                              | 35             | 85              | 86             | 951           | 891           |
|                                                              | 25             | 85              | 83             | 928           | 864           |
|                                                              | 10             | 79              | 85             | 856           | 840           |
| 1.5\times10^6                                                | 50             | 94              | 91             | 886           | 891           |
|                                                              | 35             | 95              | 92             | 856           | 599           |
|                                                              | 25             | 90              | 91             | 786           | 511           |
|                                                              | 10             | 91              | 88             | 723           | -             |

Microhardness values for coatings on copper and steel are correlated with the values of current efficiency. For both types of substrates, regardless of the current density there is a general tendency of reduction of microhardness of coatings with increasing concentration of additive of the microcapsules in the electrolyte from 7\times10^5 to 1.5\times10^6 pieces/ml. This can be explained by the fact that the inclusion of particles of the polymeric nature in the deposits reduces internal stresses in nickel coatings. Increasing current density probably leads to a decrease in the average crystal size of nickel, causing an increase of microhardness.

Evaluation of morphology of obtained coatings and calculation of number and size of the codeposited microcapsules were produced by means of optical and scanning electron microscopy. Micrographs of nickel composite coatings on copper substrates are presented in Figs. 2-4.

Surface of composite coatings is a dense layer of fine-grained nickel with rounded microcapsules protruding above the main surface.

![Micrographs](image1)

Fig. 2. Micrographs of nickel CECs with microcapsules on copper substrates, deposited at different current density, mA/cm\(^2\): a – 10; b – 25; c – 35; d – 50. Concentration of microcapsules in the electrolyte – 7\times10^5 pieces/ml.
Fig. 3. Micrographs of nickel CECs with microcapsules on copper substrates, deposited at different current density, mA/cm²: a – 10; b – 25; c – 35; d – 50. Concentration of microcapsules in the electrolyte – 1.5×10⁶ pieces/ml.

Fig. 4. SEM micrographs of nickel CEC with microcapsules on copper substrate, deposited at 35 mA/cm² with specifying zone of EDX analysis: a – zone of matrix layer; b – zone of microcapsule. Concentration of microcapsules in the electrolyte – 1.5×10⁶ pieces/ml.

At the concentration of microcapsules in the electrolyte of 7×10⁵ pieces per ml, with deposition current density increasing from 10 to 50 mA/cm², the number of microcapsules on the coating surface increases from 4189 to 28957. However, at a concentration of 1.5×10⁶ pieces per ml, as the current density increases, the number of microcapsules increases, reaching maximum at \( i = 25 \) to 35 mA/cm², and decreases thereafter.

Micrographs of nickel CECs, obtained with a scanning electron microscope are shown in Fig. 4. Deposited microcapsules are spherical formations with a diameter of 15 to 50 microns, partially covered by layer of nickel, which corresponds to the data of optical microscopy.

The composition analysis of investigated CEC was carried out by means of energy dispersive X-ray spectroscopy (EDXA), which allowed us to estimate the mass and atomic proportion of main elements of the coating. The results of analysis are presented in Fig. 5 and Table 2.

As seen from Table 2, the content of carbon in the zone of partially overgrown microcapsules is markedly higher than the content of carbon in the zone of pure nickel layer. This indicates the successful and effective codeposition of microparticles (microcapsules) with organic nature into the coating.

The number and sizes of the microcapsules deposited on a specific surface area of the nickel coatings were determined by micrographs, the distribution curves of the microcapsules by their diameters were determined, depending on current densities (Figs. 6 and 7).
Table 2
EDX analysis of composite coatings

| Concentration of micro-capsules in the electrolyte, pieces per mL | $i$, mA/cm$^2$ | Element | wt.% | At, % |
| --- | --- | --- | --- | --- |
| $1.5 \times 10^6$ | 35 | Nickel layer | 98.27 | 93.39 |
| | | Microcapsule | 89.98 | 65.89 |
| | | O | 1.24 | 4.32 |
| | | C | 0.49 | 2.29 |
| | | Ni | 98.27 | 65.89 |
| | | Microcapsule | 89.98 | 65.89 |

Effect of Current Density on Electrodeposition of Nickel Composite Coatings

When processing the curves of size distribution of microcapsules, included into the coatings, we see that they have a sufficiently large spread of values and similarity of the forms of curves in general. All of this allows approximate the distribution at different current densities to a common regularity that is typical for all current densities. We see this pattern in Fig. 8, which shows the averaged values for different current densities.

Fig. 5. EDXA spectra of nickel CEC with micro-capsules on copper substrate, deposited at 35 mA/cm$^2$: a – zone of matrix layer; b – zone of microcapsule. Concentration of microcapsules in the electrolyte – $1.5 \times 10^6$ pieces/ml.

Fig. 6. Diagrams of size distribution of codeposited microcapsules for coatings, deposited at different current density, mA/cm$^2$: a – 50; b – 35; c – 25; d – 10. Concentration of microcapsules in the electrolyte – $7 \times 10^5$ pieces/ml.

Fig. 7. Diagrams of size distribution of codeposited microcapsules for coatings, deposited at different current density, mA/cm$^2$: a – 50; b – 35; c – 25; d – 10. Concentration of microcapsules in the electrolyte – $1.5 \times 10^6$ pieces/ml.

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Fig. 8. Diagrams of averaged size distribution of the microcapsules for all current densities, in the coatings and in the initial electrolyte at different concentrations of microcapsules in the electrolyte. 1 – Distribution in the initial electrolyte; 2 – Distribution in the nickel CEC at the concentration of microcapsules in the electrolyte $7 \times 10^5$ pieces/ml; 3 – Distribution in the nickel CEC at the concentration of microcapsules in the electrolyte $1.5 \times 10^6$ pieces/ml.

As can be seen from a comparison of the size distribution of the microcapsules on the surface of the coating at different values of the concentration of microcapsules, suspended in the electrolyte (Fig. 8), there is no significant difference between them, so the distribution can be considered to be independent of concentration. However, the total amount of microcapsules deposited on the surface markedly depends on the concentration of the microcapsules in the electrolyte.

Comparison of the microcapsules’ size distributions in the composite coatings and in the initial suspension of microcapsules indicates a shift of the maximum of the distribution to the area of larger capsules for composites, compared to the suspension. If the original suspension of the microcapsules has a maximum at 25 microns, then on the surface of deposited composites the maximum exists at 35 microns. Smaller microcapsules are weakly bound to the substrate surface; therefore, they are more easily extruded from the surface during nickel deposition.

Determination of the surface concentration of the microcapsules was carried out from the micrographs, obtained by means of optical and electron microscopy. The calculations of mass and volume fractions of microcapsules in composition of nickel CECs were performed gravimetrically by the difference of the masses of the electrode before and after electrodeposition, taking into account the current efficiency (Table 3).

As can be seen from Table 3, the values of the mass and volume fractions of the microcapsules, contained in the coating, at the concentration of microcapsules in the electrolyte of $7 \times 10^5$ pieces per mL, increase with increasing deposition current density from 10 to 35 mA/cm$^2$ and decline thereafter during further increase in current density. However, at the concentration of microcapsules of $1.5 \times 10^6$ pieces per mL, as the current density of electrodeposition increases, the values of the mass and volume fraction of the microcapsules, contained in the coating, decrease.

The highest concentration of the microcapsules in the coating is achieved due to the implementation of the most favourable conditions for the efficient capture of microcapsules by layer of growing matrix.

It is an interesting fact that a lower concentration of microcapsules in the electrolyte corresponds to its higher content in a matrix. The explanation of this phenomenon might be due to the fact that the electrolyte of lower concentration contains less dissolved gelatine, which acts as a surfactant and shifts the reduction potential of nickel to the cathodic area, which creates a large internal stresses in a matrix and extrudes the adsorbed microcapsules out of galvanic coating.

### Table 3

Quantitative composition of composite coatings

| Concentration of microcapsules in the electrolyte, pieces per mL | Current density, mA/cm$^2$ | Number of microcapsules on the surface of coatings | Mass fraction, % | Volume fraction, % |
|---------------------------------------------------------------|-----------------------------|-----------------------------------------------|-----------------|-------------------|
| $7 \times 10^5$                                               | 10                          | 4189                                          | 2.6             | 12.0              |
|                                                               | 25                          | 15371                                         | 12.2            | 57.0              |
|                                                               | 35                          | 22781                                         | 11.3            | 53.0              |
|                                                               | 50                          | 28957                                         | 9.9             | 46.0              |
| $1.5 \times 10^6$                                            | 10                          | 5078                                          | 4.7             | 23.0              |
|                                                               | 25                          | 5299                                          | 3.6             | 18.0              |
|                                                               | 35                          | 10028                                         | 3.8             | 20.0              |
|                                                               | 50                          | 2190                                          | 0.8             | 4.2               |

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This hypothesis also confirmed by the significant difference in dependency of surface and volume concentration of the microcapsules in the coating on the current density, since the surface concentration has been fixed at the beginning of electrolysis, when the capsules were still not covered and volume – at the end. At higher current densities, the effect of surfactants on the internal stresses is more pronounced, resulting in a larger amount of microcapsules that have been extruded out of the matrix during their covering.

Study of the Corrosive Resistance of the Coatings

To assess the corrosive resistance of coatings obtained by the electrochemical method, a series of curves of anodic dissolution of coatings and cathodic reduction of hydrogen on them was obtained. A 3% neutral solution of sodium chloride (pH ≈ 6.3) was used as the corrosive medium. According to corrosive diagrams (Fig. 9) currents and potentials of corrosive dissolution of coatings were calculated, as well as the protective effect \( Z \) and protective factor \( \gamma \) for nickel CECs with organic microcapsules were calculated.

The highest corrosive resistance was demonstrated by the coatings deposited at 35 mA/cm\(^2\). Protective effect of this coating is 72% and the protective factor is 3.6 (Table 4) i.e. this coating is more than three and a half times more resistant in the environment of NaCl, than pure nickel coating.

Table 4
Current density, protective effect and protective factor for nickel CECs with organic microcapsules on steel substrates

| Current density of electrodeposition of coatings, mA/cm\(^2\) | Mass fraction of microcapsules in the coatings, % | \( i_{corr} \), mA/cm\(^2\) | \( Z \), % | \( \gamma \) |
|-------------------------------------------------------------|-------------------------------------------------|-----------------|----------|------|
| 10                                                         | 2.6                                             | 0.110           | 34       | 1.5  |
| 25                                                         | 11.0                                            | 0.085           | 47       | 1.9  |
| 35                                                         | 10.0                                            | 0.045           | 72       | 3.6  |
| 50                                                         | 9.0                                             | 0.068           | 58       | 2.4  |

The obtained values of the protection coefficients are in good agreement with the content of microcapsules in the composition of the nickel CECs. With the increase of current density of electrodeposition to 35 mA/cm\(^2\) the corrosive resistance of coatings increases and at 50 mA/cm\(^2\) the content of the microcapsules in the CECs reduces, which causes corresponding decrease of corrosive resistance.

In general, the correlation between the content of the microcapsules and the corrosive rate is observed for the entire range of current densities (Fig. 10).

As it is seen in Fig. 9, the corrosive potential shifts towards more negative values for coatings containing microcapsules, it indicates increase of corrosive resistance of the CEC, primarily due to the increase of hydrogen evolution polarization. The only exception is the CEC, deposited at 10 mA/cm\(^2\) and containing a small fraction of included microcapsules.

![Fig. 9. Corrosive diagrams of nickel CECs with microcapsules on steel substrate in 3% solution of NaCl (pH = 6.3). Current density of electrodeposition, mA/cm\(^2\): 1 – 10; 2 – 25; 3 – 35; 4 – 50; 5 – pure nickel coating, 25 mA/cm\(^2\). Concentration of microcapsules in the electrolyte – 7×10\(^5\) pieces/ml.](image)

![Fig. 10. Dependence of corrosion current density of CECs from the surface concentration of microcapsules in composition of nickel CECs.](image)
Conclusions

Coatings of satisfactory quality with embedded microcapsules were obtained. The inhibitory ability of these coatings was shown. The deposition of composite electrochemical coatings based on nickel, containing microcapsules of inert organic matter in a gelatine capsule was carried out.

The microcapsules for obtaining the composites were synthesized using the method of formation of a solid polymer shell on the surface of microdroplets of the emulsion of the organic matter in water.

The distribution of microcapsules in the coatings and morphology of the coatings were investigated by means of optical and electronic microscopy.

Size distribution of the microcapsules does not depend on their concentration in suspension in the electrolyte and on the current density. Surface and volume concentrations of the microcapsules in the coatings strongly depend on their concentration in suspension in the electrolyte and current density of electrodeposition.

The highest mass fraction of codeposited microcapsules was noted for the coatings deposited at $i = 25$ and $35$ mA/cm$^2$ at the concentration of microcapsules $7 \times 10^5$ pieces per mL. However, at the concentration of microcapsules in the electrolyte of $1.5 \times 10^6$ pieces per mL, mass fraction decreases with increasing deposition current density from 10 to 50 mA/cm$^2$.

Increasing the content of microcapsules in coatings increases the corrosion resistance of CECs. The interrelation between the protective effects and protective factors and the content of the microcapsules in structure of nickel CECs was shown.

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