



ON THE CORROSION BEHAVIOR OF ORGANIC NANOCOMPOSITE COATINGS

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ABSTRACT

Recently, researches on composite coatings of organic nature with the addition of metallic oxide nanopowders have shown an increasing corrosion resistance of metallic materials. Carbon steel shows an improved behavior in corrosive environments when it is covered with an organic layer that includes nanoparticles of titania. This was shown by several measurements of electrochemical corrosion in aqueous solution of 3% NaCl, such as polarization resistance, corrosion potential, corrosion current and electrochemical impedance. The explanation of the improved behavior of carbon steel samples starts from the assumption that the presence of titania leads to a decrease of gas permeability through the composite organic coatings and an improvement of the adherence between the cover and the sample surface.

KEYWORD: steel, corrosion, organic coating, titania, EIS

1. Introduction

There are several methods and techniques for protecting the surface of metallic materials against aggressive action of environment. One of them refers to surface modification of metallic substrates by covering with non-organic, organic coatings. In this way, certain surface properties of metallic materials such as resistance at corrosion, oxidation and wear processes become enhanced.

The deposited coating can be considered as an effective barrier between the metal and its environment. For example, an enrichment of metallic surface by a compound containing chromium leads to a superior behavior into corroding medium. However, due to the health and environmental concerns, this kind of material is recommended to be substituted by an alternative material without ecological or biological impacts. Lately, the researches in field have been focused a using organic coatings, being mostly a good anticorrosive agent.

In the domain of organic coatings having protective character, there can be mentioned polymers including polyurethanes [1], epoxy resins [2], polyesters [3]. These coatings have a protective function being a physical barrier against aggressive species such as ions of hydrogen or molecules of oxygen. Other type of organic coatings such as

polypyrrole [4], polythiophene [5] or polyaniline [6] have also a protective character due to their redox catalytic properties they lead to formation of metal oxide layer on metallic substrate having a passivation role. All these assumptions are accepted only when the organic coatings are without intrinsic defects.

In numerous cases, it was found that even neat organic coatings are not permanently impenetrable because small defects can appear and they can be considered as attack zones of various corrosive species. Therefore in such areas a localized corrosion will occur. One of method for removal of this inconvenient consists in introducing into coating of certain impurity of the type Me_xO_y having the role to increase the length of diffusion pathway for oxygen and water decreasing the permeability of the coating [7-9]. In this way, the adherence of composite coating to metallic substrate becomes stronger due to apparition of a further bond between coating and metallic surface, being of the type Fe-O-Me.

In this paper are reported some results concerning the behavior into corrosive environment of carbon steel samples covered with a coating obtained by hydrothermal method. For this aim, amino-titania nanoparticles were introduced into hybrid of fluorinated polyimide-titania followed by a conventional thermal polymerization reaction that occurs during hydrothermal deposition, as it is

presented in many papers [10-12]. It is reported that the F⁻ ions protect the metal from corrosion, at lower temperature, but at higher concentration or at higher temperature, fluoride accelerates the attack on the metal. The main goal of this paper is to present the corrosion protection performance of fluorinated polyimide-titania hybrid sol-gel coating deposited on carbon steel sample. To achieve this objective, Voltalab 40 and Voltalab 21 instruments were used and the following studies were performed: polarization resistance, corrosion potential, corrosion current, corrosion rate and electrochemical impedance spectroscopy (EIS).

2. Experimental research

Electrochemical measurements of polarization resistance, corrosion potential, corrosion current, corrosion rate and electrochemical impedance spectroscopy of uncoated and coated carbon steel samples were performed by using standard instruments. The electrochemical corrosion cell consists of stainless steel rod counter electrode, reference electrode and working electrode that is uncoated or coated carbon steel sample having dimension of 10x10mm. The thickness of prepared coatings ranged around 20µm and the corrosion solution consists of aqueous solution of 3% NaCl.

The polarization resistance, R_p ($k\Omega/cm^2$), was determined by sweeping the applied potential from 20 mV below to 20 mV above the E_{corr} at a scan rate of 500mV/min and the corresponding current change was recorded. The value of the polarization resistance was obtained from the slope of the potential-current plot, as in fig1.

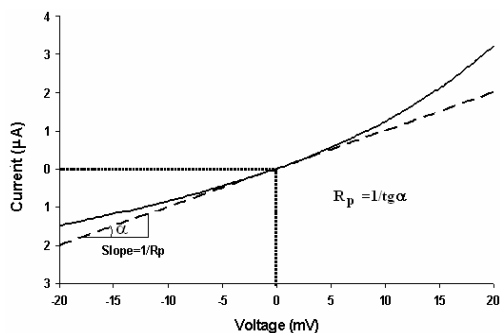


Fig.1. How to calculate the polarization resistance

Tafel curves were plotted by scanning the potential from 250 mV below to 250 mV above the E_{corr} at a scan rate of 500mV/min and allowed to determine the corrosion current (i_{corr}). Corrosion current has been determined by drawing a straight line along the linear portion of the cathodic or anodic

curve and by extrapolating it through E_{corr} . Corrosion rate (R_{corr} , in millimeter per year) was calculated from the following equation :

$$R_{corr} (mm / y) = \frac{0.051 \cdot I_{corr} \cdot (e.w.)}{A \cdot \rho} \quad (1)$$

where e.w. is the equivalent weight (in g/eq.), A is the area (in cm²) and ρ is the density (in g/cm³).

By using the Stearn-Geary equation can be determined the polarization resistance, R_p , namely

$$R_p = \frac{b_a b_b}{2.303 \cdot (b_a + b_b) \cdot I_{corr}} \quad (2)$$

where b_a and b_b are the Tafel slopes $\Delta E / \Delta \log I$ for positive and negative domains of Tafel curve as presented in fig. 2.

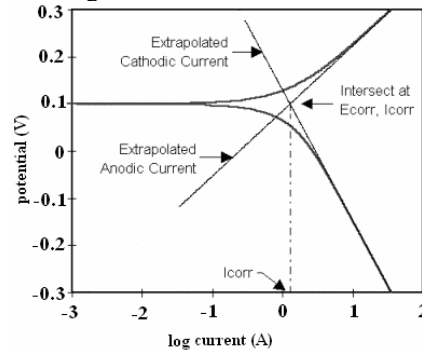


Fig. 2. Analysis of Tafel curve

The value of the protection efficiency, P_{ef} (%), can be used to measure the corrosion protective effect of prepared coatings. For this aim it is recommended [13] to use the relation

$$P_{ef} (\%) = \frac{R_p(c) - R_p(unc)}{R_p(c)} \cdot 100\% \quad (3)$$

where $R_p(c)$ and $R_p(unc)$ are, the values of polarization resistance for coated and uncoated sample, respectively.

3. Results and discussion

The corrosion protection effect of prepared coatings was studied at both neat polymeric coatings and hybrid coatings. Electrochemical corrosion parameters such as corrosion potential, corrosion current, polarization resistance and protection efficiency were determined for each kind of coating allowing for its anticorrosive characteristics. The anticorrosion properties of prepared coatings resulted from the analysis of Tafel curves which are presented in fig.3. By analyzing the curves 1 and 2, results the corrosion protecting effect of the coated sample with flourinate polyimide.

3.1. Tafel curves

As shown in fig.3, the corrosion potential in case of coated sample (flourinate polyimide) is 634.3 mV, that is more positive than that for uncoated sample being of 688.7 mV. Moreover, the corrosion current is $1.62 \mu A/cm^2$ in case of uncoated sample and the same size is $1.08 \mu A/cm^2$ for coated sample (flourinate polyimide). These data show that the coating with flourinate polyimide has a real protection effect. In addition, the distribution of the Tafel remaining curves in relation to the first two discussed demonstrate the superiority of using coatings containing titania nanoparticle in corrosion protection.

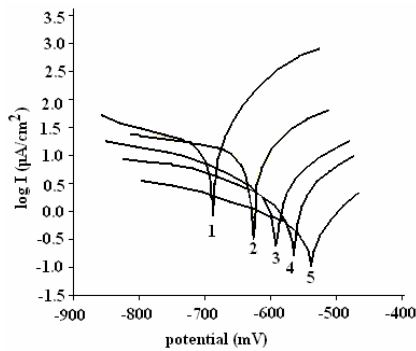


Fig.3. Tafel curves for prepared coatings:
1- uncoated sample, 2- coated sample (flourinate polyimide), 3- coated sample (flourinate polyimide + titania 5%), 4- coated sample (flourinate polyimide +5% titania nanoparticle), 5- coated sample (flourinate polyimide +10% titania nanoparticle), 6 –coated sample (flourinate polyimide +15% titania nanoparticle).

3.2. Polarization resistance

The polarization resistance, R_p , is an other important size in order to characterize the performance of anticorrosive properties of coatings. This was estimated from Tafel plots, according to the Stern-Geary equation.

The values of this size are increasing from sample 1 up to sample 5 being, respectively, $R_p = 2.68(k\Omega \cdot cm^2)$,

$2.98(k\Omega \cdot cm^2)$, $3.22(k\Omega \cdot cm^2)$, $5.62(k\Omega \cdot cm^2)$,

$8.88(k\Omega \cdot cm^2)$, $10.12(k\Omega \cdot cm^2)$ showing that by increasing of titania nanoparticles content, the anticorrosive properties of coating get bigger.

3.3. Protection efficiency

The protection efficiency, $P_{ef}(\%)$, was calculated for uncoated sample and for all coated samples. The obtained values are increasing with increase of the content of titania nanoparticle concentration. The obtained values are $P_{ef} = 0\%$, 16.77% , 52.31% , 70.15% , 73.81% . These data show that the efficiency of prepared coatings at corrosion starts to become increasingly larger with the increase of nanoparticles concentration.

3.4. Corrosion rate

The corrosion rate was calculated for each sample taking into account the value of I_{corr} obtained from Tafel curve by superimposing a straight line along region of the negative or positive curve and extrapolating it through E_{corr} . The obtained values are, respectively $R_{corr} = 43.37(mm/y)$, $6.12(mm/y)$, $4.22(mm/y)$, $3.12(mm/y)$, $2.89(mm/y)$. Increasing the concentration of titania nanoparticles in coating leads the significantly decreasing of corrosion rate.

3.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy can be used in order to evaluate the corrosion activity variation of all coated samples, noted from 1 to 5. Any electrochemical bath together with its electrodes introduced into AC circuit having a frequency (ω) is characterized by the following sizes: an impedance (Z) that depends on the charge transfer resistance (R_{ct}), a solution resistance (R_s), a capacitance (C_{dl}) of the electrical double layer [14-16] by relation

$$Z = \frac{R_s + R_{ct}}{1 + (R_{ct}C\omega)^2} + j \frac{R_{ct}^2 C_{dl} \omega}{1 + (R_{ct}C\omega)^2} \quad (4)$$

Figs. 4 and 5 display the Nyquist and Bode plots, respectively, for samples immersed in aqueous solution of NaCl (3%) having a temperature of 25°C.

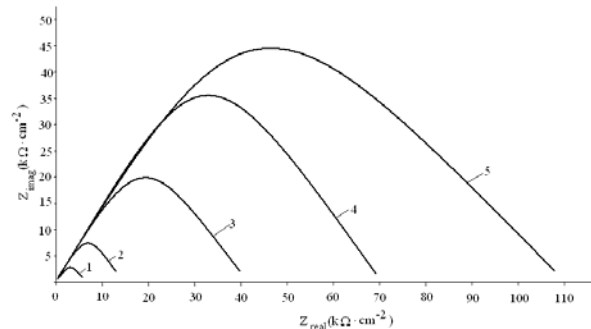


Fig. 4. Nyquist curve for studied samples

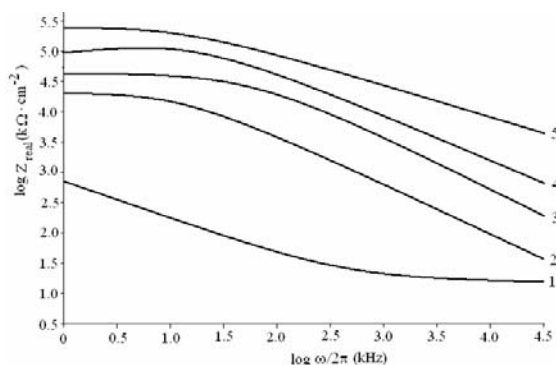


Fig. 5. Bode curves for studied samples

The charge transfer resistances of samples were determined by subtracting the intersection of the high-frequency end from the low-frequency end of the semi-circle arc with the real axis (1) - (5) such as $6.21 \text{ k}\Omega \cdot \text{cm}^{-2}$, $13.08 \text{ k}\Omega \cdot \text{cm}^{-2}$, $40.07 \text{ k}\Omega \cdot \text{cm}^{-2}$, $70.03 \text{ k}\Omega \cdot \text{cm}^{-2}$, and $109.38 \text{ k}\Omega \cdot \text{cm}^{-2}$, respectively. Moreover that, the larger the semicircle diameter correspond to the lower the corrosion rate and the Bode plots depend on impedance versus frequency of samples (1)-(5). These plots show that the 5 coated samples exhibit a better corrosion protection.

4. Conclusions

In this paper, preliminary investigations for the corrosion protection effect of certain organic composite coatings onto carbon steel electrode were presented. For this aim, a series of electrochemical corrosion measurements such as polarization resistance, corrosion potential, corrosion current, corrosion rate and EIS in corroding media have been performed. The obtained data show that by increasing the titania nanoparticles concentration in organometallic composite coatings through the sol-gel

process, an improved behavior of covered carbon sample into corroding environment consisting of an aqueous solution of 3% NaCl. This can be explained by a decreasing in gas permeability of organic composite coatings and improvement of adhesion between the interface of coatings and surface of metallic sample. This research will continue and it aims at confirming the EIS results by microscopic studies.

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