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THE ELLIPSOMETRICAL STUDY OF ADSORPTION-DESORPTION OF THE CORROSION INHIBITORS ON METALLIC SURFACES

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Abstract. In this paper we present the experimental results of ellipsometric measurements regarding the adsorption of corrosion inhibitors on steel. The superficial films were studies by means of a very exact optical method: the ellipsometry. After the immersion of the steel sample in the inhibitor solution the change of thickness for the superficial inhibitor films is noticed. The thickness of the films decreases, because of the inhibitors desorption from the surfaces of the samples, when the sample is maintained in air.

Key words: corrosion inhibitor, adsorption, desorption, ellipsometry.

1. INTRODUCTION

Corrosion protection of metals with corrosion inhibitors is one of the appropriate methods of corrosion protection used in many industrial plants. A simple application of the corrosion inhibitors, results in uniform protection of the whole surface. The industrial installations protected with corrosion inhibitors do not have special maintenance problems. The number and diversity of corrosion inhibitors is continuously increasing due to the advantages offered, and to the diversity of industrial processes where it may be applied [1, 2].

The corrosion inhibitors most frequently used are organic, containing functional groups which serve as the "function-anchor" on the adsorption centers of metal surface.

The adsorption ability depends on the molecular structure and the concentration of inhibitor, as well as on the metal surface condition. The anticorrosive protection efficiency of industrial installations depends on the time of inhibitor desorption on the metal surface. This, in turn, depends on the type of inhibitor and the washing of the surface by different reagents used in the chemical plants in operation.

The evaluation of the effectiveness of anticorrosive protection is generally made by electrochemical or gravimetric methods which focus on the corrosive action of various corrosive media [3, 4].

The thickness of the inhibitor on the metal surface and its temporal variation during adsorption or desorption can be achieved by optical methods. One of the nondestructive and highly refined methods is ellipsometry. It is possible to detect various adsorbed layers with thicknesses in the order of nanometer size [5, 6].

The ellipsometrical method is based on the analysis of changes in the state of polarization of a monochromatic radiation of wavelength λ, after reflection on a clean or film-covered, homogeneous, isotropic, and evenly thick surface, represented schematically in Fig. 1 [7].

The fundamental equation of ellipsometry:

$$\mathrm{tg}\Psi e^{i\Delta} = f\left(n_0, \varphi_0, \lambda, \overline{n}_f, \overline{k}_f, d_f, \overline{n}_s, \overline{k}_s\right) \quad (1)$$

links the measurable sizes Δ and Ψ to the optical constants $\overline{n}_s, \overline{k}_s$ of the substrate and of the superficial film $\overline{n}_f, \overline{k}_f$.

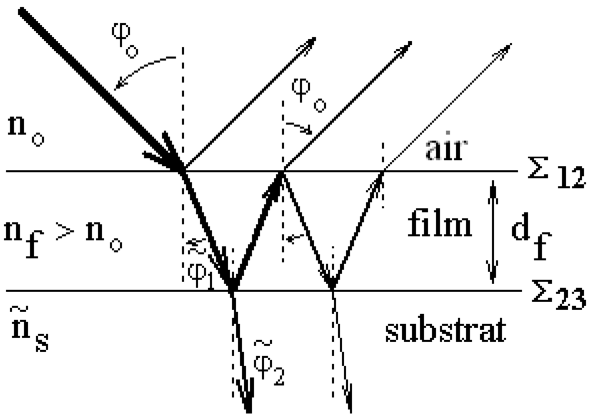

Fig.1 – The reflection of a monochromatic radiation on reflecting surfaces covered with surface films.

For superficial, optically non-absorbent films, it is possible to determine the thickness d_f of the film surface and its optical properties if the optical properties of the film-free substrate are previously known.

They are determined before placing the film, with additional measurement of the Δ^0 and Ψ^0 ellipsometrical sizes for film-free substrate before depositing the film.

In this case, the fundamental equation:

$$\tan\Psi^0 e^{i\Delta^0} = f(n_0, \varphi_0, \overline{n}_s, \overline{k}_s) \quad (2)$$

is resolved.

For the thin superficial film of corrosion inhibitors we can suppose, in a good approximation, that they are optically non-absorbent.

Ellipsometry allows the accurate determination of thickness for superficial films only when their thickness is less than:

$$d_f = \frac{\lambda}{2\sqrt{n_f^2 - n_0^2 \sin^2 \varphi_0}}. \tag{3}$$

Reference literature presents in detail the working technique and the processing of the data resulting from experimental measurements [5, 8, 10].

In case there is a surface covered with a surface film, as shown in Fig. 1, the fundamental ellipsometric equation is as such:

$$\tan\Psi \cdot e^{i\Delta} = \frac{\tilde{r}_{pf} + \tilde{r}_{ps} \cdot e^{i2\tilde{D}}}{1 + \tilde{r}_{pf} \cdot \tilde{r}_{ps} \cdot e^{i2\tilde{D}}} \cdot \frac{\tilde{r}_{sf} + \tilde{r}_{ss} \cdot e^{i2\tilde{D}}}{1 + \tilde{r}_{sf} \cdot \tilde{r}_{ss} \cdot e^{i2\tilde{D}}}, \tag{4}$$

where: $\tilde{r}_{pf}$ and $\tilde{r}_{sf}$ are the reflection coefficients at the interface air-film, corresponding to the two radiation components:

$$\tilde{r}_{pf} = \frac{\tilde{n}_f \cos\varphi_0 - n_0 \cos\tilde{\varphi}_1}{\tilde{n}_f \cos\varphi_0 + n_0 \cos\tilde{\varphi}_1}; \quad \tilde{r}_{sf} = \frac{n_0 \cos\varphi_0 - \tilde{n}_f \cos\tilde{\varphi}_1}{n_0 \cos\varphi_0 + \tilde{n}_f \cos\tilde{\varphi}_1}; \tag{5}$$

– $\tilde{r}_{ps}$ and $\tilde{r}_{ss}$ are the reflection coefficients at the interface film-substrate, corresponding to the two radiation components:

$$\tilde{r}_{ps} = \frac{\tilde{n}_s \cos\tilde{\varphi}_1 - \tilde{n}_f \cos\tilde{\varphi}_2}{\tilde{n}_s \cos\tilde{\varphi}_1 + \tilde{n}_f \cos\tilde{\varphi}_2}; \quad \tilde{r}_{ss} = \frac{\tilde{n}_f \cos\tilde{\varphi}_1 - \tilde{n}_s \cos\tilde{\varphi}_2}{\tilde{n}_f \cos\tilde{\varphi}_1 + \tilde{n}_s \cos\tilde{\varphi}_2}; \tag{6}$$

– $\tilde{\varphi}_1$ and $\tilde{\varphi}_2$ are the complex angle of incidence at the interface air-film and at the interface film-substrate, respectively, defined by Snellius's refraction law. These angles have been used as mathematical artificial means so that, for optical absorbing media, the relationship given by Snellius' law is observed; they should not be confused with the real refractive angles φ_0, φ_1 and φ_2 in Fig. 1.

$$n_0 \sin\varphi_0 = \tilde{n}_f \sin\tilde{\varphi}_1; \quad \tilde{n}_1 \sin\tilde{\varphi}_1 = \tilde{n}_s \sin\tilde{\varphi}_2, \tag{7}$$

$\tilde{n}_f = \overline{n}_f - i \cdot \overline{k}_f$ is the film complex refractive index;

$\tilde{n}_s = \overline{n}_s - i \cdot \overline{k}_s$ is the substrate complex refractive index.

The complex parameter $\tilde{D}$ is expressed in terms of the wavelength of the incident radiation λ and film thickness by the relationship:

$$\tilde{D} = \frac{-2\pi}{\lambda} d \sqrt{\tilde{n}_f^2 - n_0^2 \sin^2 \varphi_0} . \quad (8)$$

In case of transparent films ($\bar{k}_f = 0$) n_f, φ_1 and $\tilde{D}$ are real. The film thickness *d* and refractive index n_f can be determined through a single elipsometric measurement (Δ, Ψ).

When the thickness d_f or the refractive index n_f of the surface film are not known, is resolved the relationship expressed by equation (4). Rearranging the terms, we obtain a quadratic of the form:

$$C_1 \left(\exp \tilde{D}\right)^2 + C_2 \left(\exp \tilde{D}\right) + C_3 = 0, \quad (9)$$

where C_1, C_2 and C_3 are complex functions of the refractive indexes (n_0, and n_f), the angle of incidence φ_0 and the ellipsometrical quantities, experimentally measured (Δ and Ψ) [10].

2. EXPERIMENTAL

The surface of OL-37 steel samples on which the corrosion inhibitor superficial films were deposited, was mechanically polished and then burnished into a perfect mirror. IC-2000 and ICI-2010 corrosion inhibitors were used. They are organophosphoric corrosion inhibitors: amino trimethylene phosphonic acid (ATPM) and 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP). The concentrations of the inhibitor solutions were 1 ‰.

The ellipsometrical measurements were performed by means of an IFTAR photoelectric ellipsometer in PCSA assembly, using monochromatic radiation with $\lambda = 562.5$ nm at 60^0 and 70^0 incidence angles.

Before each measurement, the surfaces of the steel samples were prepared by fresh polishing, and then they were washed with benzene.

The metal surface without the superficial film was ellipsometrically measured after it had been burnished and washed. Then steel samples were immersed for 40 minutes in solutions of inhibitors and were again ellipsometrically measured.

The new ellipsometrical measurement of the metallic surface with the inhibitor film adsorbed, correlated with ellipsometrical measurement of the film-free metal surface, allows us to determine the thickness and refractive index of the superficial film [10].

The steel sample with the corrosion inhibitor adsorbed on the metal surface was kept in the measurement device of the ellipsometer in order to see, by measurements at different time intervals, the desorption kinetics of the corrosion inhibitor.

The optical constants of the metal surface without surface films were calculated using the program developed by McCrackin [9]. This computer program written in Fortran IV was adapted to be run in Visual FORTRAN for Windows.

On the basis of the optical constants of the film-free metal surface, we could calculate the thickness and the optical constants of the superficial film, by means of the same computer program.

3. RESULTS AND DISCUSSION

Figure 2 shows the time variation of the thickness for corrosion inhibitor films adsorbed on the surface of OL-37 steel.

We used IC-2010 and IC-2000 inhibitors. There is an increase in the adsorbed film thickness up to values of about 10 nm.

The inhibitor adsorbed on the metal surface will be desorbed if the metal surface is not kept immersed in the inhibitor solution. If the metal surface is maintained covered with inhibitor film in ambient atmosphere, there will be a time desorption of the inhibitor. Thus, the protective action on the metal surface will decrease.

Figure 3 presents the time variation of the thickness of an IC-2000 inhibitor film because of its desorption from the surface of steel.

A decrease of the inhibitor film thickness up to the order of 2 nm thickness is observed. This thickness is constant, after a sufficiently long time but the value of the inhibitor thickness is insufficient in some cases to ensure a better protection of the metallic surface, especially in highly corrosive media.

The study of desorption kinetics shows a simple 1st order kinetics. The rate constant, determined from the experimental measurements set, shown in Fig. 3, is $k = 2.17 \cdot 10^{-2}$ min^{-1}. It depends on the nature of the inhibitor.

It is also possible to study the desorption of the corrosion inhibitors by the simple observation of the time variation of Δ and Ψ ellipsometrical sizes. This is possible for superficial film thicknesses below 10 nanometers [10].

Figure 4 shows the variation of ellipsometrical sizes Δ and Ψ due to a decrease of the inhibitor film thickness during desorption.

We present the theoretical curves of variation of ellipsometrical sizes Δ and Ψ for surface films with refractive indices whose values vary between 1.5 and 1.8. On the same graph are represented the experimental measurements.

During the desorption of the inhibitor film the value of Δ increases while the value of Ψ decreases when the inhibitor film thickness decreases. The measured refractive index of the corrosion inhibitor film which is desorbed from the metal surface is $n_f = 1.63$.

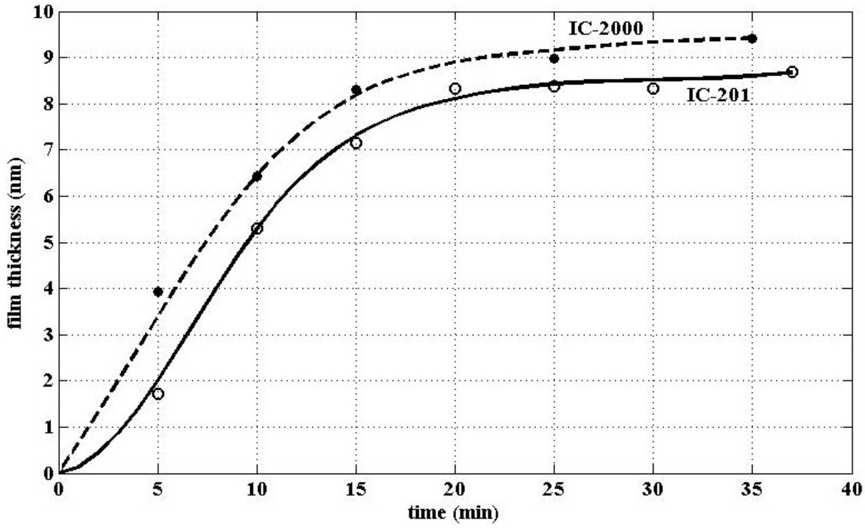

Fig. 2 – The adsorption of the corrosion inhibitors films on the OL-37 steel surface.

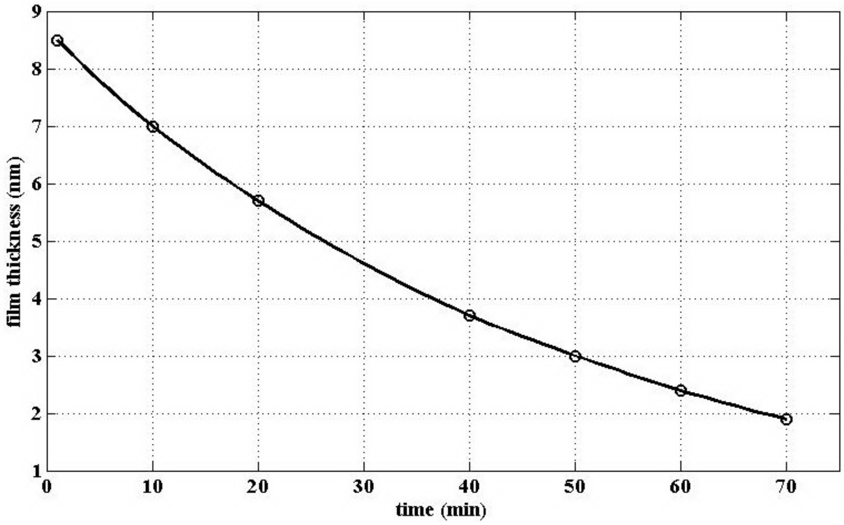

Fig. 3 – Desorption of the IC-2000 inhibitor film from the OL-37 steel surface.

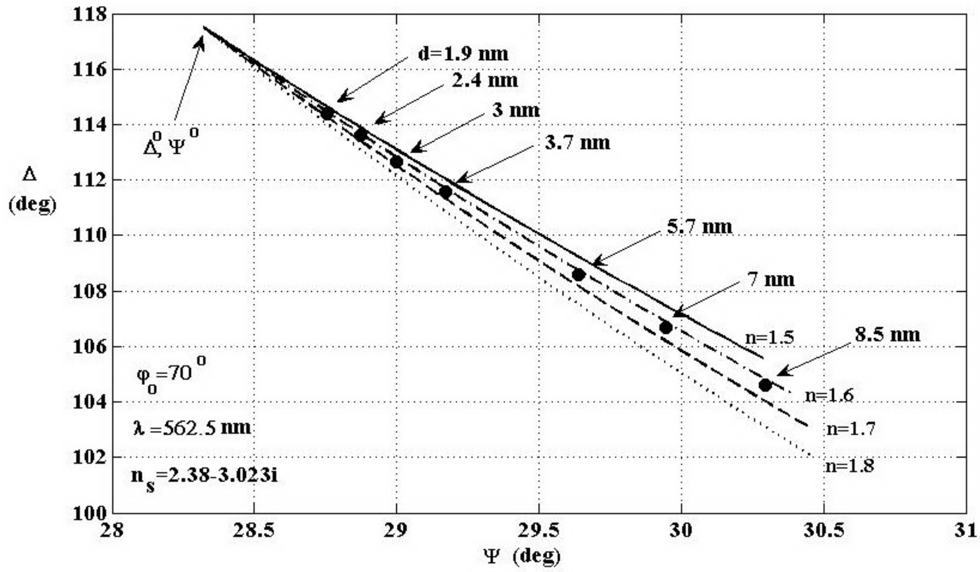

Fig. 4 – Change in Δ and Ψ ellipsometrical sizes during desorption of the IC-2000 corrosion inhibitor on OL-37 steel surface.

Figure 5 shows the inhibitor desorption phenomena in three-dimensional coordinates (Δ, Ψ, d_f).

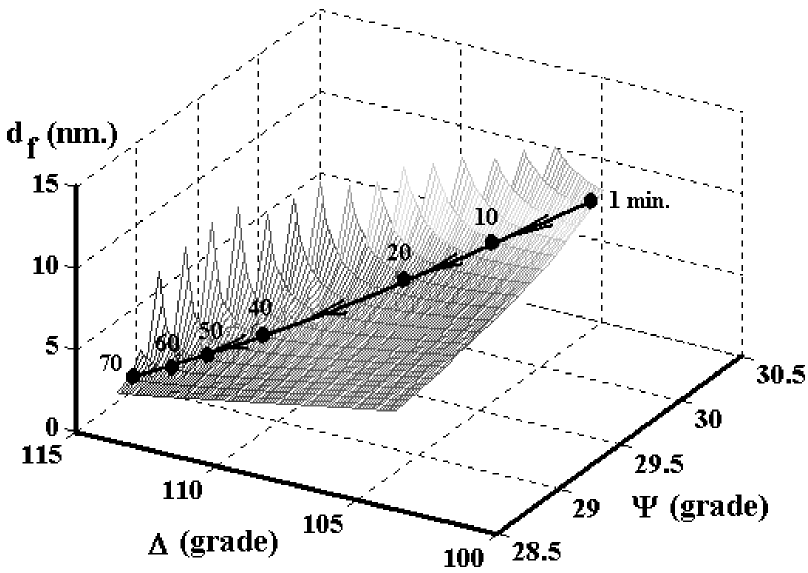

Fig. 5 – Desorption of the IC-2000 inhibitor film from the OL-37 steel surface.

The three-dimensional graphical representation allows a better observation of the desorption phenomenon, in which the superficial film thickness decreases with time and the ellipsometrical sizes will be changed. The values of time were marked on the figure from the time of the steel sample removal from corrosion inhibitor solution.

4. CONCLUSIONS

The corrosion inhibitors have an important role in corrosion protection of industrial plants, particularly those in the chemical industry.

The study of metallic surface protection, ensured by corrosion inhibitors can be achieved by several methods. The optical methods of research on metallic surfaces covered by protective films are nondestructive, allowing the study of protective coatings "in situ".

The ellipsometrical method of surface analysis is of great sensitivity, allowing the study of surface films of nanometer or tenths of nanometer thickness. It is possible to determine by this method the thickness and optical constants (refractive index and absorption index) of surface films. You can also study the kinetics of adsorption or desorption of the corrosion inhibitor films.

The thickness of inhibitor films adsorbed on metal surface increases with time, to a constant value which depends on the inhibitor used and its concentration.

The thicknesses of films that do not ensure an effective protection is obtained after a sufficiently long time, during desorption.

The study of desorption shows a first order kinetics with a rate constant whose value depends on the type of inhibitor.

The ellipsometrical method that we have used, coupled with measurements of corrosion, allows drawing conclusions on the protection efficiency provided by a particular type of inhibitor.

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