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UNIVERSITATEA
„ALEXANDRU IOAN CUZA“
din IAȘI

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ELECTROCHEMICAL STUDIES OF THE CORROSION OF METALS AND ALLOYS IN DIFFERENT ENVIRONMENTS

Summary of PhD thesis

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- Iaşi, 2013 -

Introduction

Most people are familiar with various types of corrosion phenomena, in particular rust. Whether there is a rusty nail or affecting cars, roofs or other materials, corrosion is everywhere around us.

Although there is an abundance of publications and reference documents on aspects about the science and engineering of corrosion, it is considered a current problem because often, the inspection and monitoring of materials located in corrosive environments and less accessible (e.g. the pipelines for the transport of oil and natural gas) is very expensive. Preventing this process is mainly based on early diagnosis of problems and the development of optimal actions to protect materials.

In the study of corrosion we can also talk about the impact of the corrosion on the environment, not only on the economic component. As the environment affects metallic materials also the corrosion and corrosion products formed affect the environment. This can lead to the release into the environment of considerable amounts of metal ions, fragments of destroyed metal and at worst can lead to ecological disasters.

For the present thesis as corrosive environment was considered the water. The experimental data presented in this paper refers to the study of waters corrosivity on metals and alloys for a short time, under laboratory conditions. Primary objective was to study the corrosion process that occurs by immersing the metals in water from the Bahlui River (AB), but for comparison were taken into account also samples from the tap water (AR) and double distilled water (ABD). The water from the Bahlui River is used for the first time as aggressive environment in the study of the corrosion process, given that the Bahlui River crosses Iasi, one of the main cities of Romania.

Regarding the literature, a particular importance was given to study the corrosion phenomenon of steel in salt water for short and long term immersion. Corrosion of steel in the river water is less studied because it is not as severe as that of sea water.

Another element of novelty of this thesis is the method of electrochemical impedance spectroscopy (EIS) applied in the study of corrosion into the river. In the majority of research in the field of corrosion, the EIS method is applied in the study of corrosion in different environments, such as sea water, acid media, NaCl or NaOH, and in particular, for protective coatings and inhibitors; the investigation of the corrosion process in river water by EIS being a less discussed topic.

The PhD thesis expands on 160 pages and it is structured into introduction, seven chapters, conclusions, bibliography and appendices. It contains 85 figures, 16 tables and 185 bibliographic indexes. At the end of each chapter are mentioned the conclusions drawn from experimental measurements.

In the **introduction** are mentioned the main monographs and articles with the subject of the corrosion of metallic materials in different environments, particularly water.

For a better understanding of corrosion phenomena, the first two chapters present aspects about corrosion, its mechanism and methods for monitoring and analysis.

The first chapter refers to the corrosion of metals and alloys in aqueous environment and includes the general considerations related to corrosion, the kinetics and thermodynamics of the process, but also aspects related to metallic materials, aqueous corrosive environments and the influence of various factors. In the chapter 1, it is also written about the impact of corrosion on the environment.

The second chapter covers the theoretical aspects of the corrosion monitoring techniques used in the current study: cyclic voltammetry (CV), linear voltammetry (LV), hydrodynamic voltammetry (HV) and electrochemical impedance spectroscopy (EIS), used for determining the corrosion rate of the alloy and to characterize the corrosion damage, and by scanning electron microscopy coupled with electron dispersion X-ray (SEM), optical microscopy, and Fourier transform infrared spectroscopy (FTIR), used for identifying and characterizing the nature of the corrosion products.

In the **third chapter** it is presented the type and the composition of metallic materials and it is described the equipment and the working procedures. This chapter also includes the characterization of water samples used as corrosion environments.

Starting with the **fourth chapter** is presented the experimental data obtained by studying the corrosive character of water on some metals and alloys, for short time immersion, under laboratory conditions.

Chapter 4. Characterization of the mild steel behavior in river water from Bahlui River by voltammetry

The main objective of this chapter was to characterize the corrosivity of three types of water (ABD, AR and AB) and to study the corrosion behavior of 7 mild steel alloys using the voltammetric techniques.

After plotting the cyclic voltammograms, it was observed the appearance of a hysteresis loop, which is correlated with the susceptibility to localized corrosion. There have been also highlighted the breakdown potential and the potential ranges where the alloys exhibit a corrosion resistance.

It has been shown that the water from Bahlui River is the most aggressive from the three studied environments, in the CV obtained in river water being pointed out more defined breakdown potentials and larger hysteresis loops than those obtained from the immersion in double distilled water and the tap water.

To assess the corrosion damage, there were obtained the corrosion parameters using the polarization resistance and the Tafel extrapolation method. It was found that alloy 2 is the most resistant to corrosion, while the alloy 6 is corroded due to the effect of the alloying elements. By analyzing the Tafel slope coefficients it was highlighted the alloys tendency to corrode.

Simultaneous determination of Fe^{2+} and Fe^{3+} ions from solution can be accomplished by electrochemical techniques applicable to systems containing multivalent cations. By using the rotating disk electrode technique (RDE) were determined the concentrations of Fe^{2+} and Fe^{3+} ions and was revealed the increased concentration of these ions in the solution after the corrosion of the alloys, which on long term would lead to environmental pollution. It was also noted that in the case of ABD and AR, the iron ions concentrations do not change over time, while in the case of AB, by repeating the measurements after a time it was noted that there is a decrease of the concentration of Fe^{2+} ions from the solution.

The cyclic voltammetry and the linear voltammetry were used to study the modification of corrosion parameters with increasing the immersion time of the alloys. From the CV was observed that keeping the samples immersed leads to lower values of the current intensity on the exchange potential.

Following the values of the corrosion parameter, it was observed an increase of corrosion resistances up to the 7th day of immersion, after which they begin to decrease. This was explained by the initial formation of a protective film due to submission of corrosion products, that by maintaining more time immersed the alloys, this protective layer changes and allows diffusion of oxygen to the alloys surface motivating the increase of corrosion rates.

Chapter 5. EIS applied in corrosion study of mild steels

This chapter aimed to the study of the corrosion products layers and their evolution with the increase in corrosion time, by using the electrochemical impedance spectroscopy method.

Following the corrosion studies by EIS method were obtained the Nyquist and Bode diagrams for the 7 alloys at the immersion in water from Bahlui River. The first information provided by these representations is the capacitive behavior of the alloys, by the appearance of one or two incomplete semicircles in Nyquist diagrams or a linear portion of the curve in the phase angle variation with frequency. To get more information about the formation of corrosion and the processes that take place, there were modeled the corresponding equivalent circuits.

It was found that for alloy 2 the equivalent circuit contains the solution resistance, a resistance and a constant phase element that corresponds to the formed corrosion products, and a resistance of the charge transfer process and a pseudo-capacitance of the electric double layer. In the case of alloys 1, 3, 4, 5 and 6, in addition in the modeled equivalent circuit it appears also the Warburg element, which corresponds to the diffusion. For the alloy 7 was modeled a circuit with two polarization resistances and two constant phase elements, corresponding to the two layers of corrosion products.

By increasing the immersion time, and hence the corrosion time (up to 15 days) was observed that the Nyquist diagrams present a second incomplete semicircle which led at modeling circuits with multiple elements.

The equivalent circuits modeled for the alloy 3 doesn’t show changes of the structure of corrosion products, for all the cases (1 day, 3, 7 and 15 days) being shaped a circuit R(RQ)(RQ) type, that corresponds to the formation of two layers. For alloys 1, 2 and 4, by maintaining the samples immersed for a longer time, in the electrochemical cell it appears the diffusion process and, by increasing the corrosion time it increases also de number of elements from the equivalent circuits, which correspond to the separation of corrosion products in several layers.

Chapter 6. Corrosion of other metals and alloys

In the current chapter was followed the corrosion behavior of 4 metals and another 4 alloys and the comparison of these with the first alloy from the seven alloys series presented previously.

It has been found that the corrosion rate of iron is greater than the one of alloy 1, because of the alloying elements present in the composition of mild steel that make it more resistant to corrosion. The values of the corrosion parameters obtained from polarization curves show that aluminum and copper are less corroded than the alloy 1, but the titanium is the most resistant to corrosion.

In comparison to copper, the aluminum has a larger potential range characteristic to passivity, but also a higher susceptibility to localized corrosion with a large hysteresis loop.

The equivalent circuits corresponding to the Nyquist diagrams of the iron and aluminum point out the formation of a single layer of products and the appearance of the charge transfer processes, and in the case of copper the corrosion products are separated in two layers. The Nyquist diagram of titanium appears as a inclined straight line to which can be assigned a circuit of RQ type.

The cyclic voltammograms of the three studied alloys for comparison to alloy 1, highlight a wide potential range for passivity for the stainless steel and a larger hysteresis loop for the welding mild steel than in the case of alloy 1. The cyclic voltammogram of the brass does not present hysteresis loop, but has a wider passivity potential range than the mild steel and the alloy 1.

After plotting the potential diagrams and obtaining the corrosion parameters it can be said that the corrosion rate obtained for the welding mild steel is approximately equal to that of the alloy 1, while the brass has a corrosion rate significantly lower, and the stainless steel is the most resistant at corrosion.

The Nyquist diagrams indicate the formation of one layer of corrosion products in the case of the brass, two layers in the case of the welding mild steel and a high corrosion resistance in the case of the stainless steel.

From the cyclic voltammogram drawn at the immersion of mild steel for sheets in the sea water, it can be noticed the existence of a large domain for passivity and also the presence of a hysteresis loop characteristic to localized corrosion. The Nyquist diagram of this mild steel immersed in sea water, appears in the form of a single incomplete semicircle which corresponds to the formation of a single layer of corrosion product, the equivalent circuit being one of the R(RQ) type.

Chapter 7. Morphological and compositional studies

By electron and optical microscopy were highlighted the two layers of corrosion products formed after 12 days of immersion in the ABD, AR and AB.

From the SEM micrographs for the corrosion products formed in AB, it was noticed a bunch structure in the outer layer and a more compact one, with smaller crystallites in the inner layer. In the case of ABD and AR, the corrosion products from the outer layer are in the form of a compact crust with smaller crystallites than the ones from the inner layer.

The micrographs obtained by optical microscopy confirm those observed by electron microscopy, ie the formation of a porous exterior layer and a compact interior layer as a result of corrosion in river water, and in the case of bidistilled and tap water, the appearance of a compact and sleek outer layer.

The FTIR spectroscopy revealed that the corrosion products structured in two layers consist in: an inner layer, of black color, which consist mainly of magnetite, and an outer layer, of reddish-brown color, which consists from lepidocrocite, goethite and hematite. The comparison of FTIR spectra of corrosion products formed in the 3 types of water revealed that in the case of corrosion in double distilled water the peaks characteristic to goethite are not found in the spectrum.

General conclusions

The main objective of this thesis was to characterize the corrosivity of three types of water (double distilled water, tap water and river water Bahlui) and study the corrosion behavior of seven mild steel alloys. The experimental determinations were based on electrochemical methods (techniques voltammetric and electrochemical impedance spectroscopy), but for a better understanding of the corrosion phenomenon were also used the non-electrochemical methods to characterize the corrosion products (scanning electron microscopy, optical microscopy and Fourier transform infrared spectroscopy).

The innovations of the thesis relate to the use of water from the Bahlui River as corrosive environment and the application of electrochemical impedance spectroscopy in the study of corrosion in aqueous environments. Also the importance of the study emerges from the fact that the alloys are mild steels used in the construction of commercial buildings and industrial plants that come in contact with aqueous media. Another important aspect presented in the paper was to determine the concentrations of iron ions which pass from the surface of the alloy in the solution after their corrosion.

After plotting the cyclic voltammograms it was found that all 7 mild steel alloys have a tendency to localized corrosion, highlighted by the appearance of a hysteresis loop. The CV also points out the potential of breakdown and the potential fields in which the alloys exhibit corrosion resistance.

The corrosion tests carried out have shown that the water of the Bahlui River is the most aggressive of the three studied media. The CV obtained in river water note more defined breakdown potential and larger hysteresis loop than those obtained from immersion in double distilled water and tap water.

By the polarization resistance method and the Tafel extrapolation method were obtained the corrosion parameters, with the aim of assessing the corrosion damage. The highest value of a corrosion rate was obtained in the case of the alloy 6 and the alloy 2 is the most resistant to corrosion of all the alloys, due to the effect of the alloying elements. From Tafel coefficient values was found that the tendency of alloys is to corrode.

The rotating disk electrode technique was used to determine the concentration of Fe2 + and Fe3 + ions that pass into solution as a result of corrosion of the alloys. It was found an increase of these concentrations, which, in the long term, would lead to environmental pollution.

From the study of the change of corrosion parameters with the increase of immersion time of the alloys, the CV revealed that maintaining the samples immersed leads to lower values for the current intensity at the return potential. From the values of the corrosion parameters was observed that the corrosion resistance increases up to the 7th day of immersion and then begin to decrease. This can be explained by the initial formation of a protective film due to the deposit of corrosion products, which changes by maintaining a longer time the alloys immersed, and allows the diffusion of oxygen to the surface of the alloy leading to an increase in corrosion rates.

For the study of the formation of corrosion product layers and their evolution with the increase of the corrosion time by EIS method, were obtained the Nyquist and Bode diagrams for all 7 alloys at the immersion in river water. The occurrence of one or two incomplete semicircles in the Nyquist diagrams show a capacitive behavior of the alloys, as confirmed in the curves of the phase angle by frequency, by the appearance of a linear portion. After modeling the equivalent circuit it was found that the equivalent circuit of alloy 2 contains the solution resistance, a resistor and a constant phase element corresponding to the formed products and a resistance of the charge transfer process and a pseudo-capacitance of the electric double layer. In the case of alloys 1, 3, 4, 5 and 6, in addition, the Nyquist diagrams present a straight line tilted at an angle of 45°, that corresponds to the diffusion process. While for the alloy 7 were modeled the circuits comprising two polarization resistances and two constant phase elements that correspond to the two layers of corrosion products formed.

The number of elements in the modeled equivalent circuits increases with increasing the immersion time, and hence the corrosion time (up to 15 days), due to the occurrence in the Nyquist diagrams of a second incomplete semicircle.

For comparison, in the present study, we studied also corrosion behavior of four metals (Fe, Al, Cu and Ti) and 4 alloys (a welding mild steel, a mild steel for sheets, a brass and stainless steel). From the experimental measurements it has been found that the corrosion rate of iron is greater than that of the alloy 1, aluminum and copper are more resistant to corrosion than alloy 1, but titanium is the least corroded.

By interpreting the Nyquist diagrams it was concluded that in the case of iron and aluminum it occurs the formation of a single layer of products and the appearance of charge transfer processes to the electric double layer, and in the case of copper the corrosion products are separated in two layers. Titanium has a high corrosion resistance, the Nyquist diagram presenting as an inclined straight line at which can be assigned a type RQ equivalent circuit.

From the cyclic voltammogram of stainless steel it is observed a broad potential field characteristic to the resistance at corrosion. The welding mild steel presents a larger hysteresis loop than the one of mild steel 1, and the brass has no hysteresis, but has a wider range for passivity than the other two mild steels.

From the values of corrosion parameters, it can be seen that the corrosion rate for the welding mild steel is approximately equal to that of the alloy 1, while the brass has a significantly lower corrosion rate, and the stainless steel is the most resistant to corrosion.

The equivalent circuits modeled for interpreting the impedance data indicate the formation of one layer of corrosion products for brass, two layers for the welding mild steel and a high corrosion resistance in the case of stainless steel.

At the immersion of mild steel for sheets in the sea water, the obtained cyclic voltammogram presents a large passive domain and a hysteresis loop corresponding to localized corrosion. In the Nyquist diagram it was observed a single incomplete semicircle of this mild steel at the immersion in sea water, which corresponds to the formation of a single layer of corrosion products, the modeled equivalent circuit being one of type R(RQ).

The scanning electron microscopy and the optical microscopy revealed the structure and the morphology of the two layers of corrosion products formed after 12 days of immersion in ABD, AR and AB.

The SEM micrographs highlights a bunch structure of the outer layer and a more compact structure , with smaller crystallites of the inner layer, for the corrosion products formed in the water from Bahlui River. In the case of ABD and AR it appears the formation of a compact crust on the exterior, which has the crystallites smaller than the ones from inner layer. The optical microscopy micrographs confirm the SEM studies, namely the formation of two layers: one layer which is porous and exterior and one interior and compact for the immersion in the AB, and in the case of corrosion in ABD and AR the appearance of a compact and sleek on the exterior and a inner layer with larger crystallites.

The FTIR spectroscopy revealed that the inner layer, of black color, is composed mainly of magnetite and the porous outer layer, of reddish-brown color, consisting of lepidocrocite, geothite and hematite. By comparing the FTIR spectra of the corrosion products formed in the 3 types of water was found that in the case of bidistilled water the goethite is not formed.

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