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Studies of Resistance to Corrosion of Selected Metallic Materials Using Electrochemical Methods

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1. Introduction

One of the main causes of degradation of metallic products during their operation time is their corrosion. The destruction by corrosion arises from spontaneous adverse chemical reactions in metallic materials with the surrounding environment. Irreversible corrosive processes damage any metallic products both, during their operation, and their storage. Economic losses due to destructive corrosive actions are very important and still growing due to increasing environmental pollution. The annual cost of corrosion and corrosion protection in the world is estimated to be in excess of hundred billion dollars. Reducing the continuing degradation of metallic materials by corrosion is one of the fundamental objectives of modern technological solutions and is still the subject of intensive research in many research centers in the world (Yang, 2008).

Metallic products in operational conditions are primarily exposed to electrochemical corrosion. Corrosion processes, which include oxidation and reduction reactions, mainly occur at the interface between the metal and the environment. Both, the structure and the properties of the metal as well as the characteristics of the environment affect the corrosive processes. The rate of corrosion processes depends on the electrochemical susceptibility of a given metal, its chemical composition, homogeneity and surface topography, on the type and chemical composition of the environment, the concentration of aggressive agents, temperature, as well as the type of corrosion products themselves. Electrochemical corrosion processes are accompanied by mass transport and flow of electric charge through the metal - corrosive environment boundary. To characterize the susceptibility of metallic materials to electrochemical degradation modern research techniques increasingly use the relationship between voltage and current intensity occurring in corrosive systems. Such studies rely on computerized measuring system, in which suitable electrical stimulation is generated numerically while the system analyzes simultaneously the response. The results are presented in the form of graphs showing the current - voltage relationships (Trzaska, 2010).

In this chapter we present the results of investigations of corrosion properties of metallic materials with different chemical susceptibilities and different crystalline structures. The main focuses are materials playing important roles in current technologies.

Two electrochemical methods were used to characterize the corrosion properties of the materials under investigation: potentiodynamic polarization and impedance spectroscopy.

2. Electrochemical methods for testing the susceptibility to corrosion of metallic materials

Both processes of oxidation and reduction simultaneously occur at the metal-corrosive environment interface during an electrochemical corrosion. The basic processes occurring during the electrochemical corrosion of metallic materials are:

- oxidation of the metal atoms: $M - ne \rightarrow M^{n+}$
- reduction of ions present in the corrosive environment: $X^{n-} - ne \rightarrow X$.

In the reduction processes in natural environments hydrogen ions H^+ and oxygen O_2 are most often involved, and the related reduction processes can be written as following:

- reduction of hydrogen ions: $2H^+ + 2e \rightarrow H_2$
- reduction of oxygen, depending on the pH of the corrosive environment:
 - in alkaline and neutral environment: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
 - in an acidic environment: $O_2 + 4H^+ + 4e \rightarrow 2H_2O$.

Oxidation and reduction processes are accompanied by the flow of electric charge through the interface metal-corrosive environment. In metals the charge carriers are electrons while in the corrosive environment charge flow is due to ions. Thus an active assessment of electrochemical corrosion processes can be achieved by assessing the electrical charge transfer process. In the reactions of corrosion that are controlled by the rate of charge transfer, the current - potential relationship can be described by the Butler-Volmer equation:

$$j = j_0 \left[\exp\left(\frac{\alpha_A n F}{RT} \eta\right) - \exp\left(-\frac{\alpha_K n F}{RT} \eta\right) \right] \quad (1)$$

where: j - current density, j_0 - exchange current density, $\eta = E - E_0$ - overpotential (voltage), n - number of electrons, α_A and α_K - transfer coefficients, respectively, at the anode and cathode, F - Faraday constant, R - gas constant and T - absolute temperature (Marcus, 2011).

The disruption of the steady state corrosion by the electrical signal and the measurement of its response to the stimulation allow determining the set of electrical quantities providing valuable information about electrochemical processes occurring in the system under study. The most common approaches for the electrochemical characterization of corrosion processes are non-stationary methods, which are easy to automate and computer-control (Trzaska & Trzaska, 2007).

The present study of corrosion processes of metallic materials uses variable current technology, namely the electrochemical polarization potentiodynamic and electrochemical impedance spectroscopy (EIS) techniques. The basis of polarization potentiodynamic electrochemical technique is the stimulation of the corrosion system by a potential, whose value varies linearly in time and the recording of the instantaneous value of current flowing in the system. The electrochemical impedance spectroscopy consists of a perturbation of the

steady state corrosion by applying the sinusoidal alternating potential signal of small amplitude, but in a wide range of frequencies and the automatic recording of current intensity responses of the system. Investigations of corrosion by those methods, based on a change in the relationship between potential and current were implemented in the three-electrode system (Fig. 1).

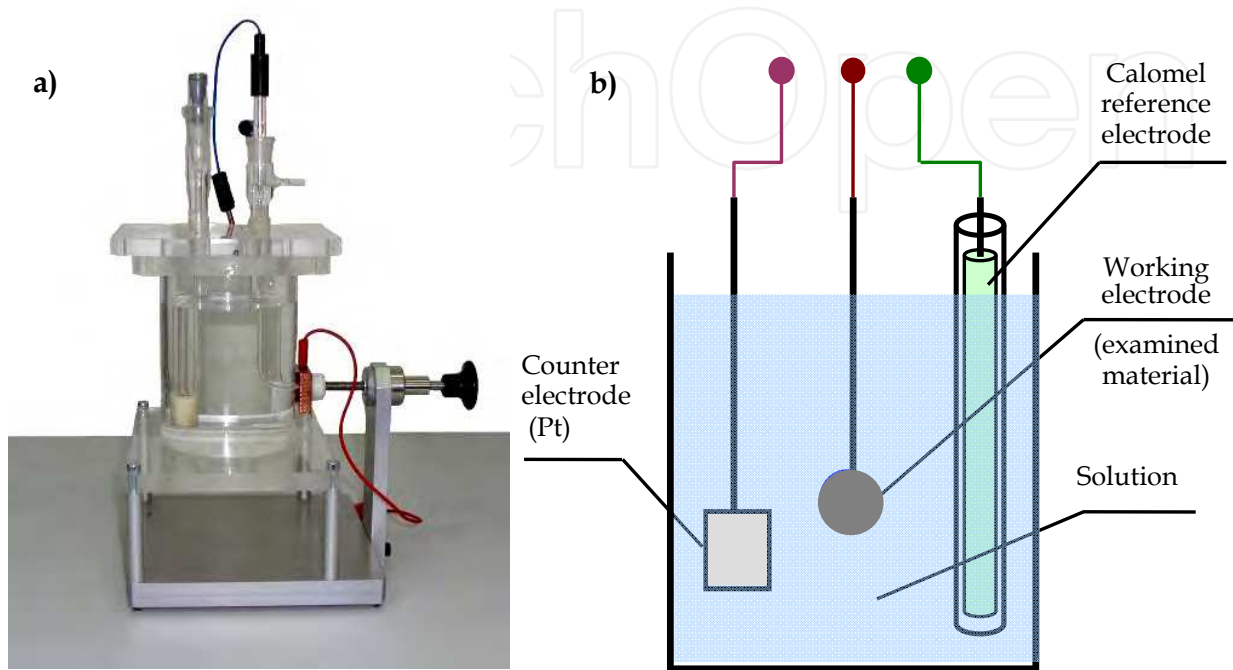


Fig. 1. Three-electrode system for corrosion studies: a) measuring system, b) circuit diagram.

Research of metallic materials corrosion was carried out by means of computerized measuring systems, which generated in a digital form an electrical signal of a certain shape to stimulate the system and simultaneously analyze the response of the corrosion test (Figs. 2 and 3).

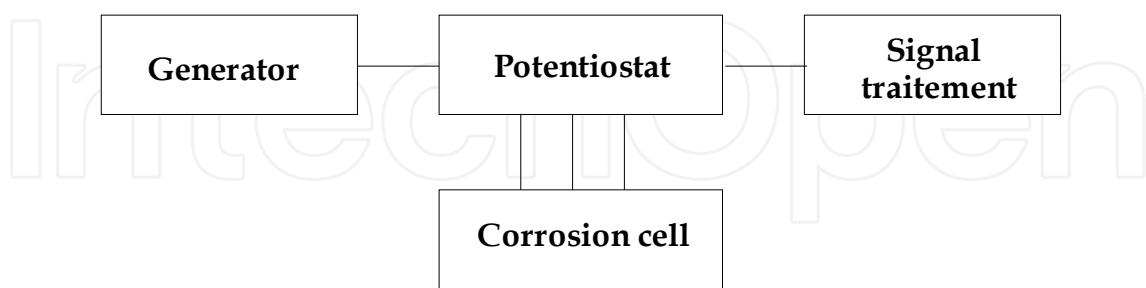


Fig. 2. Block diagram of the electrochemical corrosion tests.

In the three-electrode system, used in the current study, the examined metal takes the role of the active electrode. A calomel electrode, $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$ characterized by the potential +244 mV, was used as the reference electrode. Auxiliary electrode was made of platinum (Pt). The tests were carried out in the corrosive environment of 0.5M NaCl solution at pH = 7 and a temperature of 293K (Trzaska &Trzaska, 2010).



Fig. 3. The set of appliances for the electrochemical corrosion testing by EIS technique.

2.1 Potentiodynamic polarization method

In any process of electrochemical corrosion oxidation processes, i.e. the anodic processes, as well as the reduction i.e. cathodic processes occur on the surface of the metal. In the measurement system these processes occur simultaneously during the polarization for each of the applied potential values but at different speeds. The resultant speed of the processes constituting a sub-inflicted response to the potential changing at prescribed rate is recorded by the measurement system in the form of instantaneous current values. The characteristics $j = f(E)$ of the current intensity as function of the potential obtained in this way are called potentiodynamic polarization curves.

Potentiodynamic polarization method was applied to a wide range of potential changes to characterize the current-potential relationship $j = f(E)$ in corrosion systems under investigation. The corrosion current density j_{cor} and potential E_{cor} of tested metallic materials were further determined based on extrapolation of tangents to the curves of the cathodic and anodic polarization zones.

2.2 Impedance spectroscopy method

The perturbation of the equilibrium of the corrosive systems composed by metal - 0.5M NaCl solution, was obtained through time-varying sinusoidal signal described by the following relationship $E(t) = E_0 \cos(\omega t)$, where $E(t)$ is the instantaneous potential value [V], E_0 - potential magnitude [V], t - time [s]. The response of the corrosion system to such an interfering signal was the current intensity signal, which is the effect of transferring electrical charge between the corrosive metal - an electron conductor, and the electrolyte - ionic conductor. This response is described by the time-varying current signal $I(t) = I_0 \cos(\omega t + \varphi)$, where $I(t)$ - instantaneous current value [A], $\omega = 2\pi f$ - pulsation [rad/s], f - frequency [Hz], φ - phase shift [rad.]. The measuring system digitally generates the excitation having the above sinusoidal form and measures the current system response as a function of frequency. Then the plots of $|Z(\omega)|$ and $\varphi(\omega)$ were generated, i.e., amplitude and phase spectra of impedance, called Bode plots, and curves $X(\omega) = F(R(\omega))$, called amplitude-phase characteristics or Nyquist plots (Orazem & Tribollet, 2008), (Sword et al., 2007).

The experimental results expressing the dependence of impedance spectra on the applied signal frequency are shown by

- the Bode diagrams in the form of two plots as function of ω : $i | Z | = f_1(\log(\omega))$ and $\varphi = f_2(\log(\omega))$, where $Z(j\omega) = |Z| e^{j\varphi}$, $|Z|$ - impedance magnitude,
- the Nyquist diagrams representing relationship $Z'' = f(Z')$, where Z' is a real component and Z'' - imaginary component of input driving impedance $Z(j\omega) = Z' + jZ''$ of the corrosive systems investigated.

Impedance is an essential characterization of the current intensity response of the corrosion system to the sinusoidal perturbation of the potential applied to the metal. The results of impedance measurements made in a suitably wide range of frequencies provide valuable information about the system and electrochemical corrosion occurring therein. The majority of electrochemical as well as physical processes can be interpreted within the impedance spectroscopy method as elements of electrical circuits with appropriate time constants. Thus, to interpret the results of electrochemical impedance measurements surrogate models of electrical circuits, known as Randles models, can be used.

Experimentally determined frequency characteristics were used to map the corrosion processes using models based on suitable equivalent circuits. Each element of such a circuit models the specific process or phenomenon occurring in the corrosion system under investigation.

3. Electrochemical characteristics of corrosion resistance of metallic materials

Metals are very commonly used materials in various technologies and applications. Properties of metallic materials are shaped by their composition and structure. Moreover, most natural metals are found in chemical combination with other elements. In the current study, resistance to electrochemical corrosion tests were applied to metallic materials with different properties and structures: aluminum (Al), aluminum with a surface layer of oxide aluminum (Al_2O_3), iron (Fe), S235JR steel, nickel (Ni), microcrystalline nickel (Ni_m), nanocrystalline nickel (Ni_n), and amorphous alloy of phosphorus-nickel (NiP). The choice of these materials was due to the universality of their applications in technology.

3.1 Identification of the resistance to corrosion of aluminum

Aluminum and its alloys are materials of great technical importance. Attractive physical properties of aluminum such as low density, high ductility, good thermal and electrical conductivities, relatively low production costs and its high abundance in nature make it an indispensable metal in many industries and in numerous areas of daily life, both as a pure metal and in various alloys. Aluminum, as an element of high chemical activity, shows a significant tendency to passivity, leading to high resistance of aluminum and its alloys to corrosion in many environments with low aggressiveness (Vargel, 2004).

However, the processes of alloying and heat treatments are not always sufficient to ensure the qualities of aluminum required in the modern technical applications. One way of modifying the performance of aluminum and its alloys in order to adapt them to the

operating conditions is the production on their surfaces of a thin layer of Al_2O_3 by anodic oxidation process (Huang, et al., 2008).

Corrosion test has been applied to technical aluminum (99.9%) and to aluminum with Al_2O_3 surface layer produced by hard anodic oxidation and sealed in boiling-hot deionized water. Images of morphology and topography of the surface layer of aluminum and Al_2O_3 before corrosion tests using scanning electron microscope (SEM) are shown in Fig. 4.

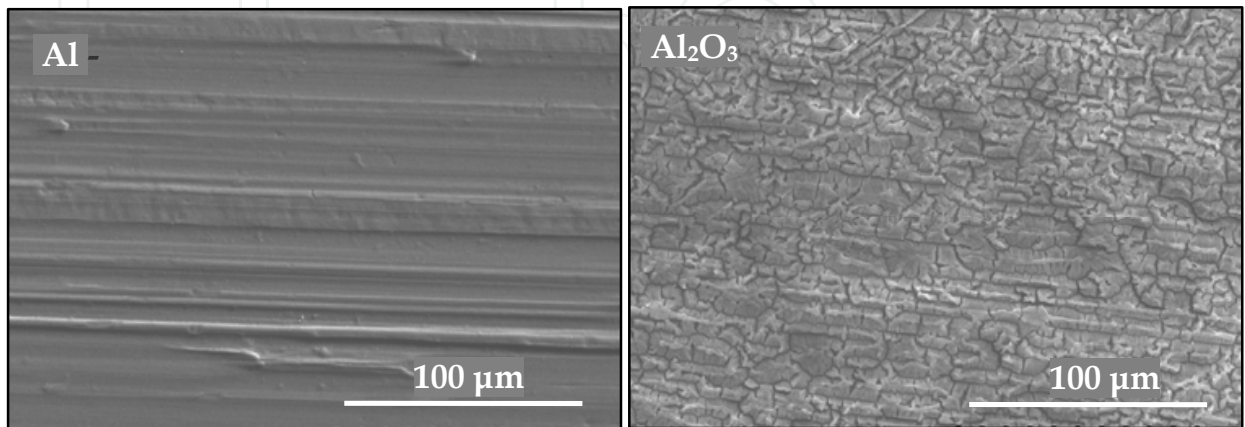


Fig. 4. Morphology and topography of the surface of Al and Al_2O_3 layer before corrosion tests.

Potentiodynamic polarization distortion of the steady state technique at the interface of both Al as well as Al_2O_3 with 0.5M NaCl solution, was applied with the change in the potential ranging from -780mV to -450mV. The rate of the potential change during the test was 0.2mV/s. Current characteristics $j=f(E)$ of test materials in the form of potentiodynamic polarization curves are shown in Fig. 5.

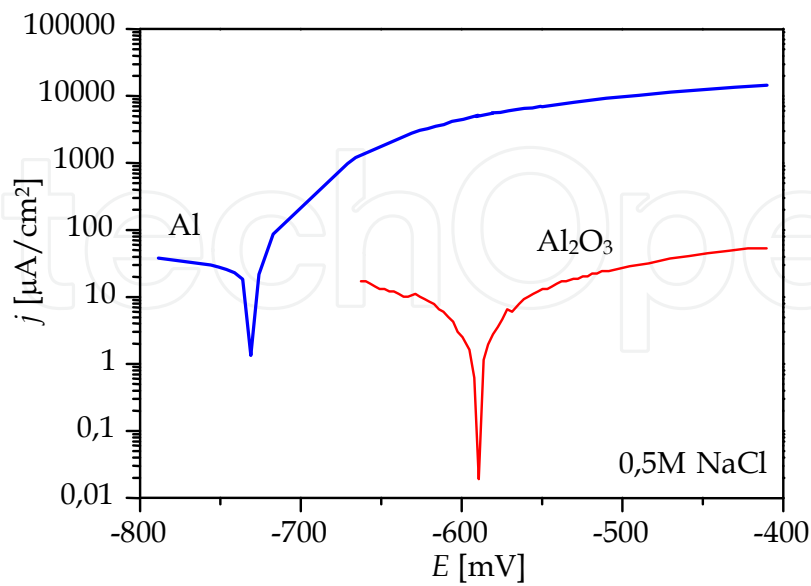


Fig. 5. Potentiodynamic polarization curves of materials of bulk raw Al and Al_2O_3 layer in the corrosive environment of 0.5M NaCl solution.

To determine the corrosion current density j_{cor} and the corrosion potential E_{cor} the tangential extrapolation method was used for the polarization curves $j = f(E)$ from the cathode and anode zones. The values of corrosion current densities and corrosion potentials for tested materials are summarized in Table 1.

Material	E_{cor} [mV]	j_{cor} [μAcm^{-2}]
Al	-719	14.9
Al_2O_3	-583	0.23

Table 1. Corrosion parameters of bulk raw Al and Al_2O_3 layer in 0.5M NaCl.

It is worth mentioning that Al_2O_3 layer has a much higher corrosion resistance compared to aluminum. Corrosion protection of aluminum using Al_2O_3 layer is guaranteed by efficient isolation of the substrate material from the corrosive environment. The effectiveness of the corrosion protection depends on the thickness and tightness of Al_2O_3 layer.

For further characterization of electrochemical corrosion processes at the interface between the environment of 0.5M NaCl solution and Al and Al_2O_3 , the electrochemical impedance spectroscopy method was applied. As stated above this method allows considering the corrosion process as a combination of equivalent electric circuits. In the case of Al the study was carried out with the amplitude of the forcing sinusoidal signal of 10mV. However, in the case of Al_2O_3 layer the amplitude of perturbing signal in the corrosion balance was fixed at 20mV. The study was conducted in the frequency range $23\text{kHz} \div 16\text{mHz}$. Measured impedance spectra of Al and Al_2O_3 layer in the corrosive environment of 0.5M NaCl solution are presented in the form of Nyquist and Bode diagrams.

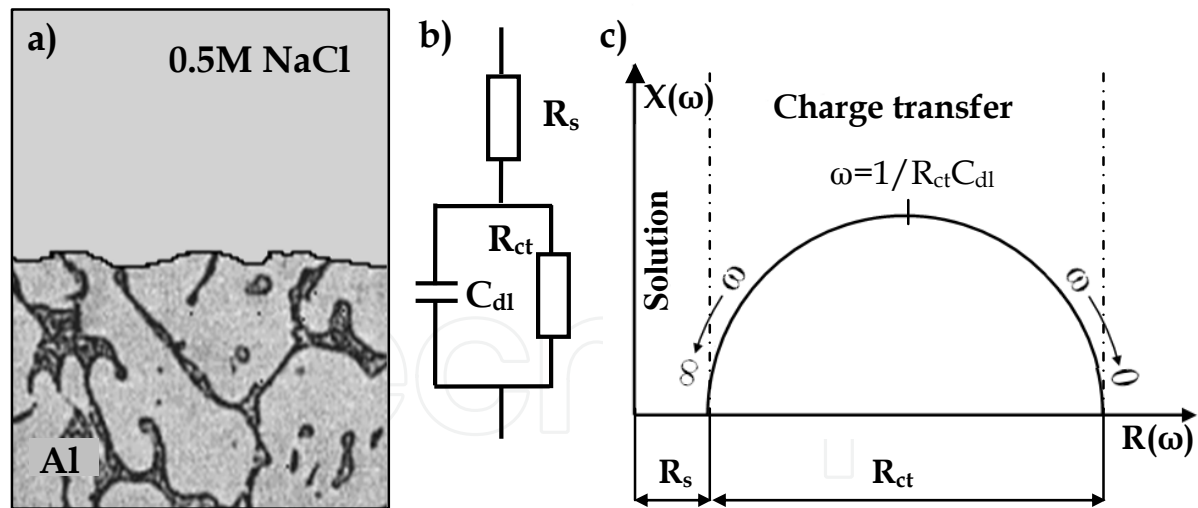


Fig. 6. Equivalent electric circuit for corrosion of bulk Al: a) corrosion system Al - 0.5M NaCl solution, b) an equivalent circuit scheme, c) Nyquist frequency characteristics

Equivalent electrical circuits obtained by minimizing the mean square error were further used for the analysis of experimentally identified frequency characteristics and a description of corrosive processes in the systems under investigation. A simple electric circuit consisting of three elements of type R and C with a single time constant was adopted as system model for Al. Figs. 6 and 7 show the circuits modeling respectively the

corrosion systems of bulk Al and Al_2O_3 surface layer deposited on aluminum in a 0.5 M NaCl corrosive environment.

Fig. 6 presents the system of Al corrosion in 0.5 M NaCl solution, its frequency impedance characteristic in the form of Nyquist plot and the equivalent electrical circuit. Individual parts of the electric circuit reflect the electrochemical and electrical characteristics of the corrosion systems. In this arrangement, the spectral characteristic of the impedance in the Nyquist plot has the shape of a semicircle, whose intersection with the real axis in the high-frequency range determines the electrolyte solution resistance R_s . Conversely, the intersection of the real axis in the low-frequency range corresponds to the sum of $R_s + R_{ct}$, where R_{ct} indicates the charge transfer resistance of the boundary metal/electrolyte, and characterizes the rate of corrosion. On the other hand, C_{dl} component of the circuit represents capacity of the double layer at the interface metal/electrolyte.

Layout of the corrosive system for aluminum with a surface layer of Al_2O_3 in 0.5M NaCl corrosive environment, and the designated equivalent circuit are shown in Fig.7.

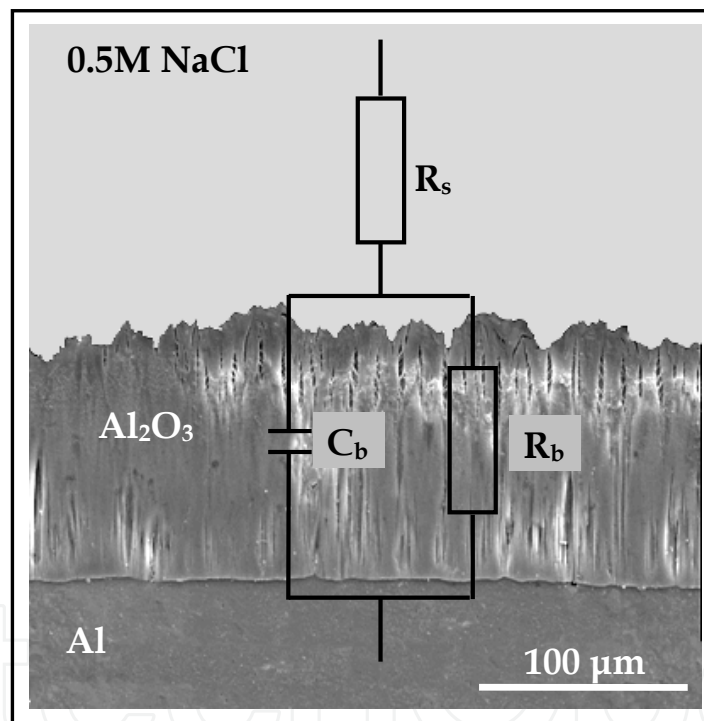


Fig. 7. Layout of the corrosive system for aluminum with a protective layer of Al_2O_3 in 0.5M NaCl environment and its equivalent circuit.

Similarly to the previous case the element R_s of the equivalent electric circuit for this corrosion system represents the resistance of the 0.5M solution of NaCl electrolyte used as the corrosive environment. Elements in parallel in the equivalent electric circuit characterize the protective properties of Al_2O_3 layer deposited on the bulk Al. The element C_b specifies the Al_2O_3 layer capacitance, which depends on the thickness of this layer and on the dielectric properties of the material. The resistor R_b in such a system represents the resistance of the protective layer, and depends on properties of the material forming the layer, and varying with the thickness of the layer and its material composition. The

value of the resistance R_b in the test case of Al_2O_3 protective layer is large and amounts to $R_b = 100 \text{ k}\Omega\text{cm}^2$.

The resulting impedance of the equivalent circuit (Figs. 6 and 7) adopted to describe the corrosion processes occurring in systems with bulk Al and Al_2O_3 layer deposited on an aluminum substrate in the corrosive environment of 0.5M NaCl solution is determined by the expression

$$Z = R_s + \frac{1}{\frac{1}{R} + j\omega C}$$

(2)

The equivalent electrical circuit approach adopted maps the processes occurring in the corrosion systems and enables the determination of parameters relevant to these processes. The parameter values of individual elements of equivalent electrical circuit representing investigated corrosion systems are summarized in Table 2.

Material	R_s [Ωcm^2]	C $\mu\text{F}/\text{cm}^2$	R [$\text{k}\Omega\text{cm}^2$]
Al	13.3	$C_{dl} = 10.0$	$R_{ct} = 0.8$
Al_2O_3	12.5	$C_b = 1.4$	$R_b = 100.0$

Table 2. Parameters of equivalent electrical circuit for corrosion processes of bulk Al and Al_2O_3 layer in 0.5M NaCl solution.

The frequency characteristics of corrosion systems of bulk Al and Al_2O_3 layer in 0.5M NaCl solution in the form of Nyquist and Bode plots obtained by the measurements and calculations based on adopted equivalent electrical circuits are shown in Figs. 8 and 9, respectively.

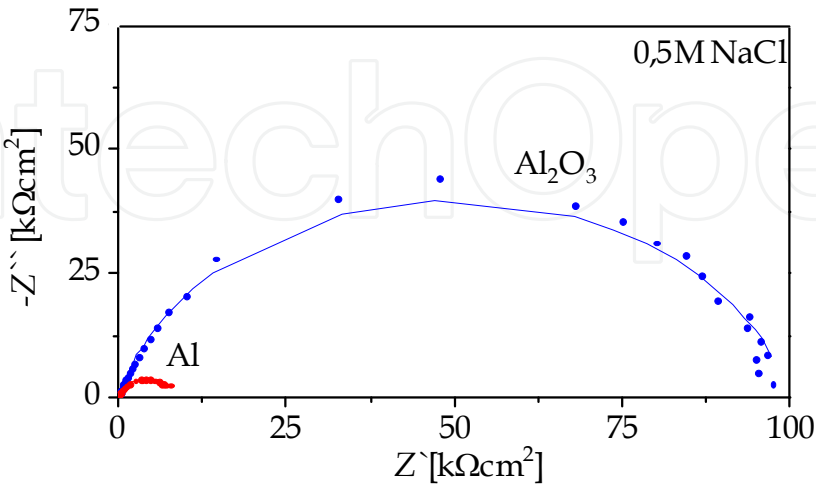


Fig. 8. Nyquist diagrams of impedance spectra of corrosion systems for bulk Al and Al_2O_3 layer in 0.5M NaCl solution determined experimentally (point line) and as a result of calculations (solid lines).

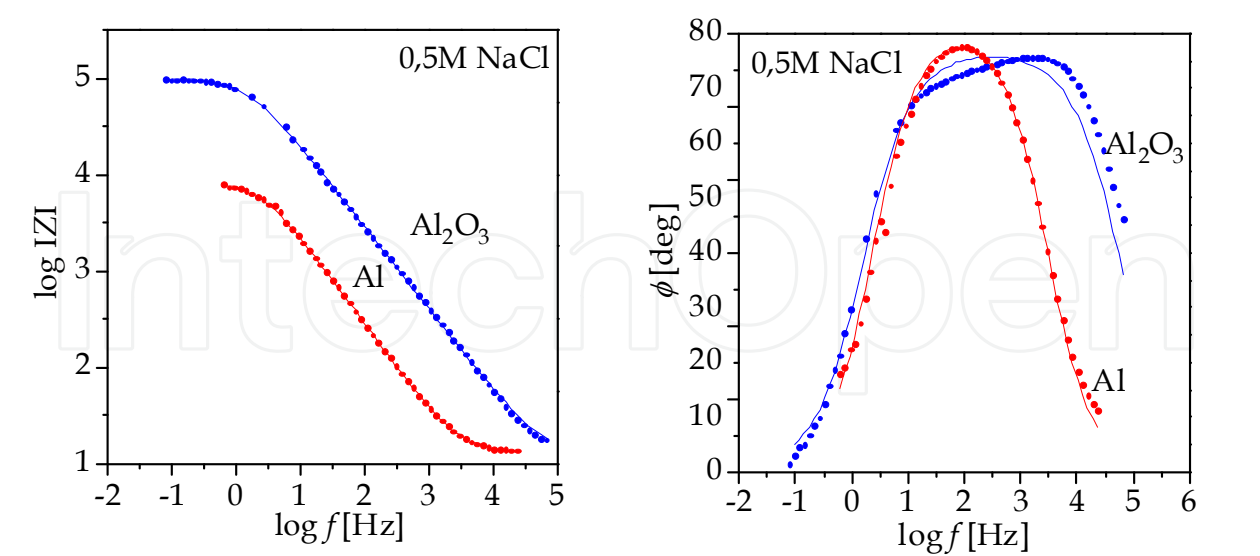


Fig. 9. Bode amplitude and phase spectra of circuit impedances for corrosion of bulk Al and Al_2O_3 layer in 0.5M NaCl solution determined experimentally (point line) and as a result of calculations (solid lines).

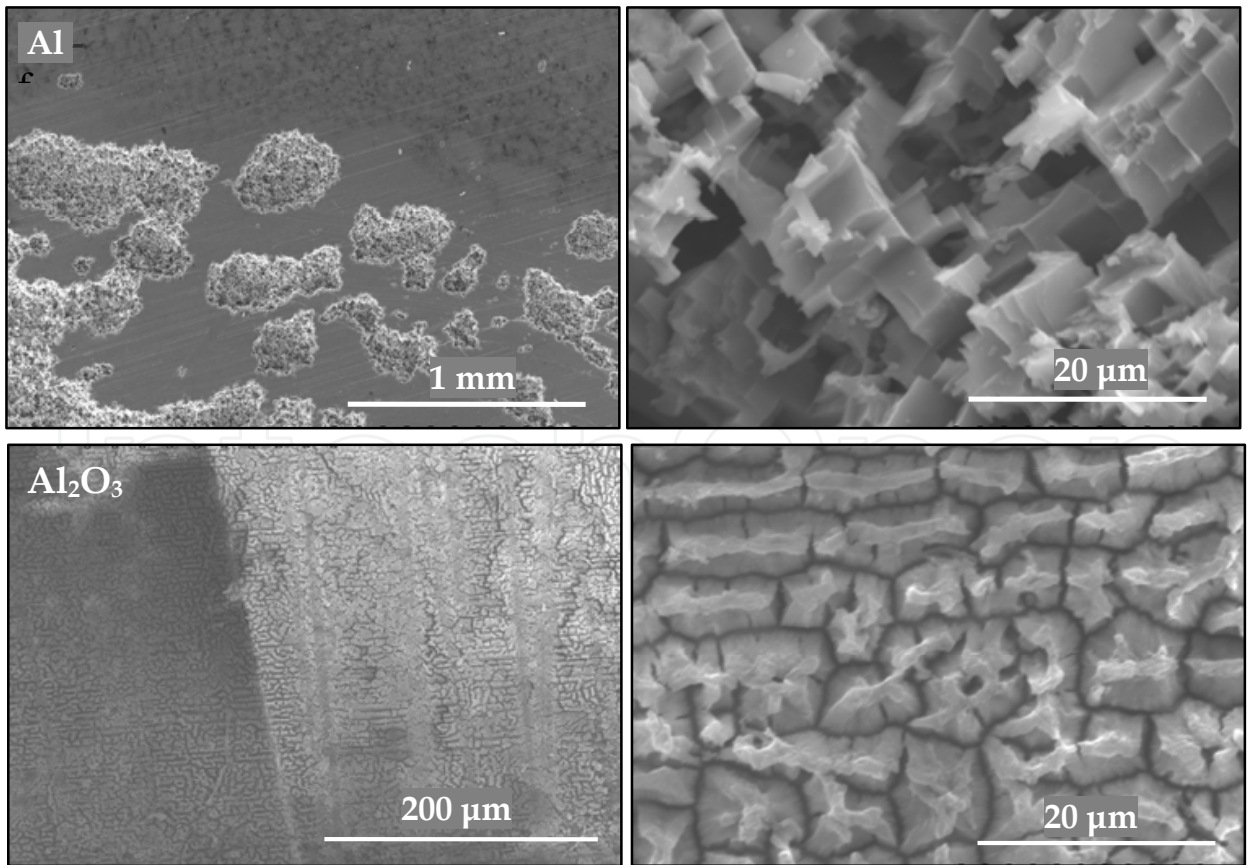


Fig. 10. SEM images of the surface of Al and Al_2O_3 materials after corrosion tests in an environment of 0.5M NaCl solution.

The comparison of plots of the frequency characteristics of corrosion systems obtained experimentally and from the calculations (Figs. 8 and 9) attests that the adopted scheme for the equivalent circuits reproduces well the impedance measurements across the whole frequency range of the forcing signal.

In addition, the circuit impedance characteristics for corrosion of bulk Al and Al₂O₃ layer in 0.5M NaCl solution confirm the results obtained from potentiodynamic polarization studies of these systems.

SEM images of material surfaces of bulk Al and surface layers of Al₂O₃ in the study of influences of corrosive environment of 0.5M NaCl solution are shown in Fig. 10. Images of the surfaces after corrosion tests show that in an environment of 0.5M NaCl solution Al substrate material undergoes pitting corrosion. However, Al₂O₃ surface layer provides a good corrosion protection for aluminum substrate.

3.2 Identification of the resistance to corrosion of iron

Iron is a metal with the greatest technical importance. Its useful physical properties include relatively high hardness, ductility and large malleability, relatively low production costs and high prevalence in nature. However, chemically pure iron has practically no direct use, while iron alloys with carbon, silicon and other metals have an enormous technical and practical importance.

Iron is a relatively reactive metal - its standard electrochemical potential is -760mV. It reacts with all diluted acids resulting in the salts of iron (II). Chemically pure iron is relatively less prone to corrosion compared to its commonly used alloys. Steels containing various alloying elements have different chemical compositions in material micro-zones. Such micro-zones in contact with the electrolyte solution lead to different electrochemical potentials and are able to create micro-cells, in which iron is most often an anode. As a result of these electrode processes the iron oxidation occurs and the formation of various corrosion products takes place, in which iron occurs primarily at two and three degrees of oxidation.

Electrochemical corrosion characteristics of iron were determined by potentiodynamic and impedance spectroscopy techniques. Tests were applied to chemically pure iron Fe made by electrocrystallization method and to carbon steel S235JR with the chemical composition shown in Table 3.

Component	C	S	P	Si	Mn	Cr	Ni	Cu
[%] weight	0.22	0.05	0.05	0.30	1.10	0.30	0.30	0.30

Table 3. The content of alloying elements in S235JR steel.

Images of topography and surface morphology of Fe iron and S235JR steel prior to corrosion tests are shown in Fig. 11.

In studies using potentiodynamic polarization perturbation of the steady state of the metal-solution the potential varied between -550mV to -10mV in the case of iron produced electrochemically, and in the range -723mV to -20mV in the case of S235JR steel. The rate of potential changes during the test was 0.3mV/s.

The characteristics $j = f(E)$ for iron Fe and S235JR steel in 0.5M NaCl solution obtained in the above potential ranges are shown in Fig. 12.

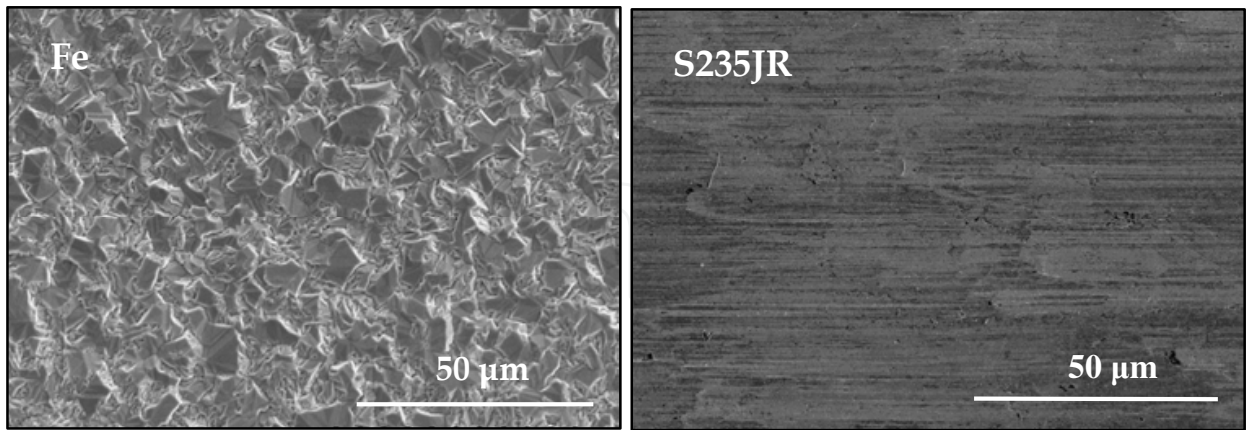


Fig. 11. Topography and surface morphology of Fe and S235JR steel prior corrosion tests.

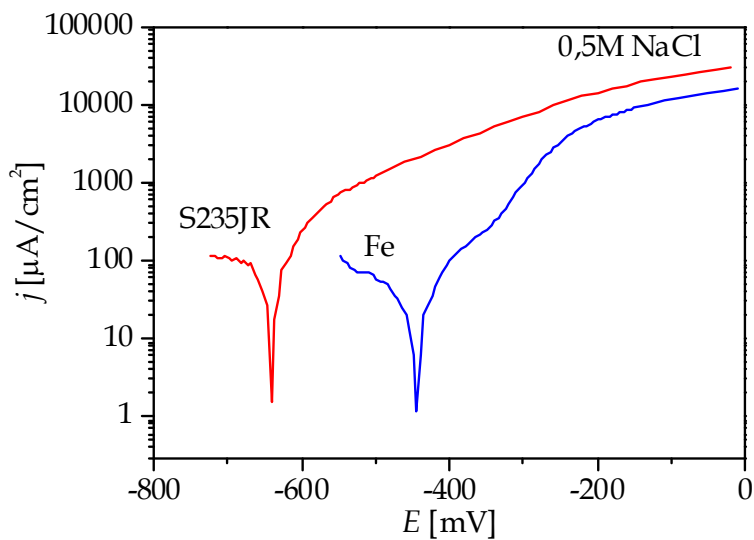


Fig. 12. Potentiodynamic polarization curves of Fe and S235JR steel in 0.5M NaCl solution.

Each of the potentiodynamic polarization curves for iron Fe and S235JR steel in the range of potentials tested consists of two parts: the cathodic and anodic segments. Part of the reduction process corresponds to the cathodic corrosive components of H^+ and O_2 occurring on the metal surface. However, part of anodic potentiodynamic polarization curve is characterized by the oxidation process of metal atoms or the process of corrosion - in the case of iron the reaction is $\text{Fe} - 2\text{e} \rightarrow \text{Fe}^{+2}$.

The corrosion test parameters of iron and S235JR steel in 0.5M NaCl solution are summarized in Table 4.

Material	E_{cor} [mV]	j_{cor} [$\mu\text{A}/\text{cm}^2$]
Fe	-445	24
S235JR	-641	93

Table 4. Parameters of Fe and S235JR steel in corrosion environment of 0.5 M NaCl solution.

The results show that pure iron produced electrochemically has much higher corrosion resistance compared to S235JR steel. Thus, alloying elements and the heterogeneity of the material in the case of carbon steel activate electrochemical processes of the material.

For further characterization of electrochemical corrosion processes at the interface of iron and S235JR steel with the 0.5M NaCl solution environment electrochemical impedance spectroscopy was used. The study consisted of perturbing the equilibrium of the corrosion system with a sinusoidal potential signal of small amplitude (15mV) across a wide frequency range (10kHz ÷ 33mHz) and recording the changes in time of system's current intensity response.

The measured frequency characteristics of electrochemically produced iron and S235JR steel in corrosive environment of 0.5M NaCl solution are presented in the form of Nyquist diagrams (Fig. 14) and Bode plots of impedance spectra (Fig. 15).

Effective modeling of complex electrochemical processes of corrosion in the systems based on iron required the use of a more complex equivalent electrical circuit, i.e., circuit containing CPE - constant phase elements. Constant phase element (CPE) is characterized by a constant angle of phase shift. Impedance of the CPE is described by the following expression: $Z_{CPE} = 1/Y_0(j\omega)^n$, where Y_0 and n are parameters related to the phase angle. The more heterogeneous the corrosion processes occurring on the metal surface the smaller value of the parameter n .

Best matching of all designated impedance spectra for experimentally studied systems of corrosion of iron and S235JR steel in the solution of 0.5 M NaCl was obtained by using an equivalent electric circuit with two time constants, whose structure is shown in Fig. 13.

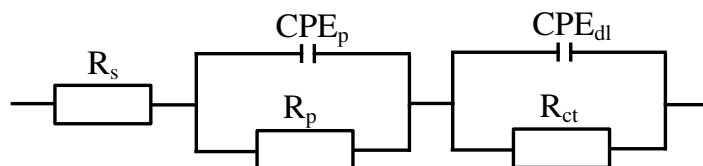


Fig. 13. The equivalent circuit for corrosion of Fe and S235JR steel in the solution of 0.5M NaCl.

This equivalent electric circuit can be described by the following relationship defining the resulting impedance, namely

$$Z = R_s + \frac{1}{\frac{1}{R_p} + Y_p(j\omega)^{n_p}} + \frac{1}{\frac{1}{R_{ct}} + Y_{dl}(j\omega)^{n_{dl}}} \quad (3)$$

Each element of this circuit appropriately models the specific process or phenomenon occurring in the system investigated. In the circuit shown in Fig. 13 the resistance element R_s represents corrosive environment, i.e., 0.5 M NaCl solution. The resistance representing the charge transfer through the interface associated with the process of oxidation of iron, i.e., the corrosion element, is described by R_{ct} , and the electrical double layer at the interface iron - 0.5M NaCl solution is characterized by a constant phase element CPE_{dl} . The use of two constant-phase elements in an equivalent electric circuit improves the quality of model fit to

the observations, as shown by Figs. 14 and 15. However, this introduces two additional circuit elements whose physical meaning can be expressed as follows: CPE_p - the capacity of the surface area of materials with high degree of surface development, R_p - resistance of electrolyte contained in the pores of the corroded material zone.

Analysis of impedance spectra with a fitted equivalent circuit allows the assessment of the variability of individual circuit elements with the change of potential and current intensity flowing in the corrosion system.

The values of the parameters of equivalent circuit elements that characterize the processes occurring in the corrosion of iron and S235JR steel in 0.5M NaCl solution are summarized in Table 5.

Material	R_s [$\Omega\text{ cm}^2$]	R_p [$\Omega\text{ cm}^2$]	CPE_p [$\mu\text{Fs}^{n-1}/\text{cm}^2$]		R_{ct} [$\Omega\text{ cm}^2$]	CPE_{dl} [$\mu\text{Fs}^{n-1}/\text{cm}^2$]	
			Y_p	n_p		Y_{dl}	n_{dl}
Fe	16.7	5.7	212.6	0.68	1513	136.5	0.76
S235JR	15.4	114	182.4	0.68	386	48.3	0.98

Table 5. Electrical circuit parameters of the corrosion systems of Fe and S235JR steel in 0.5M NaCl solution.

Compatibility of the actual processes in the system under study with a description of the corrosion with an equivalent circuit through which current flows with the same amplitude and same phase angle as in the corrosion system at a given excitation is illustrated in Figs. 14 and 15, respectively.

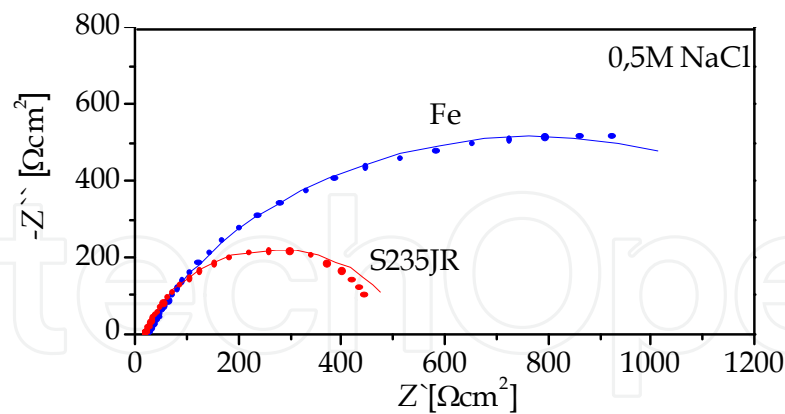


Fig. 14. Nyquist diagrams of impedance spectra of corrosive systems of Fe and S235JR steel in 0.5M NaCl solution determined experimentally (point line) and as a result of calculations (solid lines).

Nyquist diagrams (Fig. 14) in the shape of the characteristic semi-circles indicate the activation process control during corrosive material tests. Much larger diameter of the semi-circle in the case of electrochemically generated iron shows high electrical resistance at the interface metal-solution, which is the result of oxidation of iron and Fe^{+2} ions passing into the solution. This indicates a greater corrosion resistance of iron compared to steel S235JR in

the test environment, which also confirms the results obtained with the potentiodynamic polarization method.

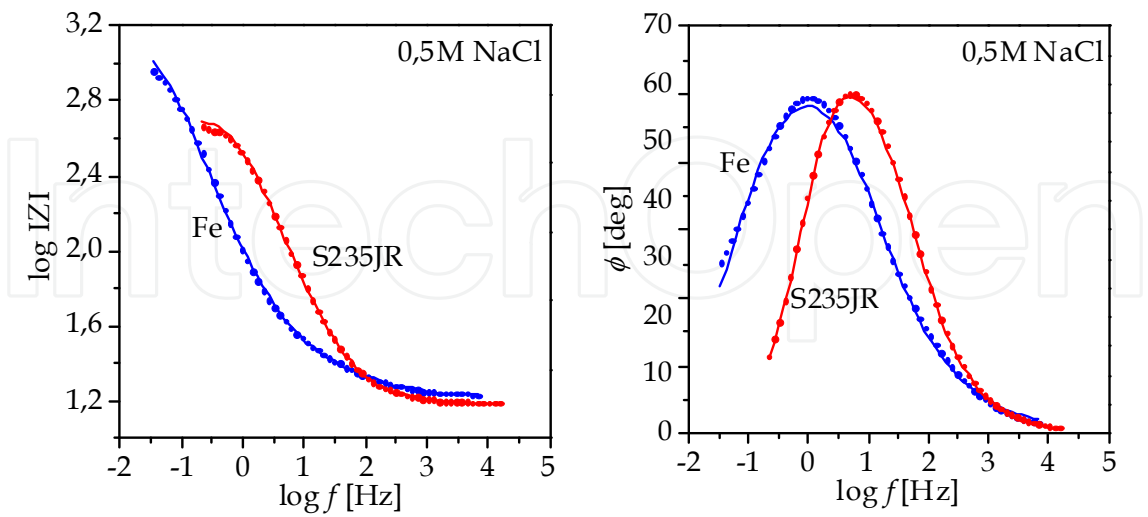


Fig. 15. Bode amplitude and phase spectra of circuit impedance and corrosion systems of Fe and S235JR steel in 0.5M NaCl solution determined experimentally (point line) and as a result of calculations (solid lines).

Images of destruction of corrosion test samples of Fe and S235JR steel after corrosion tests are shown in Fig. 16.

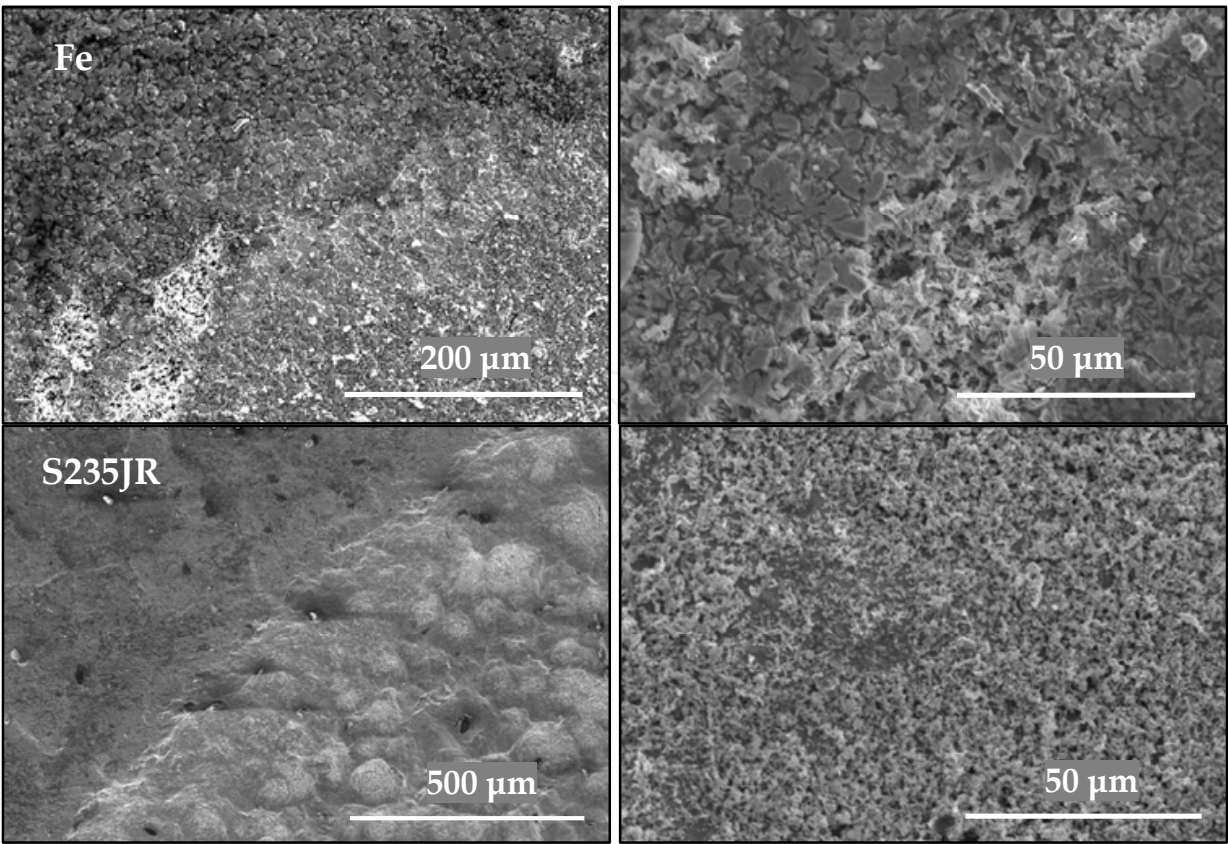


Fig. 16. Images of the surfaces of Fe and S235JR steel after corrosion tests.

Samples of iron Fe and S235JR steel subjected to corrosion test not only differed in structure and chemical composition, but also the morphology and surface topography (Fig. 11), which had also influenced the course of corrosion processes. Both the iron Fe and S235JR steel were submitted to uneven general corrosion (Fig. 16). Material pickling on the grains boundaries is clearly visible in the case of electrochemically produced iron.

3.3 Identification of the resistance to corrosion of nickel

Nickel is a metal characterized by soft, ductile, smelting and converting properties. Its standard electrochemical potential is -0.24V . The chemical compounds of nickel are mainly found in 2nd oxidation states, rather than the 3rd and 4th ones. It dissolves in mineral acids, but insensitive to bases (alkalis). In the atmospheric environment and many aqueous solutions nickel has the ability to passivity in a fairly wide pH range. Thanks to its passivity it has high resistance to corrosion in many environments (Trzaska & Moszczynski, 2008).

Nickel in pure state is used for manufacturing protective coatings of products made of other metals - mainly steel - and in its fine particle form is used as a catalyst for many chemical reactions. It is also one of the major components of many alloys, which are used in a variety of current technologies. However, restrictions in uses of nickel in various products are constantly growing due to its rarity in nature.

Electrochemical corrosion characteristics of nickel were carried out by potentiodynamic polarization and impedance spectroscopy methods. Corrosion tests of nickel produced by electrocrystallization were applied to its micrometric (Ni_m) and nanometric (Ni_n) crystalline structures and for NiP amorphous alloy of nickel with phosphorus at content of 10.7% by weight (Eftekhar, 2008), (Kowalewska & Trzaska, 2006).

Images of surface topography and morphology of nickel with microcrystalline and nanocrystalline structures and of NiP alloy before corrosion tests are shown in Fig. 17.

Potentiodynamic polarization curves of all tested nickel materials were determined in the same conditions for all the above materials: during measurements the polarization potential was increased in a wide range from -750mV to $+700\text{mV}$ with a 0.4mV/s rate.

The potentiodynamic polarization curves $j = f(E)$ of nickel with different crystalline structures and of amorphous NiP alloy determined from measurements are shown in Fig. 18.

Analysis of these curves indicates a noticeable influence of the structure of nickel and other ingredients contained in the material, on the process of corrosion in the test environment. The corrosion parameters of the tested materials obtained from the experiment are summarized in Table 6.

Analysis of these parameters shows that the greatest potential for corrosion and the smallest corrosion current density characterize nickel with the nanocrystalline structure. This highlights its highest resistance to corrosion in the test environment. Increased corrosion resistance of electrochemically produced nickel with the nanocrystalline structure in comparison to microcrystalline nickel may indicate a greater tendency to passivity of the nanocrystalline nickel. A passive layer that forms on the surface of nanocrystalline nickel

inhibits the processes of corrosion of nickel in a certain range of the potential. However, differences in the corrosion resistance of pure nickel and its alloy result from both the additive contained in the material alloy, as well as different material structures.

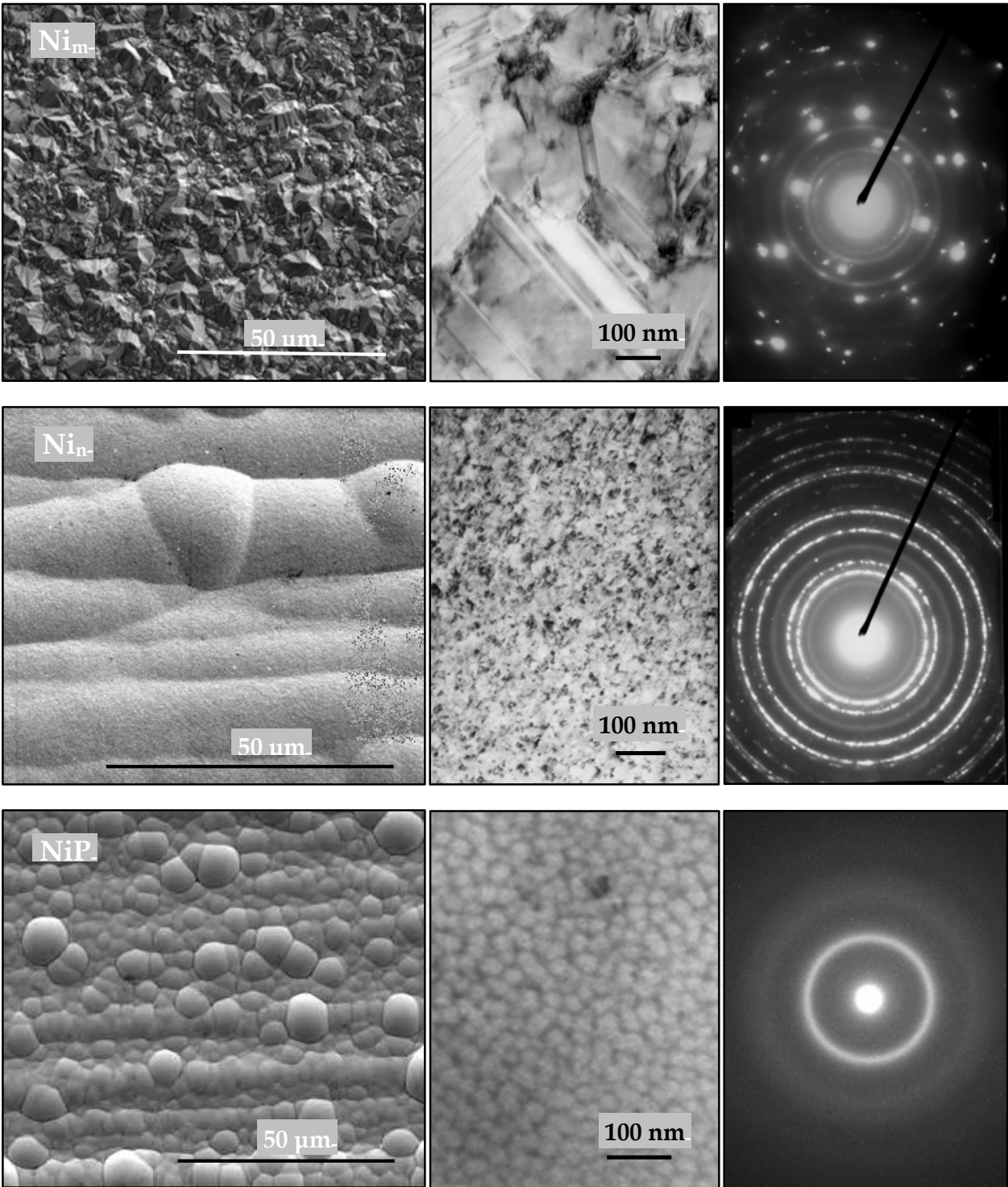


Fig. 17. Images of surface morphology (SEM), structure (TEM) and electron diffraction (SAED) of microcrystalline nickel Ni_m, nanocrystalline nickel Ni_n and NiP amorphous alloy prior corrosion tests.

Material	E_{cor} [mV]	j_{cor} [$\mu A/cm^2$]
Ni _m	-568	24
Ni _n	-340	1.5
NiP	-390	4.5

Table 6. Corrosion parameters of nickel and alloy NiP in 0.5M NaCl solution.

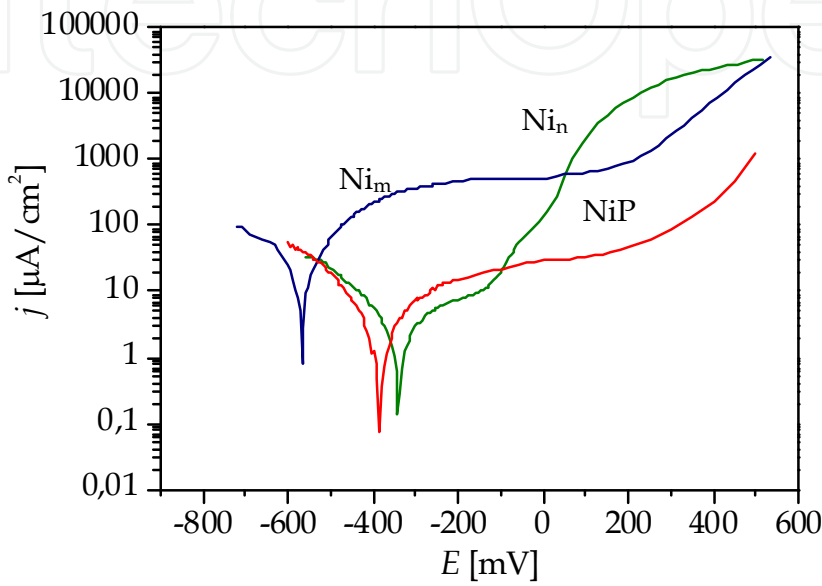


Fig. 18. Potentiodynamic polarization curves of nickel with the microcrystalline structure (Ni_m), and nanocrystalline structure (Ni_n) and of NiP alloy.

Investigations of the processes at the interface nickel-0.5M NaCl solution by impedance spectroscopy were performed with frequency changes in the range of 10kHz ÷ 2mHz. Amplitude of the sinusoidal perturbation signal was maintained at 15mV. Impedance spectra recorded for test materials are shown as Nyquist diagrams (Fig. 22) and Bode diagrams (Fig.23), in the form of two relationships: the impedance magnitude and phase angle versus frequency.

Nyquist diagrams (Fig. 22) indicate significant differences in the course of corrosion processes of the different forms of nickel and its alloy structures in the environment of 0.5M NaCl solution. In the case of nanocrystalline nickel structure and alloy NiP, the impedance spectra obtained are expressed in the form of an arc forming part of the semi-circle of very large radius. This chart indicates good corrosion resistance of nanocrystalline nickel and alloy NiP in the test environment. Impedance spectrum plot of microcrystalline nickel in the shape of semicircle of small radius ends with a fragment of straight line in the low frequency part of the forcing signal. This straight line fragment of the relationship between the imaginary component (Z'') and the real part (Z') of the impedance points to the diffusion control of corrosion processes at low frequency of the forcing signal. The smallest diameter of the semi-circle in the case of nickel with microcrystalline structure corresponds to a small value of resistance electric current flowing through the phase boundaries as a result of oxidation of nickel, which corresponds to a high rate of corrosion processes.

All obtained results of impedance measurements confirm the significant impact of the material structure and the additions of nickel alloy on the resistance to corrosion and are consistent with the results obtained by potentiodynamic polarization method.

The two methods showed that nanocrystalline nickel has the highest corrosion resistance in an environment of 0.5M NaCl solution..

Further assessment of the characteristics of the impedance at the system boundaries for nickel and its alloy in 0.5M NaCl solution was obtained by approximation of experimental data using equivalent electrical circuits. The equivalent electrical circuits most suitable to represent the measured impedance characteristics of studied systems of nickel with different structures and its alloy in corrosive environment of 0.5M NaCl solution are shown in Figs. 19, 20 and 21. The corresponding resulting impedances are described in the expressions (4) ÷ (6). For the analysis of the corrosion of microcrystalline structure nickel with the equivalent electrical circuit a simple layout shown in Fig. 19 was used.

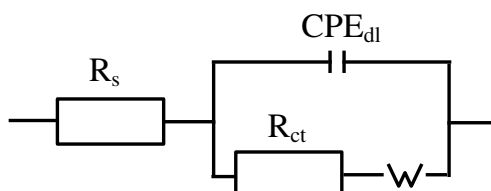


Fig. 19. The equivalent electrical circuit for corrosion of microcrystalline structure nickel in 0.5 M NaCl solution.

This system includes four elements: R_s - resistance of 0.5M NaCl solution, R_{ct} - electric charge transfer resistance for phase boundary of nickel - solution, CPE_{dl} - constant phase element characterizing the electrical properties of the double layer at the interface, and the element W - Warburg impedance, which characterizes the control of corrosion processes by diffusion of mass in the area of the electrolyte at the metal surface.

The equivalent electrical circuit is described by the resulting impedance

$$Z = R_s + \frac{1}{\frac{1}{R_{ct} + W} + Y_{dl}(j\omega)^{n_{dl}}} \quad (4)$$

Experimentally determined impedance spectra of nanocrystalline nickel corrosion (fig. 20) are well mapped by equivalent electrical circuit with two time constants described by equation (5)

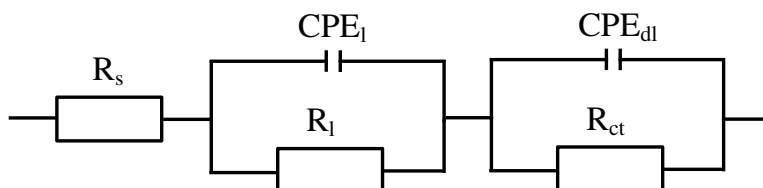


Fig. 20. Equivalent electrical circuit of corrosion of the nanocrystalline structure nickel in 0.5M NaCl solution.

$$Z = R_s + \frac{1}{\frac{1}{R_l} + Y_l(j\omega)^{n_l}} + \frac{1}{\frac{1}{R_{ct}} + Y_{dl}(j\omega)^{n_{dl}}}$$

(5)

This circuit, besides elements such as R_s , R_{ct} , CPE_{dl} which are needed in the equivalent electrical circuit to describe the corrosion of microcrystalline nickel contains two additional elements: CPE_l - modeling capacity of the passive layer on the material surface, and R_l - describing the resistance of the passive layer.

To describe the corrosion processes occurring in the system NiP- 0.5M NaCl solution the equivalent electrical circuit shown in Fig. 21 was designed with the resulting impedance expressed by (6).

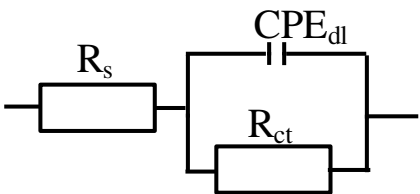


Fig. 21. Equivalent electrical circuit for corrosion of the nanocrystalline structure nickel in 0.5M NaCl solution.

$$Z = R_s + \frac{1}{\frac{1}{R_{ct}} + Y_{dl}(j\omega)^{n_{dl}}}$$

(6)

The parameters of the equivalent electrical circuits of corrosive systems of nickel materials tested in this study are summarized in Table 7.

Material	R_s [Ωcm ²]	R_l [Ωcm ²]	CPE_l [ΩFs ⁿ⁻¹ /cm ²]		R_{ct} [Ωcm ²]	CPE_{dl} [μFs ⁿ⁻¹ /cm ²]		W [Ωcm ²]
			Y_l	n_l		Y_{dl}	n_{dl}	
Ni _m	14.7	-	-	-	1420	69	0.8	705
Ni _n	14.7	4708	17.6	0.9	15317	30	0.8	-
NiP	12.6	-	-	-	20430	17	0.9	-

Table 7. The parameters of equivalent electrical circuits for corrosive systems of nickel - 0.5M NaCl solution.

The agreement between characteristics predicted by the equivalent circuit methods and those obtained from measurements are illustrated in Figs. 22 and 23.

Images of the damage on the surface of nickel samples with different structure and its alloy after corrosion tests are shown in Fig. 24.

In the case of the microcrystalline structure nickel and NiP alloy in corrosive environment of 0.5M NaCl solution, a pickling of their internal structures occurred over the entire surface exposed and even its internal structures was revealed. On the other hand, corrosion of the nanocrystalline nickel in this environment takes the form of uneven local corrosion.

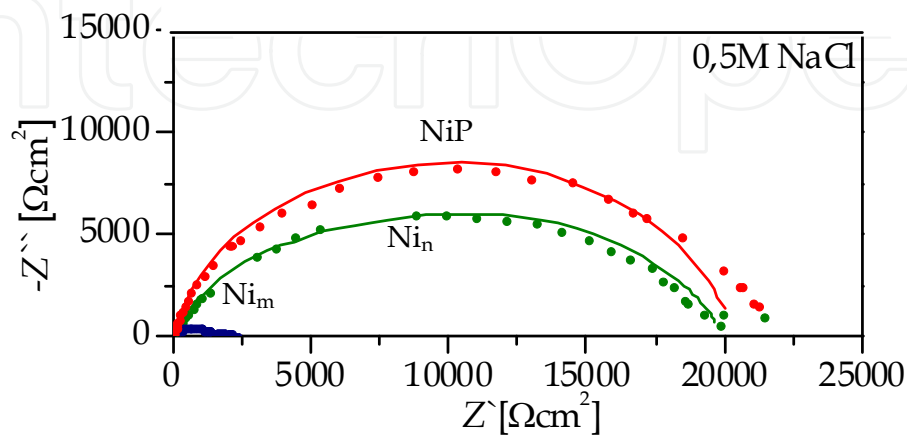


Fig. 22. Nyquist diagrams of impedance spectra of investigated corrosion systems of nickel and its alloy in the environment of 0.5M NaCl solution determined experimentally (point line) and as a result of calculations (solid lines).

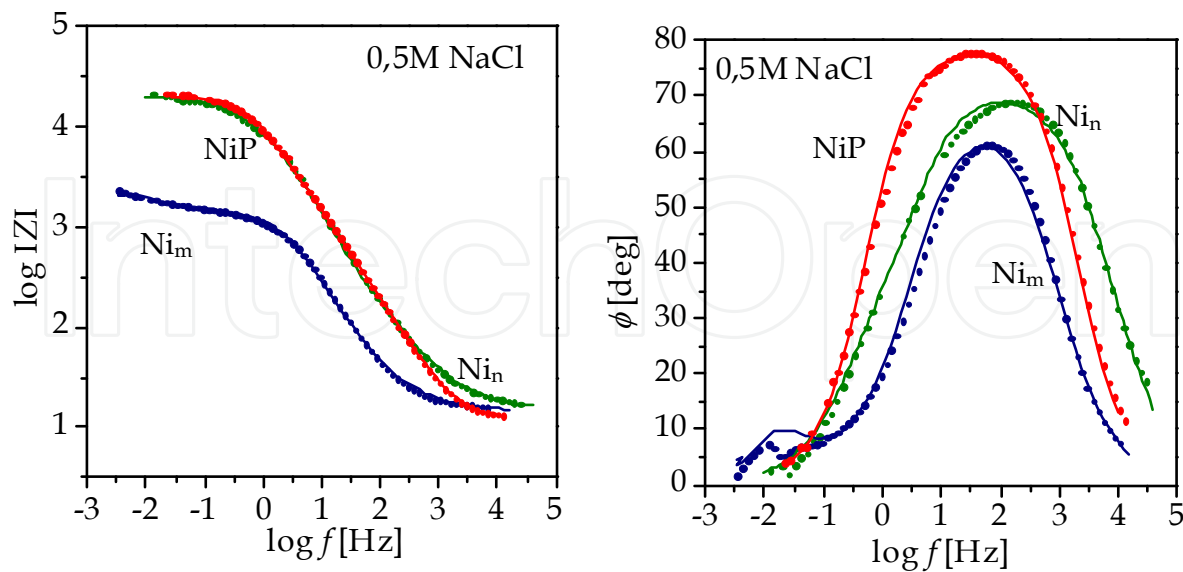


Fig. 23. Bode diagrams of impedance spectra of investigated corrosion systems of nickel and its alloy in the environment of 0.5M NaCl solution determined experimentally (point line) and as a result of calculations (solid lines).

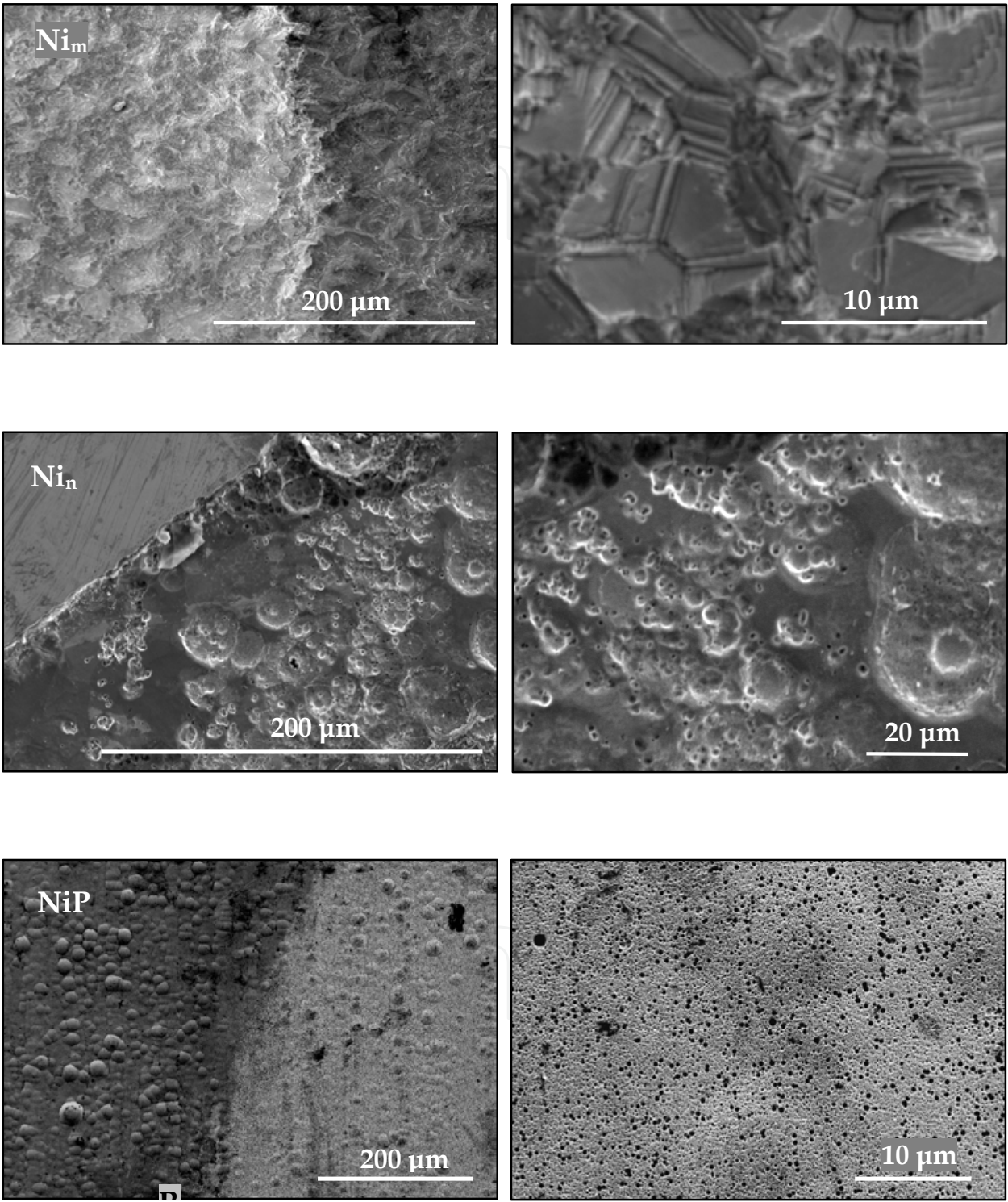


Fig. 24. SEM images of the surface of Ni_m , Ni_n , and NiP alloy after corrosion tests in an environment of 0.5M NaCl solution.

4. Summary

The rate of corrosion processes of metallic materials in a corrosive environment depends on the chemical activity of the metal and the additional components, the structure of the material as well as the degree of development of their surfaces.

Electrochemical methods for the study of corrosion processes are based on the relationships between electrical, chemical and physical properties, which are used to identify phenomena and processes at the interface metal-corrosive environment. Electrochemical potentiodynamic polarization method allows determining the corrosion potential and corrosion current density of the metallic material in a corrosive environment. Additionally, the precise measurement method using electrochemical impedance spectroscopy (EIS) generates frequency characteristics of corrosion systems and forms the solid basis to design models based on equivalent electrical circuits, which maps the processes occurring in the corrosion system under investigation. Such an equivalent electrical circuit that meets the criteria of a mathematical (and metrological) model can also be considered as a physical model describing the phenomena and the processes occurring in a given system undergoing electrochemical corrosion.

The current research of corrosion phenomena appearing at the interface metal-natural environment showed that chemical re-combination of the metals to form ore-like compounds is a natural process, because the energy content of the metals and alloys is higher than that of their ores. It has to be emphasized that there are number of means of controlling corrosion. The choice of a means of corrosion control depends on economics, safety requirements, and a number of technical considerations. However, it is necessary to learn and recognize the forms of corrosion and the parameters that must be controlled to avoid or mitigate corrosion.

Through the understanding of the electrochemical processes and how they can act to cause the various forms of corrosion, the natural tendency of metals to suffer corrosion can be overcome and equipment that is resistant to failure by corrosion can be designed. In this study we have shown that the measuring methods based on the electrochemical impedance spectroscopy are able to detect the potential corrosion spots in very early stages.

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The book has covered the state-of-the-art technologies, development, and research progress of corrosion studies in a wide range of research and application fields. The authors have contributed their chapters on corrosion characterization and corrosion resistance. The applications of corrosion resistance materials will also bring great values to reader's work at different fields. In addition to traditional corrosion study, the book also contains chapters dealing with energy, fuel cell, daily life materials, corrosion study in green materials, and in semiconductor industry.

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