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# **WORKBOOK**

# **CORROSION AND CORROSION PROTECTION**

## **LUBLIN 2014**



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NARODOWA STRATEGIA SPÓJNOŚCI



UNIA EUROPEJSKA  
EUROPEJSKI  
FUNDUSZ SPOŁECZNY



Projekt współfinansowany ze środków Unii Europejskiej  
w ramach Europejskiego Funduszu Społecznego



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First edition



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# 1. STRUCTURE AND PROPERTIES OF THE CORROSION-RESISTANT MATERIALS

## 1.1 Purpose of the exercise:

Identification of the structures of corrosion-resistant materials based on microscopic observations. Determination of relation between structural construction and properties of the materials.

## 1.2 Significant control questions:

- Iron alloys,
- Copper and its alloys,
- Aluminium and its alloys,
- Titanium and its alloys,
- Heat resistant materials.

## 1.3 Supplementary literature:

1. Baszkiewicz J., Kamiński M.: Podstawy korozji materiałów, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa 1997
2. Surowska B.: Wybrane zagadnienia z korozji i ochrony przed korozją, Wyd. PL, Lublin 2002
3. Wranglen G.: Podstawy korozji i ochrony metali. WNT, Warszawa, 1985
4. Żurek Z.: Materiał i środowisko, Wyd. Pol. Krakowskiej Kraków 1998

## 1.4 Course of the exercise:

1. Materials and equipment for testing:
  - Set of specimens from metallographic corrosion-resistant materials,
  - Metallographic microscope,
  - User manual for the microscope,
  - Microstructure atlases.

## 1.5 Course of the testing:

Before starting the exercise, every student must learn about recommendations of health and safety instruction. Course lecturer checks the knowledge of information provided in health and safety instructions, as well as the knowledge of research issues. Upon acceptance to carry out the exercise, a student must perform the following actions:

- Turn on the microscope light and using user manual check its functionality. Check the selection of magnification,
- Carry out the observation of structures of all metallographic specimens included in the set and identify them based on the atlas of microstructures,
- Draw in the report structures of corrosion-resistant materials indicated by the lecturer.

## 1.6 Development of test results and reports

- Purpose of the tests, subject of the tests,
- Brief characteristic of the tested materials,
- Type of microscope and its accessories,
- Drawings of the observed structures and their characteristics,
- Analysis of the tests results and conclusions concerning relations between structural construction and properties of corrosion-resistant materials.

## 1.7 Supplementary materials

- Atlas of copper alloys microstructures,
- Atlas of titan alloys microstructures,
- Atlas of aluminium alloys structures,
- Atlas of microstructures of alloys with special properties.

## 2. MICROSCOPE ASSESSMENT OF TYPE AND DEGREE OF CORROSION

### 2.1 Purpose of the exercise:

Identification of corrosion types and learning about the corrosion test methodology, as well as about evaluation of type and degree of corrosion.

### 2.2 Significant control questions:

- List types of chemical and electrochemical corrosion,
- Name forms of local corrosion,
- Methods of corrosion tests,
- Principles of quantitative assessment of corrosion degree,
- Methods for assessing the degree of intergranular corrosion,
- Quantitative methods for assessing the degree of pitting corrosion.

### 2.3 Supplementary literature:

1. Baszkiewicz J., Kamiński M.: Podstawy korozji materiałów, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa 1997
2. Surowska B.: Wybrane zagadnienia z korozji i ochrony przed korozją, Wyd. PL, Lublin 2002
3. Wranglen G.: Podstawy korozji i ochrony metali. WNT, Warszawa, 1985
4. Żurek Z.: Materiał i środowisko, Wyd. Pol. Krakowskiej Kraków 1998

### 2.4 Theoretical information

#### Introduction

Corrosion is a process of metal destruction due to chemical or electrochemical reaction with the surrounding environment.

Corrosion processes are classified in accordance with various criteria, whereas from the viewpoint of corrosion tests, the most rational is the systematic of corrosion phenomena depending on the process mechanism and corrosive environment. There are two basic types of corrosion: chemical corrosion and electrochemical corrosion.

**Chemical corrosion** – includes all phenomena, in which there's a physical-chemical interaction between the metallic phase and gas or liquid oxidizing environment, that is not of electrolyte nature e.g. dry gasses  $O_2$ ,  $H_2Cl_2$ , vapour of sulphur, bromine, iodine, anhydrous organic compounds (alcohols, phenols,  $CCl_4$ ).

**Electrochemical corrosion** – includes phenomena, in which there's a physical-chemical interaction at the boundary of metal-electrolyte phases. It's associated with the passing of electric charge through boundary of the phases. Electrochemical corrosion is the most common type of corrosion. It occurs in water and water solutions, in the soil and the atmosphere.

Taking into account the appearance or change in the physical properties of the metals, we can distinguish the following basic groups:

**uniform corrosion** – it is characterized by uniform oxidation of the material surface. Example of this type of destruction is rusting of the iron and high-temperature oxidation of metals;

**pitting corrosion** – it is characterized by local formation of the pitting due to different corrosion rates of the surface areas. Pits that are forming can be shallow or deep. Pitting corrosion affects, among others, acid-resistant steels and carbon steels. Corrosion damages in the form of pits also occur in the case of fretting corrosion and erosion;

**intergranular corrosion** – it is characterized by local destruction along the boundaries of metal grains. Intergranular corrosion spreads deep into the material, without causing the destruction symptoms on the elements' surface. This often results in catastrophic failures. Intergranular corrosion most commonly occurs in acid-resistant steels and aluminium alloys;

**selective corrosion** – it is based on selective oxidation of one or more alloy components, leaving a porous residue and maintaining the original shape of the element. Most common type of the selective corrosion is so called dezincification, which affects the zinc alloys. In this case the corrosion mainly affects the zinc, leaving a porous residue of copper and corrosion products. With this type of corrosion there may be no external symptoms of destruction, with the exception of tarnishing. Whereas tensile strength and particularly the ductility are significantly reduced;

**corrosion cracking** – it is a type of local corrosion occurring under the influence of tensile stresses and specific corrosive environment. The cracks are of intergranular or transgranular nature, depending on the type of environment and metal. Due to this process, damages to apparatus or structural elements are usually unexpected and occur without any external symptoms or any deterioration in functioning of the installation. Corrosion cracking affects almost all construction metals, carbon steels, corrosion-resistant steels, brass, alloys of aluminium, magnesium, titanium, nickel;

**hydrogen corrosion** – it is a group of phenomena associated with reduction of plastic and strength properties of metals under the influence of hydrogen. Hydrogen corrosion, depending on the environment conditions (temperature, pressure, chemical composition) and on material structure, can occur in the form of hydrogen embrittlement and snowflakes.

### Types of the testing methods

Depending on the test purpose and type of occurring corrosion, in accordance with PN-69/H-04609, the following assessment methods must be used:

- a.) method of visual assessment of changes in surface appearance (detailed description in the further part of this exercise);
- b.) assessment method of changes in mass and dimensions; weigh method specified by the Polish standard PN-74/H-04600 is the most popular method of tracking the progress of uniform corrosion. It is based on determination of the loss or gain of the sample weight. Gravimetric designations are also conducted on the isolated (mechanically or chemically) layers of the corrosion products e.g. to determine their thickness. This method is especially useful in selection of materials for construction. This is because it enables us to express the rate of change in cross-section of metal structure, resulting from corrosion progress and assessment of corrosion resistance group based on scale of resistance;
- c.) assessment method for determining the frequency of occurrence of corrosion changes and depth of corrosion changes;
- d.) assessment method of changes in mechanical properties – tests of: stretching, impact strength, formability, bending. Bending test consists of bending the sample (cooked in the solution and fixed in a vice) to an angle of  $90^{\circ}$  by hitting it with a hammer. Rounding radius of the vice jaws or the holder should be equal to 3 mm in the case of sample with the thickness up to 1 mm; 3-times the thickness of the sample in the case of sample with the thickness of 1÷3 mm; and 10mm in the case of sample with the thickness greater than 3 mm. In the case of sample with the thickness of 3÷5

mm and lower, the bending test must be conducted in 2 areas of the sample, bending it to a shape of letter Z. In the case when the sample is cut from a plated element, it must be bent in such manner so that the side, which is in contact with carbon steel (or other metal) would be inside the bending.

e.) assessment method of under film corrosion;

f.) sound method, which is based on a comparison of the cooked and uncooked sample sounds, dropped from a height of 200÷250 mm onto a stone plate. Complete loss of sound by at least one sample of the tested material means that the steel has been affected by the intergranular corrosion. Sound test must be supplemented by bending test and should not be applied to samples of welded joints.

Selection of assessment method – type of method and number of methods – depends on the conditions and purpose of the test.

### Visual methods of assessing the corrosion

**Intergranular corrosion** - Microscope observations of the transverse polished section are conducted on the transverse polished sections of the straight or slightly bent samples (bent to an angle of 10÷15°), before and after the test for resistance to intergranular corrosion at a magnification of 250÷400. Steel is considered to be not resistant to intergranular corrosion, if the corrosion extends to a depth of:

- 30µm in the case of etching of all grains that are located in the field of microscope vision;
- 50µm in the case of etching of single grains' boundaries in 1/3 field of microscope vision at a magnification of x250.

For individual cases of the equipment use, reserved in the technical conditions of the delivery and agreed between the supplier and the ordering party, a steel is considered as prone to intergranular corrosion when its intergranular corrosion reaches the agreed lesser depth.

#### Calculation of the average corrosion rate $V_c$ or $V_p$ :

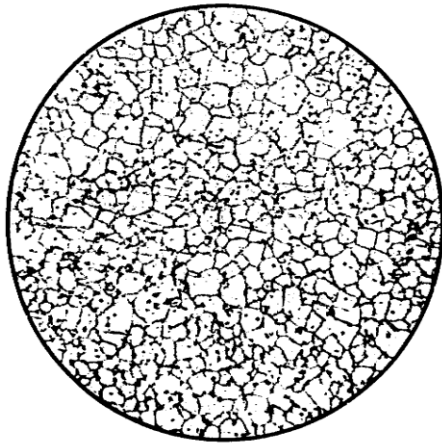
Average corrosion rate  $V_c$  or  $V_p$  is calculated in accordance with PN-85/H-04640 for each cooking period. If after any of 48-hour sample cooking periods, the rate of corrosion exceeds  $43,5 \text{ g/m}^2 \times \text{day}$  or 2mm/year, then the steel is considered to be not resistant to intergranular corrosion.

#### Microscope observation of the etching spot:

**Etching spot** is observed under a microscope with at least x30 magnification. In the case when observation of the spot using the microscope is not possible, it is allowed to observe it using magnifying glass or other optical device that is equipped with at least x20 magnification. The steel is considered as not resistant to intergranular corrosion, if the grains in a place of anodic etching are surrounded by continuous grid of little channels – as shown in the following figure.



A)



B)

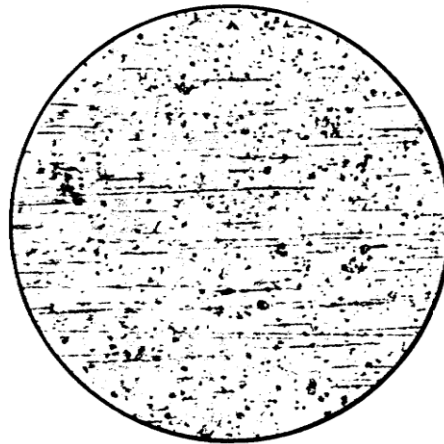


Fig.1. Etching spot (x50): a) for steel not resistant to intergranular corrosion, b) for steel resistant to intergranular corrosion (wg PN-66/H-04630)

In the case when such grid does not occur, the banding visible on the spot of anodic etching is not the indicator of steel's tendency for intergranular corrosion.

In the case of very intensive etching of the tested sites (which may indicate the uniform corrosion or very small resistance to intergranular corrosion), the tests must be repeated on these samples with the use of other methods.

#### **Pitting corrosion**

The assessment is based on visual observation of the corrosion damages and evaluation of the corrosion test using visual method (macro), as well as on the calculation of spots and corrosion points using square method or determination of the corroded places on the given surface with the use of linear-differential method.

#### **Linear-differential method:**

Assessment of corrosion must be conducted on the samples affected by the changes in the form of spots and strong corrosion. On the tested surface using etching-needle, you need to draw parallel lines in the distance not smaller, than the smallest corrosion spot, while the size of the tested surface should at least be equal to 25 cm<sup>2</sup>.

**Degree of corrosion ( $S_k$ )** in percents must be calculated according to the following formula(1):

$$S_k = \frac{n_L}{N_L} \times 100 \quad (1)$$

where:

$n_L$  - total length of the lines covered with corrosion products (on the tested surface), mm

$N_L$  – total length of all lines on the tested surface, mm

Degree of corrosion in percents ( $S_k$ ) corresponds to the degree of corrosion resistance ( $O_L$ ) in accordance with the scale provided in table 1.

Table 1. Relation between degree of corrosion resistance  $O_L(O_Q)$  and degree of corrosion  $S_k (S'_k)$  according to PN-78/H-04610

Degree of corrosion resistance $O_L(O_Q)$	Degree of corrosion $S_k (S'_k)$ [%]
10	Without corrosion changes
9	Up to 1,0
8	above 1,0 to 2,5
7	above 2,5 to 5,0
6	above 5,0 to 10,0
5	above 10,0 to 30,0
4	above 30,0

### Square method

Corrosion assessment must be carried out on the samples prepared in accordance with paragraph 3, while the minimum size of the tested surface should be equal at least to 25 cm<sup>2</sup>.

Elastic, transparent template must be placed on the tested surface and on it, a scale must be applied with the squares sides of 1×1 or 5×5 or 10×10 mm. Size of the squares on the scale is selected depending on the size of points and spots occurring on the sample. Size of the square side should be equal or smaller than corrosion spot or point that occurs most frequently on the sample.

In the case of scratches, long spots and smudges occurrence, you need to take into account all squares located in their areas, even when the surface corroded within the square area is smaller than 50% of the total area of the square. One point or couple of points located within one square must be counted only once.

Determination includes a number of squares, in which the corrosion products occur in relation to the total number of squares occurring within the sample, in result of applying the template.

**Degree of corrosion ( $S'_k$ )** in percents must be calculated according to the following formula (2):

$$S'_k = \frac{n_Q}{N_Q} \times 100 \quad (2)$$

where:

$n_Q$  – number of squares covered with corrosion products on the surface equal or greater, than 50% of the surface of the observed square,

$N_Q$  – total number of squares on the tested surface and these squares that cover it in 50% or more on the sides of the sample

Degree of corrosion ( $S'_k$ ) in percents corresponds to the degree of corrosion resistance  $O_q$  according to the scale provided in table 1.

**Incidence of corrosion changes ( $H_Q$ )** expressed in percents must be calculated according to the following formula (3):

$$H_Q = \frac{n}{N} \times 100 \quad (3)$$

where:

$n$  – number of corrosion points

$N$  – size of the sample surface cm<sup>2</sup>

**Depth of the pitting corrosion** is expressed as a **ratio of penetration depth  $f$** , which is a relation of the greatest depth of pits to the average depth, determined from the loss of the sample weight, in accordance with the following formula (4):

$$f = \frac{l_{\max}}{\Delta s} \quad (4)$$

where:

$l_{\max}$  – maximum depth of corrosion ( $\mu\text{m}$ , mm, cm)

$$\Delta s = \frac{\Delta m}{\rho A}$$

$\Delta m$ . – loss of weight, g

$\rho$  - density,  $\text{g/cm}^3$

A – tested surface,  $\text{cm}^2$

f coefficient shows how much the loss of thickness in the biggest occurring loss is greater than the loss of thickness, which would result from the calculation of uniform surface corrosion based on the determined loss of weight. If f is getting close to 1, then the local corrosion is becoming the uniform surface corrosion.

## 2.5 Course of the exercise:

Materials and equipment for testing:

- Set of elements and metallographic specimens after various corrosion processes,
- Stereoscopic microscope,
- Metallographic microscope,
- User manual for the microscope.

## 2.6 Course of the testing:

Before starting the exercise, every student must learn about recommendations of health and safety instruction. Course lecturer checks the knowledge of information provided in health and safety instructions, as well as the knowledge of research issues. Upon acceptance to carry out the exercise, a student must perform the following actions:

- Conduct visual assessment of the type and degree of corrosion (sample appearance, degree of corrosion, number and distribution of corrosion changes),
- Carry out the observation of elements using stereoscopic microscope,
- Carry out the observation of the structure of all metallographic specimens included in the set and identify them (type of corrosion, number and distribution of corrosion changes),
- Draw in the report elements after the corrosion process and material structures indicated by the lecturer,
- Calculate appropriate corrosion coefficients depending on the type of corrosion.

## 2.7 Development of test results and reports

- Purpose of the tests, subject of the tests,
- Brief characteristic of the tested materials,
- Type of protective cover (in case of occurrence),
- Method of surface preparation,
- Type of corrosion exposure and its duration,
- Assessment of the initial test (with possible photographs),



- 
- Assessment of corrosion changes (visual method, differential-linear method, square method),
  - Analysis of the test results and conclusions.

## 2.8 Supplementary materials

- Atlas of corrosion types and material microstructures after the corrosion.



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## 3. TESTING OF ELECTROCHEMICAL CORROSION

### 3.1 Purpose of the exercise:

Determination of the degree of material's resistance to corrosion in the given environment. Determination of environments where the given material can be used. Comparative tests concerning the resistance of various metal materials to corrosion.

### 3.2 Significant control questions:

- What is electrochemical corrosion,
- How to determine the potential of corrosion,
- Passivity of the materials,
- Polarization curves and their interpretation,
- Factors affecting the resistance to electrochemical corrosion.

### 3.3 Supplementary literature:

1. Baszkiewicz J., Kamiński M.: Podstawy korozji materiałów, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa 1997
2. Surowska B.: Wybrane zagadnienia z korozji i ochrony przed korozją, Wyd. PL, Lublin 2002
3. Wranglen G.: Podstawy korozji i ochrony metali. WNT, Warszawa, 1985
4. Żurek Z.: Materiał i środowisko, Wyd. Pol. Krakowskiej Kraków 1998

### 3.4 Course of the exercise:

Materials and equipment for testing

- Set of samples for corrosion tests,
- Set for electrochemical testing,
- User manual of the set for electrochemical testing.

### 3.5 Course of the testing

Before starting the exercise, every student must learn about recommendations of health and safety instruction. Course lecturer checks the knowledge of information provided in health and safety instructions, as well as the knowledge of research issues. Upon acceptance to carry out the exercise, a student must perform the following actions:

- Prepare electrolyte suitable for intended testing program e.g.:
  - a.) acidic solution,

- b.) alkaline solution,
- c.) neutral solution.

To perform this exercise, it is recommended to use 5% NaCl alkaline solution

Prepare the samples

- a.) immerse the samples in the epoxy resin in PCV rings, so that the exposed area would be equal to approximately  $1 \text{ cm}^2$ ,
- b.) polish and degrease the surfaces of the samples.

- Perform initial treatments:

The samples must undergo one of the following initial treatments:

- a.) immerse in electrolyte for 20 minutes in electroless conditions,
- b.) immerse in a solution of nitric acid  $\text{HNO}_3$  (in order to make it passive and clean it).

- Carry out the measurements.

a.) potentiodynamic test:

- assemble the measuring system (in accordance with the schematic),
- place the samples in measuring dish,
- determine the operating parameters of the system (in accordance with the user manual of voltage changing generator),
- determine the rate of voltage changes ( $1 - 100 \text{ mV/s}$ ),
- determine the range of voltage changes,
- conduct the measurement.

b.) potentiostatic test:

- determine constant voltage with a value exceeding the value of breakthrough potential, read from the potentiodynamic curve,
- turn on the system,
- conduct continuous measurement of the current flow for a period of 15 min.

### 3.6 Development of test results and reports

- Purpose of the tests, subject of the tests,
- Brief characteristic of the tested materials,
- Analysis of the potentiodynamic curves and determination of characteristic potentials.

From the obtained graphs (graphs of anodic polarization potentiodynamic curves) we need to read characteristic electrochemical parameters:

$i_{kryt}$  - critical passivation current,  $i_p$  - passivation current,

$E_c$ ,  $E_p$ ,  $E_b$ ,  $E_r$  – potentials of: corrosion, passivation, breakthrough, repassivation,

$(E_b - E_c)$  – area of passivity.

Measured value	material .....	material .....	material .....
$i_{kryt} \text{ [mA/cm}^2\text{]}$			
$i_p \text{ [mA/cm}^2\text{]}$			
$E_b \text{ [mV}_{NEK}\text{]}$			
$E_r \text{ [mV}_{NEK}\text{]}$			
$E_p \text{ [mV}_{NEK}\text{]}$			
$E_c \text{ [mV}_{NEK}\text{]}$			
$E_b - E_c \text{ [mV]}$			

*Caution:* Sometimes the obtained curves have different shape than typical

Alloys with high corrosion resistance, which are easily self-passivated in the given environment, do not exhibit the temporary increase in current density  $i_{kryt}$ , which causes the passivation. Passivation occurs immediately after crossing the corrosion potential  $E_c$ .

- Analysis of the test results and conclusions concerning the relations between structural construction and properties of the materials (corrosion resistance).

## 4. TESTING OF THE SELECTED CORROSION PROCESS – TESTING IN THE CORROSION CHAMBER

### 4.1 Purpose of the exercise:

Testing issues of the corrosion processes. Determination of the degree of material's resistance to corrosion in the given environment. Determination of environments where the given material can be used. Comparative tests concerning the resistance of various metal materials to corrosion.

### 4.2 Significant control questions:

- What is corrosion,
- Types of corrosions,
- Testing method of corrosion resistance,
- Accelerated laboratory tests,
- Methods for assessing the degree of corrosion.

### 4.3 Supplementary literature:

1. Baszkiewicz J., Kamiński M.: Podstawy korozji materiałów, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa 1997
2. Surowska B.: Wybrane zagadnienia z korozji i ochrony przed korozją, Wyd. PL, Lublin 2002
3. Wranglen G.: Podstawy korozji i ochrony metali. WNT, Warszawa, 1985
4. Żurek Z.: Materiał i środowisko, Wyd. Pol. Krakowskiej Kraków 1998

### 4.4 Course of the exercise:

#### Materials and equipment for testing

- Set of metal elements (materials), materials with applied protective coatings – designed for testing in corrosion chamber.
- Corrosion chamber.
- User manual for the corrosion chamber.

### 4.5 Course of the testing

Before starting the exercise, every student must learn about recommendations of health and safety instruction. Course lecturer checks the knowledge of information provided in health and safety instructions, as well as the knowledge of research issues. Upon acceptance to carry out the exercise, a student must perform the following actions:

- Prepare the materials designed for testing in corrosion chamber (check state of the material, determine sample dimensions, carry out the measurements of sample weight),



- Prepare the corrosion solution (5% NaCl),
- Place the samples in holders (in corrosion chamber),
- Set the test parameters (humidity, temperature and duration of the test),
- After the test completion, conduct the inspection of individual samples, carry out the photographic documentation.
- Clean the surface of the samples,
- Measure the weight of individual samples.

#### **4.6 Development of test results and reports**

- Purpose of the tests, subject of the tests.
- Brief characteristic of the tested materials.
- Method of sample preparation, applied corrosive environment, etc.
- Table summarization of the samples dimensions, weight of the samples before and after tests.
- Photographic or schematic representation of corrosive changes on the surface of the tested materials.
- Determination of the corrosion degree of materials.
- Analysis of the tests results and conclusions concerning relations between type of the materials, method of surface modification and corrosion resistance.