THE CHARACTERIZATION OF IONITRIDED LAYERS FROM THE POINT OF VIEW OF CORROSION MECHANISMS

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Abstract
The researches and experiments for the characterization of ionitrided layers from the point of view of corrosion mechanisms have passed three stages: the determination of potential curves based on the value of parameters measured in a galvanic pile, the drawing of Edeleanu-Evans charts for the tested steels and solutions and the interpretation on potential curves and of the Edeleanu-Evans charts in correlation with the structure of layers obtained by ionitriding.

The experiments have been carried out on steels micro-alloyed with boron and titanium and on steels used in nuclear power plants, subjected initially to ionitriding.

For the determination of the electromotive force (the only value which can be determined experimentally) and for the drawing of the potential curves, there was used an installation with a universal polarograph OH-15 and the corrosion speed was determined through the electrolytic method. Simultaneously, following parameters have been measured: applied potential, current intensity and anodic potential.

The Edeleanu-Evans charts offer information on the nature, thermodynamics and kinetics of corrosion processes and are obtained by representing the potential curves in the coordinates anodic potential – lg i. The kinetic corrosion parameters have been calculated: current density ($i_{cor}$), corrosion speed ($k_g$) and the penetration index ($P_{min}$).

1. THEORETICAL CONSIDERATIONS
Metals corrode in the working space as result of oxidation and reduction reactions. The oxidation reaction is also called the anode reaction and the reduction reaction is called the cathode reaction. These two reactions are complementary. The rate of these reactions depends on the electrode potential.

A metal, in contact with an aggressive medium, has the role of an electrode with two kinds of reactions. These two reactions act in an alternative manner.

Every electrochemical reaction is characterized by an equilibrium electrochemical potential ($\varepsilon$). For the oxidation reactions and the reduction reactions the electrochemical potentials can be written [3]:

\[
\varepsilon_1 = \varepsilon_1^0 + \frac{RT}{nF} \log[M^{n+}]
\]
(1)

\[
\varepsilon_2 = \varepsilon_2^0 + \frac{RT}{pF} \log \frac{O_{1/2}}{R_{ed}}
\]
(2)

where: $\varepsilon_1^0$ and $\varepsilon_2^0$ - the standard potentials of oxidation and reduction reactions;

R – the perfect gas constant;

T – the medium’s temperature, [°K];

F – Faraday’s constant;

n – the valence of metallic ion;
The activity of metallic ions into the solution; 
the oxidant form of a constituent into the solution; 
the reduced form of the same constituent into the solution; 
the number of electrons needed for the reduction of the oxidant agent.

According to the electrochemical theory, the corrosion exists if \( \varepsilon_2 > \varepsilon_1 \), which means that into the solution exists a reduction system that has an equilibrium potential higher than the equilibrium potential of metal’s solubilization process. In this case the metal-solution potential is established to a value between the two equilibrium potentials and it represents the corrosion potential of the metal into the considered solution.

The polarization represents the displacement of the equilibrium potential to a new value under the influence of the electric current produced by the electrochemical reactions of electrode. The polarization decreases the corrosion process because the corrosion speed highly decreases. After an attack period, thin layers of pure metal appear on the material’s surface with a protection role.

To predict the corrosion behavior of a metallic material the polarization curve tracing is necessary by using a reference electrode and measuring the electromotive power of a galvanic cell with two electrodes: the reference electrode and the studied material electrode.

The metal’s potential, measured in relation with the reference electrode, will vary as a function of applied current. If it doesn’t change the electrolyte’s composition or the surface condition, the value of the electromotive power is calculated with the formula (Tafel’s law):

\[
E = m + n \log i \quad (3)
\]

By progressive variation of the applied potential, the kinetically potential curve can be sketched.

2. THE DETERMINATION AND THE INTERPRETATION OF POTENTIAL CURVES.

2.1. The equipment and the measuring conditions.

To determine the electromotive power (the only industrial measurable parameter) and to trace the potential curves it was used a specific installation using the following components:

- universal polarograph OH-105 with the reference potential of -4V and the starting potential of 1,6V; 
- electronic digital voltmeter RFT DC-AC-R which allow the measurement of the anodic potential; 
- reference electrode of calomel (mercury/mercuric chloride). 
- electrolytes : NaCl aqueous solution with 3% concentration and H₂SO₄ aqueous solution with 10% concentration at 22°C temperature; 
- the experimented steels were:
  - micro alloyed steel with bohr and titan (0,41%C; 0,13%Mn; 0,04%Cr; 0,04%Ni, 0,04%Ti; 0,03%B) thermo-chemically treated by ionic nitriding at 520°C temperature for 10 hours;
  - A541 steel 6th class (0,30%C; 0,54%Mn; 0,22%Si; 2,33%Cr, 0,36%Ni; 0,97%Mo) thermo-chemically treated by ionic nitriding at 520°C temperature for 10 hours and used to build coupling flange for fittings for the nuclear power plants;

The following parameters have been measured:

- applied potential, [V];
- intensity of the current, [mA];
- anodic potential, [V].
2.2. Trace and interpretation of kinetic potential curves.

The condition for the solution/metal interface to be in electrochemical equilibrium is the equalization of the partial anode current with the partial cathode current, also an exterior current or a net current equal with zero (null).

For every type of steel and electrolyte it were measured and recorded: the values of the potential applied to the galvanic cell, the intensity of the current and the anode potential and calculated the densities of the current (reported to the material surface).

With these values, it was sketched the kinetic potential curves of the micro alloyed steel in a 3% NaCl solution (fig. 1) which allow the interpretation of the behavior at corrosion of the steel as follows:

- the increase the of the applied potential lead to an increase of the intensity of the anode current (\(I\)), low at the beginning, then increasing with high rates (while de anode potential is positive), followed by an interval where the current (\(I\)) is constant, as a consequence to the forming of some salt layers on the surface (\(I_{\text{max}} = 0.98\ \text{mA}, \ i_{\text{cor}} = 0.032\ \text{mA/cm}^2\)).
- the increase of the applied potential over this critic value induce an abrupt decrease of the intensity of the electric current, resulting a passive steel;
- the passive steel continue to dissolve at a low rate, at a negative anodic potential, but the salt layers did not breakdown, which means the passivity remains.

The kinetic potential curve of the same steel into a 10% H\(_2\)SO\(_4\) solution (fig. 2) shows the following characteristics:

- the increase of the applied potential associated with the slow increase, but continuous, of the anodic potential values and the intensities of the current until the \(I_{\text{max}} = 38.6\ \text{mA}\) value is reached, with the corresponding intensity of current \(i_{\text{cor}} = 12.2\ \text{mA/cm}^2\);
- a decrease of the current intensity follows, which means the steel become passive.
- the sample remains passive at the continue increasing of the applied potential (\(I = \text{constant}\)).

It could be establish that the current density value (\(i_{\text{cor}}\)) necessary to obtain the passive steel is 380 x higher rates during the acid solution determination.

![Figure 1. Polarization curve of micro-alloyed steel in a 3% NaCl solution.](image-url)
The recorded parameters for the A541 steel into the galvanic cell allow the trace of the potential curves (fig. 3 and fig. 4), which leads to the following results:

- into the 3% NaCl solution, the increase of the applied potential is associated, at the beginning, with a low increase of intensity of the current up to the 0 (zero) value, maintaining the constant value in the interval [+0.9 ... -0.6V], followed by a quick increase of the current intensity up to the value $I_{\text{max}} = 1.22$ mA ($i_{\text{corr}} = 0.04$ mA/cm$^2$).
- next, an abrupt decrease of current intensity appear, to the zero value, leading to the passive steel;
- the specific potential curve for the 10% H$_2$SO$_4$ solution shows a continuous depolarization on the anode side and a continuous polarization on the cathode side, that indicates a very good stability of the A541 steel treated with ionic nitriding into the acid solutions.
2.3. The determination and interpretation of Edeleanu-Evans diagrams.
The Edeleanu-Evans diagrams show the nature, the thermodynamics and kinetics of corrosion process and it can be raised by tracing the potential curves into the anodic potential – logarithmic (lg i) coordinates. Based on these diagrams, considering the Tafel regime, it was computed the kinetic parameters of the corrosion process: current density (i_{corr}), the corrosion rate (k_e), penetration coefficient (P_{min}) and the transfer coefficient (α).

For the micro-alloyed steel with boron and titan, the Edeleanu-Evans diagram, using the 3% NaCl solution as an electrolyte (fig. 5), shows the control of the process by the oxidation and reduction processes in equal proportions and using the 10% H_2SO_4 solution, the Edeleanu-Evans diagram (fig. 6) shows a complex control of the corrosion processes.
Figure 6. Edeleanu-Evans diagram for the micro-alloyed steel (10% H₂SO₄ solution).
In the table 1. the kinetic parameters of the corrosion process are systematized as follows:

Table 1. The kinetic parameters of the corrosion of the microalloyed steel.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(i_{\text{cor}}) [mA/cm²]</th>
<th>(K_g) [g/m²·h]</th>
<th>(P_{\text{min}}) [mm/year]</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% NaCl</td>
<td>0,032</td>
<td>0,042</td>
<td>0,047</td>
<td>0,512</td>
</tr>
<tr>
<td>10% H₂SO₄</td>
<td>12,219</td>
<td>1,543</td>
<td>0,175</td>
<td>6,244</td>
</tr>
</tbody>
</table>

For the A541 steel, the 6th class, the Edeleanu-Evans diagram for the 3% NaCl solution (fig. 7) shows a very weak cathode polarization of the sample’s surface and for the 10% H₂SO₄ solution of electrolyte, the Edeleanu-Evans diagram (fig. 8) shows that the corrosion process have a complex control, both, anode and cathode processes.

The main kinetic parameters of the corrosion process reactions for the A541 steel are showed into the table 2.

Table 2. The kinetic parameters of the corrosion of the A541 steel.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(i_{\text{cor}}) [mA/cm²]</th>
<th>(K_g) [g/m²·h]</th>
<th>(P_{\text{min}}) [mm/year]</th>
<th>(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% NaCl</td>
<td>0,041</td>
<td>0,055</td>
<td>0,067</td>
<td>0,895</td>
</tr>
<tr>
<td>10% H₂SO₄</td>
<td>0,194</td>
<td>0,549</td>
<td>0,583</td>
<td>1,023</td>
</tr>
</tbody>
</table>
Figure 7. Edeleanu-Evans diagram for the A541 steel (3% NaCl solution)

Figure 8. Edeleanu-Evans diagram for the A541 steel (10% H₂SO₄ solution)


The study of the potential curves and the Edeleanu-Evans diagrams presented allows establishing the correlations between the electrochemical corrosion behaviors and the plasma nitriding layer structure obtained and the conclusions:

- The micro alloyed steel, after the ionic nitriding process, shows a layer formed by the combination zone (a sub-layer), which contain the $\gamma$ nitride (Fe$_4$N) and the $\varepsilon$ nitride (Fe$_{2.3}$N), in massive quantities fine dispersed and from the diffusion zone ($\alpha$ nitro ferrite).
- Into the 3% NaCl solution the steel become passive for the low values of the current density ($i_{\text{cor}} = 0.032 \text{ mA/cm}^2$), because of the presence of the combination zone ($\gamma' + \epsilon$) but also the non-aggressivity of the corrosion medium. The Edeleanu-Evans diagram proves de corrosion stability of the nitriding layer by reactions with equal rates for both anode and cathode electrodes.

- Into the 10% H$_2$SO$_4$ solution, with a more aggressive corrosion process, the passive steel come at higher values of the current density ($i_{\text{cor}} = 12.2 \text{ mA/cm}^2$) and for a positive anode potential.

- The A541 steel shows into the nitriding layer, composed by the combination zone ($\gamma' + \epsilon$) and the diffusion zone ($\alpha$), small quantities of chrome carbides and nitrides.

- Into the 3% NaCl solution the steel shows and excellent stability at corrosion process ($i_{\text{cor}} = 0.04 \text{ mA/cm}^2$) and the Edeleanu-Evans diagram shows a complex control of the both anode and cathode processes.

- The 10% H$_2$SO$_4$ solution produce a continuous corrosion of the samples with low rates until current density have large values ($i_{\text{cor}} = 0.194 \text{ mA/cm}^2$), then the steel become passive. The passive process is caused by the $\epsilon$ phase is present into the exterior zone of the ionic nitriding layer.

**BIBLIOGRAPHY**

