Corrosive effect of sea water on the superficial layers obtained by electrical sparking

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Abstract: - The experimental research was made on superficial layers laid-down through electrical sparking on the steel carbon OLC 45 samples, the used electrode being made from corrosion resistant material (Aluminum and Copper). The corrosion speed was determinate through gravimetrical method and the polarization curves method. The superficial layers subjected to corrosion were analyzed by the use of an atomic force microscope.

Key-Words: - corrosion, superficial layers, electrical discharge, aluminum, copper

1 Introduction
The superficial treatment through impulse electrical discharges is a procedure through which the proprieties of the metallic materials can be improved. Process consist in discharges (short period) and the erosion of the cathode takes place a transfer of erosion products on the treated surface.
The proprieties of the superficial layers obtained through this procedure are the same as the electrodes material being used or very close to this one, the properties resulting from micro alloying and the diffusion of the electrode material in the sample of steel [3].

2 Problem Formulation
The experiments where done for the superficial treatment through impulse electrical discharges, made with the ELITRON 22A equipment, using Al and Cu electrodes of some parallelepiped samples with the surfaces of 0,00127512 m², from steel carbon OLC 45 brand, the probes plane surfaces where previously prepared. Preparing the surfaces presumes a thorough treatment and degrease with a powerful solvent.
The treatment through electrical discharges where made manually, the active electrode is under a 60° angle with the treated surface.
When making treatment with electrical discharges, a significant importance in the formation of the superficial layer and the quality, has the electrode section surface, influence that will be manifested at the working regime temperature variation and at the current density which passes through the electrode.
In the experiments wasn’t specified the electrode vibration amplitude value because this does not influence neither the layer thickness, or the structure, the only importance is to be big enough to prevent the solder of the electrode with the surface which will be treated. In table 1 are presented the recommended values for the electrode cross section in regard to the work regime of the ELITRON – 22A equipment and the current value at every regime.

<table>
<thead>
<tr>
<th>Electric work regime</th>
<th>Electrode cross section value [mm]</th>
<th>Work current [A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ELITRON – 22A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.8</td>
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<tr>
<td>3</td>
<td>4÷6</td>
<td>1.3</td>
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<td>4</td>
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<td>1.8</td>
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<tr>
<td>5</td>
<td>6÷9</td>
<td>2.3</td>
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</tbody>
</table>

Through the corrosion research process using the gravimetrical method, the parallelepiped samples superficial treated with electrical sparking, with the surface of 0,00127512 m² where suspended with an synthetic line (nylon) of \(\phi = 0.2\, mm\) in a plastic material tub at 4 cm above the tubes liquid level (sea water), being immersed 285 days in static see water at the environments temperature [2].
The samples on which the superficial treatment was made through impulse electrical discharges where individually weighted on the analytic balance at different time intervals, determining the corrosion process speed.
For the corrosion testing through the electrochemical method, the steel carbon samples, OLC 45 brand with Al and Cu electrodes sparking, at three work regimes of the ELITRON 22A equipment:R1 – 0.5 A, R2 – 1.3 A
and R3 – 2.3 A, where inserted in a raylon holder so that they can be mounted to the electrode equipment. The corrosion potential and marking the polarization curves (linear and cyclic) [2] was determined with an advanced electrochemical system type VOLTALAB 32. The acquisition and processing of experimental data was made with the help of the specialized software VOLTMASTER 2. The samples subjected at electrochemical corrosion have the circular plane surface, cylinder shape from steel carbon OLC 45, the probes plane surfaces where previously prepared. Preparing the surfaces presumes a thorough treatment and degrease with a powerful solvent. The fine determining of the topography surfaces exposed to the action of the corrosive environment was made using the atomic force microscope (AFM) [1].

3 Experimental research
The speed corrosion variation results from immersed samples in sea water (285 days), is presented in figure 1 and figure 2.

[Graphs showing corrosion rate for OLC 45 sparking with Al and Cu electrodes]

The samples from OLC 45 carbon steel sparking with Al and Cu electrodes are corrosion resistant, having the estimated scale of 4 (according to STAS 9684-82), the corrosion speed between 0.21 – 1.0 g/(m².day) in comparison to the steel used as original probe which has the estimated scale 5, and the corrosion speed between 1.0 – 2.1 g/(m².day) [4]. In the first stages of corrosion (0-30 days) corrosion rate increases rapidly and corrosion test results in the short term are inconclusive for the long term corrosion. On the superficial layers subjected to see water, initially you can observe a progressive increase of the corrosion speed, because of the oxygen absorption. After the effect of microorganism, the corrosion drops to an almost stationary value. This is because of the fact that microorganisms eliminate oxygen from the surfaces, but a anaerobic corrosion still persists. The corrosion potential was determined using the Evans diagram: \( E = f(\log I) \) (figures 3, 4).

[Graphs showing linear polarization curves for Aluminum and Copper sparking probes]

Fig. 3. Linear polarization curves for the Aluminum sparking probes

Fig. 4. Linear polarization curves for the copper sparking probes
The support but also the sparking probes, present the same type of corrosion; a general corrosion, which in the initial moments is represented by the appearance of corrosion dots.

With the quality of the Cu sparking OLC 45 probes there can be accentuated the same conclusions as in the case of the open circuit potential: the copper has a good protection, also taken into account the way of the sparking regime influence the protection; the copper residue is better in the R1 and R2 regime (at low currents);

The corrosion process analysis was made also based on the cyclic polarization curves (figures 5, 6).

![Fig. 5. The cyclic polarization curves for the support probe and for the probes covered with Aluminum at different sparking regimes (R1 - 0,5 A ; R2 –1,3 A ; R3 – 2,3 A)](image)

With the majority of the sparking probes the cathode branch is slightly moved forward compared to the anode branch, but it is still linear. This movement can be because of the fact that the scanning speed of the electrodes potential is relatively big (20 mV/s) and the presence of the metal on the surface induces a certain inertia.

Linear dependency current-voltage and the absence of some passivity bearing or some corrosion characteristic curves through the points indicate the fact that in the sparking probes the material, which suffers the corrosion process is also the iron in the supports. This is a certain proof that the covering the support with sparking material it is not perfect, the reduced corrosion speed is probably because of the reduced free surface of the support.

The “wave-mode” from the AFM microscope on the probes superficial treated with the Al and Cu electrode present the surface relief through color tone. The light color zones are the highest ones.

![Fig. 6. The cyclic polarization curves for the support probe and for the probes covered with Copper at different sparking regimes (R1 - 0,5 A ; R2 –1,3 A ; R3 – 2,3 A)](image)

![Fig. 7. Superficial treated sample with Al electrode "wave mode" image – 2d on an scanned area of 20x20 µm](image)

![Fig. 8. Superficial treated sample with Al electrode-"wave mode" image – 2d on an scanned area of 10x10 µm](image)

The extension of the observation area on the scanned...
surface of 10 \( \mu \text{m}^2 \) and presented in three dimension as in the figure 4, emphasizes the appearance of some dark color zones which denote the discontinuity of the laid layer. These areas represent a possible way in of the corrosive agent to the sample material. The presented images are not in accordance with the thickness of the residue layer. The 2.631 \( \mu \text{m} \) dimension refers to the distance between the lowest area of the layer and the highest one.

Images presented evidence of good behavior by a layer against corrosive environment which ultimately leads to a very good corrosion protection of the sample OLC 45. AFM investigations on samples sparking with Copper electrode (figures 9 and 10) show that layer on the sample surface is not uniform presenting discontinuities allowing corrosive environment to attack the substrate material.

Fig. 9. Superficial treated sample with Cu electrode “wave mode” image – 2d on an scanned area of 10x10 \( \mu \text{m} \)

Fig. 10. Superficial treated sample with Cu electrode - "wave mode" image – 3d on the same scanned area

4 Conclusion
The uniformity and thickness of the deposition layer are harder to control in manual deposition, and this has a large influence on the behavior of the corrosion layers.

Measuring the open circuit potential it can note that copper electrode sparking of the OLC 45 steel, regardless of the working regime, leads to an improvement of material quality in comparison with the corrosion thermodynamic probability.

The carbon steel probes of OLC 45 brand sparked with copper electrode show a generalized corrosion, which in the initial stages is represented by the appearance of some corrosion dots.

The cyclic voltamograms obtained, in the case of the OLC 45 support and the sparking probes are typical for the generalized corrosion (uniform corrosion on the entire surface). This aspect is more evident for the steel supports, for which the cathode branch (return) is overlapped over the anode branch (positive polarization);

From the cyclic polarization curves can be observed that in the sparking probes, the material is subjected to the corrosion process, is all the iron in the supports, this certifies that the deposition electric sparking process is not uniform.

The superficial layers laid through Al and Cu electrodes sparking proves a improved corrosion resistance to see water compared to the base steel, specially for long term tries, when the corrosion speed is stabilizing remaining almost constant.

Throughout the interval studied, the stability is preserved, the less stable is steel coated with the Cu electrode.

The investigations, through atomic force microcopy, made on the probes tested for long term corrosion, emphasize the conclusion that the samples have compact and homogenous surfaces areas which had not permitted the corrosive agent to interact with the base material.

The wave-mode images present the discontinuities of the superficial laid layers which represent a possible way in for the corrosive agent to the probes material.

References: