Changing the surface properties on naval steel as result of non-thermal plasma treatment

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Abstract. The problem of corrosion, related to Biofouling formation, is an issue with very high importance in the maritime domain. According to new rules, the paints and all the technologies for the conditioning of naval materials must fulfil more restrictive environmental conditions. In order to solve this issue, different new clean technologies have been proposed. Among them, the use of non-thermal plasmas produced at atmospheric pressure plays a very important role. This study concerns the opportunity of plasma treatment for preparation or conditioning of naval steel OL36 type.

The plasma reactors chosen for the experiments can operate at atmospheric pressure and are easy to use in industrial conditions. They are based on electrical discharges GlidArc and Spark, which already proved their efficiency for the surface activation or even for coatings of the surface. The non-thermal character of the plasma is ensured by a gas flow blown through the electrical discharges. One power supply has been used for reactors that provide a 5 kV voltage and a maximum current of 100 mA. The modifications of the surface properties and composition have been studied by XPS technique (X-ray Photoelectron Spectroscopy).

Differences were found between atomic concentrations in each individual case, which proves that the active species produced by each type of plasma affects the surface properties of the treated naval steel.

1. Introduction

Corrosion is a major issue for the maritime domain. The most important parameter of the corrosion phenomenon is the Biofouling process. This process takes place in 4 steps and in order to limit, to delay or to prevent it, one intervention must be applied since early phase of its formation. The main protection factors of the naval steel are the primer and the paint covering the naval steel surface. Because of new rules protecting the environment imposed by IMO, new methods must be taken into
consideration, as addition to chemical properties of the paints. One possible solution concerns the use of the non-thermal plasmas that have already proved their efficiency for decontamination applications or for conditioning of surfaces in order to apply subsequent treatments, [1], [2]. For the second case, a plasma treatment of naval steel before any other operation could signify a more homogeneous distribution of marine paint applied later, or a surface conditioning for applying a special sol-gel instead of the paint, [3]. This work aims to study the modifications of the surface of naval steel samples, because of the plasma treatment. There have been chosen for the treatment three types of electrical discharges producing non-thermal plasma at atmospheric pressure. The first one is a Gliding Spark, the second one is a GlidArc and the third one is a special type of GlidArc, called Mini-torch plasma. All three types of electrical discharges are well known for the production of the electrochemical active species, very effective at the interface between the plasma and the target to be treated, [4], [5]. These properties are ensured by geometry of the plasma reactors, by the parameters of the power supply (high voltage, low electrical current) and by a gas flow.

The samples treated by non-thermal plasma have been analysed with a special spectroscopic method, called XPS, indicating the atomic concentration of the elements as carbon, oxygen, iron, chromium, silicon, on a shallow depth of the sample.

2. Experimental Setup

The power supply used for all types of the electrical discharges producing the plasma treatment has the voltage of 5 kV and the electrical current of maximum 100 mA. A flow of gas ensures the character of non-thermal plasma and its value was 65 l/min. The treatment time was chosen to 12 minutes because active species from the discharge have maximum impact after about 8 minutes. The distance between the top of the electrodes and the metal samples was chosen of 2 cm in the case of GlidArc and Mini-torch Plasma, respectively of 0.5 cm in the case of the Gliding Spark.

The treated samples are made of naval steel. Their square section has the side of 1 cm and their length was about 2 cm. Before the plasma treatment, one side of each sample was sanded with a vibration machine using sandpaper with different granulation. The last had the finest granulation of P800 and this operation was performed until obtain the metal gloss.

The first type of plasma reactor, called Mini-torch GlidArc is composed by a closed cylindrical chamber, equipped with a nozzle on the exit. The nozzle has a diameter of 3 mm. The flow of air is introduced through a side opening and is pushed towards the nozzle through a sieve. The first electrode is placed along the symmetry axis of the cylinder, having a sharp shape at its end. The second electrode is connected to the nozzle. In figure 1 it is shown a photo while the reactor is operating.

![Figure 1. Mini-torch GlidArc reactor.](image)

The second type of plasma reactor is based on a Gliding Spark. It was obtained by cutting the mass electrode of a classical spark plug electrode until the edge of the thread and placing it in a special enclosure. The enclosure has a thread for the spark plug on the bottom side, 2 windows on the opposite
sides and 2 gas fittings on the other 2 opposite sides. One of the gas fittings is used as input and the air is forced to pass through the electrodes before to be evacuated. In such way the electrochemical species are produced and right away evacuated from the reactor. They are used to treat certain targets placed at the gas output. A photo of the electrical discharges obtained with this reactor is shown in figure 2.

![Photo of a Gliding Spark.](image)

Figure 2. Photo of a Gliding Spark.

The last type of plasma reactor is based on GlidArc, see figure 3. The high voltage of the power supply is applied between two electrodes having divergent shape. Where the distance between electrodes is the shortest, an electric discharge is started, according to the Paschen law. Because of the air flow the discharge is elongated along the electrodes.

![Photo of a Gliding Spark.](image)

Figure 3. Photo of a Gliding Spark.

This discharge is maintained as long as the power supply provides enough energy in order to maintain a threshold value of the specific energy (energy on unit volume). The length of the discharge continues to increase because of the air flow and when the threshold energy is overcome, the discharge is extinguished. At the same moment at the shortest distance between the electrodes, all the conditions
are accomplished to start a new discharge and the cycle of the discharge is repeated. Because of the limited current provided by the power supply and of the air flow, the produced plasma is a non-thermal one. The easy active particles as electrons, photons etc. have a very important energy, but the other heavy physical species have low energies, so they remain almost at ambient temperature, [6].

The XPS technique used for analysis of the treated samples relays on exciting photoelectron emission using an X-rays beam and measuring the energy and number of the electrons escaping the sample surface.

In our experiments, done on a ULVAC-PHI, Inc. PHI 5000 Versa Probe scanning XPS microprobe, a monocromated Al Kα X-ray source \((hν = 1486.7 \text{ eV})\) with a spot size of 100 \(\mu\text{m}^2\) was used to scan each sample while the photoelectrons were collected at a 45-degree take-off angle. The calibration was made using the carbon C 1s XPS peak at 284.6 eV as reference. The peaks deconvolution has been done by the means of PHI MultiPak 8.2 C software that analyzes peak areas to find the atomic concentration on the surface.

3. Experimental results

The purpose of this work is to investigate the influence of non-thermal plasma treatments presented above on the properties of naval steel surface.

For our investigation were used specimens with low carbon percentage, having ferrite grain structure obtained after hot rolled annealing process. The superficial structure of the witness sample is shown in figure 4.

![Figure 4. Witness specimen A36.](image)

X-ray photoelectron spectroscopy is a powerful concept to identify different chemical states of compounds in depth profiles, important for obtaining information underneath surfaces or at layer interfaces. We are getting several spectrum surveys for each specimen corresponded to each non-thermal plasma treatment. A survey is one spectrum acquired from a quick, high-sensitivity scan of a wide energy range (for us we applied 117.40 eV) to survey the elements presented over an area.
XPS survey spectrum of naval steel surface shows that the dominant signals are from Cr, Fe, C and O. Elemental surface composition analysis for witness specimen indicates that C content is about 65 at.%, O 25.3 at.%, Fe 8.7 at.% and Cr 1 at.% as listed in figure 4 and table 1.

| Samples/Treatments      | Cr at% | Fe at% | O at%  | C at% |
|-------------------------|--------|--------|--------|-------|
| Witness A36 steel       | 1      | 8.7    | 25.3   | 65    |
| Mini-torch              | 4.2    | 8.9    | 35.8   | 51.1  |
| Gliding Spark           | <.1    | 1.7    | 6.8    | 89.5  |
| GD with dry air         | 0.9    | 18.2   | 38.6   | 42.3  |
| GD with CO₂             | 1.7    | 5.2    | 29.1   | 49.3  |

We were expecting that the amount of carbon and oxygen decreases significantly with depth. It is possible that the reaction with residual gases in the spectrometer chamber or the ionic transport causes the remained oxygen contents in the first layer of surface. Both Cr and Fe contents increase significantly with depth for three types of plasma treatment, as indicated in other references, [7].

The surface is exposed to the plasma ambient, oxygen and carbon are quickly adsorbed on the surface because iron has a high affinity for oxygen and carbon. The plasma treatments performed by torch with GlidArc, GlidArc (GD) with dry air and GD with CO₂ (figure 5, figure 7, figure 8) increase the oxygen surface content despite of Gliding Spark method (see figure 6).

Similarly the plasma treatments produced by torch with GlidArc, GlidArc with dry air and GlidArc with CO₂ (figure 5, figure 7, figure 8) decrease the carbon surface content despite of Gliding Spark treatment (figure 6).

For all verified spectrums the Cr% and Fe% peak become very weak (<.1 for Cr% at Gliding Spark treatment). This indicates that the outermost layer of naval steel surface is chromium oxides, iron oxides and carbon contamination layer.

In reference [8] it is shown that the potential modification of chemical state of expected corrosion products call for a systematic investigation. For an exact understanding it is mandatory to examine at first the stability of pure reference materials in order to be able to reliably evaluate the composition of real samples with industrial background.

In the case of the chosen non-thermal plasma corrosion protection treatments, an insufficient number of studies was conducted to date for the relevant reference compounds comprising Cr₂O₃-Cr(III) oxide, CrO₂-Cr(VI) oxide, FeO-Fe(II) oxide, Fe₂O₃-Fe(III) oxide, and Fe₃O₄-Fe(II III) oxide. A corrosion product, chromium (III) oxide may be found on the surface. In figure 9, a Cr (III) sample spectra in shown, proposed by [8].
Figure 5. Torch with GlidArc.

Figure 6. Gliding Spark.
Figure 7. GlidArc with dry air.

Figure 8. GlidArc with CO₂.
The sharp structure directly located on the right side of the Cr2p3/2 peak at the surface level is related to a multiplet splitting due to the fact that Cr₂O₃ has unpaired electrons [9], also causing the asymmetric shape on the left side of the peak (figure 10a). In the spectra of Cr3s also a multiplet splitting can be observed (figure 10b). Since only Cr (III) - out of the possible oxidation states of Cr - shows a really pronounced multiplet splitting, these features are a reliable proof for the presence of the correct reference material. This type of spectrum profile with Cr2p3/2 peak and (570-592 eV) binding energy interval we can find for Torch with GlidArc treatment with maximum (Cr%=4.2) surface chromium composition shown in figure 5.

![Figure 9](image_url)

**Figure 9.** XPS depth profiling of Cr (III) oxide, with high resolution scans of the (a) Cr2p and (b) Cr3s levels [8].

If the corrosion process is well defined, the metallic iron at the interface starts to oxidize and form corrosion products, which are also necessary to be taken into account. In reference [8] Fe (II), Fe (III) and also Fe (II, III) oxides were investigated with the spectra of the Fe2p photoelectron level, where the 2p1/2 and 2p3/2 peaks as well as correspond for all spectrums except for Gliding Spark treatment with minimum (Fe%=1.7) surface iron composition, shown in figure 6.

### 4. Conclusions
The analysis X-ray photoelectron spectroscopy has detected the major elements on the surface (carbon, oxygen, chromium, iron) in high energy resolution mode to determine their binding energies and then to make some inferences about the compounds present on the surface. This measurement determines the relative amounts of metals versus oxides for chromium and iron.

High C% and O% are typical on steels exposed to the Mini-Torch with GlidArc (O%=35.8, C%=51.1), GlidArc with dry air (O%=38.6, C%=42.3) and GlidArc with CO₂ (O%=29.1, C%=49.3).

High content of chromium on specimen exposed to the Torch with GlidArc (Cr%=4.2) rises a lot of questions; from where did Cr% come on surface? If we are expected that Cr% is coming from electrodes, we can assume a real superficial thin layer of chromium enrichment which gives an increased corrosion resistance.

The investigation of non-thermal plasma influence on the naval steel surface presented above is not achieved and for the next experimental research it will be taken into account the depth profiling experiments.
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