Corrosion protection of 1020 steel by conducting films electrodeposited in methanesulfonic acid

DOI: 10.30609/JETI.2018-1.5303

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Abstract

1020 steel is widely used in the industrial sector, however it is a reactive metal and susceptible to corrosion, being necessary to use surface coatings to protect the metal in corrosive media. The polyaniline and polypyrrole are conducting polymers that have the ability to inhibit corrosion when deposited in organic media. In this work, corrosion protection was investigated through polyaniline and polypyrrole films electrodeposited in methanesulfonic acid medium. The films were electrodeposited by chronoamperometry and the corrosion tests were performed by potentiodynamic polarization in aggressive sodium chloride medium. The surface of the films was analyzed by scanning electron microscopy. From the polarization it was observed that the polypyrrole film, in relation to the polyaniline film, showed better performance against corrosion. The MEV indicated that the polypyrrole film is homogeneous and adherent, while the polyaniline film showed flaws, allowing the interaction of the metal with the corrosive medium.

Keywords: Polypyrrole, Polyaniline, Steel, Methanesulfonic acid
1- Introduction

Steel is a metal widely used in the industrial sector, mainly made up of iron and carbon. The mechanical properties of the steel differ in the extent to which the carbon content varies, ranging from 0.2% to 1.8% in its composition. Currently 1020 steel is one of the most used materials due to its low temperability, excellent forging, low cost, ductility and higher tensile stress [1]. This metal presents numerous applications, such as the manufacture of screws, fasteners, shafts and gears, these components is important in the safe operation of a machine [2]. As other metals, steel is susceptible to the effects of corrosion, which leads to a decrease in service life and possible mechanical failure in the set where it is inserted.

The corrosion protection of the steel is performed by different surface treatments, primarily the phosphatization and the chromatization. The basic compositions of phosphatizing solutions require catalysts using heavy metals as nickel (Ni) and copper (Cu) in their composition and moreover, contains phosphorus based compounds, which cause eutrophication of water resources when discarded in an inadequate form. The compounds based on hexavalent chromium are toxic and carcinogenic. Research groups seek an alternative to the phosphating processes and the use of Cr$^{6+}$, presenting as substitutes the conducting polymers [3]. Conductive polymers, such as polypyrrole (PPy) and polyaniline (PAni), have a wide range of applications in their doped or partially oxidized state, and present interesting results in the corrosion protection effect of steel [4]. These polymers are electrically conductive and may be called active coatings, as chemical or electrochemical interactions may occur with active metals [5].

The synthesis of PPy and PAni films can be performed chemically or electrochemically, in aqueous or organic media. PPy films are advantageous because have good mechanical properties, low roughness, flexibility and low production cost. Besides these properties, the PPy stands out for its chemical stability and high electrical conductivity, when doped. All these characteristics associated to the atoxicity make these polymers advantageous to act in protection corrosion of oxidizable metals, as 1020 steel [6].
Both the direct electrochemical polymerization of pyrrole and the aniline in steel electrodes has been reported as complicated due to the oxidation of the metal, which can occur simultaneously with the oxidation of the monomer and can inhibit the growth of the polymer or reduce the adhesion of the polymers to the metal [7]. In this electrochemical process, the electrolyte selection is fundamental to prevent it from promoting the oxidation of the metallic substrate [8].

Previously developed studies have shown that homogeneous films were formed electrochemically on aluminum surfaces, when methanesulfonic acid was used as electrolyte [9]. This work investigated the electrodeposition of PPy and PANi on the surface of 1020 steel in aqueous medium containing methanesulfonic acid. The performance of the corrosion films, electrodeposited on the metal were analyzed by potentiodynamic polarization tests in aqueous medium containing chloride ions.

2- Experimental

For the electrochemical tests, a Potentiostat / Galvanostat model MQPG-01 of Microchemistry was used, connected and controlled by a microcomputer. The tests were carried out in an electrolytic cell containing three electrodes: working electrode (1020 steel, embedded in teflon and exposed area of 0.53 cm²); reference electrode (Ag / AgCl); and auxiliary electrode (platinum rod). The composition of the steel 1020 is shown in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>0,18/0,23</td>
<td>0,30/0,60</td>
<td>0,04</td>
<td>0,05</td>
</tr>
</tbody>
</table>

Before each test, the steel surface was polished and then the steel electrode was rinsed with distilled water.

The polymeric films were electrodeposited using an aqueous solution containing 0.1 mol.L⁻¹ monomer and 0.2 mol.L⁻¹ methanesulfonic acid.
The PPy and PANi electrodepositions were performed by cyclic voltammetry, varying the potential from -1.0 to 2.0 V vs Ag / AgCl, with a scanning speed of 5.0 mV.s\(^{-1}\). The respective films were also electrodeposited by chronoamperometry, applying the potential of 1.2 V vs Ag / AgCl for 30 minutes.

The morphology of the surfaces coated with the PPy and PANi films were analyzed by Scanning Electron Microscopy (SEM) using the Jeol JXA-840A equipment.

The corrosion protection of the steel surfaces, covered with PPy film and covered with PANi film, were investigated by potentiodynamic polarization tests in 0.1 mol.L\(^{-1}\) NaCl solution (pH = 6.4), at room temperature of 25 ° C.

3- Results and Discussion

Initially, cyclic voltammetry were performed, varying the potential from -1.0 to 2.0 V vs Ag / AgCl at 5.0 mV.s\(^{-1}\). The Fig.1 shows the first potential scanning cycle for PPy electrodeposition (curve 1). Note that the anodic currents began to increase from + 1.0V, indicating the oxidation of monomer.

![Figure 1: Voltammogram for steel: in the presence of PPy (1) in the absence of PPy (2)](image)

The electrodeposition of PPy and PANi films also were performed by chronoamperometry applying the potential of 1.2 V vs Ag / AgCl, established from
the voltammogram of pyrrole, for 30 minutes that completely covered the working electrodes, resulting in the formation of both black and homogeneous films for polypyrrole and polyaniline. Fig.2 shows the current versus time curves obtained in these experiments.

![Graph showing current versus time for PPy and PAni](image)

**Figure 2**: Growth of the PAni (1) and PPy (2) film by applying 1.2V.

It was observed in Fig.1 that after the application of the 1.2 V potential, current values increased and remained elevated over time, indicating the formation of the conducting films on the surface of the steel electrodes. The PAni presented current values of approximately 0.033 A.cm\(^{-2}\), while PPy remained in the current range of approximately 0.005 A.cm\(^{-2}\).

The surfaces morphology of 1020 steel coated with PPy and PAni films were analyzed by Scanning Electron Microscopy. Fig. 3 shows the SEM for the surface of the steel covered with PPy and PAni films.
To analyze the corrosion performance of PPy and PAni films, were done Potentiodynamic polarization tests in aggressive NaCl 0.1 mol.L$^{-1}$ medium. Fig.3 shows the Tafel curves for these tests.

![Figure 3: SEM for steel surfaces: PAni coated steel at 1.2 V (a) and PPy coated steel at 1.2 V (b).](image)

![Figure 4: Tafel curve for the steel surfaces coated PPy(1), PAni(2) and polished(3).](image)

The corrosion potential of the polished (1) steel was approximately -0.73 V, the PAni coated steel has a lower potential than the polished steel, around -0.75 V, whereas the steel coated PPy has a potential of corrosion potential of approximately -0.51 V. The
displacement of the corrosion potential to the positive direction indicates anodic protection
by the polymer film [11].

It was observed in Fig.4 that the densities of anodic currents, associated with metal
oxidation, were lower for steel coated with PPy. If we consider in the graphs of Fig.3, at the
potential of 0.5 V, the anodic current density for the PPy-coated surface is equal to 10.05
mA.cm\(^{-2}\), whereas for the surface only polished and covered with PANi are values close to
35 mA.cm\(^{-2}\). Previous studies conducted in our laboratories have indicated that PPy films
electrodeposited with higher potential values result in a polymer chain with defects, making
the film not as a barrier against corrosion and therefore is inefficient against aggressive
medium of chloride [12].

4- Conclusions

This work has shown that the polymeric films electrodeposited on 1020 steel
were homogeneous and adherent. The corrosion test in aggressive sodium chloride
medium showed that the PPy film is effective in metal corrosion protection, while the
PAni film did not perform well. Tafel curves showed that the PPy film can provide anodic
protection to the steel, unlike PAni that has values of corrosion potential similar to
polished steel, indicating the oxidation of the metal. Therefore, in these conditions, PAni
does not offer protection against corrosion. From these data, it was concluded that PPy
can act as a protective barrier inhibiting corrosion while intact and without failures.

5- References

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