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ANTICORROSIVE POLYMERIC COATINGS

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Abstract. *In order to improve the anticorrosion protection properties, polypyrrole thin films were deposited on silicon steel plates. The anticorrosive protection effect of the polypriol coating was evaluated by electrochemical measurements in two different aqueous solutions of potassium chloride and hydrochloric acid. Polypyrrole-coated silicon steel plates were immersed for one and seven days, respectively. The obtained results show that the thin layer of polypyrrole ensures effective protection of silicon steel against corrosion, especially in aqueous potassium chloride solution.*

Keywords: *polypyrrole, silicon steel, coating, thin film, anticorrosion*

1. INTRODUCTION

The method of protecting metal surfaces against corrosion with the help of polymeric materials is a classical field of research, but which can always be enriched with research and news. I have reported research on some aspects raised by thin layers of polypyrrole deposited on metallic materials, such as steel or non-ferrous alloys. [2–5]. Thus, for the present research theme, polypyrrole was chosen as an anti-corrosion protection layer, a conductive polymer that I have also researched under other aspects, and the protected material is silicon steel plates, a material widely used in the electro technical field.

If it covers the surface of a metal material with a thin film of conductive polymer, this coating provides protection against corrosion because of the free potential that the redox character of the polymer confers.

In the case of steels, all kinds of protective coating methods have been presented in the literature to solve the corrosion problem, of which two important types stand out: one method consists in introducing an anion into the electrolytic solution, and it will form complexes with the Fe^{2+} cations from the electrodissolution of the superficial layers of the steel. The result is the creation of a protective film that prevents the further dissolution of Fe^{2+} and favors the deposition of polypyrrole. [9,10]. This method also has disadvantages because the reaction initiation time is long and losing Fe^{2+} ions in the solution cannot be avoided. Another method comprises passivation of the metal with an acid (example: hydrochloric, nitric) and polymerizing the pyrrole on that surface [11].

In this work, it is described the deposition of polypyrrole on silicon steel plates. The structures and morphology of the coatings have been investigated through several characterization techniques: FTIR, optical and electronic microscopy. The protective capabilities of polypyrrole against the corrosion of silicon steels were studied by determining the free potential, by electrochemical cycles by immersion in saline or strongly acidic aqueous solutions. The obtained results are interesting and presented in the following.

2. EXPERIMENTAL

2.1. Materials

Silicon steels used in electrotechnics, especially with oriented grains, are ferromagnetic alloys with the following specific properties: high values of magnetic induction and permeability, low coercivity, low hysteresis and eddy current losses. In order to maintain these very useful magnetic properties, an efficient anti-corrosion protection is necessary, in order to not change the chemical composition and therefore, the magnetic properties.

As it was presented in the previous works [1, 12-14], polypyrrole, a polymer made up of several connected pyrrole rings (figure 1), shows electrical conductivity because of the possibility of electronic jumps between polymer chains, but with the condition of being stimulated by anionic doping.

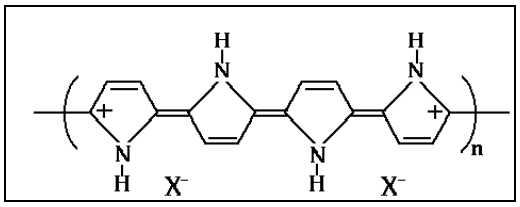


Figure 1. Polypyrrole structure

Polypyrrole can be obtained easily through a chemical method of polymerization of pyrrole in solution with a dopant anion (X^-), whose concentration of the incorporated part during the synthesis determines its adhesion characteristics to the steel surface and electrical conductivity properties.
Polypyrrole was the first in the family of conductive polymers that show high conductivity [1, 6-8, 12-14].

To realise the experiments it has been used: pyrrole (C_4H_4NH), silicon steel plates, ferric chloride anhydrous ($FeCl_3$), potassium chloride (KCl), and hydrochloric acid (HCl), it purchased all from Merck. In all experiments it has been used distilled water.

2.2. Polypyrrole deposition on silicon steel plates

Initially, all silicon steel plates were cleaned and degreased, for the best adhesion of polypyrrole to their surface. The polypyrrole thin films were synthesized with ferric chloride aqueous solution at 5 °C, on different silicon steel plates. The concentrations of pyrrole and ferric chloride solution were maintained constant each in all experiments. After coating with a thin layer of polypyrrole, the silicon steel plates were washed with distilled water and left to dry on filter paper.



Figure 2. Silicon steel plates coated with polypyrrole, left to dry

This coating method produces polypyrrole with a fairly high conductivity for a conducting polymer, but it is possible for the iron in the silicon steel to pass into solution before the pyrrole (monomer) begins to oxidize.





Figure 3. Silicon steel plates coated with PPy films

Polypyrrole coatings are uniform and black, but after 500 seconds of coating, slight blue reflections were observed. After the deposition of thin layers of polypyrrole, the plates were placed in aqueous solutions of KCl (40g/l) and HCl (1M) for 1 day and 7 days, respectively (Figure 4).



Figure 4. Silicon steel plates coated with polypyrrole, in aqueous solution of KCl (40g/l)

3. RESULTS AND DISCUSSIONS

3.1. Adhesion tests of polypyrrole films deposed on silicon steel plates

The tests to verify the adhesion of the polypyrrole coatings on the silicon steel plates were made by incisions with a cutter, and then a calibrated adhesive tape was stuck on each plate. After that, the tape was peeled off and, depending on what remained on the metal plate and on the tape, the adhesion was estimated on a scale from 0 (nothing on the tape) to 5 (over 33%). Adhesion tests confirm the good adhesion of these polypyrrole coatings to silicon steel, approximately 2 on the scale.

3.2. FTIR spectrum

To perform the FTIR spectrum, we used a Jasco 4200 spectrophotometer, using powder samples pastilled with KBr. The FTIR analysis aimed to show the polymerization of pyrrole on the surface of silicon steel plates. Thus, a spectrum (figure 5) was obtained that shows absorption bands characteristic of pyrrole. The characteristic bands of polypyrrole were identified according to the theory of effective coordination conjugation (ECC), which predicts that the intensities and positions of the IR bands change the size of the delocalization along the polymer chains.[15] The band at 1560 cm^{-1} was due to the stretching of the C–C and C=C

bonds and the band at 1480 cm^{-1} was due to the stretching of the C–N bond in polypyrrole. C. R. Martin explained this situation because the ratio of the two bands is inversely proportional to the conjugate length and the doping level of polypyrrole [16].

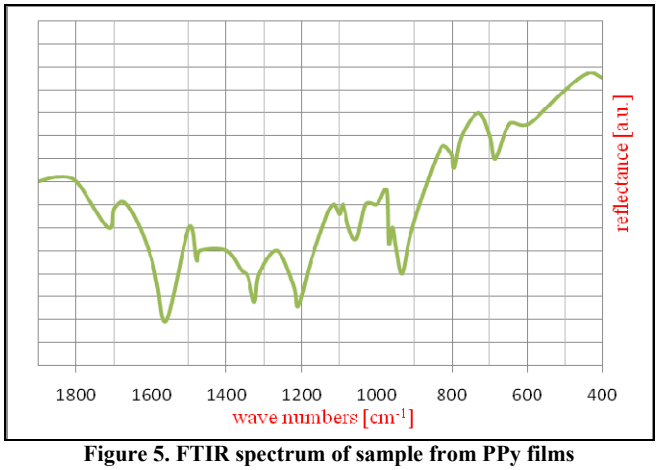


Figure 5. FTIR spectrum of sample from PPy films

3.3. Electrochemical behavior of the polypyrrole coatings

It has been investigated the electrochemical behavior of coatings in either potassium chloride solution or an aqueous solution of hydrochloric acid. The choice of Cl^- ions to the detriment of NO^{3-} ions is due to the fact that corrosion processes are generally accelerated by chloride ions. Figure 6 shows the low scan speed voltammograms of a silicon steel plate not coated with polypyrrole (S-S) and of a silicon steel plate covered with a thin layer of polypyrrole (S-S/PPy), in aqueous potassium chloride solution. Following the analysis of the electrochemical behavior, it is observed that the silicon steel plates oxidize quickly compared to those coated with polypyrrole. In the case of silicon steel plates covered with polypyrrole, the electrochemical activity of polypyrrole in concert with protecting the plates is clearly highlighted.

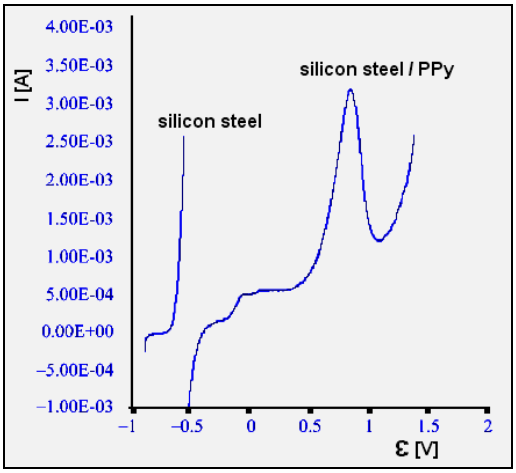


Figure 6. Voltampermetric curves obtained in KCl (40 g/l) aqueous solution of coated silicon steel plates

The thin layers of polypyrrole deposited on the silicon steel plates act as a transport barrier against the mobile charges involved in the electrochemical reaction. As expected, the same thing is observed in the presence of a hydrochloric acid solution as a supporting electrolyte. It is known that protons, although they can improve the corrosion processes, do not have any important effect on the electroactivity of polypyrrole [17]. If the free potential is analyzed for each sample, the stability of the anti-corrosion protection is highlighted more (figure 7). Because of the high free potential, thin layers of polypyrrole offer good protection to silicon steel plates.

After about 850 seconds, the potential drops almost instantly because the thin layer of polypyrrole has lost

its ability to protect against corrosion. If the experimental conditions are changed in the sense that the study is carried out in a 1M aqueous solution of hydrochloric acid, it is observed that the thin layer of polypyrrole does not offer protection because the free potential is close to that of silicon steel not covered with polypyrrole. Again, this shows, even more clearly than in the previous experiment with Kal, that there is the protective action of the polypyrrole.

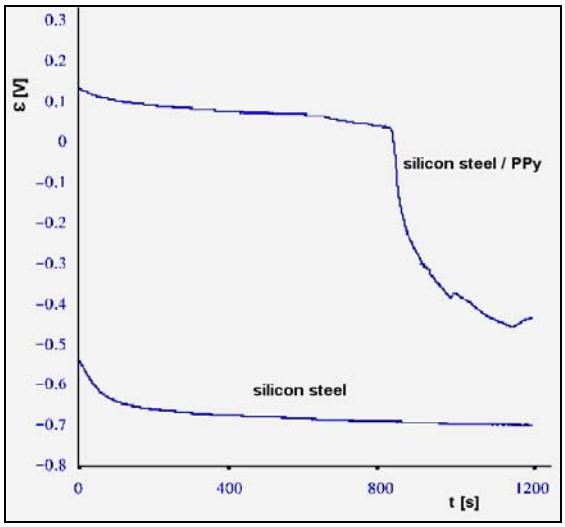


Figure 7. Variation of free potential as a function of time, in KCl (40 g/l) aqueous solution

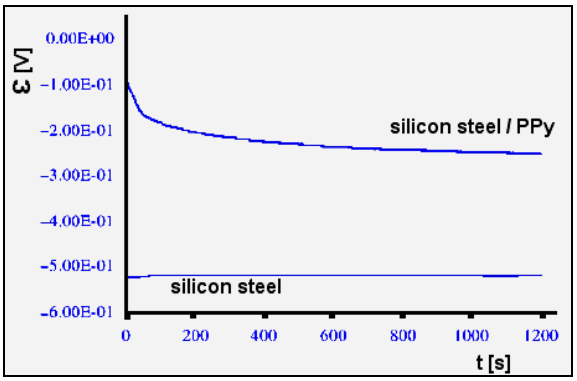


Figure 8. Variation of free potential as a function of time, in HCl (1 M) aqueous solution

3.4. Corrosion investigations

3.4.1. Determination of the metal dissolution

After the electrochemical study, experiments were carried out for the quantitative determination of the corrosion products, i.e. the determination of the amount of iron ions dissolved in the solution following the corrosion of the metal substrate of each sample, both in the case of using the potassium chloride saline solution (40 g/l), as well as in the case of using the aqueous solution of hydrochloric acid (1 M) (figure 9). If with using the potassium chloride saline solution, the corrosion is slow, especially if the polypyrrole protective layer is present, with the hydrochloric acid solution, there is practically no protection.

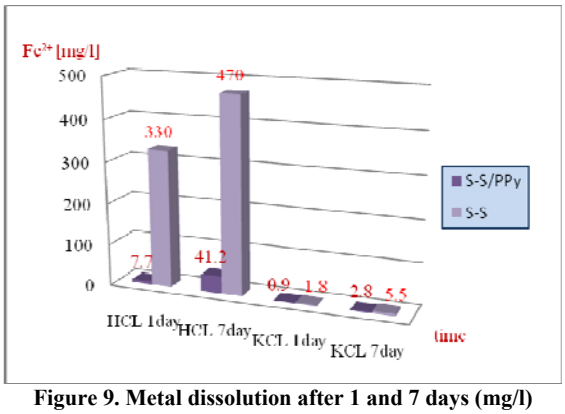


Figure 9. Metal dissolution after 1 and 7 days (mg/l)

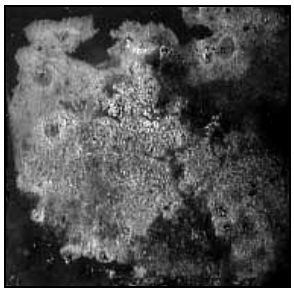
3.4.2. Microscopy study before and after corrosion tests

Silicon steel plates coated with thin layers of polypyrrole were characterized by optical microscopy (figure 10) and SEM (figure 11). It is clearly observed that the polypyrrole corrosion degrades thin layers in the hydrochloric acid solution.

Initially, the coatings with thin layers of polypyrrole were adherent and smooth, but after the corrosive action of the 1M hydrochloric acid aqueous solution, they undergo visible changes. Thin layers of polypyrrole change color from black to brown and rust spots appear. Moreover, the adhesion of the polypyrrole layer is lost. The most representative microscopic images are shown in the figures 10 and 11.

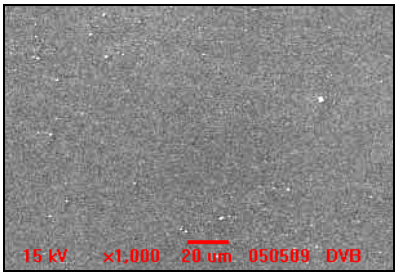


a.

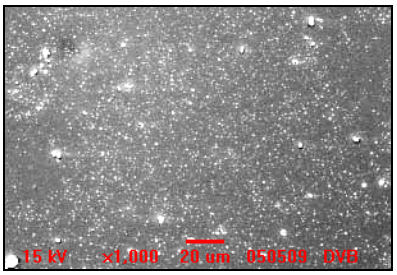


b.

Figure 10. After immersion in HCl (1 M) solution for 7 days: a) Image of S-S/PPy plate (1000 seconds of coating); b) optical micrographs of a representative area on the same S-S/PPy plate



a.



b.

Figure 11. SEM images of S-S/PPy: (a) before, and (b) after immersion in HCl solution (1 M) for seven days

4. CONCLUSION

The experimental research carried out aimed to demonstrate the role of anticorrosive protector of a conducting polymer deposited thinly on silicon steel plates.

For these experiments, polypyrrole was chosen because obtaining it through the polymerization of pyrrole is easy when using an aqueous medium that contains chlorine anions.

After depositing the thin protective layers of polypyrrole on the surface of the silicon steel plates, it was demonstrated by FTIR analysis that the polymerization of pyrrole was successfully carried out. Then the adhesion of the polypyrrole layers was studied, which was good.

The experimental study of the anti-corrosion protection capacity of the thin layer of polypyrrole was done by electrochemical measurements in an aqueous solution of potassium chloride (40 g/) and, respectively, in an aqueous solution of hydrochloric acid (1M). The action time of the corrosive solutions was 1 day and 7 days, respectively.

When potassium chloride solution was used, the protection offered by the polypyrrole layer proved effective, but with using hydrochloric acid solution, the results were very poor.

The morphology of thin layers of polypyrrole deposited on silicon steel plates was studied, both by digital optical microscopy and by scanning electron microscopy, the images obtained strengthening the conclusion that the efficiency of covering silicon steel plates with thin layers of polypyrrole is manifested only against the action of corrosive of the aqueous salt solution of potassium chloride.

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