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Studies on the preparation, characterization and corrosion behavior of injection molded 316L steel electrochemically coated by poly{*trans*[dichloro (4-vinylpyridine) ruthenium]}

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Abstract: The present work describes the studies on corrosion of powder injection molded 316L stainless steel potentiostatically coated by poly{*trans*[$RuCl_2(vpy)_4$]} where vpy (4-vinylpyridine) acts as ligand. Scanning Electron Microscopy (SEM) coupled to an Energy Dispersive X-Ray Analysis (EDAX) characterized the coated electrodes. Anodic polarization tests were performed in 3% NaCl to estimate the anodic dissolution current density of the electrode coated by the polymeric material. In addition, the specimens were exposed to salt spray and acid rain simulated environment. The microestrutural analysis indicated that the films were approximately 58 μm thick. Cyclic voltammetry experiments were carried out in 0.1M HTBA/methyl isobutyl ketone solution. The results revealed a scan rate dependent wave corresponding to a Ru^{2+}/Ru^{3+} redox reaction, thus confirming the presence of ruthenium as metallic center in the polymer backbone. Pitting corrosion was observed in coated specimens only after thirty days of exposure to salt spray and after two days of exposure to acid rain simulated environment.

Introduction

An increasing interest in corrosion protection of metallic components during transport and storage has stimulated the development of novel protective coatings. A new and attractive method consists of electrodepositing polymeric films on metallic substrates. The approach has attracted the attention of several research groups since Mengoli *et al.* [1] described this possibility. A great number of studies [2-6]. including a recent review [7] have been reported in literature. Beck [8] described a method to electrochemically deposit polypyrrole on oxidizable substrates such as aluminum and mild steel. The oxidative polymerization of monomers on active metals is somewhat troublesome as the polymerization reaction and anodic dissolution of the substrate are competing processes. Hence, the electropolymerization on active metal surfaces depends on a cautious choice of the synthesis conditions. Our research staff has studied the synthesis of a new class of polymers such as poly{*trans*-[$RuCl_2(pmp)_4$]} (where pmp = 3-(pyrrole–1–ylmethyl) pyridine [9-10] and poly{*trans*-[$RuCl_2(vpy)_4$]} to coat metallic sintered surfaces [11] . One of the aspects of the use of *vpy* is that this ligand allows polymerization by reduction of vinyl groups, thus avoiding the dissolution of the metallic substrate during synthesis. Complexes containing vinyl pyridine (as well as vinyl bipyridine) were first described by Murray and co-workers [12 - 16] and others [17 – 18a] in the early 1980s. Extensive literature is now available on these and other related materials [18b-18c]. Such studies have conclusively demonstrated that transition metal complexes containing *vpy* undergo electroreductively onset polymerization responsible for deposition of electroactive films of the corresponding monomer complex. In an electroreductive process, films are generated in the cathodic region of the substrate, yielding protective action to the steel and giving better stability upon polymerization. Our recent studies demonstrated that these monomers are also easily polymerized on Pt, Pd and sintered Fe (5-10)%-Ni electrodes yielding excellent adherence on these substrates [11]. In addition to the protective nature of the polymeric coating, the presence of ruthenium in the film plays an important role, since Ru^{2+} can be oxidized to Ru^{3+} and reduced back to its original valence state acting as a redox buffer, as a mechanism for inhibiting corrosion. Reversible anodic sites can then be formed in the film, avoiding the oxidation of the substrate. Coating stainless steel with such polymeric films improves the protective action against chloride attach, preventing localized pitting corrosion during transport and storage. The present work depicts the applicability of eletropolymerized poly {*trans*-[$RuCl_2$(vpy)$_4$]} films in the corrosion protection of 316L stainless steel. Scanning Electron Microscopy (SEM) was used to observe the morphology of the coating layer, to estimate its thickness and to assess the general aspect of corroded specimens. Energy dispersive X-Ray analysis (EDX) was carried out to determine the elementary composition of the polymer coatings. Cyclic voltammetry tests were also employed to observe the electrochemical behavior of the films. Finally, the corrosion resistance of the deposits was studied by anodic polarization and exposure to salt spray and acid rain environments.

Materials And Methods

Solutions and chemicals: The synthesis of {*trans*-[$RuCl_2$(vpy)$_4$]} has been described elsewhere [11]. Commercially available chemicals and solvents of an analytical grade were used in the synthesis of the monomer. The main chemicals employed were: 4-vinyl pyridine (Aldrich), trihydrated ruthenium chloride (Jonhson-Matthey) and solvents. Chromatographic grade solvents were employed in the electrochemical tests. The electrodeposition solution consisted of: 3 mM {*trans*[$RuCl_2$(vpy)$_4$]}$^+$ 0,1 M HTBA dissolved in acetonitrile/dichloromethane (4:1). Anodic polarization curves were conducted in 3 % NaCl aqueous solution (Grupo Química) and the cyclic voltammetry experiments were carried out with 0.1 M HTBA (Aldrich) in methyl isobutylketone. Salt spray and acid rain experiments were carried out in 5 % NaCl aqueous solution and in: 0.85 mM H_2SO_4 + 1.45 mM $(NH_4)_2SO_4$ + 1mM $NaNO_3$ + 1mM HNO_3 + 0.87mM NaCl, respectively.

Electrochemical techniques and electrodes: Electrodeposition and electrochemical tests were carried out using a potentiostat/galvanostat (EG&G PAR 283). A pseudo-reference consisting of a platinum sheet (size: 0.1 cm thick, 0.7 cm width, 2.0 cm length; exposed area to the solution: 2.1 cm^2) placed at a distance of 0.5 cm from the working electrode was used during electrodeposition and cyclic voltammetry experiments. In addition, a KCl saturated calomel electrode was used in the anodic polarization experiments. The counter electrode was a platinum sheet (size: 0.1 cm thick, 0.7 cm width, 2.0 cm length; exposed area to the solution: 2.1 cm^2). The working electrode was a 316L stainless steel injection molded specimen (size: 0.3 cm thick, 0.9 cm width, 4.2 length; exposed area: 2.1 cm^2 (electrodeposition), 0.25 cm^2 (cyclic voltammetry) and 0.95 cm^2 (anodic polarization)) with the following composition: 0.013% C; 0.80% Si; 0.20% Mn; 0.031% P; 0.003% S; 13.5% Ni; 16.40% Cr and 2.2 % Mo. Powdered steel samples were injected and sintered by the Steelinject Division of Lupatech (Caxias do Sul, Brazil). The main process parameters employed were: pre-sintering profile: 980 ^oC/1h; pre-sintering atmosphere: $H_{2;}$ sintering profile: 1300 ^oC/4h; sintering atmosphere:

vacuum, Ar and H_2; final density: 7.59 g cm^{-3}. Prior to electrodeposition, the steel specimens were surface ground using 220-600 sandpaper and polished in an aluminum slurry (ϕ = 0.3 µm to 0.25 µm), in order to obtain a good finish. The samples were then immersed in a propanone ultrasonic bath for 5 min. Poly {*trans*- [$RuCl_2(vpy)_4$]} film was potentiostatically deposited onto 316L stainless steel at an applied potential of -2.75 V during 30 min.

Polarization curves: The polymeric films were characterized according to the corrosion rate. Related parameters such as active region, passive region and transpassivation were also determined from anodic polarization plots. The initial potential was set to -0.25 V *vs.* OCP (Open Circuit Potential), and the scanning rate used was 0.8 mV/s to avoid damages on the specimens, usually caused at very slow scan rate (0.167 mV/s) as recommended from AST standards. The variation of OCP versus time, figure not shown here, reveals that after 30 minute there is no variation on the value of OCP. In this sense, the polarization curves experiments starts after 30 minutes when the OCP became steady.

Corrosion tests: Salt spray tests were performed with the 316L stainless steel specimens during 30 days, and the acid rain simulated test was carried out during 10 days. Both were performed following technical specification [20]. These tests consist basically of a salt spray conventional test and an accelerated test with alternated stages of spraying (acid rain simulated solution) and drying with airflow at 35 °C.

Morphological characterization and elementary analysis: The polymeric films of poly {*trans*- [$RuCl_2(vpy)_4$] were analyzed by a Philips XL-30 scanning electron microscope equipped with an energy dispersive spectrometer. Morphology, thickness and composition of the films were investigated. SEM determined the sample thickness after cutting the electrodes using a diamond disc with a Buehler cutting machine model Isomet 2000 (Centro de Tecnologia Cerâmica CTC-Criciuma, SC BRAZIL). After cutting the sampling no further treatment was done in order to avoid damage on the surface. Further measurements were also done using a *Digital Coating Thickness Gauge*, model Electrometer 345. (BRAMETAL - Brandão Metalúrgica LTDA, Criciuma, SC BRAZIL). The results corroborate with those obtained from SEM.

Results And Discussion

Morphological characterization, elementary analysis and adherence tests: Figure 1 illustrates some morphological aspects of a crossection of a polymeric film deposited on 316L stainless steel.

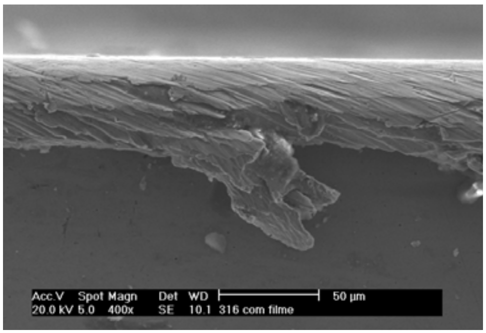


Figure 1. Morphological crossection of a polymeric film deposited on 316L stainless steel

The film is approximately 58 µm thick and essentially uniform, depicting a reddish opaque hue. It could also be noticed that the film penetrated into open pores coating, an additional area that otherwise would be exposed to corrosion attack. The influence of porosity on the corrosiveness of sintered stainless steel has been extensively documented by previous literature reports [21-25]. The excessive open porosity increases the exposed area to the corrosive environment which induces crevice corrosion with the formation of concentration cells within the pores [26-27]. The possibility to coating of open pores by poly{*trans*-{$RuCl_2(vpy)_4$} (Fig.1) is an important aspect in driving further research towards improving corrosion protection to sintered steels. Results from an EDAX analysis carried out for a 316L stainless steel specimen coated by poly-{*trans*-{$RuCl_2(vpy)_4$} indicated the presence of ruthenium in the film. Chlorine and carbon lines corresponding to axial vpy and Cl^- ligands, coordinated in ruthenium complexes, could also be observed. Relatively wide peaks corresponding to alloying elements were also observed and suggested the presence of a large number of pores and defects in the film structure (Fig. 2b). The results of the adherence tests carried out for poly{*trans*-[$RuCl_2(vpy)_4$]} films suggested nearly full adherence to the metallic substrate for every specimen analyzed.

Electrochemical characterization: cyclic voltammetry: Voltamogramms corresponding to steel samples are compared with those obtained on platinum substrates coated with a polymeric film of poly {*trans*-[$RuCl_2(vpy)_4$]} obtained in 0.1 M HTBA/methyl isobutylketone medium at a scanning rate of 0.8 mV/s (Fig. 2). Curves A (polymeric coating on platinum) and B (polymeric coating on steel) clearly show the presence of two peaks probably related to the Ru^{2+}/Ru^{3+} redox reaction. This confirms literature data obtained for the same complex deposited on platinum [11] and 17-4 PH stainless steel [28].

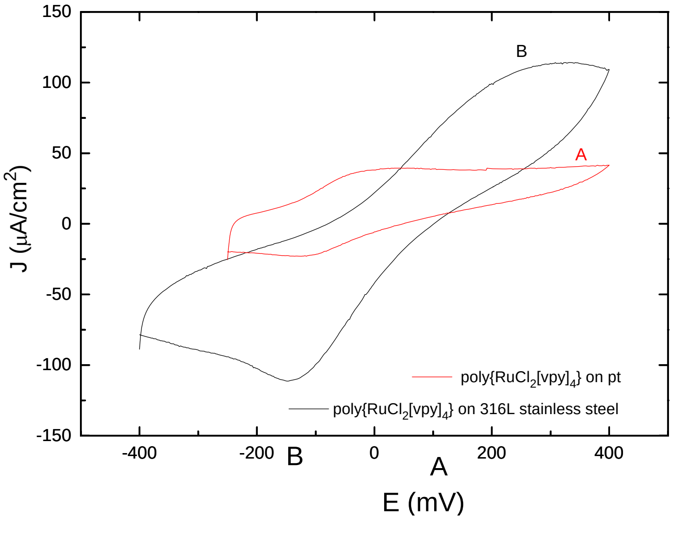


Figure 2 Cyclic voltammetric experiments of poly {*trans*[$RuCl_2(vpy)_4$]} on Pt and on 316 L steel.

In curve A, the anodic peak shows the maximum potential value (E_{pa}) at approximately –18 mV, whereas the cathodic peak (E_{pc}) is at –115 mV. A corresponding ΔE value of 97 mV is then obtained. On the other hand, E_{pa} for curve B is at 225 mV and E_{pc} at -133 mV. In this case, ΔE comes to 358 mV. Preliminary results reported in literature [11] indicated that, in contrast to those observed for 316L stainless steel coated specimens, peaks related to the Ru^{2+}/Ru^{3+} process in the Voltamogramms of the platinum sheet coated by the polymeric film are separated by ΔE of 30mV for a scan rate of 20 mVs^{-1} to exceeding 204 mV for scan rate greater than 200mVs^{-1}. The redox process is metal-centered with E_{pa} = 185 mV attributed to the *trans*-[RuCl$_2$(vpy)$_4$]$^{0/+}$ process (curve A (0.4 mV/s)). The reverse wave, observed at –48 mV corresponds to the *trans*-[RuCl$_2$(vpy)$_4$]$^{+/0}$ process. It was observed that E_{pa} values shift from 185 to 280 mV and the E_{pc} from -48 to –260 mV as the scanning rate increased from 0.4 to 2.0 mV/s. These values differ slightly from those reported by Franco *et al*. [11] for the same complex deposited on platinum. *Polarization curves:* Anodic polarization curves obtained for both bare and coated 316L steel in 3-wt% NaCl are shown in Fig. 3. The corrosion potential of the uncoated sample (curve A) was around –130 mV *vs* SCE. The coated sample (curve B) had a corrosion potential of –390 mV. It was observed a decrease in the i$_{corr}$ around 25 times in addition to a decrease in the potential about 200 mV, indicating a more pronounced effect in the cathodic reaction, related to the oxygen reduction. According to Coulomb's law, it is possible to estimate the concentration of ruthenium in the polymeric film: 7.64 x 10^{-5} mol/cm^2, which corresponds to 45.9 x 10^{18} molecules of *trans*-{RuCl$_2$(vpy)$_4$ per cm^2.

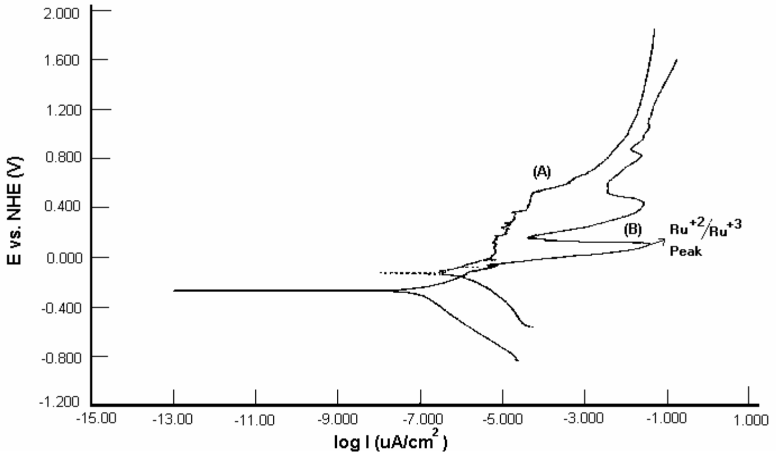
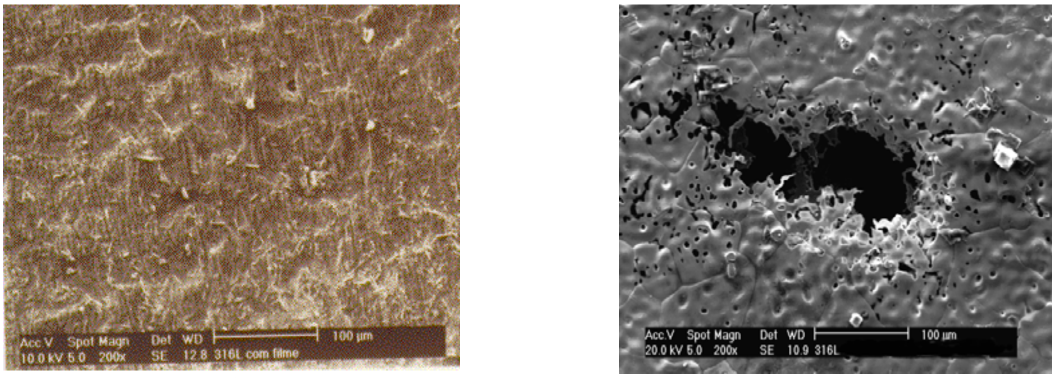


Figure 3 Polarization curves of 316L steel (A) and 316L steel coated by poly{*trans*[RuCl$_2$(vpy)$_4$]} (B) in 3% NaCl medium, at a scanning rate of 0.8 mV/s.

The morphology of the coating films remained unaffected after the polarization tests in 3% NaCl (Fig. 4 (a)) and no pitting corrosion was observed on the coated 316L steel, probably due the polymer film acting as a barrier. On the other hand, Fig. 4 (b) shows clearly that pitting occurred in the uncoated steel.



a) **b)**

Figure 4 Scanning Electron Micrograph of A) 316L steel coated by poly{*trans*-[RuCl$_2$(vpy)$_4$]} and B) 316L steel after anodic polarization experiment. Magnification 200 x.

*Salt spray corrosion tests***:** The salt spray test according to ASTM B117 showed that the coated 316L steel resisted to the corrosion attack of this aggressive atmosphere during the whole period of test (30 days). However, the samples only resisted to the acid rain environment for 2 days of exposure.

Conclusions

The results described demonstrated that the *trans*-[$RuCl_2(vpy)_4$] monomer can be electrodeposited on the surface of 316L stainless steel samples using potential-controlled techniques. SEM imaging showed that poly{*trans*{$RuCl_2(vpy)_4$]} films are essentially uniform and approximately 50 μm thick. Additionally, the coating layers tended to penetrate into open pores of the substrate. EDAX analysis of poly{*trans*-{$RuCl_2(vpy)_4$]} coated 316L steel revealed the presence of a ruthenium redox center, in addition to chlorine and carbon, related to the axial ligands of the complex. The corrosion rates of the coated 316L steel was reduced nearly 25 times comparatively to the uncoated steel. The coated specimens did not show pitting after polarization in 3% NaCl solution. The performance of coated stainless steel 316L was better in the conventional ASTM B117 salt spray test than in an accelerated test with acid rain.

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