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# Adhesion of Polyaniline on Metallic Surfaces

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## 1. Introduction

Metal corrosion can cause enormous material and economic damages to general infrastructures, airplanes, reservoirs, tanks, ships, etc. The development of new materials and the association of different materials for corrosion protection have been an important area of research. In the literature, the use of conducting polymers can provide corrosion protection to metals in different environments (acid and basic aqueous media). Among the several intrinsic conducting polymers, polyaniline (PAni) stands out due to its processability, chemical stability, low cost and easy polymerization.

This chapter discusses corrosion processes and their prevention using conducting polymers, especially polyanilines, and the advantages of the use of adhesion promoters, which improve the efficiency of the coatings. The experimental results used to discuss this matter are those obtained by using iron (stainless and carbon steels) and aluminium alloys.

## 2. Corrosion

Corrosion is the deterioration of materials by either chemical or electrochemical action of the medium, and may or may not be associated with surface strain. When considering the use of materials in the construction of equipment or facilities, those must resist the action of the corrosive environment, as well as provide appropriate mechanical properties and manufacturing characteristics. Corrosion can be associated with different types of metallic or non-metallic materials. Considering the particular case of metallic materials, their degradation is called metallic corrosion (Fontana, 1986; Jones, 1991; Trethewey & Chamberlain, 1995).

Studies on metal corrosion are based on their importance to the increasing use of metals in all fields, specifically in the technological one. The use of large metal buildings, more susceptible to corrosion than stone structures, an increasingly aggressive environment in areas of usual applications (water, polluted air) and industrial areas (processes involving aggressive and hazardous reagents) and the use of rare and expensive metals, in some special applications (e.g., atomic energy and aerospace) are the most indicative examples of the metallic corrosion importance. Depending on the action of the corrosive medium on the material, the corrosive processes can be classified into two major groups, covering all cases of deterioration by corrosion, electrochemical corrosion and chemical corrosion. The processes of electrochemical corrosion are more common in nature and are basically characterized by their occurrence in the presence of liquid water at different temperatures with the formation of a corrosion cell in function of the movement of electrons in the metal.

### *Protective coatings against corrosion*

Passivation is the modification of an electrode potential towards less activity (more cathodic or more noble) due to the formation of a corrosion product film, called passivating film. Some examples of metals and alloys that are passive-forming protective films are: *i*) chromium, nickel, titanium and stainless steel (passive in most corrosive media), *ii*) lead (passive in the presence of sulphuric acid), *iii*) iron (passive in the presence of concentrated nitric acid and non passive in the presence of dilute nitric acid) and *iv*) the majority of passive metals and alloys in the presence of facilities, with the exception of amphoteric metals (Al, Zn, Pb, Sn and Sb).

Besides passivating films, surfaces can be protected against corrosion by different types of protective coatings. These films are applied to metal surfaces hindering surface contact with the corrosive environment, in an attempt to minimize the degradation by the action of species on the medium. The length of protection given by a coating depends on several factors, such as type of coating (chemical nature), forces of cohesion and adhesion, thickness and permeability to the passage of electrolyte through the film.

The main mechanisms for the protection of coatings are: a barrier, anodic inhibition and cathodic protection. If protection is only a barrier as soon as the electrolyte reaches the metal surface, the corrosion process starts, whereas if there is an additional mechanism of protection (anodic inhibition or cathodic protection), the life of the coating is extended.

Different types of protective coatings can be applied to metal surfaces: *i*) anodization, which is the thickening of the protective passive layer existing in some metals, especially aluminium (the surface oxidation can be performed by either oxidants or electrochemical process and aluminium is a very common example of anodizing material), *ii*) shading, which is the reaction of the metal surface with slightly acidic solutions containing chromate (the chromate passivating layer increases the corrosion resistance of the metal surface to be protected), *iii*) phosphatization, which is the addition of a phosphate layer of the metal surface (the phosphate layer inhibits the corrosive processes and constitutes, when applied even as a thin layer, an excellent base for painting due to its roughness. The phosphating process has been widely used in the automobile and appliance industries. After the process of the metal surface degreasing, the phosphate layer is applied, followed by painting) and *iv*) organic coatings, which is the interposition of a layer of organic nature between the metal surface and the corrosive environment.

Painting is an industrial coating, usually organic, widely used for corrosion control in various types of structures and also in overhead structures, and to a lesser extent, on buried or submerged surfaces. However, there exist different types of damage leading to the deterioration of the protective film: mechanical damage caused, for example, by knocks and scrapes, damages caused by the natural action of time, such as discoloration, fading, corrosion, microcracks, etc., damages from chemical attack caused by industrial and urban pollution, damages by biological action, such as those caused by drops of resin from the trees or loose-leaf vegetation or by secretions of insects and birds.

## **2.1 Adhesion**

When two surfaces are close to each other, an interface takes place by the action of physical and chemical forces defining an interfacial phenomenon called adhesion. The degree of attraction between the two phases defines the adhesion strength.

Considering the particular case of organic coatings, the adhesion occurs either mechanically or chemically. In the mechanical adhesion the coating penetrates the surface in its defects as

pits and crevices, establishing a bond which can be improved by increasing the number of defects on the surface or its roughness. On the other hand, the chemical adhesion occurs at the metal/organic coating interface when interatomic bonds take place. These bonds can be primary (covalent or ionic bonds), secondary (dispersion forces, dipole interactions or van der Waals forces) or hydrogen bridge type. It is important to mention that metal/polymer interfacial bonds are generally secondary or hydrogen bridge type, except for epoxy resins and zinc silicates.

Adhesion problems between metallic substrates and top coats exert strong influence on the corrosion protection of a metallic surface and are caused by different factors, such as excessive film thickness and insufficient superficial cleaning. Poor adhesion allows the electrolyte to diffuse more easily into the region between the surface and the coating. The permeability of oxygen into a coating permits the occurrence of the oxygen reduction reaction, hence, an increasing  $\text{OH}^-$  concentration, which could break the metal/coating bonds. This fact leads to an increase in the polymer film detachment and further growth of blisters.

Seré et al. (Seré et al., 1996) analysed the relation between adhesion strength and corrosion resistance of carbon steel/chlorinated rubber varnish/artificial sea water systems. The authors pointed out that the adhesion of chlorinated rubber varnish onto carbon steel depends directly on the substrate surface roughness, before exposure to aggressive aqueous environments.

After immersion in aggressive environment, those samples with lower adhesion loss show a minimum corrosion level, i.e. there is a direct relationship between adhesion loss and corrosion resistance. Therefore, adhesion strength depends not only on the metal/coating system, but also on the environment characteristics (Seré et al., 1996).

### 3. Polyaniline as corrosion inhibitor

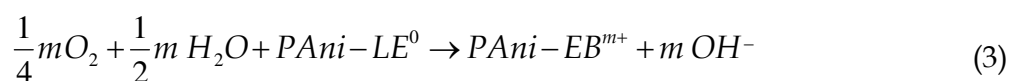
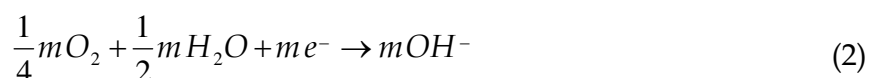
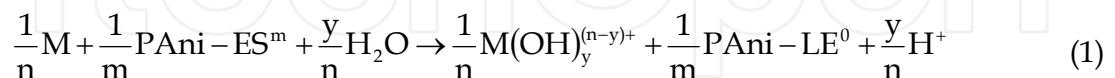
Many studies have reported the use of conducting polymers as coatings (Bernard et al., 1999; Santos et al., 1998; Talman et al., 2002). Particularly, PANi has been extensively used due to its ability to protect metals against aqueous corrosion (Santos et al., 1998; DeBerry, 1985).

PAni can be obtained by either chemical or electrochemical oxidation of aniline (Trivedi, D.C., 1997). In the chemical method an oxidizing agent must be used (for instance, ammonium persulphate) and the product is obtained in powder form. In the electrochemical method, PANi is obtained in the form of ordered thin films on the electrode surface.

DeBerry (DeBerry, 1985) was the first to indicate the possibility of using PANi as a corrosion inhibitor. The author studied the electrodeposition of PANi on 410 and 430 stainless steels. He observed an anodic protection that significantly reduced the corrosion rate in sulphuric acid solution by maintaining the metal in the passive state and repassivating the damaged areas. The advantage of PANi was its effective use in acidic environments.

According to different authors (Dominis et al., 2003; Cook et al., 2004), at least three different configurations of PANi used as a corrosion protector have been reported: coatings alone, such as solution cast PANi films formed or electrochemically synthesized (Santos et al., 1998; Huerta-Vilca et al., 2003b, 2004a; Fahlman et al., 1997), coatings as primer with a conventional polymer topcoat (Dominis et al., 2003; Talo et al., 1997), and PANi blended with a conventional polymer coating or polymer coatings containing PANi as an additive (Galkowski et al., 2005; Samui et al., 2003; Sathiyarayanan et al., 2009).

Kinlen et al. (Kinlen et al., 1997) and other authors (Spinks et al., 2002; Oliveira et al., 2009) observed that the electrochemically produced conducting polymers, as PANi, shift the corrosion potential ( $E_{\text{corr}}$ ) of the metal to the passive region, maintaining a protective oxide layer on the metal and minimizing the rate of metal dissolution (Eq. 1). The reduction of oxygen to hydroxide (Eq. 2) shifts from the metal surface to the polymer/electrolyte interface and probably involves the re-oxidation of the conducting polymer (Eq. 3), stabilizing polymer coatings from cathodic disbondment. According to the above reaction sequences, the conducting polymer catalyses the oxide layer growth, protecting the metallic surface against corrosion (Oliveira et al., 2009).



Thus, the polymer serves as a mediator between the anodic current passive layer and the reduction of oxygen in the polymer film.

#### 4. Steels and polyanilines

Steel is the most important material in engineering followed by aluminium. Its popularity is due to the low-cost manufacturing, forming and processing and the abundance of raw materials and their mechanical properties. It can be offered in a huge number of different chemical compositions and heat treatments, microstructures, terms of conformation, geometry and surface finish. Carbon steel is steel without intentional addition of other elements, containing only carbon and four trace elements (manganese, silicon, phosphorus and sulphur) always found in steels, remaining in their composition during the manufacturing process. Stainless steels are defined as ferrous alloys that have a minimum chromium content of 11% in their constitution, because this is the element that provides corrosion resistance in certain environments.

There are many studies showing the capability of PANi acting as corrosion protection for steels in different environments. Le et al. (Le et al., 2009) deposited different PANi coatings onto 316L stainless steel, varying the cycle numbers of cyclic voltammetry (2-, 3- and 4-cycles) by electro-polymerization in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution containing fluoride. The authors concluded that the corrosion resistance of the 316L substrate was considerably improved by the PANi coating and that the increase in the number of voltammetric cycles increased the thickness and enhanced the performance of the PANi coating due to low porosity.

Hermas et al. (Hermas et al., 2005) used electrodeposited PANi onto 304 stainless steel as protective coating in a deaerated 1.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> medium at 45°C. PANi improved the passivity of the steel, which remained passive in this aggressive medium for several weeks. After removing the PANi layer, the exposed passive oxide resisted the corrosion in acid solution for several days, in comparison to an anodically passivated film in stainless film, which broke down at once. Mrad et al. (Mrad et al. 2009) obtained PANi films on 304L



stainless steel by cyclic voltammetry in different media: 0.3 mol L<sup>-1</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or 0.3 mol L<sup>-1</sup> KNO<sub>3</sub> (slightly basic). The authors concluded that both types of PANi coatings were able to offer a noticeable enhancement of protection against stainless steel corrosion process carried out in 0.5 mol L<sup>-1</sup> NaCl. However, PANi electrosynthesized in oxalic acid showed the highest electroactivity, but the most porous structure properties. Also, the polymeric film synthesized in KNO<sub>3</sub> medium showed a better barrier property than the polymeric film obtained in oxalic acid medium.

Cook et al. (Cook et al., 2004) investigated the capacity of solution-cast PANi coating to protect mild steel in 0.1 mol L<sup>-1</sup> NaCl and 0.1 mol L<sup>-1</sup> HCl. The authors concluded that PANi in emeraldine base form protected mild steel in acidic and near neutral environments via inhibition of the active corrosion process rather than by anodic protection in the form of passivation.

Santos et al. (Santos et al., 1998) showed the capability of PANi in the emeraldine oxidation state to protect carbon steel and stainless steel against corrosion, in 3% NaCl aqueous solutions saturated with air. The authors related that the polymeric film is strongly adherent to the metallic substrate studied (carbon and stainless steel). The PANi film shifts corrosion potential to more positive values for both carbon steel (~100 mV) and stainless steel (~270 mV) when compared with the bare metal.

Fahlman et al. (Fahlman et al., 1997) studied the use of the emeraldine base form of PANi as a corrosion protecting undercoat on A366 cold rolled steel and iron samples when exposed to a corrosive environment consisting of a humidity chamber at 70 or 80 °C, and the performance of the PANi coatings was analyzed by X-ray photoelectron spectroscopy (XPS). The authors concluded that the mechanism for corrosion protection is anodic, the polymer passivated the metal and there was an increase in the corrosion protection when the top and interfacial oxide layers were removed prior to the polymer deposition.

Moraes and Motheo (Moraes & Motheo, 2006) deposited composites of PANi and carboxymethylcellulose (CMC) on AISI 304 surface by cyclic voltammetry using different concentrations of aniline and CMC. The authors observed that CMC interacts with PANi throughout hydrogen bonding and the morphology of the composite becomes less porous and more packed with increasing CMC concentration. The film of the composite obtained protects the surface of the steel, shifts the corrosion potential to more positive values and decreases the corrosion current. In another study, Moraes et al. (Moraes et al., 2002) synthesized PANi by chemical and electrochemical methods in phosphate buffered media. The chemically synthesized PANi was solubilized in N-methyl-pyrrolidone and was applied on stainless steel (AISI 304). By electrochemical via, a film was deposited on the steel surface by cyclic voltammetry. The efficiency of the PANi films to inhibit the corrosion action was then studied. The authors concluded that chemically prepared PANi protects more efficiently the stainless steel in its doped state. Moraes et al. (Moraes et al., 2003a, 2003b) also showed the role of phosphate buffer solution as a moderator of the local pH variations at the polymer/electrolyte interface and the possibility of forming homogeneous and strongly adherent films. The PANi applied as coating on stainless steel acts as a corrosion inhibitor in 3% NaCl, shifting the  $E_{\text{corr}}$  to more noble values.

To illustrate the efficiency of PANi films in the corrosion protection of carbon and stainless steels, Fig. 1 depicts the potentiodynamic polarization curves for AISI 1020 carbon steel and AISI 304 stainless steel covered or not with PANi film, in NaCl 0.6 mol L<sup>-1</sup>. The PANi film was formed by casting 7% (m/V) of undoped PANi solubilized in N-methyl-pyrrolidone. Corrosion studies were carried out with a potentiostat (EG&G PAR model

273A) using a saturated calomel electrode as reference, Pt plate as counter electrode and  $0.5 \text{ mV s}^{-1}$  sweep rate.

The value of  $E_{\text{corr}}$  determined for AISI 1020 carbon steel is  $-0.545 \text{ V}$ . As this potential is already an oxide layer formed on the surface, with increasing potential (above the  $E_{\text{corr}}$ ), this layer begins to dissolve and other processes, as pitting corrosion begin to occur. The  $E_{\text{corr}}$  of AISI 1020 coated with PANi is  $-0.446 \text{ V}$  and pitting potential ( $E_{\text{pit}}$ ) is  $-0.214 \text{ V}$ . The protective action of PANi on the carbon steel causes the change in  $E_{\text{corr}}$  to more positive values (Fig. 1), compared to the uncoated electrode ( $E_{\text{corr}} = -0.545 \text{ V}$ ), due to the inhibition of redox reactions that occur at the metal/electrolyte interface. For AISI 304 stainless steel (Fig. 1),  $E_{\text{corr}} = -0.340 \text{ V}$  and  $E_{\text{pit}} = +0.087 \text{ V}$ . When AISI 304 is coated with PANi, there is a shift of corrosion potential to more positive values - this behaviour is similar to that of AISI 1020 carbon steel. However, for AISI 304 coated with PANi, the corrosion potential variation ( $\Delta E_{\text{corr}} \cong 0.295 \text{ V}$ ) is greater than that of the uncoated surface. This change can be justified, as described by Santos Junior et al. (Santos et al. (Santos et al., 1998)), as the attack of the species in the electrolyte, passing through the polymer layer, forming a passivation layer and interrupting the corrosion process. Fig. 2 depicts images of AISI 1020 carbon steel before and after the corrosion tests. Fig. 2a shows the risks due to the mechanical polishing and points, which can be attributed to structural defects. After the corrosion tests, the surface seem to be attacked showing (Fig. 2b) a large number of pits (corrosion points) and intergranular corrosion. The surface, which was smooth before the tests, becomes irregular and flat. The surface of AISI 1020 carbon steel, shown in Fig. 2b, is easily corroded when no corrosion protection is applied.

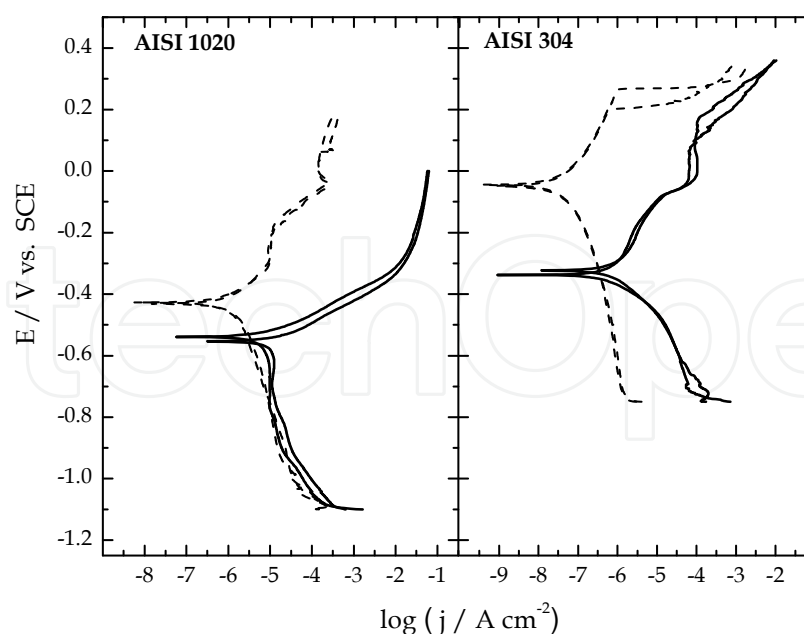


Fig. 1. Potentiodynamic polarisation curves for carbon steel AISI 1020 (left) and stainless steel AISI 304 (right) coated with PANi film (---) and bare (—) in the presence of  $0.6 \text{ mol L}^{-1}$  NaCl aqueous solution saturated with air. Sweep rate:  $0.5 \text{ mV s}^{-1}$ .

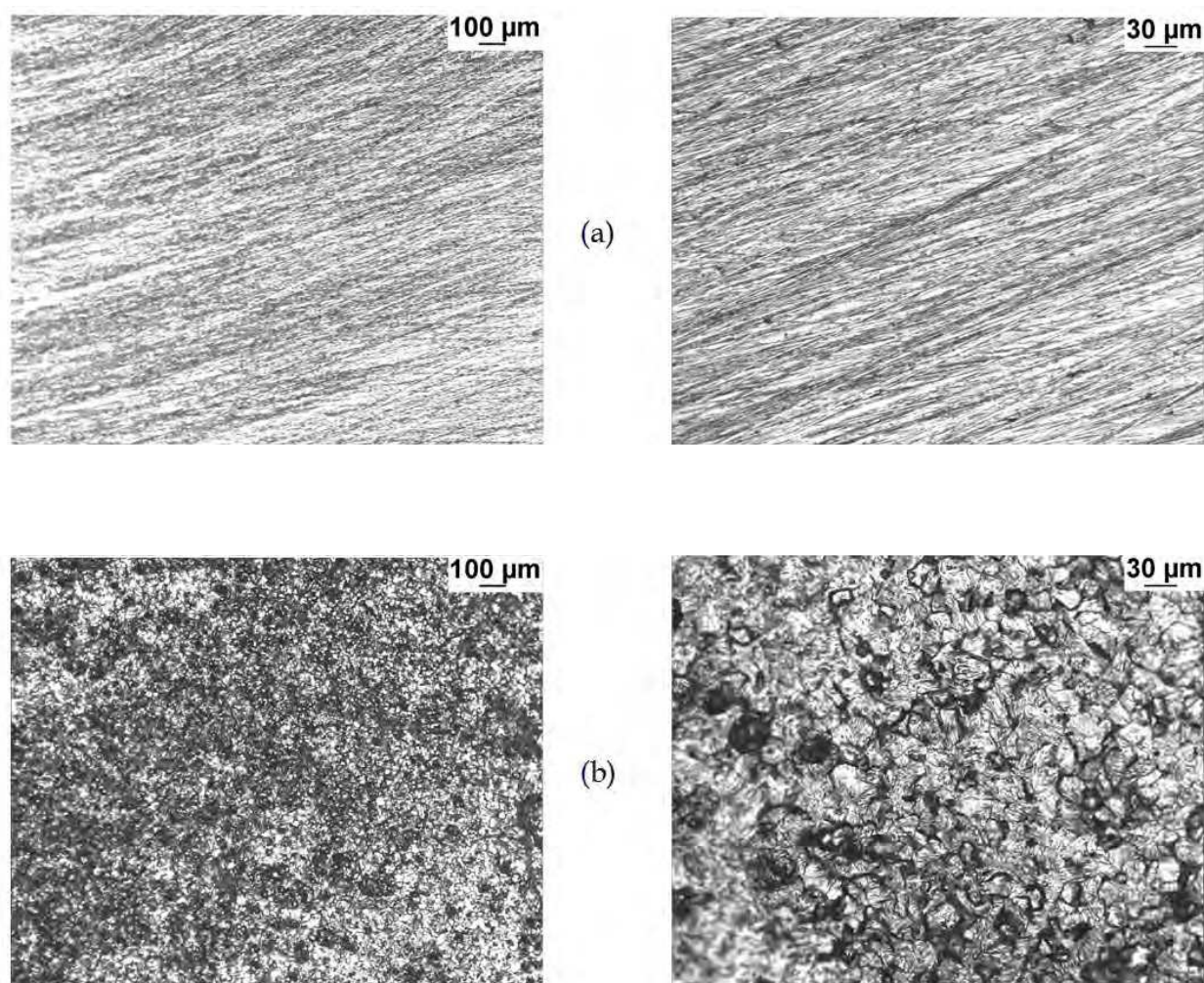


Fig. 2. Optical images of AISI 1020 carbon steel uncoated (a) before and (b) after corrosion tests. Magnification: 50x (left) and 200x (right).

Fig. 3 shows images of AISI 1020 carbon steel with the PANi film before (Fig. 3a) and after the corrosion tests (Fig. 3b) and images of the surface after removal of the PANi film (Fig. 3c). In Fig. 3a, the PANi film covering the carbon steel electrode is compact and heterogeneous.

The characteristics of the PANi film formed on the substrate depend on the characteristics of the surface of carbon steel (Fig. 3a). During the drying of the PANi film, the surface of carbon steel undergoes corrosion processes, thus forming a heterogeneous film. After the corrosion tests there is no change in the structure of the PANi film (Fig. 3b). When the PANi film is removed (Fig. 3c), it is possible to observe that the surface has been protected from corrosion, in comparison with unprotected carbon steel.



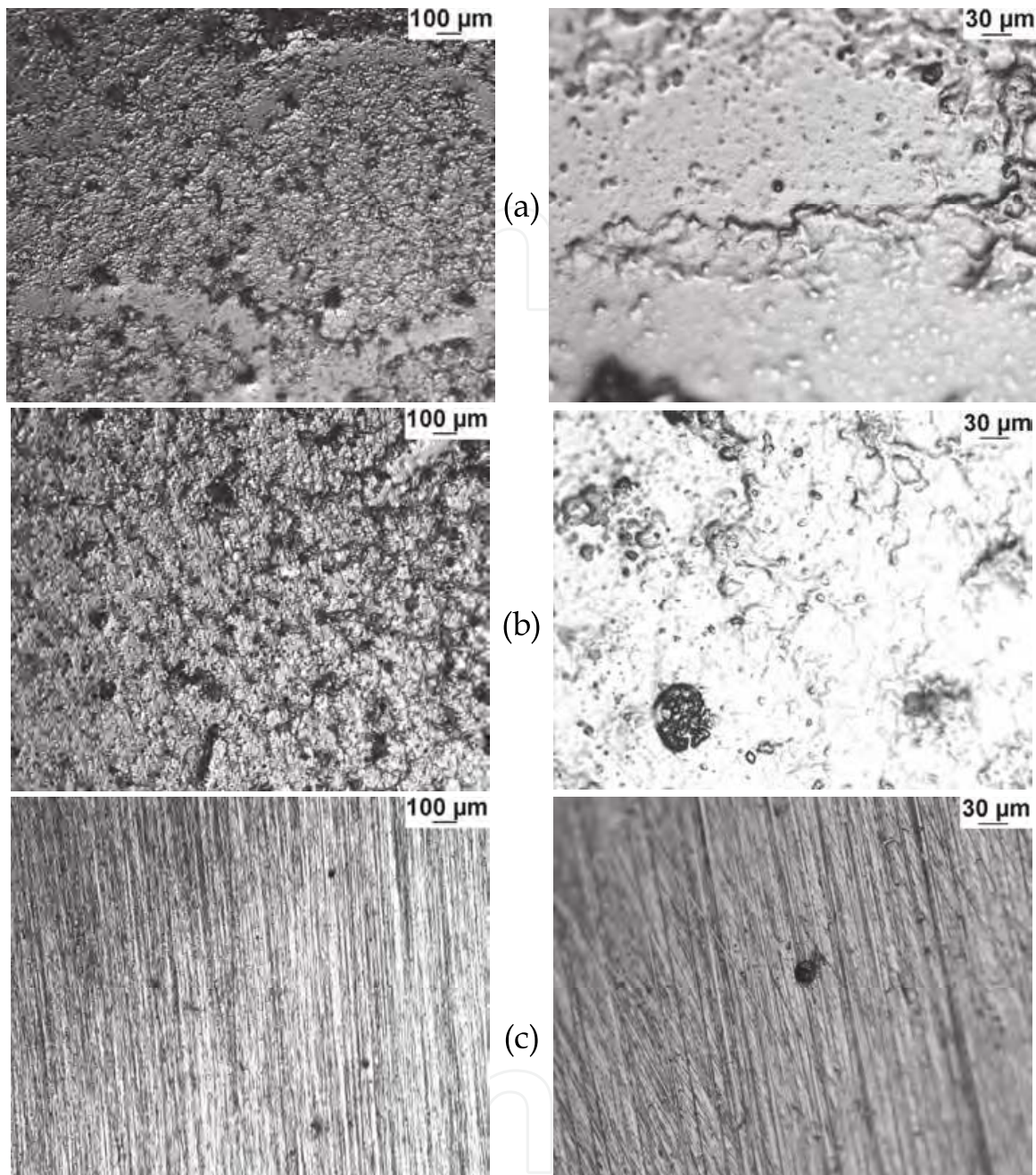


Fig. 3. Optical images of AISI 1020 carbon steel coated with PANi film (a) before and (b) after corrosion tests. (c) carbon steel surface after removal of PANi film. Magnification: 50x (left) and 200x (right).

Fig. 4 shows the images of AISI 304 stainless steel before and after the corrosion tests. The presence of risks is attributed to the mechanical polishing and the points to structural defects. After the corrosion tests one can see that the stainless steel has been attacked by chloride ions, which is evidenced by the presence of pits. Unlike what occurs in carbon steel, due to the formation of protective film of  $\text{CrO}_3^{2-}$ , for stainless steel only few pits are observed in function of the presence of chloride ions.

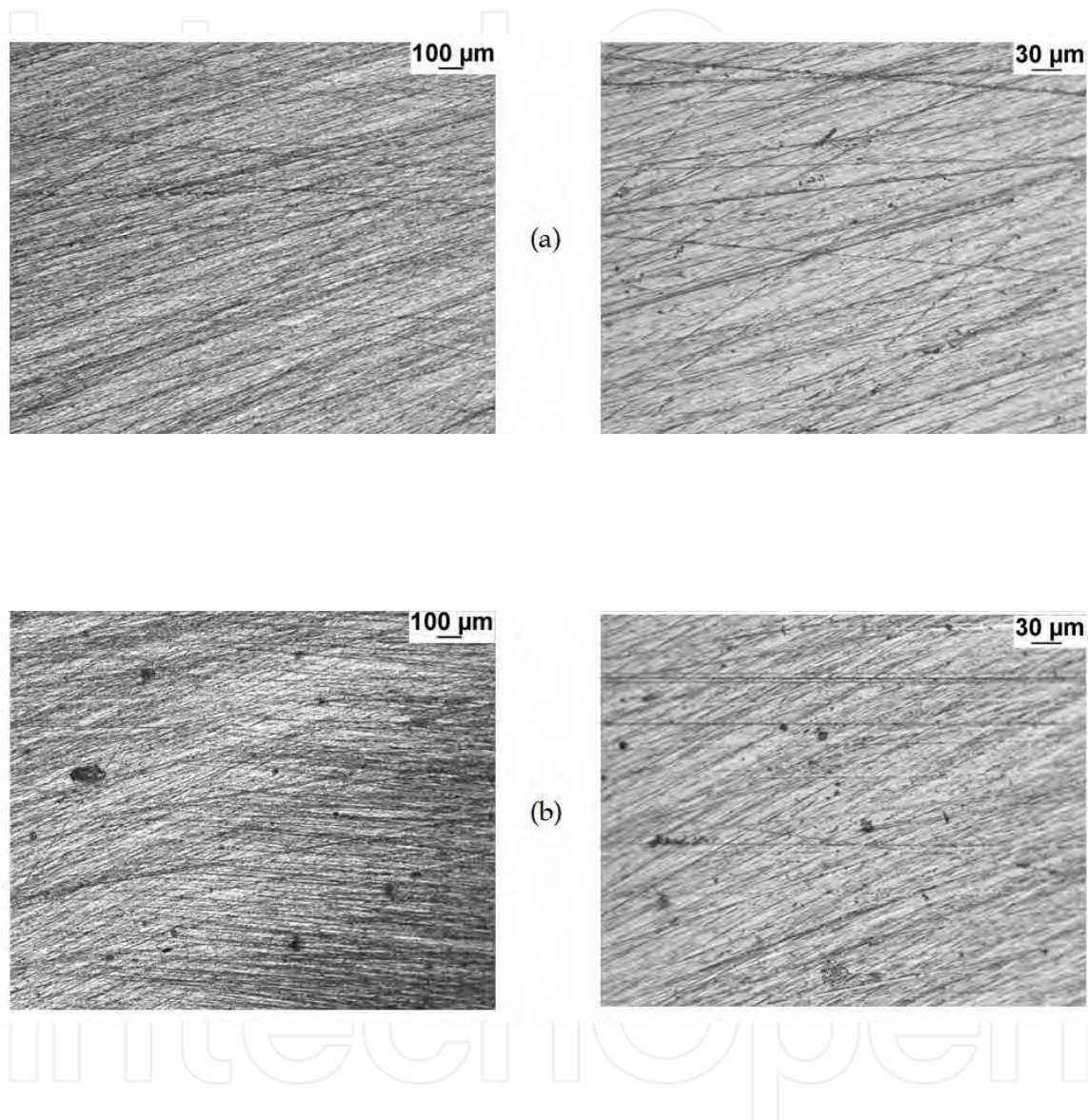


Fig. 4. Optical images of uncoated AISI 304 stainless steel (a) before and (b) after corrosion tests. Magnification: 50x (left) and 200x (right).

The PANi film formed on the surface of stainless steel is compact, uniform and homogeneous, as shown in Fig. 5a. After the corrosion tests, multiple bubbles emerged on the surface of the polymer (Fig. 5b). When the PANi film is removed (Fig. 5c), the surface does not present too many points of corrosion, evidencing the protection of the PANi film. These examples support many studies in the literature, showing the capability of PANi to protect steel surfaces, by not only barrier effect, but also anodic protection.



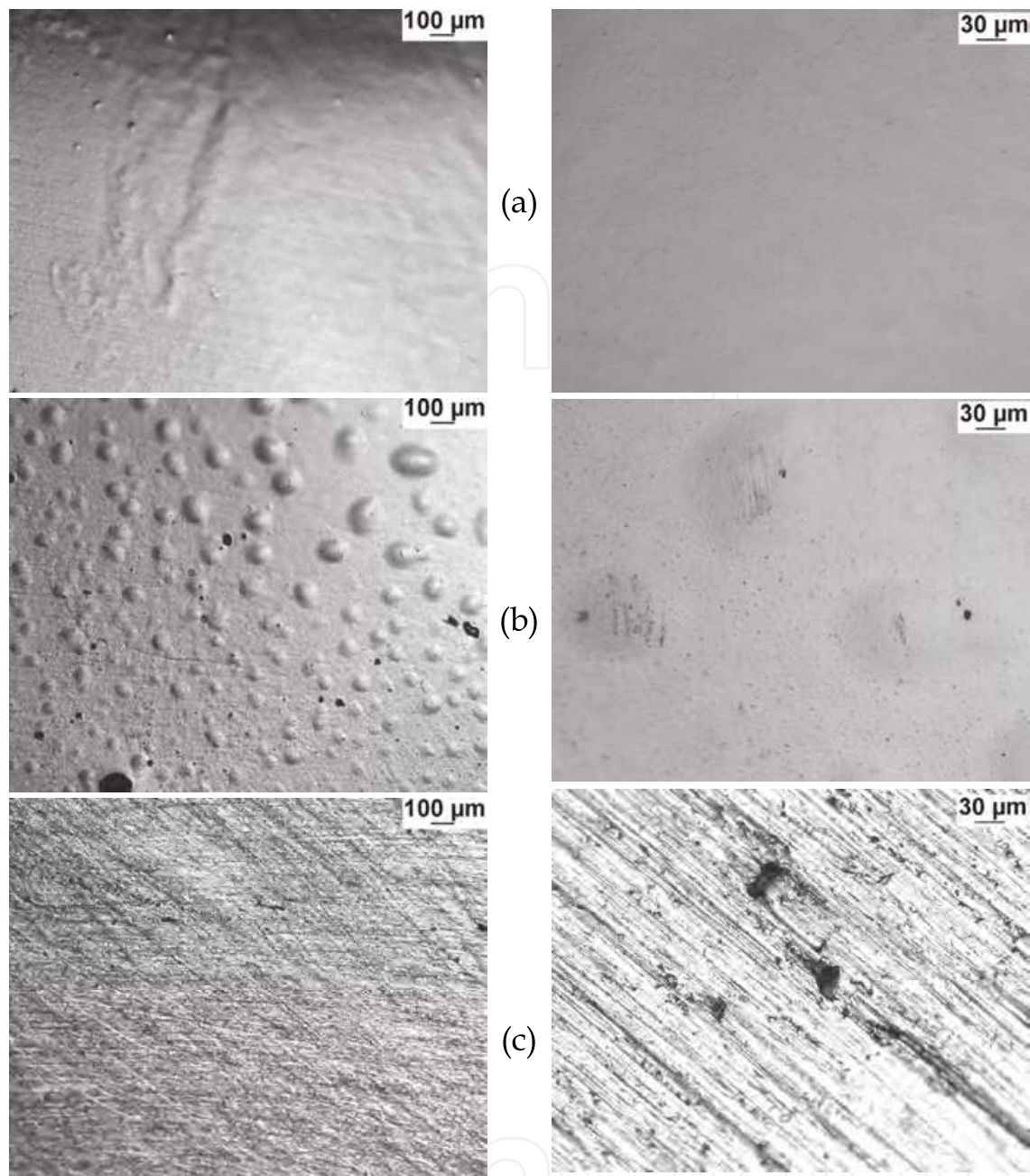


Fig. 5. Optical images of AISI 304 stainless steel coated with PANi film (a) before and (b) after corrosion tests. (c) stainless steel surface after removal of PANi film. Magnification: 50x (left) and 200x (right).

## 5. Aluminium, aluminium alloys and polyanilines

As presented in the latter sessions, many researchers have studied the corrosion protection of different types of steels by using chemically or electrochemically synthesized PANi, in its conductive and insulate form. Another commodity metal with increasing application is aluminium. To improve the mechanical properties, small quantities of alloying elements are added to pure aluminium, forming different aluminium alloys; however, the protection afforded is reduced by the natural passive layer.

The corrosion protection of aluminium and its alloys, especially in environments containing chloride ion, is very important, because of the increasing health risks and environmental problems with conventional coatings, like chromate and phosphate. Therefore, the coating of aluminium by PANi can become an alternative solution to the problem.

The electrodeposition of aniline on pure aluminium surface was described by Conroy and Breslin (Conroy & Breslin, 2003). The PANi films were obtained from a 1.0 mol L<sup>-1</sup> tosylic acid solution containing aniline (0.132 or 0.174 mol L<sup>-1</sup>) at a constant potential (1.25 V vs. SCE). After the deposition, the coated aluminium was exposed to a highly aggressive 0.5 mol L<sup>-1</sup> NaCl, pH 5.85 electrolyte, using the anodic polarization technique. The PANi films shifted the  $E_{\text{corr}}$  to more positive values, with a slight increase in the corrosion resistance of aluminium. The authors related that chloride anions diffuse across the polymer and react at the underlying substrate.

Kamaraj et al. (Kamaraj et al., 2009) reported the electropolymerization of aniline on AA7075 alloy in 0.1 mol L<sup>-1</sup> oxalic acid and 0.5 mol L<sup>-1</sup> aniline by galvanostatic polarization (using 20 and 15 mA for 1h). The AA7075 alloy coated with the PANi in emeraldine salt form was tested in aerated 1% NaCl by potentiodynamic polarization and impedance technique. For the film obtained using 15 mA, the corrosion current density and  $E_{\text{corr}}$  were not significantly changed in relation to the uncoated sample. For the film obtained using 20 mA, a small shift to more positive values was observed in  $E_{\text{corr}}$ . The result also confirmed the slight improvement in the corrosion protection performance. However, the authors concluded the poor corrosion resistant behaviour was due to the galvanic action of PANi and related it to the use of cerium in the post-treatment to improve the corrosion protection offered by PANi coatings.

Martins et al. (Martins et al., 2010) related the deposition of PANi films on AA6061-T6 alloy in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 0.5 mol L<sup>-1</sup> aniline using cyclic voltammetry and potentiostatic polarization. In both methods, the films obtained were adherent and presented a cauliflower structure. However, the corrosion resistance of PANi in naturally aerated 0.5 mol L<sup>-1</sup> NaCl solutions showed a slight increase in the  $E_{\text{corr}}$  for coated substrate, when compared with bare metal.

The study about the capability of PANi in the emeraldine base form and self-doped sulfonated PANi form as corrosion protection of AA2024-T3 alloy was performed by Epstein et al. (Epstein et al., 1999). The results showed the efficiency of the coatings to reduce the corrosion rate when the coated alloy was exposed to 0.1 mol L<sup>-1</sup> NaCl solution. The X-ray photoelectron spectroscopy analyses indicated a reduction in the copper concentration at the surface of the coated AA2024-T3 alloy samples. The authors concluded that the PANi in the different studied forms facilitated the extraction of copper from the surface of the AA2024-T3 alloy, reducing the galvanic couple between aluminium and copper, and decreasing the corrosion processes.

Fujita & Hyland (Fujita & Hyland, 2003) investigated the use of PANi (emeraldine base form) as anti-corrosion coatings for AA5005 alloy. The PANi obtained in the 1 mol L<sup>-1</sup> HCl and ammonium peroxydisulfate as an oxidant was solubilized in N-methyl-pyrrolidone. This dispersion was deposited onto the alloy surfaces. The alloy substrates, uncoated and coated with PANi films, were exposed to 80% relative humidity and 30 °C for up to 4 weeks in a humidity chamber. After the corrosion tests, the samples were characterized by XPS and the authors observed that the amount of oxide grown was much smaller for coated samples than uncoated ones. However, the PANi in emeraldine base form can provide some corrosion resistance for the AA5005 alloy.

According to the classification system for aluminium alloys adopted by the Aluminum Association (Davis, 1999), zinc is the main alloying element in the AA7075 alloy (Al-Zn-Mg-Cu), while for the AA8006 alloy, the main alloying elements are iron and manganese.



The AA7075 alloy has been frequently studied because of its widespread use in the aerospace industry. On the other hand, AA8006 alloy has been successfully used for packaging and microelectronics industries, due to its high ductility and resistance to large plastic deformation in the lamination process.

Corrosion studies performed on AA7075 and AA8006 alloys uncoated and coated with PANi films were performed using potentiodynamic polarization in 0.6 mol L<sup>-1</sup> NaCl aqueous solution at 0.5 mV s<sup>-1</sup>. The measurements were taken with a potentiostat and a saturated calomel electrode as reference. The PANi film was formed from casting solution (undoped PANi dispersed in N-methyl-pyrrolidone).

Fig. 6 depicts the potentiodynamic polarization curves obtained for AA7075 and AA8006 alloys coated and uncoated with PANi films. The  $E_{\text{corr}}$  for AA8006 alloy was -0.913 V, while for the AA7075 alloy it was -0.768 V. These results show that the surface of the AA7075 alloy is more noble than that of the AA8006 alloy. The alloying elements present in the AA8006 (Al-Fe-Mn) provide this alloy with more susceptibility to corrosion than for the AA7075 alloy.

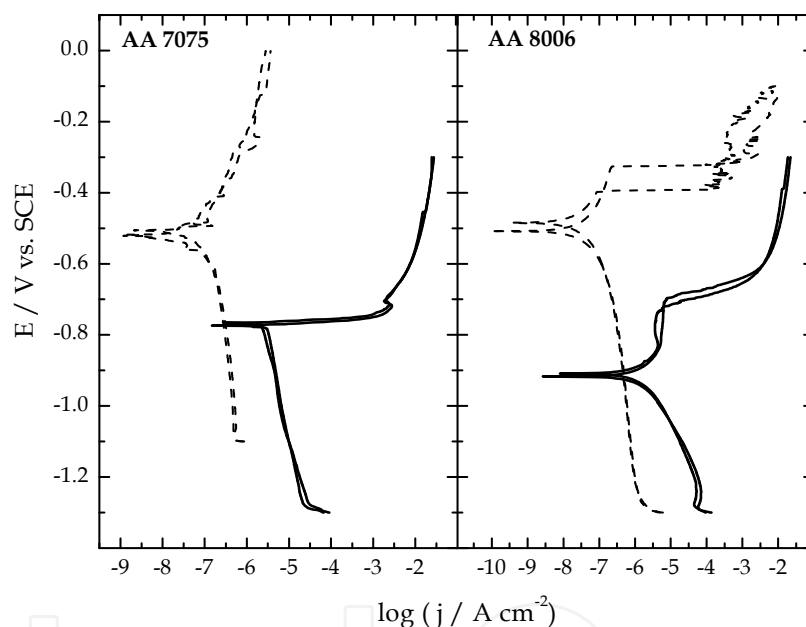


Fig. 6. Potentiodynamic polarisation curves for aluminium alloys AA7075 (left) and AA8006 (right) coated with a PANi film (---) and bare (—) in the presence of 0.6 mol L<sup>-1</sup> NaCl aqueous solution saturated with air. Sweep rate: 0.5 mV s<sup>-1</sup>.

For the AA8006 alloy, the pitting potential observed was -0.681 V. However, for the AA7075 alloy,  $E_{\text{pit}} = -0.763$  V is very close to the value of  $E_{\text{corr}}$ . This result shows that for this alloy, the pitting corrosion occurs almost simultaneously with the uniform corrosion, i.e., while the passivation layer is formed, the aggressive species (Cl<sup>-</sup> ions in the solution) attack the surface and the pitting corrosion occurs.

As observed in Fig. 6, when PANi is used as a protective coating on AA7075 and AA8006 alloys, the corrosion and pitting potentials are shifted to more positive values in relation to the uncoated electrode, providing protection anode. For the AA7075 alloy coated with PANi,  $E_{\text{corr}} = -0.516$  V and  $E_{\text{pit}} = -0.455$  V, while for AA8006 alloy coated with PANi,  $E_{\text{corr}} = -0.501$  V and  $E_{\text{pit}} = -0.257$  V.

Fig. 7 shows optical images of the surface of AA7075 and AA8006 alloys, before and after the polarization curves. Before immersion in 0.6 mol L<sup>-1</sup> NaCl solution, the surfaces of the AA7075 and AA8006 alloys were homogeneous and showed some imperfections (due to the mechanical polishing). After immersion in a corrosive solution and the polarization tests, some irregularities (holes) were observed on the surfaces, which appeared to be deep. The AA7075 alloy showed a larger number of pits in comparison with the AA8006 alloy, possibly because the values of  $E_{\text{pit}}$  and  $E_{\text{corr}}$  were very close.

The PANi film formed on the surface of the aluminium alloy is compact and uniform, covering the irregularities of the surface, as shown in Fig. 8a. After the corrosion tests, bubbles emerged on the surface of the polymer (Fig. 8b)

When the polymer film had been removed the images obtained for both alloys became similar. Fig. 8c shows the formation of a smaller number of defects on the surface coated with PANi in comparison to the uncoated one, however, the geometry of the defects was more defined.

Comparing the micrographs of the metal surface after the corrosion tests with and without coating, we can conclude that the defects are deeper when PANi is not used. On the other hand, the defects are more superficial on the surface coated with PANi.

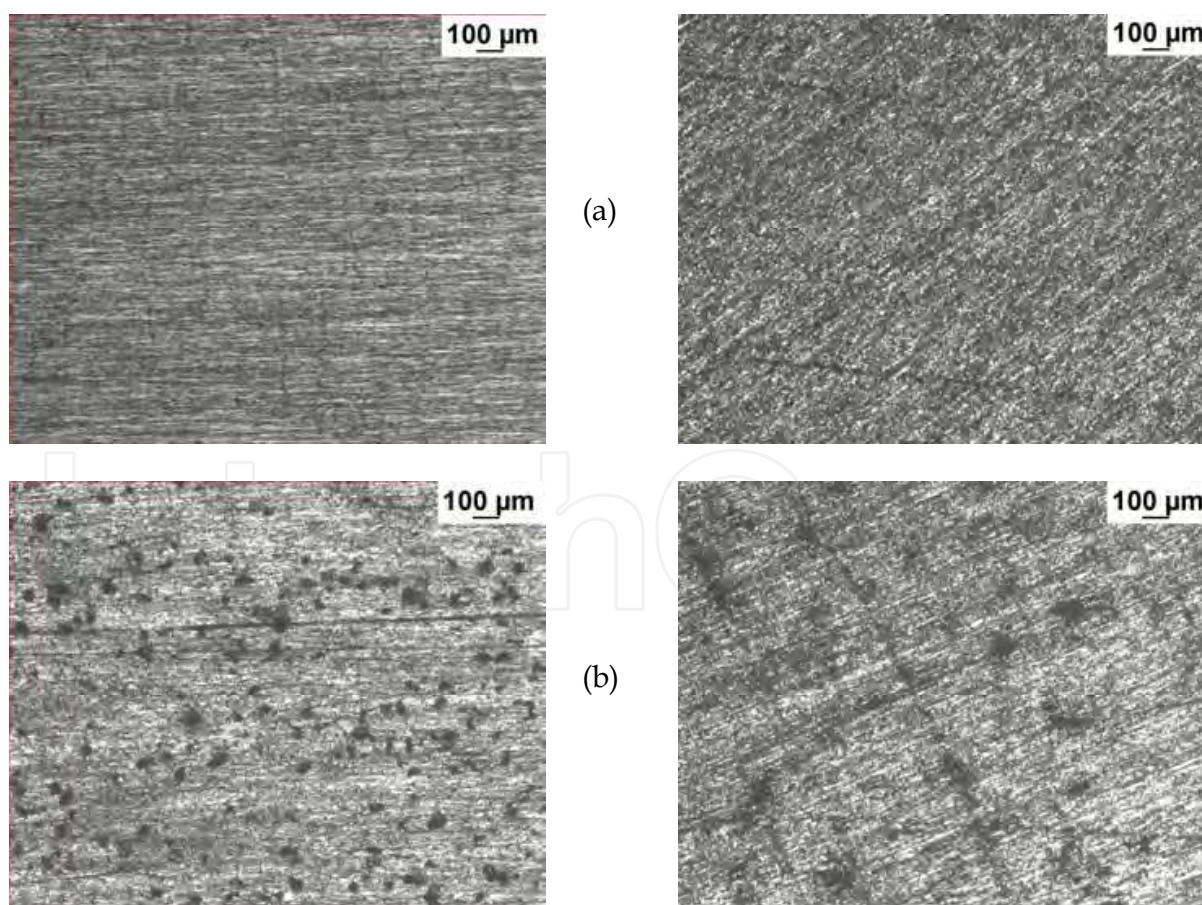


Fig. 7. Optical images of uncoated AA7075 (left) and AA8006 (right) (a) before and (b) after corrosion tests.



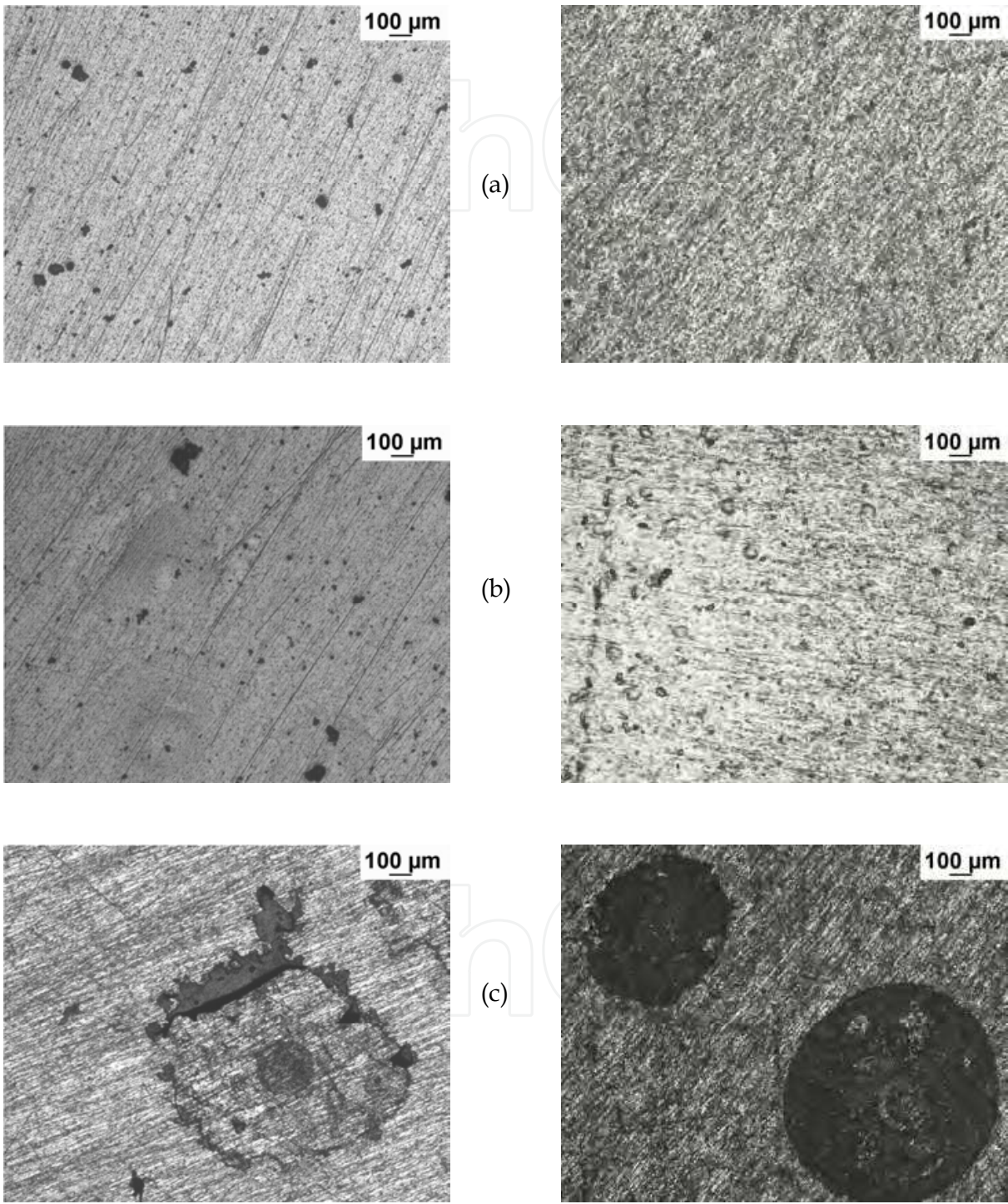


Fig. 8. Optical images of AA7075 (left) and AA8006 (right) coated with PANi films (a) before and (b) after corrosion tests. (c) aluminium alloys surface after removal of PANi film.

## 6. PANi adhesion on aluminium surfaces

To improve the corrosion protection of aluminium and alloys surfaces different pre-treatments, such as chromium plating, phosphating, and organic/polymeric coatings have been used. The pre-treatment of the substrates is necessary due to the natural oxides formation in passivating metals, which protect the active surface and hinder the coating adhesion. Considering that the hexavalent chromium is carcinogenic, the chromium plating or chromate conversion coatings have been abolished, and there has been a high demand for environmentally friendly surface treatments. Nevertheless, the use of organic compounds is limited because the adhesion of these materials on aluminium surfaces is very poor, requiring the use of adhesion promoters.

Among the many alternative pre-treatments, we can cite the use of SAMs (Self-assembled monolayers) and chelating agents as adhesion promoters and potential replacements for chromium-based pre-treatments. Among the SAMs, the organo-functional silanes can be employed to improve the adhesion of organic coatings to the aluminium surface. These adhesion promoters contain various functional groups, including amino, epoxy, vinyl and alkyl groups.

Bonding mechanisms of silanes to metal surfaces have been reported by different authors (Cecchetto et al., 2008; Hintze & Calle, 2006). A general mechanism can be described in the following stages: *i*) immersion of a metal into a dilute silane solution for few seconds; *ii*) spontaneous adsorption of the silanols groups (SiOH) on the surface through hydrogen bonds; *iii*) formation of covalent metallo-siloxane bonds from -SiOH groups and metal hydroxyls (HO<sub>Sub</sub>). The excess of SiOH groups, adsorbed on the surface, also condenses to form a siloxane, Si-O-Si. The formed covalent bonds are assumed to be responsible for the excellent bonding of the silane film to the metal substrate.

Silva et al. (Silva et al., 2010) studied the coating combining self-assembled monolayers and PANi on AA2024 alloy. The use of octadecyltrimethoxysilane/PANi and propylmethoxysilane/PANi recovering AA2024 alloy shifted the values of corrosion and pit potentials to more positive, and the double films composed of SAM and PANi were more effective in comparison to the single SAM and PANi. The authors concluded that the double film of octadecyltrimethoxysilane/PANi presented the best corrosion protection due to the anodic protection associated with the barrier effect.

Mohseni et al. (Mohseni et al., 2006) studied the influence of amino and vinyl-silane-based treatments on the adhesion performance of an epoxy coated AA1050 alloy. The authors reported that the wettability of the AA1050 alloy increased with the use of silane-based treatment, and the surface became more hydrophilic. The adhesion strength of epoxy coated samples shows an increase in the presence of silane pre-treatment, which can be explained by the relative increase in the surface free energy of the substrates in comparison with the sample without any treatment (blank sample).

Pathak and Khanna (Pathak & Khanna, 2009) studied the combined organosilane-polyester-based waterborne coatings (SiE) using methyltrimethoxysilane, 3-glycidoxytrimethoxysilane and polyester resin for corrosion protection of AA6011 alloy. The authors observed that an increase in the concentration of organosilane in SiE coatings improved the corrosion resistance, hydrophobicity, weathering stability and hardness. The corrosion current of the SiE coated substrates decreased approximately two orders of magnitude in comparison with



the bare substrate in 3% NaCl because the coating inhibited the anodic process and acted as a barrier, blocking the contact between the electrolyte and the metal surface.

Hinze and Calle (Hinze & Calle, 2006) reported the deposition of SAMs formed from *n*-decyltriethoxysilane (DS) and *n*-octadecyltriethoxysilane (ODS) on AA2024-T3 alloy and studied their use as corrosion protection in 0.5 mol L<sup>-1</sup> NaCl solution. The  $E_{\text{corr}}$  values for the modified surfaces were shifted to more positive potentials with respect to the bare surface, indicating a slight corrosion protection. However, the authors also observed that organosilanes form SAMs with a large number of defects on AA2024-T3 alloy, which probably occur over copper enriched particles found on the alloy surface.

Cecchetto et al. (Cecchetto et al., 2008) used 3-aminopropyl-triethoxysilane (APS) as primer to promote the adhesion between the AA5182 alloy substrate and PANi (in emeraldine base) coating in order to improve the corrosion protection. Potentiodynamic studies using samples coated with APS and PANi showed a reduction in the corrosion current when compared with the bare surface. The authors concluded that APS improves the adhesion of PANi coating on the alloy surface and that the corrosion resistance of PANi-coated AA5182 substrate is improved when the surface is pre-treated with an APS.

Other promoters of adhesion are the chelating agents. They have been used in the pre-treatment of metallic surfaces in the electroplating industry in order to produce decorative aluminium surfaces. Such agents can be hydrophilic or hydrophobic and can lead to the passivation of the metal by a salt or a simple formation of a blocking compound (Huerta-Vilca et al., 2003a, 2005). These authors studied the alizarin as a chelating agent in electrodeposition of PANi on aluminium surfaces (Huerta-Vilca et al., 2003a). The use of this chelating agent suppressed the evolution of hydrogen and allowed the establishment of anchor points for the growth of the polymer film. The authors also concluded that under these conditions, it is possible to electropolymerize aniline on aluminium alloys surfaces using lower aniline concentrations.

## 7. Anodizing

As described by Talboat and Talboat (Talboat & Talboat, 1998), anodizing is the formation of thick oxide films on metal substrates, driven by an anodic potential applied to the metal in a suitable electrolyte. The process involves the immersion of the clean metal in an acid solution, as anode, with a potential value that can be constant and appropriated or gradually increased to a maximum value. It leads to superficial films with properties that vary from a soft and porous deposit, which can be sealed to improve the corrosion resistance, to a hard one, when prepared at room temperature. Aluminum is the most commonly anodized metal and the electrolyte used could be sulphuric, phosphoric, chromic, oxalic, or boric acid (Droffelaar & Atkinson, 1995).

The morphology of the oxide formed is controlled by the nature of the electrolyte and anodizing conditions used. For example, Coz et al. (Coz et al., 2010) studied the preparation of anodic films on aluminium substrates from phosphoric acid solution. The authors were able to obtain self-supported films (without the aluminium substrate) with thickness reaching up to 130 nm, amorphous characteristics and partial hydration. The composition was determined as Al<sub>2</sub>O<sub>3</sub>, 0.186AlPO<sub>4</sub> · 0.005H<sub>2</sub>O and unchanged structure to temperature values up to 900 °C.

Anodizing is one of the most important processes for the corrosion protection of aluminum. Two types of anodic films can be produced: barrier and porous films. According to Mert et al. (Mert et al., 2011), the first can be formed in boric acid, ammonium borate, and ammonium tetra borate in ethylene glycol ( $5 < \text{pH} < 7$ ). The authors studied the synthesis of compact oxide films on aluminium, which can act as good corrosion protection, by anodizing process. The anodizing of aluminium was performed by electrolysis in  $0.4 \text{ mol L}^{-1} \text{H}_2\text{SO}_4 + 0.145 \text{ mol L}^{-1} \text{H}_3\text{BO}_3$  solution at  $20^\circ\text{C}$  and the corrosion of non-anodized and anodized aluminium was investigated in 3.5% NaCl solution. The authors concluded that the ideal anodizing potential was 15 V and the convenient anodizing time was 30 min. The anodized samples (obtained in 15, 30, 60, and 120 min) shifted the  $E_{\text{corr}}$  to more positive values in relation to non-anodized aluminium. However the oxide film obtained in 30 min of anodizing showed the largest displacements of  $E_{\text{corr}}$ .

The second type is porous films and can be obtained in, for instance, sulphuric, phosphoric, chromic and oxalic acids. If the anodic oxide is slightly soluble in the electrolyte, then porous oxides are formed. This porous coating may also be coloured using organic dyes, pigment impregnation, or electrolytic deposition of various metals into the pores of the coating. After coloration, the coating is sealed. This coloured anodized aluminium combines decorative purposes with corrosion resistance, and can be used in many applications.

Based on the knowledge about porous films, Huerta-Vilca et al. (Huerta-Vilca et al., 2004b) showed a method to improve the adherence of PANi on aluminium alloys. After a galvanostatic activation in nitric acid, PANi was electrodeposited from  $0.4 \text{ mol L}^{-1}$  aniline in  $0.5 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  by cyclic voltammetry. In the galvanostatic pre-treatment the surface was covered by a thick oxide layer with homogeneously distributed pores. When PANi was electrochemically synthesized, the deposition occurred in these pores having the substrate as an anchor point. This anchorage permitted an expressive improvement in the adherence and the formation of closed polymer films covering the electrode surface with consequent improvement in the corrosion resistance. The substrate (AA1050) coated with PANi obtained by this method presented greater corrosion resistance than the samples with films growth without pre-treatment.

Another paper that illustrated the polymerization of aniline into the anodic alumina films and better corrosion protection properties was presented by Zubillaga et al. (Zubillaga et al., 2009). These authors reported the syntheses of anodic alumina films containing PANi and  $\text{TiO}_2$  or  $\text{ZrO}_2$  nanoparticles on AA2024-T3 alloy. The authors showed that the PANi coatings with  $\text{TiO}_2$  nanoparticles improved the corrosion protection of the AA2024-T3 alloy in  $0.005 \text{ mol L}^{-1} \text{NaCl}$  and  $0.1 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4$  solution.

## 8. Conclusions

PAni has been extensively studied as a corrosion inhibitor in both doped and undoped forms on steels, aluminium and aluminium alloys surfaces. It acts as a barrier against corrosion and also anodic protection, maintaining the metal in a passive potential region. For steels, the literature has reported the good adherence of the PANi films obtained either electrochemically or by casting solution. However, to improve the adherence between PANi film and aluminium and alloys surfaces it is important to use adhesion promoters,

such as SAMs and chelating agents. The adherence can also be promoted by the anodization of the surface under specific conditions. This method is usually applied in the industry to protect surfaces as well as to colour them. There still exist many possibilities to be investigated using PANi as a component in corrosion protection systems, such as blends and composites. Concerning composites, it is important to mention some preliminary researches using natural resins/PANi composites for corrosion protection, in order to improve the adherence of the film and its plasticity. The adherence of deposits as well as its influence on the corrosion protection are well known in the electroplating industry. Regarding conducting polymers, the problem is the same and the development of paints containing PANi with good adherence is already a reality. However, a new generation of coatings, called smart coatings, superior to those involving conducting polymers is in evidence. Many advantages will be attributed to them, but the adherence will be always a matter to be analysed.

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