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The influence of surface microstructure and chemical composition on corrosion behaviour in fuel-grade bio-ethanol of low-alloy steel modified by plasma nitro-carburizing and post-oxidizing

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ABSTRACT

The interaction of bio-ethanol on steel surfaces modified by plasma-assisted diffusion technologies is studied for the first time. The influence of surface microstructure and chemical composition on corrosion behaviour of AISI 4140 low-alloy steel in fuel-grade bio-ethanol was investigated. The steel surfaces were modified by plasma nitro-carburizing followed plasma oxidizing. X-ray diffraction, scanning electron microscopy, optical microscopy, X-ray dispersive spectroscopy, and glow-discharge optical emission spectroscopy were used to characterize the modified surface before and after immersion tests in bio-ethanol up to 77 days. The main corrosion mechanism is pit formation. The pit density and pit size were measured in order to quantify the corrosion resistance which was found to depend more strongly on microstructure and morphology of the oxide layer than on its thickness. The best corrosion protection was observed for samples post-oxidized at 480 °C and 90 min.

1. Introduction

In the oil crisis of the seventies decade of last century, Brazil started to diversify its energy matrix by the implementation of the Pro-Alcohol National Program [1]. Nowadays, bio-ethanol obtained from sugarcane is an important fuel component in Brazil, where the automobile fleet uses variable quantities of such biofuel mixed with regular oil fuel in proportions from 20% (E-80) up to 100% (E-100) of bio-ethanol.

Considering the production, transportation and final use of bio-ethanol, one notices that it enters in contact with different metallic parts. On one hand, pure bio-ethanol does not corrode steels and alloys based on zinc or aluminium which are used to build stock tanks and auto parts that bio-ethanol is usually in contact with. On the other hand, different metals show corrosion processes taking place on the surface during immersion in bio-ethanol [2,3]. The key parameters, in qualitative and quantitative terms, are the impurities and their respective concentrations. Depending on each national law around the world, bio-ethanol is defined as a liquid solution containing maximum limits of different impurities such as chlorides, acetic acid, water, iron, and others. Impurities and contaminants may come from diverse sources like production and transportation chains, the metals and chloride contents in the soil where the sugarcane is cultivated [4], and others.

The presence of impurities such as water, acetic acid, and chloride starts corrosion processes, taking place through different mechanisms, according to their concentrations [5]. Chloride and dissolved oxygen promote both stress corrosion cracking (SCC) initiation and growth as well as pitting corrosion in X-65 and ASTM A36 steels [6,7]. Moreover, an increase in water concentrations leads to change the corrosion mechanism from SCC to pitting in X-65 steel [6]. Water seems to have an important role in determining the corrosion mechanism in carbon steels, since concentrations above 5 wt.% lead to change again the corrosion mechanism from localized (pits) to uniform corrosion [5,8]. In addition, for a relatively high concentration of acetic acid (0.1 M) in ethanolic solution, the acetate ion acts as an inhibitor of the corrosion process in low carbon steel [9]. Assuming passive conditions for carbon steels, a pH higher than 8 is required to guarantee corrosion protection in an ethanol solution containing 1 mg l^{-1} SO_4^{2-} and 4.8% (v/v) H_2O

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[10]. Lower contents of chloride and water promote SCC instead of pitting corrosion, which is generally observed when higher contents of those impurities are presented in the bio-ethanol. Moreover, acetic acid is an oxidation product of bio-ethanol as well, and; therefore, it induces iron dissolution in steel by redox reaction.

Plasma-assisted diffusion technologies are able to modify metallic surfaces by incorporation of light elements such as carbon, nitrogen, boron, and oxygen. Indeed, such surface engineering techniques are widely used in the automobile industry due to the diversified properties given on the surfaces of auto parts [11]. For example, carbon and nitrogen have been used to improve the hardness and wear resistance of ferrous alloys owing to the surface formation of tough iron carbonitride ceramics [12]. On one hand, plasma-assisted diffusion technologies such as plasma nitriding, nitro-carburizing, and oxidation in ferrous alloys produce modified layers that can functionalize material surfaces [13], combining high hardness with wear and corrosion resistances. On the other hand, many studies have been devoted to investigate the corrosion behaviour of ferrous alloys modified by plasma-assisted diffusion technologies.

In the case of plain and low-alloy steel, a duplex process of plasma nitriding/nitrocarburizing followed by plasma oxidation can grow a metallurgical system of two well-defined layers where an underneath hard and wear resistant layer is combined with an outermost corrosion resistant and low-friction layer [14,15]. For hot work steels, either plasma nitriding or nitro-carburizing can improve the pitting corrosion resistance in aqueous solutions containing NaCl by nitride/nitrocarbides layers consisting of ε-$Fe_{2-3}(C,N)$ and γ'-Fe_4N phases [16,17]. Currently, engine injection valves that are in contact with fuels are made of low-alloy steels and are treated by plasma nitro-carburizing and post-oxidizing [11,13].

Although many articles in the literature [2–10] have discussed the corrosion behaviour of carbon steel and alloys based on zinc or aluminium in bio-ethanol with different content of impurities, we were able to find only one article [18] about surface protection technologies of steel and other above mentioned alloys in contact with bio-ethanol. In such work, anodizing and electrolytic oxidation techniques were used to improve the corrosion resistance of Al6061 and Al304 aluminium alloys by creating a protective outermost oxide layer. Therefore, the interaction of fuel-grade bio-ethanol with steel surfaces modified by duplex process of plasma nitro-carburizing followed by plasma post-oxidizing was not yet studied.

In the present work, we studied the influence of surface microstructure and chemical composition on corrosion behaviour in fuel-grade bio-ethanol of AISI 4140 low-alloy steel after surface modification, namely plasma nitro-carburizing followed by post-oxidizing. The present study includes a full analysis of crystalline structure, microstructure, morphology, and chemical composition of the nitrocarbide and oxide layers before and after corrosion attack.

2. Experimental

2.1. Nitro-carburizing and post-oxidizing process

The samples were cutted from the same 1 mm diameter AISI 4140 plain steel bar (C, 0.45; Si, 0.22 P, 0.03; S, 0.03; Mn, 0.18; Cu, 0.02; Cr, 0.02; Ni, 0.01; Mo, 0.002; A, 0.03; V, 0.001; balance Fe (wt.%)). The substrates were mirror polished using standard metallographic techniques. Plasma nitro-carburizing was performed in a laboratory-scale chamber. The chamber base pressure was <2.6 Pa ($P_{O_2} < 5.3 \times 10^{-1}$ Pa). The chamber was pressurized with the feeding gases using mass flow controllers, where a Pirani gauge was used to monitor the pressure. The total gas pressure was kept at 125 Pa and the gas mixture was fixed at 88.5% N_2; 8.5% H_2; 3% CH_4 during the nitro-carburizing process. The substrate temperature during nitro-carburizing was kept at 550 °C for 5 h. A DC power supply with mean voltage 420 V and current 0.3 A was used. Following nitro-carburizing, post-oxidation was performed in the same chamber, without opening to air. The set of samples was exposed for various oxidation times from 30 to 180 min at a constant temperature of 480 °C. The total gas pressure was kept at 200 Pa and the gaseous mixture had a N_2/O_2 ratio of 7, with a H_2 proportion of 25%. The DC power was used with mean voltage 750 V and current 0.3 A.

2.2. Crystalline structure, chemical composition, microstructure and morphology

The crystalline structures of plasma-modified layers were characterized by X-ray diffraction (XRD) at an incidence angle of 2°, thus inspecting only the outermost layer. The samples were rotated during analysis in order to reduce grain orientation and texture effects. In the case of analyzing the corrosion product after immersion tests, an incidence angle of 1° was used. A Shimadzu XRD-6000 diffractometer with Cu Kα (V = 4 kV and I = 3 mA) radiation was used. The surface chemical composition was evaluated in-depth by glow discharge optical emission spectroscopy (GD-OES). A GD Profiler-2 from Horiba Jobin-Yvon was used. The technique was used in qualitative mode. Plain view and cross-section micrographs of nitro-carburized and post-oxidized layers, before and after immersion tests, were recorded using a Shimadzu SSX-550 scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). Samples for SEM were mounted in conductive Bakelite (Bakelite + copper powder) and mirror-polished with colloidal silica, mesh size = 0.05 m. The nitro-carburized and post-oxidized layers were revealed at room temperature by chemical etching (2%, v/v nitric acid in absolute bio-ethanol). Finally, the pit size and pit density were measured by using an A1 Zeiss Axio Scope optical microscope and by means of an image analyzer software.

2.3. Immersion corrosion tests

The solution was made using absolute bio-ethanol obtained from sugarcane at the maximum level of impurities allowed by Brazilian regulations (bio-ethanol 94.5 vol.%, methanol 1 vol.%, water 4.5 vol.%, acetic acid 3 mg l^{-1}, chloride 1.3 mg l^{-1}, sulphate 5 mg l^{-1}, iron 6.3 mg l^{-1}, sodium 2.5 mg l^{-1}) [19]. This final solution is denominated in the Brazilian energetic market as hydrated fuel-grade bio-ethanol and is used mainly by the flex automobile fleet. Immersion corrosion tests were carried out following the Brazilian standard NBR 8265 which is specific for bio-ethanolic medium [20]. In such standard, the nitro-carburized and post-oxidized samples were immersed in ethanolic solution that was added in a 100 ml glass flask, without stirring, which is provided by a cover, where a glass tube connects both outer and inner atmospheres. The samples were left for 77 days in duplicate. The temperature and humidity were fixed at 23 °C and 50%, respectively. For comparison purposes, the untreated and the nitro-carburized only AISI 4140 low-alloy steels were also tested. Each week, the samples were removed from the glass flasks and immediately rinsed with acetone in order to clean and dry tem surfaces. After that, the same routine of measuring the overall weight loss, pit size and pit density was performed. Pitting data reported for each sample and obtained each week were taken in the same areas of 8 selected regions where the average value and the standard deviation (SD) were calculated.