Corrosion and Micro-abrasive Wear Behaviour of 2524-T3 Aluminium Alloy with PAni-NPs/PSS LbL Coating

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In this paper, we present an alternative method to obtain thin films for coating protection on the surface of the AA2524-T3 Al-alloy by using the Layer-by-Layer (LbL) technique. The LbL films were fabricated by alternated immersion of the Al-alloy into a poly(styrene sulfonate) (PSS) and polyaniline nanoparticles (PAni-NPs) solutions, obtaining a PAni-NPs/PSS bilayer architecture. The LbL films were characterized by ultraviolet-visible spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), electrochemical and micro-abrasive wear tests. The results show that the number of bilayers promotes shifts to less negative potentials, indicating an optimized system, in which the best performance was observed for a 15-bilayer PAni/PSS LbL film. The pitting potential (E_{pit}) values shifted 130 mV (from -610 mV to -480 mV) in comparing a bare Al-alloy. The predominantly wear mechanism for AA2524-T3 with PAni-NPs/PSS bilayers was scratching whereas for the bare material there was an equivalence between scratching and rolling mechanisms. The results proved that the incorporation of PAni-NPS by the LbL method may be propitious as protective coating against corrosion in AA2524-T3 alloy.

Keywords: 2XXX series aluminium alloys, LbL technique, PAni nanoparticles, micro abrasive wear tests, aircraft fabrication.

1. Introduction

Nowadays, great attention has been given to the study of aluminium and its alloys since its applications include civil construction, energy transportation, aeronautic and automotive industry. As reported by Costenaro et al., aluminium alloys from the 2xxx series are very favorable for aircraft applications due to their low density, high mechanical resistance and durability. However, aluminium alloys present a high amount of intermetallics (IMs) leading to an increase of localised corrosion. The IMs are formed during alloy solidification and their size and number in the metal matrix depend on several factors such as impurity content, chemical composition and the solid solution solubility. Thus, in order to improve the durability of the aircrafts, the aeronautical industry has been constantly working on development of new advantageous aluminium alloys.

The AA2524-T3 (Solution Heat Treated and Cold Worked) alloy produced by ALCOA may be used as fuselage skin material and represents a potential replacement for the AA2024 alloy, widely used by the aircraft industry. Recent studies have shown that the fatigue behaviour of the AA2524-T3 alloy depends on experimental conditions (e.g., applied stress, loading rate, environment as well as the crystalline orientation of the sample). With regarding to the electrochemical tests, it was possible to verify that the corrosion potential (E_{corr}) and the pit nucleation potential (E_{pit}) values are quite similar and the variation in the ratio of passive/active areas and/or cathode/anode, which may be related to the presence of different types of IMs. Studies developed by Birbilis et al. confirm that the electrochemical characteristics of IMs vary significantly in terms of corrosion potential (E_{corr}), disintegration, reduction of oxygen and dissolution reactions. Other work in the literature describes the galvanic coupling between the IM particles and the aluminium matrix. In this way, the use of protective coatings appears as a possible alternative
against the advancement of the corrosion process of the AA2524-T3 alloy.

In this context, chromatization is the most effective conversion coating for Al-alloys \cite{22}. However, the tailings from the treatment process are highly toxic, which makes their use unfeasible \cite{22}. Several reports have shown that conductive polymers can be useful in corrosion protection as a form of coating onto metals and metal alloys by using electrochemical deposition techniques \cite{5,23,24,25}. Fang et al \cite{25} and Cao et al \cite{26} reported that polyaniline (PAni) conducting polymer is attractive due to their stability, tunable conductivity, controllable structure, ease of synthesis as well as protective coating or as corrosion inhibitors. Moreover, mostly of the studies involving the formation of PAni films on the surface of metallic materials were obtained by using electrophoretic deposition techniques. Gomes et al \cite{27} studied the influence of multilayer coating using layer-by-layer (LbL) method on the corrosion behaviour of 2024-T3 aluminium alloy and verified by potentiodynamic polarization, chronoamperometry and electrochemical impedance spectroscopy (EIS) techniques an increase of corrosion resistance in the chloride containing environment for the surface coated with 08 (Poly (vinylsulfonic acid, sodium salt/PAni) bilayer. To date, polymer coatings obtained via the LbL self-assembly technology are scarce in aluminium alloys used by aircraft materials, evidencing the need for new studies.

Here, we present an alternative deposition method to obtain thin films on the surface of the AA2524-T3 Al-alloy by using the LbL technique as a potential substitute of traditional techniques as chromium conversion coatings (CCCs) and electropolymorization (EP) for instance. The LbL technique is a pervasive method for fabricating ultrathin coating in polymers, colloids and biomolecules substrate \cite{28}. The films of PAni-NPs/PSS coated on the surface of AA2524-T3 alloy were characterized by using ultraviolet-visible spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), open circuit potential (OCP), potentiodynamic polarization curves (PPc) and micro-abrasive wear tests (MAWTs).

2. Experimental

2.1 AA2524-T3 aluminium alloy

The alloy used was a 1.2 mm-thick 2524-T3 Al plate with nominal composition (%w.t) of 3.84% Cu, 0.04% Si, 0.06% Fe, 1.31% Mg, 0.56% Mn, 0.029% Ti, 0.01% Zn with the made up of Al. Further information regarding the chemical composition of the AA2524-T3 alloy can be found in \cite{12}.

2.2 Preparation of Polyaniline Nanoparticles (PAni-NPs)

PAni-NPs were prepared according to the procedure described by Cao et al \cite{29}. First, 2 mL of aniline hydrochloride solution (93.1 g mol$^{-1}$ and density of 0.9 g cm$^{-3}$) were dissolved in 200 mL of deionized water previously mixture with chlorhydric acid (36.5 g mol$^{-1}$ - 37%). The solution was slowly stirred until a homogenous mixture was obtained. In a second part, 1.6 g of ammonium peroxydisulfate ($\text{NH}_4\text{S}_2\text{O}_8$) was dissolved in 200 mL of deionized water. The aniline hydrochloride solution was maintained in an ice bath with ammonium persulphate solution in 1:1 proportion. This new solution was stirred at 4°C for 24 h and filtered. The resulting material was washed exhaustively and dried in vacuum. The dried powder obtained (PAni) was agitated in an ultrasound bath (dispersed in propanol) during 2 h in order to obtain PAni-NPs.

2.3 Fabrication and characterization of the LbL film

Prior obtaining thin film, the surfaces of the AA2524-T3 Al-alloy were ground with SiC abrasive paper to 2400#, degreased with acetone, rinsed exhaustively with deionized water and dried using nitrogen jet. The coating was built up atop the 2524-T3 alloy surface by using the layer-by-layer (LbL) technique. Firstly, the AA2524-T3 alloy was dipped for 3 min in the H$_2$SO$_4$ + H$_2$O$_2$ solution (3:1) and then washed with water. The LbL films were fabricated by alternated immersion of the AA2524-T3 alloy into a PAni and poly(styrene sulfonate) (PSS) solutions, obtaining a PAni-NPs/PSS bilayer architecture. The repetition of this process permitted to prepare films in a multilayer fashion with 1, 5, 10, 15 and 20 bilayers.

The film growth was monitored by ultraviolet-visible spectrophotometry (UV-Vis) by using an Avantes AvaSpec-2048 fiber optic spectrometer and the topography of the film was investigated by atomic force microscopy (AFM) using a SPM-9700 Shimadzu in dynamic mode at room temperature. Fourier transform infrared spectroscopy (FTIR) was performed to analyze the chemical bonds and interactions between PAni-NPs/PSS in the film formed on the surface of the AA2524-T3 Al-alloy using an Agilent Cary 600 Series FTIR Spectrometer. It is important to mention that PAni-NPs/PSS LbL films were fabricated onto indium-tin-oxide (ITO)-coated glass substrates (used as blank) for the UV-Vis analysis. A schematic representation of PAni-NPs/PSS LbL films architecture and a digital image of the films prepared with different bilayers is illustrated in Figure 1.
2.4 Electrochemical tests

The electrochemical characterizations were performed by open circuit potential (OCP) and potentiodynamic polarization curves (PPc) in sodium chloride medium (0.6 mol L\(^{-1}\) NaCl). A single-compartment electrochemical cell based on a typical three electrodes consisting of a work electrode (WE) of AA254-T3 alloy coated with PAni-NPs/PSS film with 1 cm\(^2\) exposed area, a counter electrode of platinum (CE) and a reference electrode (RE) of silver chloride (Ag/AgCl/3M KCl) were used for the electrochemical tests. Data results were obtained by using an AutoLab 128N potentiostat/galvanostat (Metrohm Autolab, Switzerland). The corrosion potential (E\(_{\text{corr}}\)) of the samples was monitored during 3600 s. Regarding to the PPc tests, the measurements were made in the range of -1.4 to -0.4 V with a potential sweep rate of 0.5 mV s\(^{-1}\).

2.5 Micro abrasive wear tests (MAWTs)

The MAWTs were performed using a fixed ball microwear device. A fixed frequency was set up of 80 rpm with normal load of 0.5 N and test time of 3 min. The MAWTs were realized in all samples (coated and uncoated) with no abrasive or lubricant liquid. After tests, all the samples were analysed by optical microscope Leica, model MC170 HD, with camera and software analysis, which was used to measure the diameters and the crater radio generated in a coated system by rotation of the ball. In this way, the volume of wear and coefficient of friction (COF) were determined. Figure 2 presents the microwear device used for the MAWTs. It is important to mention that the micro abrasive tests were carried out in triplicate in order to ensure a good reproducibility.

3. Results and Discussion

Figure 3 (a) presents the UV-Vis spectra of PAni-NPs/PSS LbL films at different number of bilayers. It is possible to verify the presence of a broad band in the region of 190 to 355 nm due to the \(\pi-\pi^*\) transition of the PSS aromatic ring. While the band extended between 350 and 510 nm may be corresponding to the transition \(\pi-\pi^*\) in benzenoid rings and the transition \(n-\pi^*\) in quinoid rings of PAni.\(^{30-33}\) A linear growth of bilayers for PAni-NPs/PSS LbL films (Abs at 450 nm) can be verified as shown in Figure 3 (b). The increase in absorbance with the number of bilayers is due to the growth associated with electrostatic interactions between sulfonate functional group (SO\(_3^–\)) of PSS and amine groups (NH\(_3^+\)) from PAni. Furthermore, the linear increase of the absorbance suggests that the amount of material deposited for each bilayer is proportional.

The characteristic of the Pure PAni, PAni-NPs/PSS film before and after corrosion tests were determined by using FTIR as shown in Figure 3 (c). In agreement with the literature\(^{34-37}\), a broad band around 3700 - 2500 cm\(^{-1}\) is assigned to an overlap of N-H stretching (secondary amine, from PAni) and
O-H deformation bands (adsorbed water). The FTIR spectra of Pure PANi also presents C=C stretching bands at 1577 and 1485 cm\(^{-1}\) characteristic of benzene ring, the bands also referring to the secondary amine at 1300 and 1242 cm\(^{-1}\) are related to the C-N and C=N stretching modes, respectively, and bellow 1190 cm\(^{-1}\) there are some broad bands assigned to C-H deformation in the benzene ring. The characteristics bands of C=C, C-N stretching and C-H deformation shift to lower modes ~10 cm\(^{-1}\) in the PANi-NPs/PSS film before and after corrosion tests, in addition the relative intensity of C=N stretching reduces considerably in the films, indicating a strong interaction between the Pure PANi and PSS film. On the other hand, there are no significant changes in the film spectra after corrosion testing. This latter indicates that the films are strongly incorporated onto the AA2524-T3 Al-alloy, demonstrating that the LbL method may be propitious to form coating films resistant to corrosion.

In order to investigate the topography of the PANi-NPs/PSS on the surface of AA2524-T3 Al-alloy, AFM images over a scan 2.0 x 2.0 µm were verified, as can be seen in Figure 4. A rugged morphology characterized by risks from the mechanical cleaning of Al-alloy as well as different type of IMs \(^{12}\) prevenient from the solution heat treated and cold worked alloy process may be observed in all structures (Figure 4 (a)), resulting in an average rugosity of 5.98 nm. With regarding to the coated Al-alloy (Figure 4 (b)) it is possible to observe that the presence of PANi-NPs are responsible for a considerable increase in the average rugosity (~31.33 nm) in relation to the uncoated Al-alloy. The average diameter of PANi-NPs is about 36.00±1.73 nm and it was determined using a modular program for scanning probe microscopy (SPM) named as Gwyddion. The agglomerates identified in AFM images allow us to conclude that PANi-NPs were formed. In fact, the results obtained by AFM show that was a considerable
modification on the surface of the coated Al-alloy by using PANi-NPs. The morphological study of the 2524-T3 Al-alloy surface containing PANi-NPs will help us to understand the corrosion and micro-abrasive processes as will be discussed in the following sections.

Figures 5 (a) and 5 (b) show the results of OCP and PPC of the AA2524-T3 Al-alloy containing different PANi-NPs/PSS LbL films in 0.6 mol L\(^{-1}\) of NaCl. The OCP curves show the dependence of potential with time is linked to the stochastic evolution of pitting events and to the resulting variations in the ratio of passive/active areas and/or cathode/anode, which may be related to the presence of different types of IMs. The corrosion potential (\(E_{\text{corr}}\)) shifted to less negative values by increasing the number of bilayers. In addition, the pitting potential (\(E_{\text{pit}}\)) values got shifted from ~ -610 mV SCE for bare Al-alloy to ~ -480 mV SCE for PANi-NPs/PSS coating. This shift of 130 mV indicates that PANi-NPs/PSS films acted as a system of blocking aggressive species on the metal surface, protecting the substrate from the localized corrosion process. In other words, PANi was able to repair the defects present in the oxide layer and maintain its integrity and natural character of protection against the corrosion process. Figure 5 (c) confirm that even after the electrochemical tests there are regions on the surface of the AA2524-T3 Al-alloy that exhibit PANi-NPs/PSS films.

The results obtained in the present work, since using an alternative and more “structured” technique to obtain the PANi coating of the AA2524-T3 Al-alloy, corroborates the Zubillaga et al\(^{38}\), Bernhard\(^{39}\), Domingo et al\(^{40}\) and Martins et al\(^{41}\). Zubillaga et al\(^{38}\), synthesized electrochemically anodic alumina films containing PANi and TiO\(_2\) or ZrO\(_2\) nanoparticles on the surface of AA2024-T3 alloy and verified the positive influence of the nanoparticulate system on the polarization curves in 5 mM NaCl and 0.1 mol L\(^{-1}\) Na\(_2\)SO\(_4\) solution. In a similar way to this work, the nanoparticle-containing coating of TiO\(_2\) acts as a barrier layer that blocks the pores of anodic alumina\(^{38}\). Bernhard\(^{39}\) deposited PANi electrochemically on the surface of stainless steel and verified an anodic form protection due to the PANi coating. Domingo et al\(^{40}\) prepared by electrodeposition of aniline, adherent PANi films on the 2024-T3 Al-alloy surface and suggested a decrease in the corrosion process protecting the alloy. Martins et al\(^{41}\), studied the production of PANi films on the AA6061-T6 Al-alloy used by aircraft industry by electropolymorization of aniline and reinforce the need for new coating systems that may replace bared in chromates, which have been classified as hazardous to environment and human health. The corrosion prevention of 2024-T3 aluminium alloy with a polyaniline/poly(γ-glycidoxypropyltrimethoxysilane) bi-layer coating was studied by Mrad et al\(^{42}\). These authors showed that poly(γ-glycidoxypropyltrimethoxysilane) layer served as an effective barrier against the penetration of corrosive species and the results corroborate with those found in this work.

Figure 6 shows a comparison of the wear volume for the AA2524-T3 Al-alloy with and without PANi-NPs/PSS film. It can be noticed that both materials showed similar values of wear resistance. As reported by Cao et al\(^{26}\), the tribological performance of additive solids depends on the thickness of the film produced. In this work, possibly the small film thickness associated with its debris may have contributed to this similar result. Thus, it can be concluded that thin films do not act as tribofilms, while thick films function as abrasives. The coefficient of friction (COF) as a function of time for the material with and without coating is presented in Figure 7. It was observed that the COF of the AA2524-T3 alloy with PANi-NPs/PSS film reached a stationary state from the beginning of the test and the present peaks are due to the production of debris during the micro abrasive wear tests. The differentiated behavior in wear of the materials may be related to the modification of the mechanism acting in each condition. For the bare

![Figure 4](image-url)  
(a) and (b) Top view AFM images at a 2.0 x 2.0 μm scanned area, (a) uncoated AA2524-T3 Al-alloy and (b) PANi-NPs/PSS LbL films with 15 bilayers and the profile.
Figure 5. (a) OCP curves for the AA2524-T3 alloy in aerated 0.6 mol L⁻¹ aqueous solution for a period of 3600 s of immersion, (b) PPc for the AA2524-T3 alloy in aerated 0.6 mol L⁻¹ NaCl aqueous solution at scan rate of 0.5 mV s⁻¹, (c) images of surface alloy by optical microscopy and SEM in the pitting potential (E_{pit}) for a 15 bilayer PAni-NPs/PSS film. EDX analysis confirms the presence of PAni-NPs/PSS films on the surface of the AA2524-T3 alloy.

Figure 6. Wear volume for the AA2524-T3 alloy with and without PAni-NPs/PSS bilayers.
material, a low coefficient of initial friction is observed. This latter increases due to the production of the oxidized wear debris, increasing the severity of wear. It should be emphasized that the high values of COF correspond to those related to the occurrence of abrasive wear by scratching. The predominant wear mechanism for AA2524-T3 with PANi-NPs/PSS bilayers was scratching whereas for the bare material an equivalence between the scratching and rolling mechanisms was observed. These wear mechanisms can be verified through SEM images in figures 8 (a) and 8 (b).

Figure 8 (a) and 8 (b) show the micrographs of the AA2524-T3 alloy and the bare material coated with PANi-NPs/PSS LbL after the micro abrasive wear tests, respectively. As can be verified in the images, the debris of the bare material became brittle and being hard, they fragment due to wear,
this is characteristic of oxidized particles. With regarding to the AA2524-T3 alloy coated with PANi-NPs/PSS LbL film, the wear debris is exclusively the tearing of the film from the wear region, which is concentrated in the sample edge. By means of X-ray dispersive energy spectroscopy (EDX) technique, it was possible to verify that the wear region is rich in Al (bare material) and the region of concentration of debris is formed exclusively by the film removed from the surface (coated material).

4. Conclusions

The aim of this work was to study an alternative way to obtain PANi thin films on the surface of 2524-T3 Al-alloy using the LbL technique. The results demonstrated that the incorporation of the LbL method may be suitable as a coating against corrosion in aircraft materials. We can conclude in this work that 15 bilayers made the electrode more resistive against corrosion in aircraft materials. We can conclude in this work that 15 bilayers made the electrode more resistive against corrosion in aircraft materials. We can conclude in this work that 15 bilayers made the electrode more resistive against corrosion in aircraft materials.

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6. References


