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Surface modification of aluminium alloys by atmospheric pressure plasma treatments for enhancement of their adhesion properties

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ABSTRACT

This work deals with surface modification of aluminium alloy AA7075 by two types of atmospheric pressure plasma: dielectric barrier discharge (DBD) and atmospheric pressure plasma jet (APPJ) with the purpose to enhance the adhesion of polyurethane coating on the alloy. The surface characterization was performed by using water contact angle, roughness and surface free energy measurements. Quality of the coating was tested according to the adhesion tape test (ASTM D3359) and evaluated by electrochemical techniques. The aluminium alloy showed great improvement of the surface wettability after plasma treatments. While, the adhesion tape test presented excellent results with perfect adhesion, meaning that both plasma treatments were efficient in improving the adhesion of the polyurethane coating to the AA7075. The Fourier Transform Infrared Spectroscopy (FTIR) results demonstrated that the plasma treatment cleaned the Al alloy surface by removing hydrocarbon contaminations. Both polarization curves and Electrochemical Impedance Spectroscopy (EIS) results showed better characteristics of corrosion resistance for polyurethane-coated AA7075 than untreated coated samples.

1. Introduction

Aluminium (Al) alloys have been one of the most employed materials in aircrafts structures, due to their light weight, high mechanical resistance, good corrosion properties and low cost. The 7000 series (Al—Zn—Mg—Cu) shows higher strength when compared to other classes of Al alloys. Therefore, they are specifically used in the fabrication of upper wing skins, stringers and stabilizers of aircrafts [1,2]. To endure critical conditions in aeronautic applications some chemical processes, such as, conversion coatings, anodizing and chromatization are often applied as pre-treatment for Al alloys to improve corrosion resistance and enhance adhesion properties. However, the hexavalent chromium [Cr^{+6}] generated by these techniques is known to be toxic and hazardous to humans and the environment. In order to find methods environmental-friendly with the same efficiency as the chromates, several researches have been developed to modify Al alloys for aeronautic and aerospace purposes [3–6].

Atmospheric pressure plasmas are clean and environmental-friendly type of process that can be easily applied in in-line production, the capital cost is relatively low when compared to other methods [7–9].

Dielectric barrier discharge (DBD) is considered one of the most popular cold atmospheric plasma sources that generates non-equilibrium plasma [10]. Typical DBD configuration consists of an electrode arrangement where one or both electrodes are covered by a dielectric material like glass, quartz or ceramics [11]. When a high voltage (typically tens of kV in the frequency range of 50–10^4 Hz) is applied between the electrodes, the gas breakdown occurs and a large number of short-lived current filaments, known as microdischarges appear in the inter-electrode gap. Most industrial applications of DBD operate in this filamentary mode [12]. DBD has been applied for ozone generation, sterilization, flat plasma displays, excimer UV lamps, surface modification [13], and most recently in biomedical [14] and agriculture [15] applications.

Atmospheric pressure plasma jet has recently been a topic of great interest, since it can generate non-equilibrium plasma in open space rather than in a confined discharge gap. The plasma jet operation usually depends on the working gas and on the electrical excitation, which can vary from DC power supply to sine-wave signal with frequency from tens of Hz to MHz (radio frequency) and to GHz (microwave) [16]. The separation of the generation region from the application region enables the direct exposure of thermosensitive substrates, including local treatment in complex geometries substrates [17]. Therefore,

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plasma jets have been employed to materials surface modification [18] and in biomedical application (bacteria inactivation, cancer treatments and skin therapy) [19].

In this work, two types of atmospheric pressure plasmas (DBD and plasma jet) were used to pre-treat the aluminium alloy (AA7075) to enhance the adhesion of a polyurethane coating on the AA7075 alloy, avoiding the use of any chemical process typically applied in the industry. In this way the process becomes environmental-friendly, human contamination risks are reduced and the costs are decreased as well.

2. Materials and methods

Plasma treatments were performed on as-received aluminium alloy AA7075-T7351 (89.6% Al) with dimensions of Ø15 × 3 mm. No metallographic surface preparation was used to enhance the mechanic anchorage between the Al alloy surface and paint coating. Prior to plasma treatments, samples were ultrasonically cleaned in distilled water for 15 min and than in isopropyl alcohol for 10 min to remove contaminants from the surface. To evaluate the reproducibility of the experiments, all tests were done in duplicate.

The DBD reactor was consisted of two parallel aluminium electrodes with diameter of 9.5 cm, where both electrodes were covered by a Mylar sheet of 0.5 mm thickness. The bottom electrode was connected to a high-voltage source while the upper electrode was grounded. Plasma was generated by an AC power supply (60 Hz) in airflow (8 L/min). The inter-electrode gap was fixed to 4 mm and the applied voltage used was 30 kVp-p. Samples were exposed to air-DBD plasma for 5 min, 7.5 min, 10 min and 15 min. The schematic diagram of the DBD system can be found elsewhere [20].

Argon plasma jet was generated in a glass tube using a 16 mm horn-like nozzle. The nozzle to sample distance was fixed to 1 mm and the applied voltage used was 12 kVp-p. Samples were exposed to plasma for 20 s, 30 s, 40 s and 60 s. The plasma jet system details and experimental configurations are available in [21].

The AA7075 alloy surface characterization was carried out by measuring contact angle and surface free energy (SFE) with a Rame-Hart 300 goniometer, using the sessile drop method and the DropImage software, provided by the manufacturer. Deionized water and diiodomethane were used as test liquids, the volume of each liquid drop was set as 2 μL, the average value of at least 3 drops from each liquid was calculated (for each drop the contact angle was measured 5 times). SFE evaluation was performed using the Surface Free Energy tool in DropImage software, which is based on the Owens-Wendt model for two liquids (deionized water and diiodomethane) using the geometric mean method.

The chemical composition of the substrates was analyzed by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) performed on a PerkinElmer Spectrum 100 spectrometer. The spectra were acquired from 650 cm^{-1} to 4000 cm^{-1} with spectral resolution of 2 cm^{-1}. Each spectrum was obtained as an average of 40 scans.

After plasma treatments, samples were painted with polyurethane paint JETGLO® from Sherwin-Williams manufacturer. The painting was performed no more than 10 min after the treatments and dried in room temperature for 48 h prior to any measurement.

Quality of the coating was evaluated according to the adhesion tape test ASTM D3359 [22] and electrochemical techniques, which were performed by an AUTOLAB Potentiostat (302N) using a three electrode electrochemical cell, consisted of reference electrode (Ag/AgCl), counter-electrode (Pt) and working electrode (AA7075 alloy with area of 0.64 cm^2). All electrochemical experiments were conducted in 3.5% NaCl solution at room temperature, in the following order: Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS) and Polarization Curves (PC). Before any measurement all electrodes remained inside the electrochemical cell in immersion for 20 h to reach stationary conditions. After immersion time, the OCP was measured as a function of time for more 3 h. EIS spectra were collected from 10^5 to 10^{-2} Hz frequency range, using a perturbation signal of 10 mV and acquisition data scanning of 10 points per decade. Polarization curves were obtained with a potential scan rate of 0.33 mV/s from −1.2 V up to 0.6 V.

3. Results and discussion

3.1. Surface characterization (contact angle, SFE and FTIR)

Water contact angle values of the AA7075 alloy were affected significantly by both plasma treatments as can be seen in Fig. 1. Water contact angle of the control (CT) untreated sample was 89° ± 2°, whereas after plasma treatments water contact angle decreased up to 5° ± 1° and 19° ± 1° for DBD and plasma jet, respectively. Decrease of the contact angle values after plasma treatments was observed for both test liquids, water and diiodomethane.

On the other hand, AA7075 samples treated by DBD and plasma jet exhibited a substantial increase on the surface free energy (SFE) when compared to the CT sample. Fig. 2 shows SFE values of AA7075 samples for all conditions, before and after plasma treatments. SFE of plasma treated samples has similar value around 70 mJ/m^2, which is about 2.5 times higher than the one of control sample.

Although, the polar component exhibited the highest accession after plasma exposure, (around 10 times more than the CT sample), the dispersive component also tends to increase after plasma treatments. After plasma treatment, the Al alloy surface became more hydrophilic, as can be seen in Fig. 1 by the decrease of the water contact angle, resulting in a lager spread of the liquid drop on to the alloy surface. Similar results were found by some authors [23,24] using different arrangements of plasma sources and Al alloys. These authors inferred that the increase of the SFE polar component is due to the generation of polar groups on the Al alloy surface after plasma treatments.

The FTIR spectra for CT and plasma jet treated sample (60 s) are displayed in Fig. 3. Since the spectrum obtained for DBD treated samples was similar to the one of plasma jet, only one curve was inserted in the graph. Note that the signal intensity obtained from the aluminium alloy samples is very weak and in some wavenumber regions it is comparable with the noise generated by the ATR element (diamond crystal). Therefore, the region from 2390 to 1920 cm^{-1} was excluded from graph.

Control samples had several peaks that were related to surface hydrocarbon contaminants: CH_2/CH_3 vibration peaks (as. str. CH_3 at 2964 cm^{-1}, as. str. CH_2 at 2929 cm^{-1}, s. str. CH_3 at 2857 cm^{-1}, ass. bend. CH_3 at 1460 cm^{-1} and s. bend. CH_3 at 1376 cm^{-1}), C═O (str. 1742 cm^{-1}), and C═C (s. str 1649 cm^{-1}). The peak of H-bonded OH (3328 cm^{-1}) is related to the humidity condensation, while the

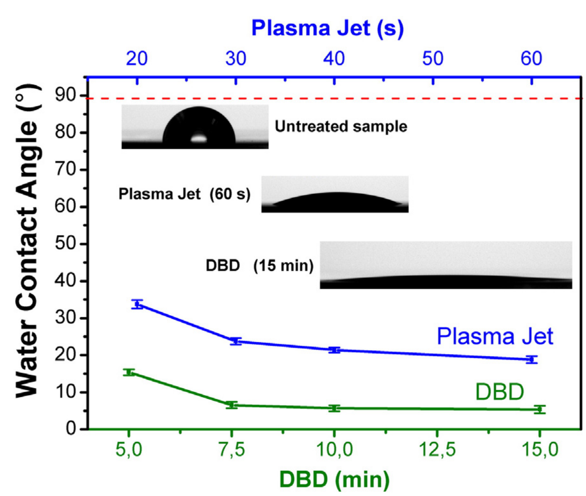

Fig. 1. Water contact angle values.

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