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Atmospheric plasma torch treatment of aluminium: Improving wettability with silanes

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ABSTRACT

This study investigates the effect of atmospheric pressure plasma torch (APPT) treatments on the surface of aluminium alloys. The influence of torch-to-sample distance, speed of treatment and ageing time is analyzed in terms of contact angles and surface energy. Results show that APPT treatment strongly increases the surface energy and wettability of aluminium surfaces. This is related to the formation of polar groups, as Fourier transform infrared (FTIR) spectroscopy has confirmed. In all conditions, hydrophobic recovery of aluminium surfaces takes place. Finally, the compatibility of the APPT treated aluminium substrate with γ-methacryloxypropyltrimethoxysilane (MPS) has been evaluated through adhesion work and spread tension, showing that it is possible to achieve a spontaneous wetting process of silane on aluminium.

1. Introduction

The effect of aluminium surface pretreatment dramatically influences the formation of thin non-functional silane films [1]. The adsorption of silane is affected by the amount of OH groups on the aluminium surface [2]. Untreated aluminium surfaces have low amounts of available OH groups [3], and require pretreatments that, more than cleaning the surface, modify it. Acid pretreatments provoke pickling and oxidation of the surface, leading to the formation of —OH groups on the surface, hence increasing Al—O—Si bonds between substrate and silanes. However, picking leads to non-homogenous distribution of silanes on aluminium alloys [4].

In recent years, studies on the reliability of environmentally friendly pretreatment techniques have increased. Plasma stands out as one of them [5]. Some plasma processes require vacuum conditions that make treatment processes expensive and difficult. Atmospheric pressure plasma processes are attractive and adaptable to large-scale production. Most economical is the use of air as plasma generating gas to improve the wettability of metallic surfaces like aluminium. The ability of cold plasmas to remove carbon contaminants on the surface of AA 7075 and AA 2024 aluminium alloys has been demonstrated [6]. These pretreatments increase the wettability of these alloys [7,8].

For example, the use of corona pretreatments on aluminium base materials has demonstrated its ability to clean the surface of aluminium wires [9], or to form protective oxides on AA1050 alloy [5,10].

The use of atmospheric pressure plasma torch (APPT) treatments allows a homogeneous treatment of surfaces, minimizing processing time and costs. Its effect on glasses [11,12] or polymers is better known than its effect on metals, increasing their wettability and the adhesion properties [13]. It has been recently used on metallic surfaces to remove organic contaminants, modify the surface and improve the adhesion of organic coatings [14]. In particular, atmospheric plasma has demonstrated those effects on AA 2024 [14] and AA 6061 [15] aluminium alloys.

Its use as pretreatment for sol–gel coatings on aluminium has also been evaluated [16], demonstrating an increase in the corrosion resistance of materials. Moreover, the increase of adhesion properties of epoxy coatings on aluminium [17] has been explained as plasma enhances the wettability of aluminium substrates.

The objective of this research is to optimize APPT treatments on an AA6063 aluminium alloy. Moreover, the ageing process of the aluminium pretreated surface will be analyzed. Finally, the increase in wettability will be applied to a particular silane solution in terms of work of adhesion.

2. Experimental procedure

6063-T6 aluminium alloy plates were selected for APPT treatment. The plates were degreased and pickled with 3% Alcid-92 solution (Alsan, Valencia, Spain) in order to remove 2 g/m^2 weight from the aluminium alloy surface, thus removing all oxides. Alcid 92 is a sulphuric acid based solution. Immediately afterwards, the

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samples were APPT treated with a PlasmaTreat GmbH (Steinhagen, Germany) device. The particular setup includes an FG3001 plasma generator and an RD1004 rotating nozzle. The setup operated at a frequency of 17 kHz and a high tension discharge of 20 kV. Air plasma was generated at a working pressure of 2 bar inside the rotating nozzle (1900 rpm) by a non-equilibrium discharge and expelled through a circular orifice onto the samples. The system contained an electronically speed-controlled platform on which the samples were placed. Two different speeds of the platform were selected (1 and 10 m/min). These speeds allow the comparison between a very aggressive condition (1 m/min) and a less aggressive one (10 m/min). The former increases cleaning but samples could suffer some heat. The latter could lead to incomplete cleaning and activation of the surface, depending on the torch-to-sample distance. Those parameters have also been assessed on steels [18]. Moreover three different distances between the sample and the plasma torch nozzle were analyzed (2, 6 and 10 mm). Samples were stored during the ageing process at 25 °C and 50% relative humidity in dust-free conditions up to 48 h.

Contact angle measurements were carried out on treated materials, as well as on pickled aluminium. Sample wettability was evaluated using OCA 15 plus (Dataphysics, Neurtek Instruments, Eibar, Spain) equipment. Sample test pieces were placed in the isothermal (25 °C) chamber of the apparatus, previously saturated with the vapour of the liquid for at least 5 min. The liquids used were bi-distilled water, diiodomethane (CH_2I_2) and tribromopropane ($C_3H_5Br_3$). Liquid drops (3 μl) were placed on the surfaces with an endflat micrometric syringe. At least six drops were measured and averaged on each sample. Contact angle measurements were used to calculate the surface energy of the materials following the Owens–Wendt–Rable–Kaelble (OWRK) method [19]. This method enables the determination of both additive contributions of the dispersive (due to London type forces) and polar (which accounts for the dipole–dipole and hydrogen bonding interactions) components of the surface energy [20], fitting a linear equation which derives from Fowkes's expression [21]. These calculations were performed using image analysis software (SCA20, DataPhysics Instruments, Filderstadt, Germany) and a computer coupled to the equipment.

Changes in the chemical bonds on the surface were evaluated with Fourier transform infrared (FTIR) spectroscopy. A Brucker Tensor 27 (Brucker Optik GmbH, Ettlingen, Germany) spectrometer was used to obtain the infrared spectra of both pickled and APPT treated samples. The attenuated total reflectance (ATR) technique was used to analyze the surface chemical modifications. A diamond prism was used and the incident angle of the IR radiation was 45°. Thirty two scans with a resolution of 4 cm^{-1} were obtained and averaged. Spectra were recorded from 600 to 4000 cm^{-1}.

Because of the huge amount of data, a statistical analysis called clustering [22] was used to group treated materials. This technique groups the 54 studied conditions (combining two speeds, three torch-to-sample distances, and ageing times up to 48 h) in the desired number of groups. The groups (clusters) are formed by objects (treated materials) which have similar properties, being different from materials in other groups. Objects forming a cluster are substituted by a centroid that will be used to measure distances between clusters. This process was carried out in two phases. The first one was a hierarchical clustering, grouping the nearest couple of materials by its centroid, until the desired number of clusters is obtained (five in this case). The second phase was a non-hierarchical clustering. Previous clusters were used as seeds for the new ones, grouping materials again in the final number of desired clusters (four in this case). A k-mean algorithm was used iteratively to achieve a convergent solution.

Moreover, some APPT treated samples were coated with a silane solution. γ-Methacryloxypropyltrimethoxysilane (MPS) silane was selected. 1% MPS was hydrolyzed for 60 min in water at pH 4 [23,24].

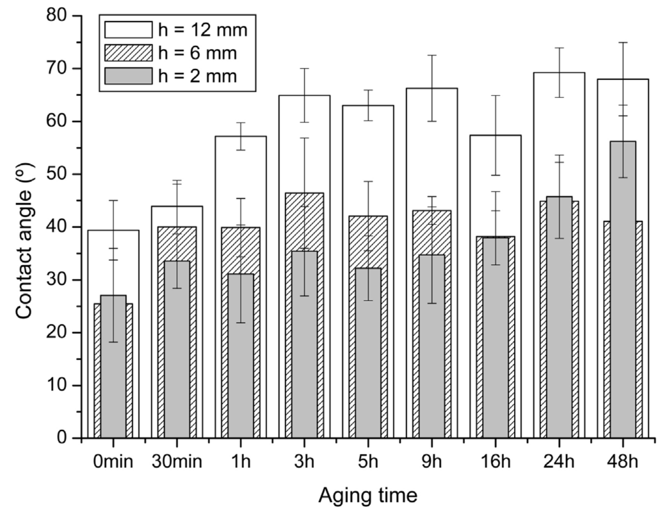

Fig. 1. Contact angle of water on atmospheric plasma treated aluminium, at 10 m/min speed and 2 mm, 6 mm and 12 mm torch-to-sample distance.

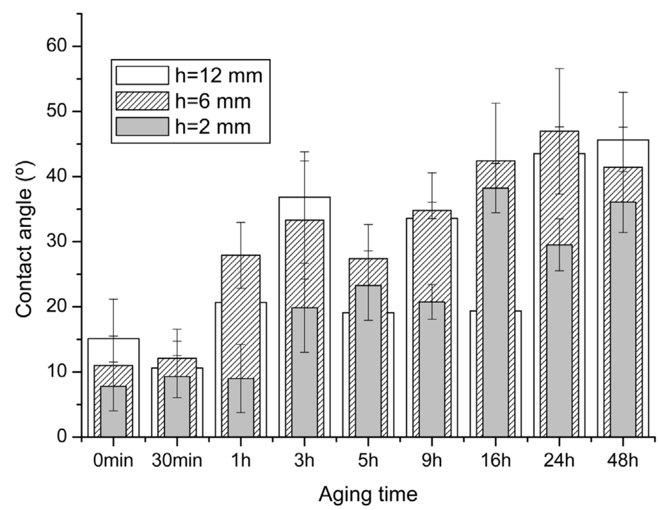

Fig. 2. Contact angle of water on atmospheric plasma treated aluminium, at 1 m/min speed, and 2 mm, 6 mm and 12 mm torch-to-sample distance.

Compatibility of the APPT treated substrate with the silane solution was studied in terms of surface tension of the solution and surface energy of the treated aluminium, evaluating the adhesion work and spread tension to achieve a spontaneous wetting process.

3. Results

3.1. Properties of the substrate after APPT

The first effect of APPT treatment is observed on the contact angle of water drops with the surface for both treatment speeds (Figs. 1 and 2). All values are lower than those found in pickled aluminium (Table 1). This behaviour is expected [25], as APPT cleans and physically–chemically modifies the surface of aluminium, as

Table 1
Water contact angle and surface energy with its polar and dispersive components for pickled aluminium.

Water contact angle	74.6°
Surface energy σ (mN/m)	34.2 ± 6.1
Polar component σ_P (mN/m)	8.7 ± 5.6
Dispersive component σ_D (mN/m)	25.5 ± 2.4