

PTFE-Coated Anodized Aluminum Alloy 6061 With Icephobic Properties

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Abstract - In order to protect the aluminum ground wires and phase conductors of overhead power lines against ice adhesion and excessive accretion, and thus ensure safe and reliable power transmission during winter periods, a new coating with icephobic characteristics and satisfactory mechanical properties was developed. The method consisted in depositing poly(tetrafluoroethylene) (PTFE) coating on an Al₂O₃ under-layer produced by anodizing with either sulfuric, phosphoric or oxalic acid electrolyte. PTFE impregnation was carried out at low temperature (320 °C) to prevent, as much as possible, PTFE degradation and Al 6061 alloy structure modifications. PTFE coatings on bare aluminum were unsuccessful. Coating adhesion was assessed using tape and bend tests. For both phosphoric and oxalic acid pre-treatment, highly hydrophobic surfaces were developed with water contact angles lying between 130° and 140°. Ice shear stress was reduced by a factor of almost 2.5, and the PTFE coatings remained active after seven ice-shedding events. Morphologies and chemical compositions were studied using scanning electron microscopy, energy dispersive X-Ray analysis, as well as Fourier Transform Infra Red and X-Ray photoelectron spectroscopy. To further decrease ice adhesion strength, an etching of Al₂O₃ before PTFE impregnation will also be described.

Keywords: Aluminum, anodizing, PTFE, impregnation, icephobicity, superhydrophobicity.

I. INTRODUCTION

Accumulation of ice on exposed surfaces may cause serious problems to the integrity of outdoor equipment such as transmission cables, telecommunication towers and aircraft. The two main strategies to deal with this issue are as follows: i) active de-icing methods such as thermal, electrical or mechanical techniques [1, 2], and ii) passive ones by protecting the exposed surface with icephobic coatings to significantly reduce or eliminate ice adhesion strength [3-9]. Currently these coatings have few industrial applications, but are environmentally friendly compared to de-icing

fluids, and cheaper than active methods which are energy hungry and expensive to make and operate.

Usually, low dielectric constant materials exhibit low ice adhesion strengths [10, 11] and Poly(tetrafluoroethylene) (PTFE or Teflon[®]) is actually one of the best materials to reduce ice adhesion strength with its $\epsilon \approx 2.1$ [4, 12]. PTFE coatings on aluminum usually need an anodizing step to create an oxide underlayer to improve polymer adhesion [13-15]. PTFE deposition on aluminum for icephobic applications was never thoroughly studied. The choice of a suitable coating process has to take into account important scientific and engineering aspects: Al₂O₃/PTFE coatings must have excellent adhesion to the Al alloy since wear can occur during cable installation, fretting between Al wires composing the cable, and ice shedding. Additionally, during PTFE coating any heat-treatment should be performed at low temperature to avoid any structural changes in the alloy [16]. As far as hydrophobic properties are concerned, the influence of polymer surface morphology is very important to consider since certain kinds of roughness may decrease ice shear stress [7, 8]. Finally, icephobic properties should be higher than those of bare Teflon[®] [4].

In this research, sulfuric, phosphoric and oxalic acid anodizing processes were studied by varying electrolyte concentrations and electrolysis voltages. Five different heat-treatments were tested for PTFE impregnation. Coating adhesion, morphology, chemical composition, hydrophobic and icephobic properties were measured and analyzed. To increase hydrophobicity, pre-etching of Al₂O₃ before PTFE impregnation was successfully performed.

II. EXPERIMENTAL

6061 aluminum alloy coupons (2.54 cm x 2.54 cm x 0.15 cm) were used to prepare all the coatings. Alloy 6061 is a silicon-rich alloy (Cu 0.07 wt %, Mg 0.33, Si 1.3, Mn 0.07, Cr 0.03, Zn 0.02 and Fe

0.2). Samples were either mirror polished or used without any surface treatment. The counter electrode was a 5.08 x 7.62 cm 6061 Al alloy plate and the electrochemical reaction was carried out at constant voltage. The PTFE suspension solutions were prepared using 200 nm nanoparticles from Polysciences Inc. ($M_w = 80000$ g and surface area = $10 \text{ m}^2 \text{ g}^{-1}$). A volume of 0.1 mL of ZONYL FS-300 was added to the 100 mL aqueous suspension to generate dispersion. The FS-300 solution was provided by the DuPont Company and is composed of 40 % non-ionic fluoro surfactant and 60 % water. Anodized coupons were placed in small aluminium trays, PTFE suspension was then poured over the coupons before heat-treatment (HT) in a tube furnace. The heating ramp was $10^\circ \text{ C min}^{-1}$, HT duration was 30 min and the sample was allowed to cool naturally. The water contact angle (CA) experiments were carried out using a Kruss DSA 100 goniometer system. Ice adhesion strengths were evaluated using the centrifuge adhesion test (CAT) method [12, 17]. Using the CIGELE refrigerated wind tunnel at $T = -10^\circ \text{ C}$, wind velocity = 9.30 m s^{-1} , air and water pressure = 103 and 414 kPa, respectively. Ice was deposited on the sample fixed at one end of an aluminum beam. The beam was allowed to spin at increasing rotational speeds an enclosure at -10° C and the resulting centrifugal force was used to detach the ice. The shear stress and the adhesion reduction factors can be calculated from the centrifugal force, ice mass, beam radius, rotation speed and surface area. The PTFE coating adhesion tests were performed using the ASTM D3359-02 X-cut test tape method [18]. Using a scalpel, an "X" was etched in the PTFE coating. Standard adhesive tape was then applied to the surface and peeled off at an 180° angle. Two chemical etching solutions were prepared [19]: solution #1, H_3PO_4 (35 mL.L^{-1}) and chromic acid (20 g.L^{-1}) used at 80° C and solution #2, HNO_3 (27 % wt) and HF (2 % wt) used at room temperature.

III. RESULTS AND DISCUSSION

A. Anodizing step

To obtain adherent PTFE coatings on aluminum, it is very important to create a porous Al_2O_3 underlayer by anodizing [13-15, 20]. Three different acid electrolytes used at variable concentrations and voltages were studied, see Table 1. Not surprisingly, thick, uniform coatings having variable colors depending on applied voltage were obtained: grey/black, bright yellow and white, using sulfuric, oxalic and phosphoric acids, respectively. SEM microphotographs taken for an Al sample oxidized with H_3PO_4 is shown in Fig. 1. At low magnification, see Fig. 1a, the surface is very rough with a certain degree of porosity. At high

magnification, see Fig. 1b, pores are clearly visible and have a diameter around 100 nm.

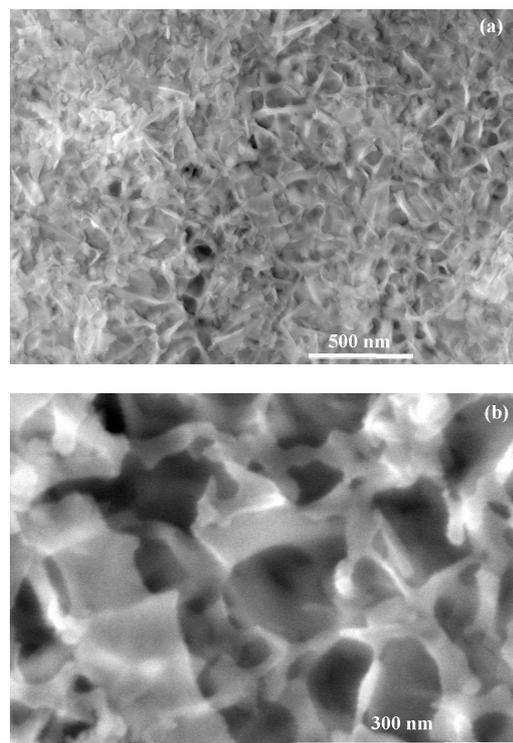


Fig. 1. SEM microphotographs of Al 6061 sample anodized in 10 % H_3PO_4 , 60 V, $t = 90$ min, $T = 18^\circ \text{ C}$. (a) low and (b) high magnifications.

Table 1. Anodizing experimental conditions and Al_2O_3 film characterization

	H_2SO_4	H_3PO_4	$\text{H}_2\text{C}_2\text{O}_4$
Concentration (% w/w)	15	10 and 30	3 and 5
Anodizing voltage (V)	20 to 40	20 to 60	40 to 80
T ($^\circ\text{C}$)	+ 5	+ 18	+ 18

Film characterization

	H_2SO_4	H_3PO_4	$\text{H}_2\text{C}_2\text{O}_4$
Concentration (% w/w)	15	10	3
Anodizing voltage (V)	30	50	60
Film thickness (μm)	34	32	38
Pore diameter (nm)	22 ± 5	111 ± 12	67 ± 8

B. PTFE impregnation

The anodic film thickness and the mean diameter of the pores for all the studied samples are displayed in Table 1. The oxide coating was relatively thick (around 30 μm) and uniform. For the H_2SO_4 process, a columnar, nanoporous Al_2O_3 structure was clearly visible and comparable to the theoretical hexagonal growth mode covered in

many textbooks on electrochemical surface treatment. In this particular case, the mean diameter of the nanopores was 22 nm. On the other hand, bigger pore diameters were observed when phosphoric acid (111 nm) and oxalic acid (67 nm) were used. The oxide surface prepared with the phosphoric acid process exhibited a rougher aspect than those prepared with the oxalic and sulfuric processes.

In a previous study, Menini and Farzaneh [20] sealed the different porous Al_2O_3 films with PTFE according to the process described in the experimental section. Figure 2 shows the hydrophobic properties (water contact angle) versus the type of aluminum chemical treatment followed by PTFE impregnation.

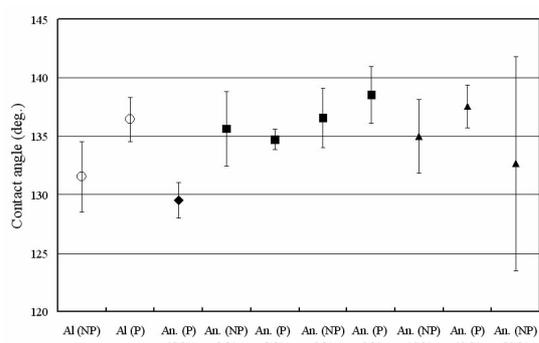


Fig. 2. Water contact angles of PTFE coatings on different Al substrates. (○): non-oxidized Al alloy, (◆): anodizing with H_2SO_4 , (■): anodizing with $\text{H}_2\text{C}_2\text{O}_4$ and (▲): anodizing with H_3PO_4 . P = Al polished samples and NP = Al non-polished samples.

While untreated aluminum followed by PTFE impregnation exhibited high hydrophobic properties ($\text{CA} > 130^\circ$) and comparable to oxidized samples, it is important to mention that PTFE adhesion to the Al substrate was very poor. On the other hand, PTFE coated anodized samples exhibited excellent mechanical properties, especially those pre-treated with the oxalic and phosphoric processes where X-cut and bend tests showed no peeling.

C. Icephobic properties

As far as icephobicity tests are concerned, Table 2 displays the shear stress force measurements (CAT method) performed on three different samples: bare Al 6061, anodized Al using a $\text{H}_2\text{C}_2\text{O}_4$ treatment, and anodized PTFE coating. Seven accumulations and measurements were performed for each sample. The shear stress (τ) was almost fell below 30 kPa, compared to the value measured by Mulherin and Haehnel on bare Teflon[®] [4]. The standard deviation was also lower compared to this work (± 103 kPa). The adhesion reduction factor ($\text{ARF} = \tau_{\text{bare Al}} / \tau_{\text{treat. Al}}$) was 2.41. This good performance could be attributed to the

fact that ice did not contact the entire rough PTFE surface. However, it is difficult to compare these data with other works in the literature since other researchers used different Al substrates, PTFE morphologies, ice accretion modes and shear stress measurement methods [4, 12 and 21]. However, the relative measurements made in the present work show that ice adhesion strength was reduced using anodizing and PTFE impregnation. It must be pointed out that PTFE layers were undamaged and remained active even after seven ice shedding CAT experiments. As concerns hydrophobicity, water contact angle measurements were performed on the different samples before and after the seven deicing experiments. The PTFE layer remained highly hydrophobic since the averaged percentage variation of the contact angle values was below 0.38 %.

Table 2. Icephobic properties of bare Al 6061, anodized Al and anodized PTFE Al using the centrifugal adhesion test method.

	Shear stress (kPa)	Deviation (kPa)	ARF
Al 6061	505	65	--
Anodized samples ¹	504	70.8	1
PTFE coatings	209.6	79.6	2.41

¹ $\text{H}_2\text{C}_2\text{O}_4$ 5 % w/w, $U = 50$ V

D. Superhydrophobic PTFE impregnation

To improve hydrophobic and icephobic properties of anodized Al impregnated with PTFE, a new step was added to the process described above. The main idea was to enhance surface roughness to reach superhydrophobicity. To achieve such a goal, two etching solutions usually utilized in industry for Al_2O_3 coating stripping [19] were used: a chromic-based solution (Etching #1) and a hydrofluoric-acid based one (Etching #2). Concerning the anodizing process, the phosphoric acid pre-treatment was chosen because it led to higher surface roughness than both the oxalic and sulfuric processes. For each etching solution, four different stripping durations were tested: 10, 20, 30 and 60 s. Water drop contact angle measurements versus etching time for PTFE impregnated Al anodized samples are shown in Fig. 3. An improvement in hydrophobicity (average gain of 20 deg) was found when either etching solution #1 or #2 was used. Although deviation tends to be important, an etching time of 60 s does not seem suitable. The chromic-based solution (#1) is the

most reliable and it should be pointed out that for $t = 10$ to 30 s, superhydrophobicity was achieved ($CA = 150^\circ$).

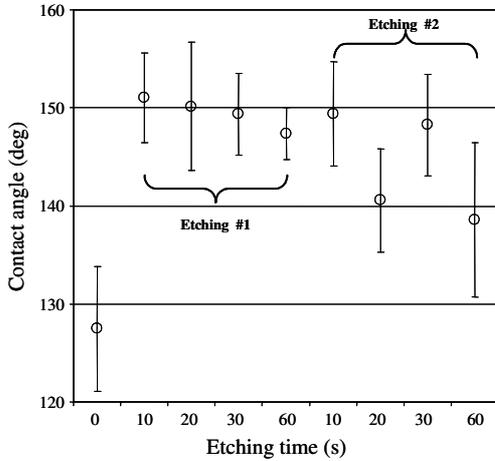


Fig. 3. Water drop contact angle measurements versus etching time for PTFE impregnated Al anodized samples (H_3PO_4 , 60 V, 90 min, $18^\circ C$).

In order to explain such improvements, atomic force microscopy imaging (in tapping mode) was performed on samples etched with solution #1 ($t = 20$ s) and subsequently impregnated with PTFE. Figure 4 shows the morphology of such a sample at relatively large scale.

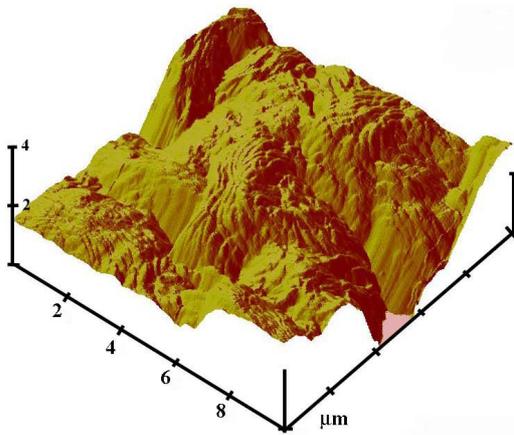


Fig. 4. Atomic force microscopy image of PTFE impregnated anodized (H_3PO_4) and etched aluminum sample (chromic acid).

From this picture, a double type or roughness can be detected: at the microscale with large asperities of 1 to $2 \mu m$ in height and at the nano scale (see for example the right hand side of the image). The nanostructure was studied using the same imaging technique and a topographical line analysis was performed on a one-micrometer-square area, see Fig. 5. Nanofeatures with heights

ranging from 10 to 100 nm were detected on such surfaces. On the line analysis shown on Fig. 5, a valley to valley height of 70 nm and a peak to valley distance of 15 nm were measured.

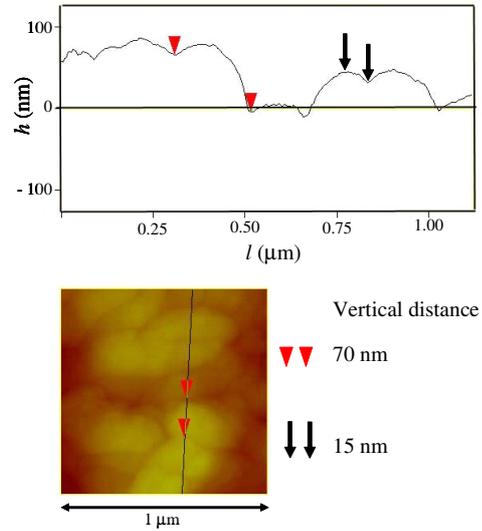


Fig. 5. Atomic force microscopy image of PTFE impregnated anodized (H_3PO_4) and etched aluminum sample (chromic acid). Line topographical analysis.

The double micro- and nano-structure is typical of superhydrophobic surfaces found in nature, such as lotus leaves for example. Superhydrophobicity is considered to be a very promising avenue towards icephobicity, as was recently demonstrated at the CIGELE laboratory of the University of Quebec at Chicoutimi, Canada [22 and 23].

IV. CONCLUSION AND FUTURE WORKS

To protect power line aluminum cables and conductors against excessive ice accumulation, new coatings with icephobic characteristics must also exhibit excellent mechanical properties. Hydrophobic and icephobic properties of aluminum alloy 6061 were improved by deposition of an extremely adherent PTFE coating on an Al_2O_3 underlayer produced by anodizing in an oxalic or phosphoric acid electrolyte. PTFE impregnation was carried out at low temperature ($320^\circ C$) to prevent, as much as possible, PTFE degradation and Al alloy structure modifications. It should be pointed out that PTFE impregnation within anodic films prepared in phosphoric acid also yielded very good results. These coatings were highly hydrophobic (superior to flat Teflon®); ice adhesion was reduced by almost 2.5 times and remained active after several ice shedding events. While some coatings have greater icephobic properties, a compromise between mechanical and icephobic properties is needed. To improve hydrophobicity, an etching step prior to PTFE impregnation was added to the process. This step

enhanced the surface porosity to such an extent that superhydrophobicity was achieved, thanks to the presence of a double micro- and nano-structure at the coating substrate. Future works will be dedicated to improving this new etching step in order to attain higher surfaces roughness. Additionally, ice strength measurements will be performed. To decrease ice adhesion strength to such an extent that ice could shed from its own weight will require further studies. However, based on the ongoing work, impregnation of different polymer compositions and/or creation of a 3-D structure to achieve superhydrophobicity are two promising avenues to fulfill this task.

V. ACKNOWLEDGMENTS

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