Ice-Repellent Performance of Alkyl-Grafted Aluminium Alloy Surfaces

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Abstract— This work aims to systematically study different alkyl-grafted aluminium surfaces as potential ice and wet-snow repellent coatings. The coatings were based on stearic acid ($CH_3(CH_2)_{16}COOH$) and octadecyltrimethoxysilane ($C_{18}H_{37}Si(OMe)_3$) on polished AA6061 and AA2024 substrates and were prepared using the wet-chemistry technique. Both the stability of such coatings in wet environments and their ice-releasing properties were carefully examined. The ice accumulated on coated samples was a glaze type prepared by spraying super-cooled water droplets in a wind tunnel at subzero temperatures. Such conditions thus simulated those of natural outdoor atmospheric icing. The ice adhesion strength and the adhesion reduction factor (*ARF*) were measured by spinning iced samples in a centrifuge maintained in a cold room, and determining the rotation speed at which ice detachment occurred. All the coatings studied are shown to gradually lose their hydrophobic properties after ~ 1000 h of immersion in water, which is associated with considerable decrease of water contact angle. Meanwhile, no significant changes in ice adhesion strength were observed on such surfaces after as many as 10 icing–de-icing cycles.

Keywords: Aluminium alloys; Ice adhesion strength; Organosilane-based layers; Icephobicity; Self-assembly; Adhesion reduction factor; Hydrophobicity.

I. INTRODUCTION

Ice and/or wet-snow adhesion on outdoor structures and equipment is a serious problem for regions subjected to extreme weather conditions in winter due to ice/snow build-ups. Atmospheric icing occurs when super-cooled water drops or snow particles come into contact with the surfaces of exposed structures, leading to potential damage and financial losses in many sectors of the economy, including power transmission and distribution, telecommunication networks, etc. Each year, numerous failures due to ice accumulation are reported in Canada, the United States, Russia, Iceland, Japan, Norway, China, and other countries. To counter this problem, various de-icing and anti-icing techniques have been developed over the past few decades [1]. As already mentioned, ice accumulation is the source of several types of damage and malfunctions; in the specific case of power transmission lines, ice or wet snow can cause serious damage due to their high adherence to both metallic and insulator surfaces. Wire sagging and short circuits are caused by static ice overloads on towers and cables. Aerodynamically unstable ice, typically a few cm thick, also increases the amplitude of wind-induced dynamic oscillations, galloping, while decreasing the damping rate, which leads to high mechanical stress on conductors, cables, insulating supports and towers. In addition, when the accumulated ice suddenly drops off from a conductor, excessive mechanical tensions are generated. All these factors cause high-amplitude movements of cables, increasing the possibility of low clearance between the adjacent cables or between cables and towers [2].

While most of the techniques currently in use are the so-called active de-icing methods (e.g. mechanical, chemical and thermal removal of ice/snow build-ups), all of them are employed where accumulations are substantial. Passive approaches to the problem, among which are the developing anti-icing or icephobic coatings that inhibit ice accumulation, are gaining in popularity [3]. Even though there is no material that completely prevents ice/snow build-ups on its surface [1], some coatings are believed to provide reduced adhesion. This is expected to result in lower ice/wet-snow accumulation on such surfaces. To be applicable, such coatings are expected to satisfy the following requirements: (1) they must seriously reduce ice/snow adhesion and (2) demonstrate reasonably long service-life (durability). The ideal solution to the problem would be the application of a durable material that reduces ice adhesion to the extent that ice falls off under the effect of natural forces [4].

Alkyl-terminated coatings, among which are alkylsilane and fluoroalkylsilane-based layers, are potential ice-releasing materials [3,5,6]. Such coatings have been tested by several groups [3,6], and reduction in ice adhesion by a factor of ~ 2 [3], compared to bare aluminium, has been reported. However, no systematic work has been done up to now. In this study, we prepared different organic coatings terminated with alkyl groups as potential ice- and wet-snow- repellent layers on the surface of aluminium alloys. More specifically, thin films of octadecyltrimethoxysilane [$CH_3(CH_2)_{17}Si(OCH_3)_3$, ODTMS] and stearic acid [$CH_3(CH_2)_{16}COOH$, SA] were layered on polished AA6061 and AA2024 substrates. Both the stability of the coatings in water and their ice-repellent performance were carefully studied. Ice adhesion was tested in order to study their performance over time.

II. Experimental

A. *Sample preparation*

The as-received AA6061 and AA2024 aluminium alloy panels were cut into smaller plates with dimensions of 1×1 and 5.1×3.2 cm^2 which were used as substrates. Prior to coating, they were mechanically polished using first 600-grit sand paper, then successively finer SiC abrasive papers lubricated with water, and finally using aqueous 1.0 μm alumina slurry to have mirror-polished aluminium surfaces. The polished aluminium plates were then cleaned and degreased in organic solvents followed by cleaning in a Turco Redoline 53D alkaline solution. The polished and cleaned aluminium plates were blow-dried in a N$_2$ gas flow and then placed in baths with different chemicals. Figure 1 is a schematic presentation of the sample preparation procedure.

The deposition baths used in this study were 5 mM stearic acid [CH$_3$(CH$_2$)$_{16}$COOH, from Alfa Aesar] in 300 ml methanol as solvent and ODTMS 1% (V/V %) [C$_{18}$H$_{37}$Si(OCH$_3$)$_3$, from Sigma-Aldrich] in methanol-water (500 ml, 90% CH$_3$OH + 9% distilled water). Prior to use, the baths were vigorously stirred for 3 h to allow for dissolution and/or hydrolysis according to the following reaction:

$$\text{R-Si(OMe)}_3 + 3\,\text{H}_2\text{O} \rightarrow \text{R-Si(OH)}_3 + 3\,\text{MeOH}$$
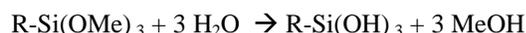
Several coatings based on stearic acid and alkylsilane were prepared on aluminium alloys. While the smaller samples were used to test the stability of the coatings in water, the larger ones were further used to evaluate their ice-repellent performance. During the sample preparation, the immersion time was 24 h for the stearic acid-methanol and 15 min for the ODTMS-methanol baths. Prior to the tests, the treated samples were removed from the solution and rinsed with copious amounts of methanol and blow-dried with N$_2$ and finally heat-treated in ambient atmosphere (80 ^{0}C) for ~ 10 h.

B. *Sample analyses*

The sample stability in water was traced by means of contact angle (CA) measurements on samples immersed in pure deionized water for different time periods, from 0 to 1200 h, and then blow-dried in N$_2$ before each CA measurement. Contact angle of a water drop on a surface determines the hydrophobicity of the surface. The more the water beads on the surface, corresponding to an elevated CA, the higher the hydrophobicity. For each sample, at least seven different spots were randomly selected on a horizontal surface and measured. CA was measured on the coated samples, after immersion in deionized water, to monitor the stability of the coatings in water over time.

The CA measurements were performed on a fully automated contact angle goniometer (DSA 100 from Krüss) with controllable volume of water drops (sessile drop method,

4 μL) on the sample surfaces. These measurements were calculated accordingly with the Young–Laplace method that is theoretically considered as the most accurate since the distorted droplet shape due to the liquid weight is taken into account [7].
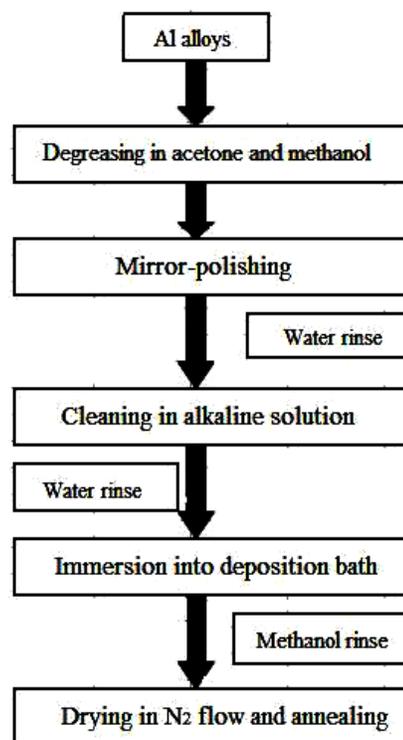

Fig. 1. Scheme of sample preparation procedure.

Scanning electron microscopy (SEM) images of the coated aluminium samples before and after immersion in water were taken using a Philips XL30FEG instrument in high-vacuum mode, typically at 15 keV. The ice-adhesion evaluation tests were conducted on Al beams with samples spun in a home-made centrifuge apparatus (see Fig.2). The samples attached to the beams were iced in a wind tunnel at a wind speed of 10 m/s, temperature -10 ^{o}C, water feed rate of 2.5 g/m^3 and average droplet size of ~80 μm to prepare glaze ice of up to ~1 cm thick over the area of ~ 3.2x3.0 cm^2. This ice geometry was enough to avoid cohesion failure and provide well reproducible results during deicing. Ice mass and area were carefully evaluated both after icing and de-icing. To balance the beam in the centrifuge, a counter-weight was used on the other side (Fig.2). The artificially iced samples were spun in the centrifuge placed in a climatic chamber at -10°C to determine the rotational speed at which ice detachment from the sample surface occurred. At the moment of detachment (detected with sensors embedded into the centrifuge walls), the adhesion strength of ice is assumed to be equal to the centrifugal force, $F = mr\omega^2$, where m is the ice mass, r is the beam radius and ω is the rotational speed in rad/s. The shear stress, correspondingly, was calculated as $\tau = F/A$, where A is the deiced area. To reduce the influence of any experimental errors, the adhesion reduction factor, *ARF*, was finally used

rather than absolute values of shear stress. *ARF* was calculated as the ratio of shear stress of ice detachment on bare Al to that on samples with coatings, $ARF = \tau_{(Al)}/\tau_{(coating)}$, provided that all the tests (for both uncoated and coated samples) were run under identical conditions.
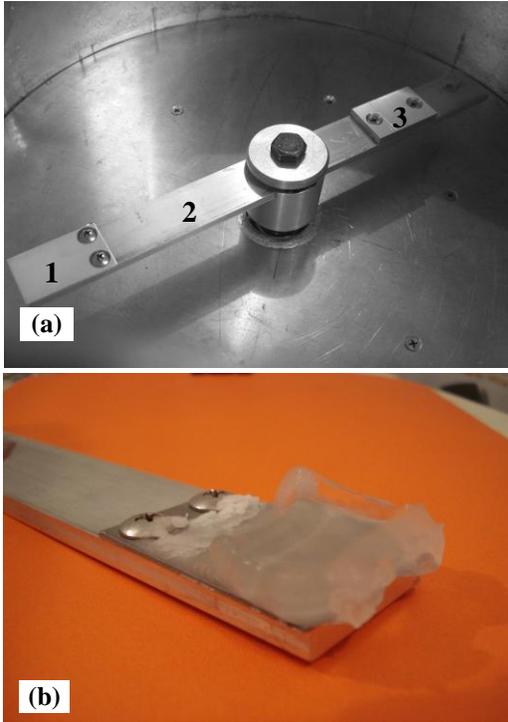

(a)

(b)

Fig. 2. (a) Sample with coating in centrifuge set-up measuring ice adhesion: (1) sample, (2) aluminium beam, (3) counter-weight. (b) Sample covered with artificial glaze ice.

For each alkyl-terminated coating studied, one sample was subjected to 10 successive icing/de-icing events. From these results, ice adhesion strength to each coating was analyzed as a function of the number of icing/de-icing cycles. On the bare Al, used as a standard reference sample, the shear stress of ice detachment value, $\tau_{(Al)}$, was measured to be 445 ± 20 kPa, in agreement with the literature data [8]. More details on this technique can be found elsewhere [7].

III. RESULTS AND DISCUSSION

Figure 3 presents CA values as a function of immersion time in water for both SA and ODTMS coatings. Both samples are seen to demonstrate initial values of CA $>100^0$ (see Fig.4, left), indicating well coated flat hydrophobic surfaces. However, it can be observed that the CA values decrease with immersion time. In fact, all the coatings studied were found to slowly lose their hydrophobic properties after ~ 1000 h of immersion in water, which is associated with a considerable decrease of their water contact angle values (e.g. Fig.4, right).
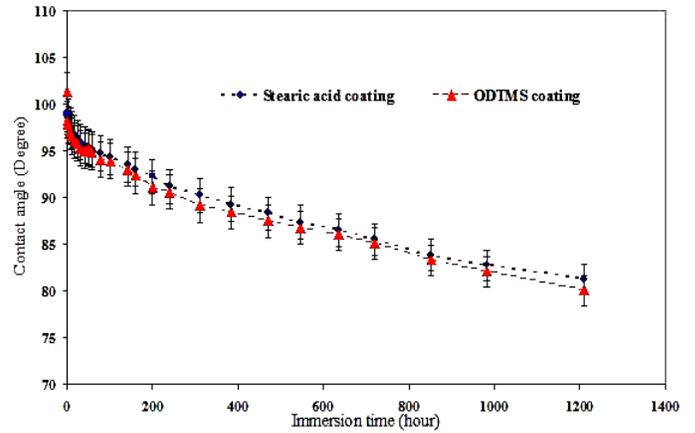

Fig. 3. Contact angle vs. immersion time in deionized water.

Figure 4 shows water droplets images on coated aluminium surfaces before (left) and after 1000 h immersion in water (right). Significant decrease in surface hydrophobicity is clearly observed in Fig.4 (right), which implies some coating layer decay.
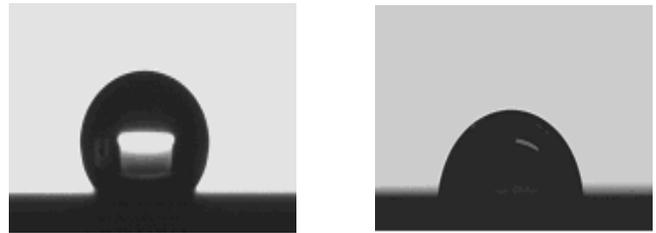

Fig. 4. Water droplet images on ODTMS coated aluminium surfaces before (left) and after 1000 h immersion in water (right).

Figure 5 shows the surface morphology of an AA2024 sample treated with ODTMS before (a) and after (b) immersion in water for 520 h. Signs of corrosion are clearly seen around a second-phase intermetallic particle, which is nobler compared to the surrounding aluminium alloy matrix. This explains well the results of the CA measurements presented in Fig.3. The ODTMS layer was not believed to be dense enough to prevent water molecules from penetrating through the coating and reaching the coating/substrate interface. This caused both the corrosion processes (whose products are seen in Fig.5b) and the hydrolysis of the Si-O-Al bond, through which the ODTMS molecules were attached to the surface. As a result, some alkylsilane molecules were removed from the surface, thus decreasing its hydrophobicity. The corrosion products (seen in Fig.5b), being oxides/hydroxides, are also believed to have contributed to the decrease in hydrophobicity observed in Fig.3 over time. Similar surface images were observed for the SA sample, both before and after immersion in water. We thus assume that similar processes contributing to the degradation of hydrophobic properties of the SA sample upon its immersion in water also occurred.

Figures 6 and 7 show the shear stress of ice detachment

on the two sample surfaces tested as a function of icing/de-icing cycles for ODTMS and SA samples. Adherence measurements were made in a cold room maintained at –10 ^{o}C, with glaze-type ice of measured density 0.87 g/cm³ ± 0.02. For each coating studied, one sample was subjected to 10 successive de-icing operations. Polished bare aluminium was used as standard reference showing shear stress of ice detachment of 445±20 kPa, which is comparable with the values in the literature [8,9]. The corresponding value for the mirror-polished aluminium surface (350±19 kPa) is also shown in Figs.6,7.

(a)

(b)
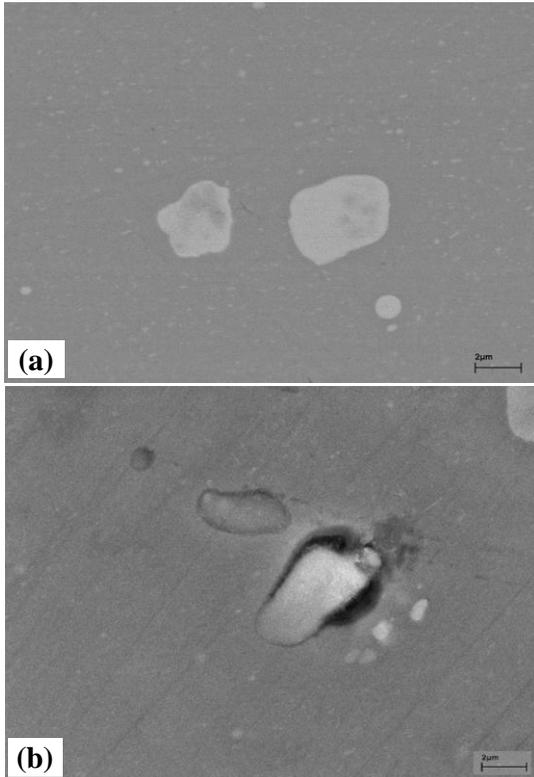
Fig. 5. Surface micrographs of AA2024 treated with ODTMS before (a) and after immersion in water for 520 h (b). (Scale bars indicate 2 µm.)
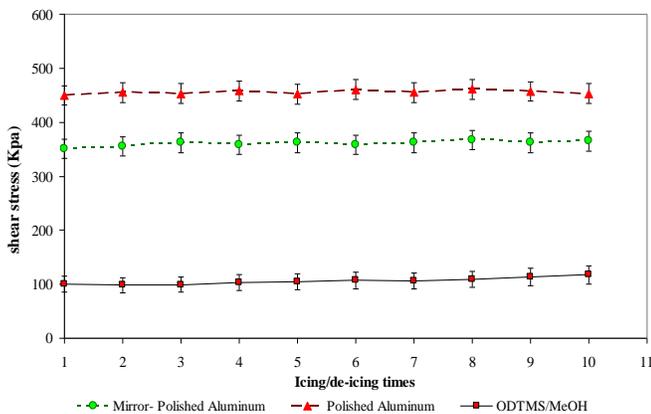

Fig. 6. Shear stress of ice detachment vs. icing/de-icing cycle number for ODTMS treated sample. The circles and triangles stand for mirror-polished and polished Al surfaces, respectively.
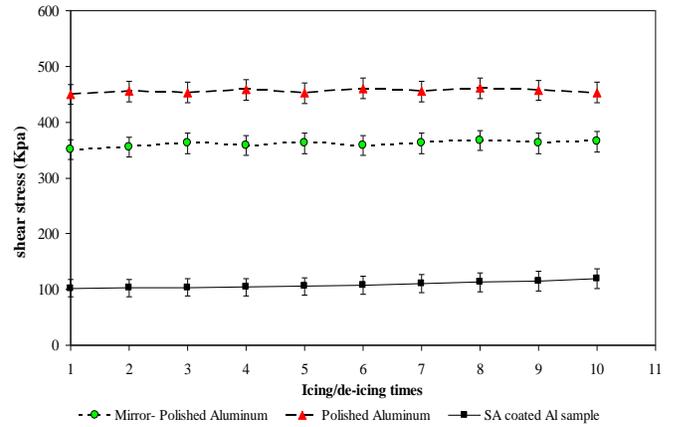

Fig. 7. Shear stress of ice detachment vs. icing/de-icing cycle number for stearic acid treated sample. The circles and triangles represent mirror-polished and polished Al surfaces, respectively.

Both coat-treated samples showed very close values of shear stress, implying very similar ice adhesion strength on both alkyl-grafted samples. The uncoated polished flat sample showed average shear stress of ice detachment of ~445±20 kPa, while its coated counterparts with alkylsilane or stearic acid coatings showed reduced values of ~100 kPa. This reduction can be attributed to the presence of the low surface energy coatings on the samples. It is observed that both samples allow for values of ice adhesion strength at least ~ 3 times lower than those obtained on the mirror-polished sample, and ~ 4 times lower than those on the polished aluminium alloy sample with rougher finish. It is also seen that the ice-releasing performance of the samples do not change much after 10 icing/de-icing cycles, as only a small increase in ice adhesion strength is observed after 10 icing/de-icing events.

Figures 8 and 9 show ice adhesion reduction factor (*ARF*) as a function of icing/de-icing cycles for the mirror-polished, ODTMS and SA treated aluminium surfaces. Only a slight decrease in *ARF* values is observed after as many as 10 icing/de-icing events on both surfaces.
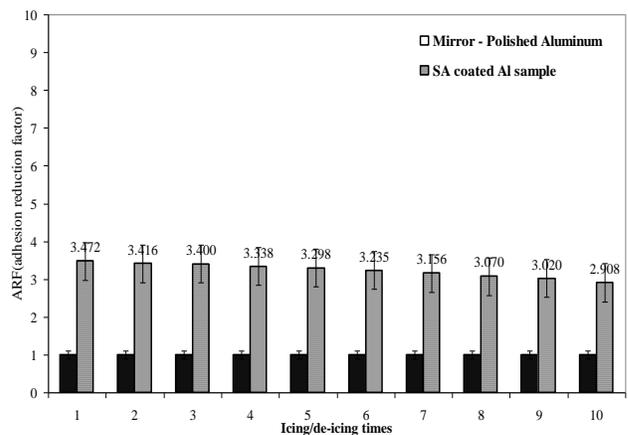

Fig. 8. Ice adhesion reduction factor (*ARF*) as a function of icing/de-icing cycles on mirror-polished and stearic acid treated aluminium surfaces.
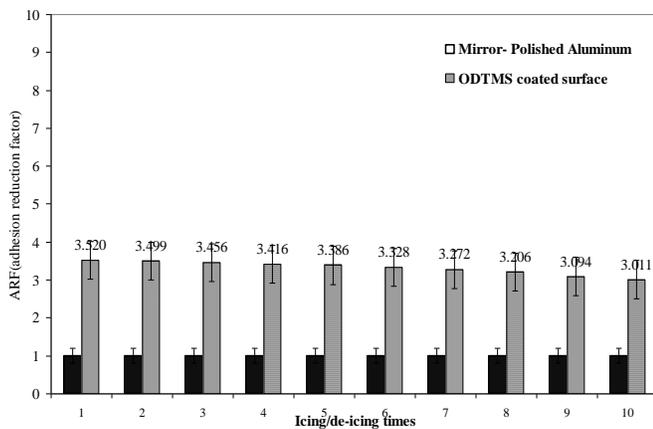
Fig. 9. Ice adhesion reduction factor (*ARF*) as a function of icing/de-icing cycles on mirror-polished and ODTMS treated aluminium surfaces.

The highest *ARF* value of 3.52 was obtained on the ODTMS treated aluminium surface compared to 3.47 on the SA treated one. These results show that ice adhesion is at least three times lower on the coatings in comparison with bare Al. The slight reduction in *ARF* values after 10 icing/de-icing events is believed to be associated with a partial decay of the coatings caused by their contact with water, similar to that observed in the above described immersion experiments.

IV. CONCLUSIONS

Alkyl-terminated surfaces were prepared by depositing layers of stearic acid and octadecyltrimethoxysilane on mirror-polished aluminium alloy surfaces. The stability of such surfaces in water was tested by means of contact angle measurements, clearly showing that they gradually lose their hydrophobicity after ~1000-h-long immersion in water, which is associated with a significant decrease of water contact angle.

Ice-releasing properties of the surfaces were investigated by accumulating glaze ice similar to that in nature prepared by spraying super-cooled micrometer-sized water droplets in a wind tunnel at subzero temperature. Both surfaces demonstrated shear stress of ice detachment values about ~ 3 times lower compared to uncoated (polished) aluminium alloy surfaces. The values remained mainly unchanged after as many as ten icing/de-icing events. The slight increase in ice adhesion strength observed can be ascribed to some degradation of the coatings upon their contact with water.

V. ACKNOWLEDGMENT

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