

## ICE-RELEASING PROPERTIES OF VARIOUS NANOSTRUCTURED SUPERHYDROPHOBIC COATINGS ON AN ALUMINIUM SURFACE

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**Abstract:** Ice or wet snow adhesion and excessive accumulation is known to sometimes cause serious problems to exposed structures in cold climate regions. To counter this problem, a variety of de-icing and anti-icing techniques have been developed over the past few decades. In this study, several nanostructured superhydrophobic coatings with different chemistry and topography were prepared and tested as anti-icing candidate materials. The samples were tested over many icing/de-icing cycles in order to assess the durability of their ice-releasing performance. The results showed that both their water-repellent and ice-repellent properties were not stable and degraded over icing/de-icing events. The possible deterioration mechanism is discussed.

### 1. INTRODUCTION

Ice and wet snow adhesion and accumulation on outdoor structures and equipment is a serious problem for cold climate regions [1]. Each year, numerous failures due to ice accumulation are reported in Canada, U.S.A., Russia, Iceland, Norway, China, and other countries. Atmospheric icing is defined as any process of ice or snow accumulation on objects exposed to supercooled water droplets or snow particles [2]. To counter this problem, a variety of de-icing/anti-icing techniques have been developed [3]. Among these, ice-repellent coatings have been recently proposed as a passive technique to reduce or prevent ice accumulation on the outdoor structures [1, 4]. Thus, the research on coatings able to reduce wet snow, frost, or ice accumulation has been going on for decades [1, 4]. Superhydrophobic surfaces with their water contact angle (CA) above 150° and low CA hysteresis (CAH) were first tested by Saito *et al.* [4] and showed promising anti-icing performance. These characteristics make superhydrophobic surfaces attractive candidates for anti-icing applications. However, the ice-releasing performance of rough superhydrophobic surfaces has not been adequately studied yet in different conditions. In this study, the ice-repellent performance of certain micro- and nano-rough superhydrophobic coatings prepared on AA6061 surfaces was investigated as the surfaces were iced and de-iced repeatedly. The samples were prepared either by etching the aluminium alloy substrate followed by further hydrophobization of the rough nanostructured surface with 1H,1H,2H,2H-perfluoro-octyltrichlorosilane (C<sub>8</sub>H<sub>4</sub>F<sub>13</sub>Cl<sub>3</sub>Si, FAS-13) or by spin-coating suspensions of a fluoropolymer (Zonyl 8740) or room-temperature-vulcanized silicone rubber (RTV SR) mixed with nanopowder of cerium (IV) oxide (CeO<sub>2</sub>). Both water- and ice-repellent behavior of the coatings were then evaluated.

### 2. RESULTS AND DISCUSSION

Based on the results of wetting characterization, all the samples tested in this study were found to be rough at micro/nano-scale and demonstrated superhydrophobicity. That is, they were all wetted in the Cassie regime [1, 6]. Artificial glaze ice was deposited on the nanostructured coated surfaces by spraying supercooled water micro-droplets with an average size of ~ 80 µm in a wind tunnel at -10 °C, thus simulating severe natural atmospheric icing. The ice adhesion strength was evaluated by spinning the samples in a centrifuge machine at constantly increasing speed until the accumulated ice detached from the samples. The initial values of shear stress of ice detachment on the as-prepared samples were ~ 3.3-6.6 times lower than those on the mirror-polished aluminium (being ~ 55 to 107 kPa), which is consistent with the Cassie wetting regime and the small ice-solid contact areas [5]. The samples were tested over repeated icing/de-icing cycles in order to assess the durability of their ice-repellent properties. After 12 icing/de-icing events, all samples demonstrated ice adhesion strengths increased by a factor of about 1.8 - 2.4 as compared with the as-prepared surfaces, which is believed to be associated with a larger ice-solid contact area on these nanostructured surfaces after 12 icing/de-icing cycles. The water repellency of all the samples increasingly deteriorated after 12 icing/deicing cycles.

### 3. CONCLUSION

Ice repellency of nanostructured hydrophobic coatings was evaluated on several samples with various surface topographies over 12 icing/de-icing cycles. The results of ice adhesion strength evaluation, after as many as 12 icing/de-icing cycles, showed that the anti-ice performance of the samples significantly deteriorated. The results showed that anti-icing performance of superhydrophobic surfaces may be limited and should be studied in more details prior to any wide applications.

### 4. REFERENCES

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# Ice-releasing properties of various nanostructured superhydrophobic coatings on an aluminium surface

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**Abstract**— Ice or wet snow adhesion and excessive accumulation is known to sometimes cause serious problems to exposed structures in cold climate regions. To counter this problem, a variety of de-icing and anti-icing techniques have been developed over the past few decades. Among these, superhydrophobic coatings have been recently proposed as a passive technique to reduce or prevent ice accumulation on the outdoor structures. In this study, the ice-repellent performance of certain micro- and nano-rough superhydrophobic coatings prepared on AA6061 surfaces was investigated as the surfaces were iced and de-iced repeatedly. The samples were prepared either by etching the AA substrate followed by further hydrophobization of the rough nanostructured surface with FAS-13 or by spin-coating suspensions of a fluoropolymer (Zonyl 8740) or room-temperature-vulcanized silicone rubber (RTV SR) mixed with nanopowder of cerium (IV) oxide ( $\text{CeO}_2$ ). Both water- and ice-repellent behavior of the coatings were then evaluated. The samples were tested over repeated icing/de-icing cycles in order to assess the durability of their ice-repellent properties. The results showed that both water-repellent and ice-repellent properties of the surfaces were not stable and degraded over icing/deicing events. The possible deterioration mechanism is discussed.

**Keywords:** Ice Adhesion; Ice Repellency; Superhydrophobicity; Ice adhesion strength; Roughness; Nanostructured coatings; Water Condensation; Durability.

## I. INTRODUCTION

Ice and wet snow adhesion and accumulation on structures and equipment is a serious problem for cold climate regions [1-5]. Atmospheric icing is defined as any process of ice or snow accumulation on objects exposed to supercooled water droplets or snow particles [6]. Atmospheric icing may lead to material damage and socioeconomic costs as it adversely affects structures like power transmission and distribution, telecommunication networks, aircraft, boats, etc. [2, 3]. Ice accumulation on high voltage power lines can lead to mechanical failure resulting from the static load of accreted ice, or from the dynamic stresses of ice shedding, as it has been reported in Canada, China, Norway, Iceland, Finland, U.S.A., Russia and Japan [1-4, 7]. To counter this problem, a variety of de-icing or anti-icing techniques have been developed over the past few decades [2, 3]. Among those, ice-repellent coatings have been recently proposed as a passive technique to

reduce or prevent ice accumulation on the outdoor structures. Such coatings provide reduced adhesion or delay water freezing on their surface [5, 7], expected to result in lower ice or wet-snow accumulation on the coated surfaces [5]. Thus, the research on coatings able to reduce wet snow, or ice accumulation has been going on for decades [5, 7]. Superhydrophobic surfaces, i.e. those characterized by water contact angle (CA) above  $150^\circ$  and low CA hysteresis (CAH), were first tested by Saito *et al.* [7] and showed promising anti-icing performance. More recently, other groups showed reduced ice adhesion [8-10] or delayed water freezing [5, 11-13] on rough superhydrophobic surfaces. These two characteristics make superhydrophobic surfaces attractive candidates for anti-icing applications.

In this research work, a number of nanostructured superhydrophobic coatings with different chemistry and topography were prepared and tested as anti-icing candidate materials. The glaze ice accumulated on the samples was prepared by spraying supercooled water micro-droplets in a wind tunnel at subzero temperatures, simulating severe natural atmospheric icing. The samples were tested over numerous icing/de-icing cycles in order to assess the durability of their ice-releasing performance.

## II. EXPERIMENTAL PROCEDURES

3.2 x 5.0 cm<sup>2</sup> aluminium alloy AA6061-T6 (Al 97.9 wt.%, Mg 1.0 wt.%, Si 0.60 wt.%, Cu 0.28 wt.%, Cr 0.20 wt.%) plates were used as substrates. Sample A was prepared by spin-coating a  $\text{CeO}_2$  nanopowder suspension in Zonyl 8740 (perfluoroalkyl methacrylic copolymer soluble in water, DuPont) [8, 9].  $\text{CeO}_2$  nanopowder (8.0 g), with a particle size < 50 nm, was mixed with 80 ml deionized water. The suspension was sonicated for 30 min, after which 5.0 ml of Zonyl 8740 was added. The final suspension was stirred for 3 h before being coated on the Al plate. Sample B was etched Al coated with 1H,1H,2H,2H-perfluoro-octyltriethoxysilane (FAS-13). The plate was first etched in 17% HCl for 5 min, after which it was sonicated in deionized water, rinsed and dried in air for 1 h. A methanol solution of FAS-13 was hydrolyzed by the addition of a 3-fold molar excess of water at room temperature. The etched metallic substrate was immersed in the hydrolyzed silane

solution for 1 h, then rinsed in methanol and heat treated at 80 °C for 2 h. The process has been described in greater detail in [14]. Nanostructured superhydrophobic sample C was prepared by spin-coating a hexane suspension of room-temperature vulcanized silicone rubber (RTV SR) doped with 3% CeO<sub>2</sub> nanoparticles over the aluminium surface [8, 9]. The silicone rubber, 1:3 v/v, was purchased from Dow Corning under the brand name of HVIC 1547. After coating, the samples were heat treated at 120 °C in air for 3 h to remove any volatile components and residual solvents. Applying spin-coating or etching allowed preparing samples with diverse surface topographies. A DSA-100 contact angle goniometer from Krüss was used to obtain the wetting characteristics reported in Table 1. Contact angle measurements were made on at least 7 different randomly selected points on a horizontal surface for each sample.

Surface topographies were analyzed with scanning electron microscopy (SEM, LEO Gemini instrument) and atomic force microscopy (AFM, Escope from Veeco). The ice adhesion evaluation tests were carried out on aluminium beams with 1-cm thick glaze ice samples spun in a centrifuge apparatus placed in a cold room at -10 °C (Fig.1) [8-10]. Glaze ice was prepared in the wind tunnel by applying a wind speed of 11 m/s, air temperature -10 °C and an average droplet size of ~ 80 μm. The samples attached to the beams were previously iced in a wind tunnel, then placed in the centrifuge and spun there with increasing rotational speed until ice detachment occurred [8-10]. It was checked carefully that the iced sample type and geometry would not allow cohesion failure, and provide well reproducible results during de-icing. Ice mass and area were evaluated both before and after de-icing. The procedure to evaluate the ice adhesion strength (as the shear stress of ice detachment) was previously reported in greater detail elsewhere [8-10]. Three duplicates were prepared for each sample in Table 1, and the results were calculated as the average of the three.

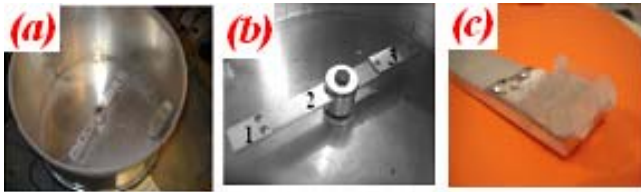


Figure 1. (a) Centrifuge adhesion test machine, (b) sample with coating in the centrifuge set-up measuring ice adhesion with (1) sample, (2) Al beam, (3) counter-weight, and (c) Sample covered with artificial glaze ice.

At the moment of ice detachment from the coated aluminium sample, 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  $\omega$  is the rotational speed in rad/s. The shear stress, correspondingly, was calculated as  $\tau = F/A$ , where  $A$  is the deiced area. Each superhydrophobic coated sample studied was subjected to 12 successive icing/de-icing events and thus, ice adhesion

strength to each coating was analyzed as a function of the number of icing/de-icing cycles.

### III. RESULTS AND DISCUSSION

Table 1 presents the wetting characteristics including both the CA and CAH values of all the prepared samples. Fig.2 shows the surface images of samples A, B and C. All the samples were found to be rough at micro/nano-scale, with root-mean-square roughness ( $R_{rms}$ ) measured via AFM of <270 nm. Thus, air was expected to be entrapped into such structures during wetting. As a result, the Cassie wetting mode was expected for these samples with high surface roughness and low-energy top layers [5, 15, 16, 18].

**Table 1:** Wetting characteristics of the prepared samples.

Sample	CA (deg.)	CAH (deg.)
A	153.4 ± 2.2	5.4 ± 1.8
B	153.2 ± 2.4	6.1 ± 1.7
C	155.3 ± 2.3	5.8 ± 1.9

The high CA and low CAH values observed with sample 2 also led to assume good surface coverage with FAS-13 molecules. The water-solid contact area on these samples was expected to be small, which is consistent with the small CAH values (~ 5-6°) and high CA values (~ 153-155°) as characteristic of superhydrophobic surfaces. Figure 3 schematically illustrates the Cassie model, where a large amount of air entrapment in the surface irregularities on a rough hydrophobic surface leads to a superhydrophobic surface. As a result, such surfaces are often referred to as ‘slippy’, as water drops are very mobile on them.

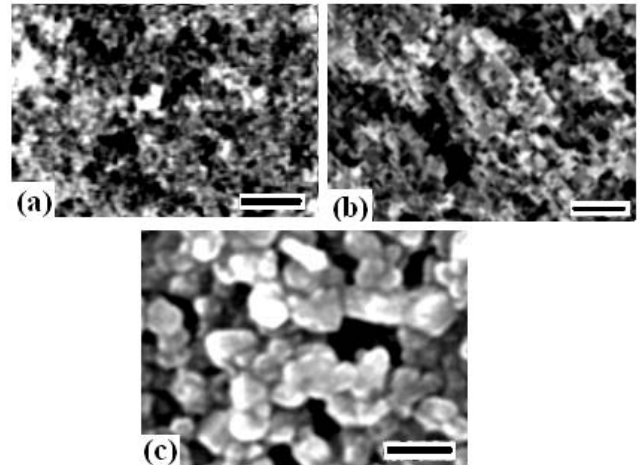


Figure 2. SEM images of super-hydrophobic samples used in this study. (a) Spin-coated CeO<sub>2</sub>-Zonyl 8740 based sample. (b) Etched Al sample passivated with FAS-13 and (c) Al spin-coated with CeO<sub>2</sub>-RTV SR suspension in n-hexane. The scale bars indicate 5 μm (b, c) and 2 μm (a).

Figure 4 illustrates the shear stresses of ice detachment values of the samples as a function of the number of

icing/de-icing cycles. The average value of shear stress of ice detachment obtained on uncoated mirror-polished Al (not shown) was  $\sim 350 \pm 20$  kPa.

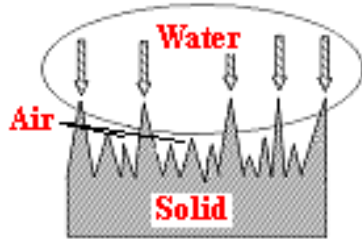


Figure 3. Schematic presentation of a water drop sitting atop a superhydrophobic surface (Cassie wetting mode). Air is entrapped underneath the water drop on the surface.

In agreement with the previous studies on low-CAH superhydrophobic surfaces [8, 9], the initial values of shear stress of ice detachment on the as-prepared samples were  $\sim 3.3$ - $6.6$  times lower than those on the standard polished Al (being  $\sim 55$  to  $107$  kPa, Fig.4), which is consistent with the above mentioned Cassie wetting regime on these surfaces shown in Fig.3. This was reported earlier to lead to small ice-solid contact areas on such surfaces [8, 9]. However, having been iced/de-iced repetitively, the samples showed gradually increased ice adherence. For instance, after 12 icing/de-icing events, all samples demonstrated ice adhesion strengths increased by a factor of about 1.8-2.4 if compared with the as-prepared surfaces. Based on the previous reports on various superhydrophobic surfaces [8, 9], the observed increase in ice adhesion strength values is believed to be associated with a larger ice-solid contact area on these nanostructured surfaces after 12 icing/de-icing cycles.

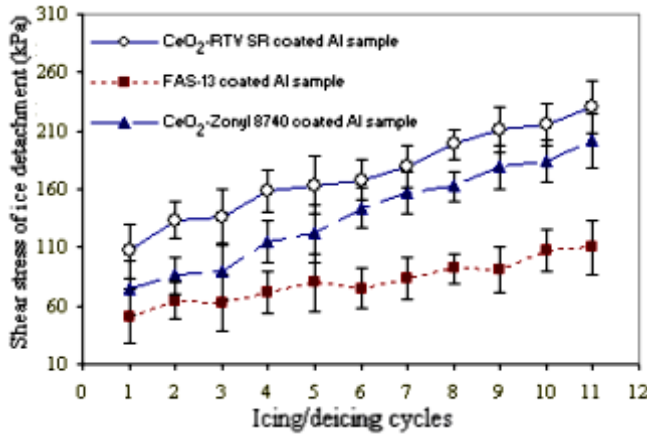


Figure 4. Shear stress of ice detachment vs. icing/de-icing cycles for coated Al surfaces with CeO<sub>2</sub>-Zonyl 8740, FAS-13 and CeO<sub>2</sub>-RTV SR.

In parallel, CA values were also measured on the samples between icing/de-icing experiments, and the results are presented in Fig.5. It is clearly seen that water repellency of all the samples increasingly deteriorated as the samples went through the icing/de-icing cycles. AFM surface analyses of samples A and B after the de-icing experiments were performed to explain these observations in terms of changes (if any) in sample topographies. Root-mean-square

roughness ( $R_{rms}$ ) was evaluated over several different locations on both samples, and the results are presented in Fig.6 as a function of the number of icing/de-icing events. A small decrease in surface roughness is observed for sample B, which corresponds well to the slightly changed ice adhesion strength on this sample over 12 icing/de-icing cycles (Fig.4). However, as it can be seen in Fig.4, a somewhat larger decrease in surface roughness was observed for sample A, which can be associated with a more remarkable increase in ice adhesion strength on this nanostructured surface during the subsequent icing/de-icing cycles.

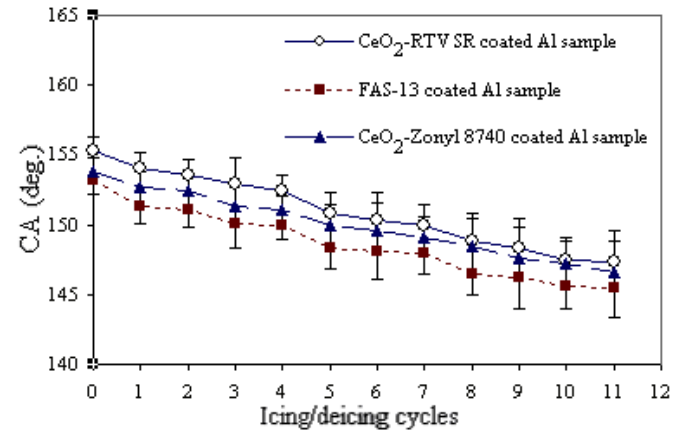


Figure 5. Contact angle versus icing/de-icing cycles for Al surfaces coated with CeO<sub>2</sub>-Zonyl 8740, FAS-13 and CeO<sub>2</sub>-RTV SR.

These decreases in surface roughness, reported in Fig.6, correlate well with the increase in ice adhesion strength on these samples, as observed in Fig.4. The results presented in Figs.4, 5 and 6 allow us to assume that the increased ice adhesion strength, somewhat deteriorated water repellency and somewhat decreased surface roughness of the repeatedly iced/de-iced samples can be related to a gradual damage of the rough structures of the sample surfaces. As the surface roughness of the samples decreased, consequently, partial switch of the wetting regime from a pure Cassie (low CAH and high CA values) to a mixed Wenzel-Cassie regime was expected on such surfaces, which had to cause the observed gradual increase in ice adhesion strength [8,9,17]. The rough nanostructured superhydrophobic surfaces tested in this study are therefore shown to demonstrate time-dependent ice-releasing performances. Their sharp tips schematically shown in Fig.3 could be (partially) broken and removed by ice during de-icing as they were believed to be indented into ice to some degree. Moreover, some damage could also be caused by icing as well, because water expansion on the solid surface caused by freezing can induce a very significant interfacial stress. This assumption is confirmed by the gradual decrease in surface roughness observed for these samples over icing/shedding tests (Fig.6). The fact that rough surface asperities get indented into a liquid (including a frozen liquid) and that their tips can be damaged during the solidification of the liquid has been recently confirmed by Ensikat and coworkers [16].

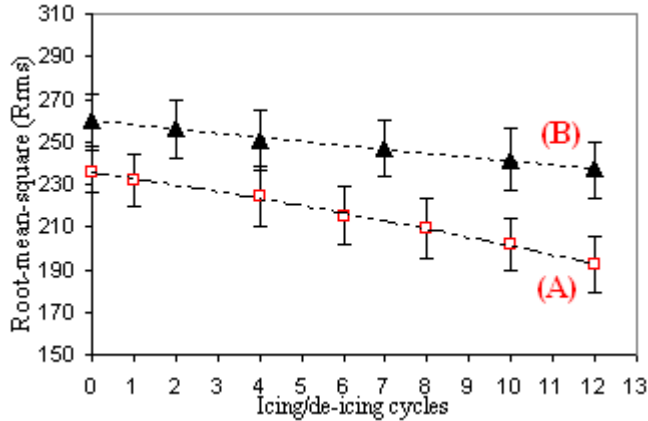


Figure 6. Root-mean-square ( $R_{rms}$ ) surface roughness of samples A and B as a function of icing/de-icing cycles.

The cryo-SEM observations of frozen droplets on both micro- and nano-structured surfaces demonstrated that asperities of both natural and artificial surfaces were indented into frozen liquids and, as a result, that their tips remained partially embedded into the liquids on the droplet removal, thus damaging the asperities [16]. All our samples were gradually affected by repetitive icing/de-icing tests and their ice-repellent performance increasingly deteriorated. The anti-ice performance of rough hydrophobic surfaces is thus demonstrated to be dependent on the number of icing/de-icing events. Therefore, the mechanical properties of such materials must be taken into account in order to further develop them for anti-icing applications. Based on the findings of the present study, it can be assumed that superhydrophobic surfaces made of very rigid or very elastic materials can demonstrate improved abrasive resistance against icing/de-icing.

#### IV. CONCLUSIONS

Ice repellency of nanostructured hydrophobic coatings was evaluated on three different materials with various surface topographies for several icing/de-icing cycles while the glaze ice used in tests was prepared under conditions similar to those in nature. The results were compared to those on uncoated polished Al as a reference. The results of ice adhesion strength evaluation, after as many as 12 icing/de-icing cycles, showed that the anti-ice performance of the samples gradually deteriorated. Even though

superhydrophobic surfaces do exhibit lower ice adhesion strength, their ice-releasing performance seems to degrade gradually during icing and de-icing. The results thus point out that the anti-icing performance of superhydrophobic surfaces may be limited and should be studied in more detail before such materials gain any practical applications.

#### V. ACKNOWLEDGMENT

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