On Self-cleaning and Anti-ice Performance of Double-layer *SAMs* Coatings with Enhanced Corrosion Resistance on AA2024 Substrate

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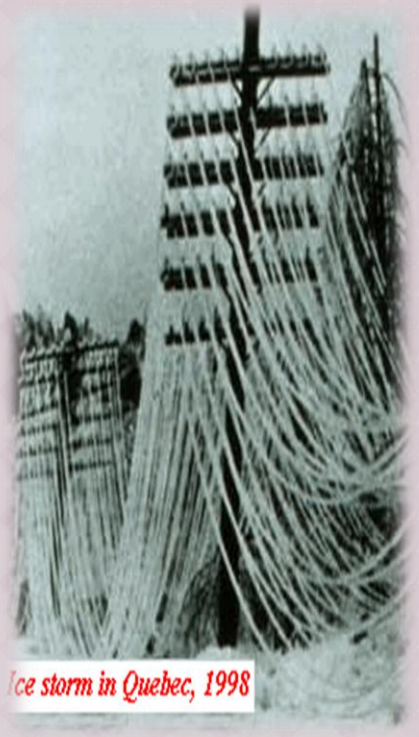
Outline

- **Introduction**
  - **Atmospheric Icing in Nature**
  - **Hydro-/superhydrophobic Properties**
  - **Icephobicity**
  - **Aluminum Alloys and Corrosion**
- **Research Objectives**
- **Methodology**
  - **Results and Discussion**
- **Conclusions**

Icing on structures

- ***Ice Storm Consequences***



Preventing ice accretion on structures

Techniques for ice removal/prevention on structures

Mechanical
- Ice-remover robot
- Shedding by shock
- …

Chemical
- De-icing fluids
- Anti-icing fluids
- …

Thermal
- Joule effect melting
- High-frequency skin effect melting
- …

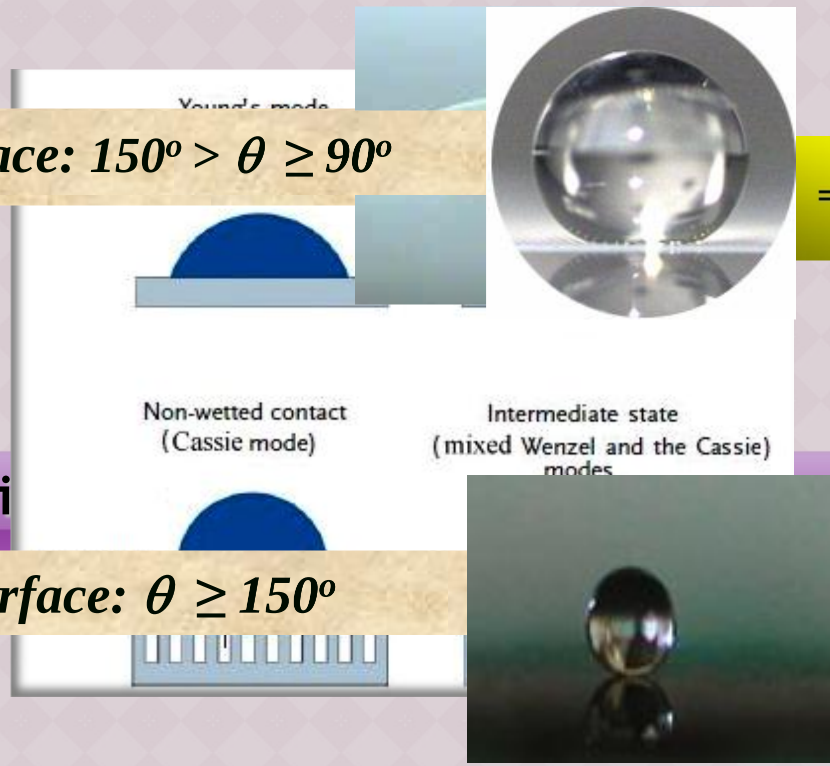
Other
- …
- …

Hydrophobicity and Superhydrophobicity

Wettability

- ☞ Characteristic of solids
- ☞ Geometrical structure and surfaces chemical composition

➢ ***Hydrophobic surface:*** $150^o > \theta \geq 90^o$



$$= \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

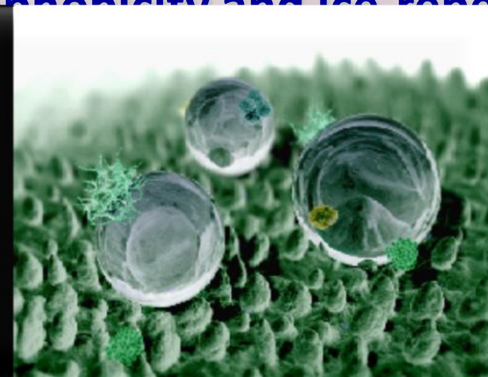
Macroscopi … **lance:**

➢ ***Superhydrophobic surface:*** $\theta \geq 150^o$

Superhydrophobicity and self-cleaning property

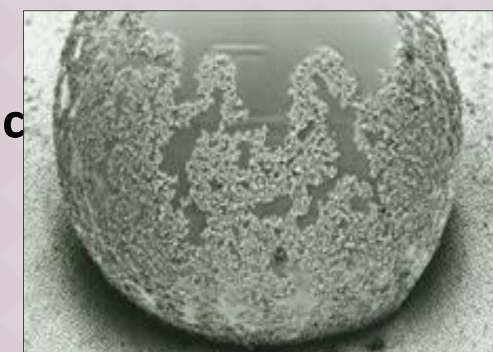
Superhydrophobicity and ice adhesion

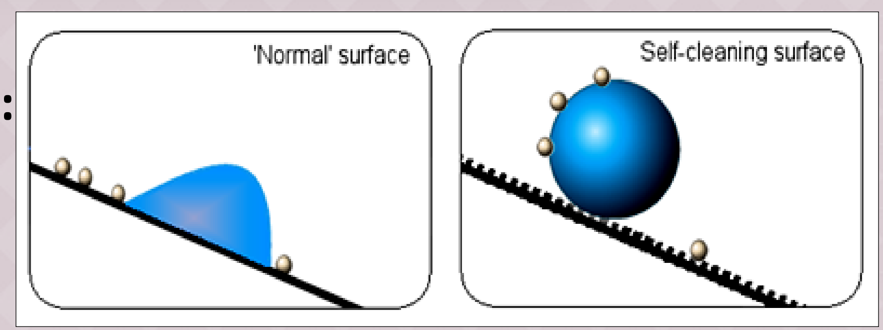
- **Good correlation between hydrophobicity and ice repellent behaviour**



- **“Self-cleaning” property … Self-cleaning of insulators**

- **Ic ngth:**





Aluminum and its alloys

- ***Worldwide use in many sectors of economy and life.***

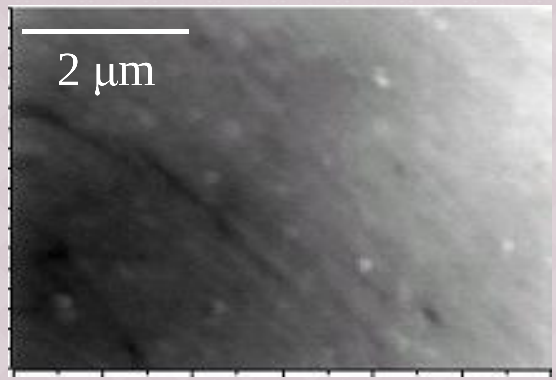
Aluminum alloys and corrosion

- When the substrate is metal ***(Al and its alloys, Fe, Mg, etc.),*** **corrosion is another concern**

- **Corrosion protection of coated metal…coating durability and performance.**

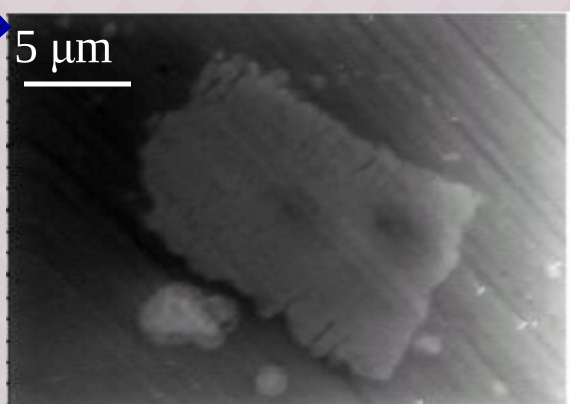
Major surface features of AA2024 *(prior to coating)*

- ***Aluminum alloy surface: <u>not homogeneous</u>***
- ***Galvanic coupling and corrosion (galvanic or localized corrosion (pitting)***



Alloy matrix

Al-Cu-Fe-Mn
Inter-metallic particle



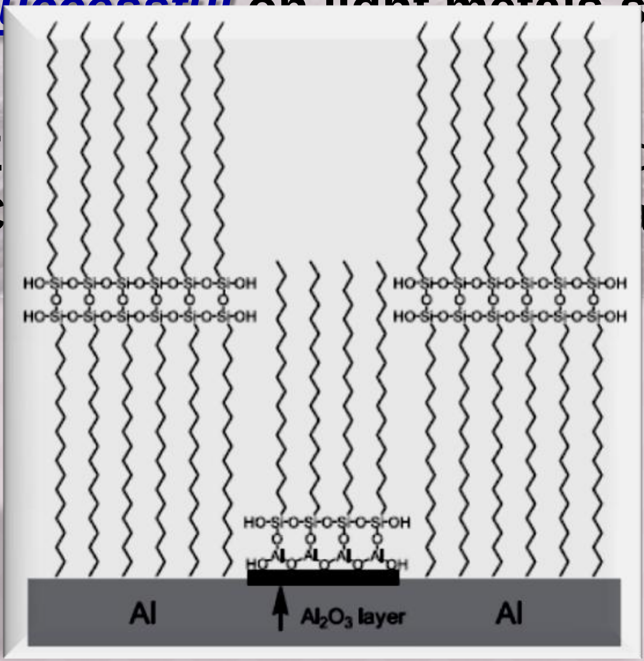
Al-Cu-Mg
Inter-metallic particle
(S phase)

Conversion coatings: simple and excellent anticorrosive performance

Self-assembled thin films: potential alternatives

- Chromate conversion coatings: ***the most successful*** on light metals so far,

- E d toxicity of C alte



Mixed multilayer film on Al surface

i. **Alkyl chains are anchored on metal surface…a multilayer film.**

ii. **Between each layer: functional groups polymerized (hydrolysis and condensation).**

coatings: ***among potential alternatives,***

- **Simple procedure**

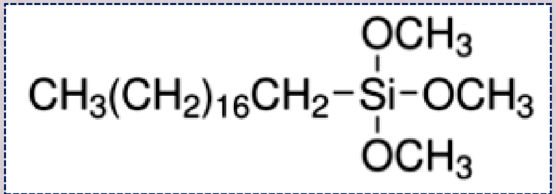
Objectives

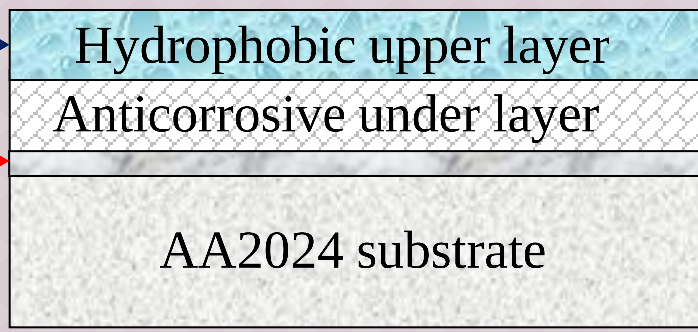
- ***Preparing single and double-layer alkylsilane-based coatings on etched AA2024; as potential ice/snow-repellent layers,***
- ***Systematically study of prepared nano-structured surfaces; morphological, compositional, wetting and self-cleaning characterization,***
- ***Studying their icephobicity,***
- ***Evaluating their durability in different pH conditions (water, basic and acidic conditions) and over repeated icing/de-icing cycles,***
- ***Electrochemical study of prepared coatings: evaluating their anti-corrosive performance (potentiodynamic polarization test and cyclic corrosion exposure as well)***

Experimental procedure

Octadecyltrimethoxysilane

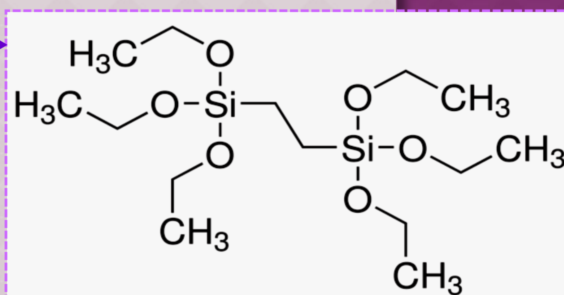
CA>150°, CAH<6°, ~ 10 nm (n:1.46)





Al_2O_3
(2-4 nm)

1, 2-Bis (triethoxysilyl) ethane ***(BTSE)***



CA ~ 41°
~ 108-119 nm
(n:1.42-1.36)

Cyclic corrosion chamber

- Programmable chamber to produce cyclic environmental conditions (*Ascott*)

☞ **3 repeating cycle** (ISO14993 - Corrosion of metals and alloys)

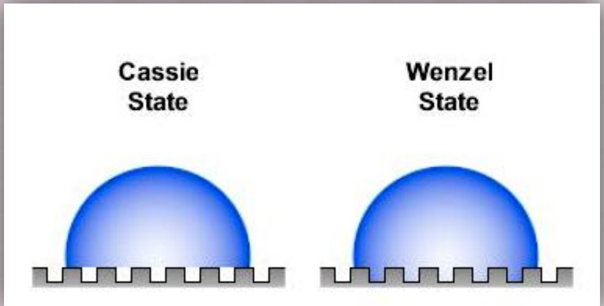
① 2-h exposure to continuous spray of salt water solution (pH: 6.5-7.2) at 35 ^{o}C.
② 4-h air drying in >30 %RH at 60 ^{o}C.
③ 2-h exposure to wetting condition of 95 to 100 %RH at 50 ^{o}C.

Results and discussion: *CA and CAH of samples*

☞ Etched Al: CA:~21.2 ± 5° and ε:~68.3 ± 1.16 (mNm^{-1}) … *Hydrophilic surface* with a native oxide layer.

$$R\text{-}Si(OMe)_3 + 3\ H_2O \rightarrow R\text{-}Si(OH)_3 + 3\ MeOH$$

- After BTSE deposition: CA: ~41°.
- After ODTMS deposition on BTSE [*double layer coating, BTSE/ODTMS*)]: CA>150° and CAH<6° ... well-coated rough Al surfaces.
- Water droplets rest at the top of rough asperities (*Cassie-Baxter wetting regime*) with a solid fraction area: %11.48 → large amount of air trapped beneath the water droplets.

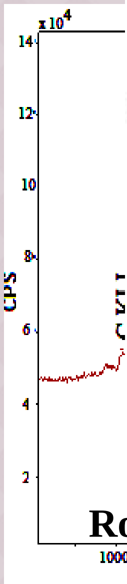


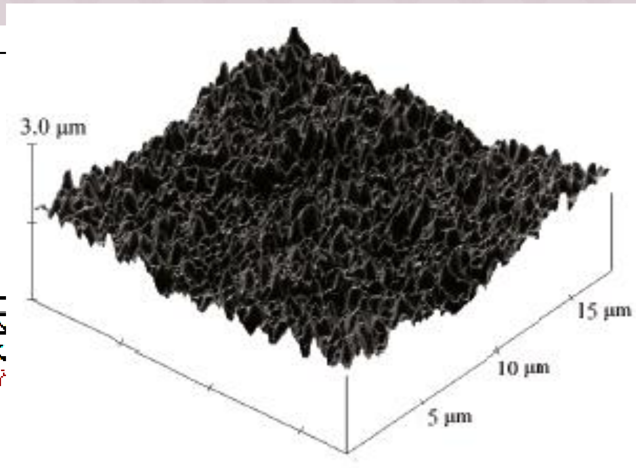
$$\cos\theta^* = f\,(1+\cos\theta) - 1$$

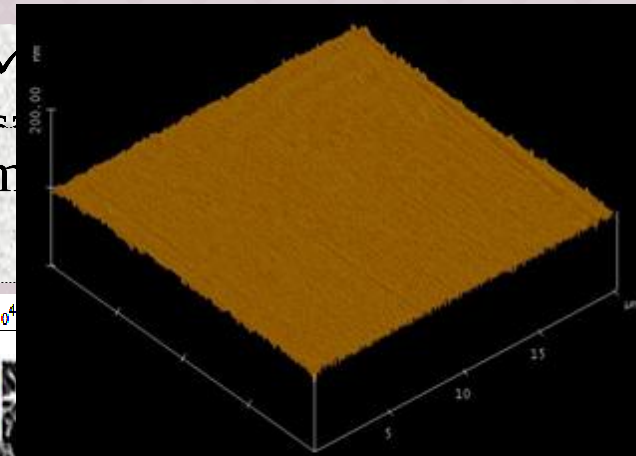
θ^* and θ are the CA of rough and flat surfaces with the same surface chemistry

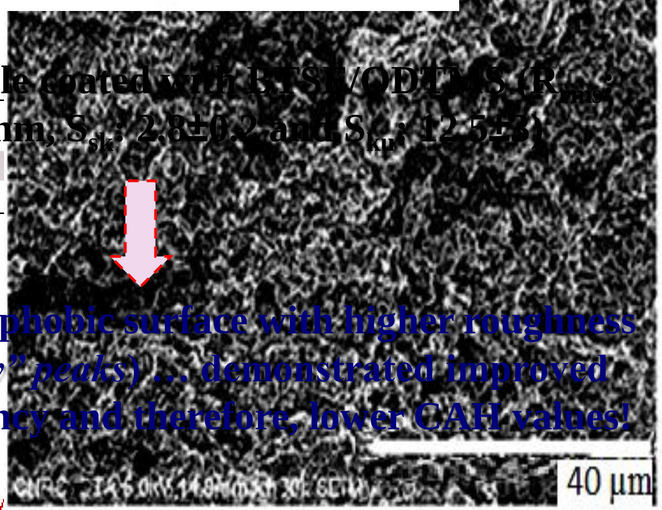
f is the area fraction of the solid surface that contacts water

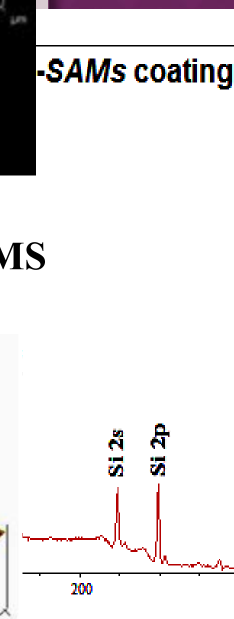
Surface characterization: AFM images







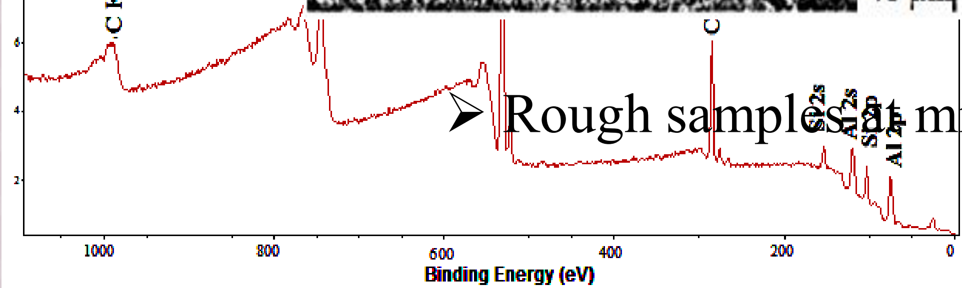


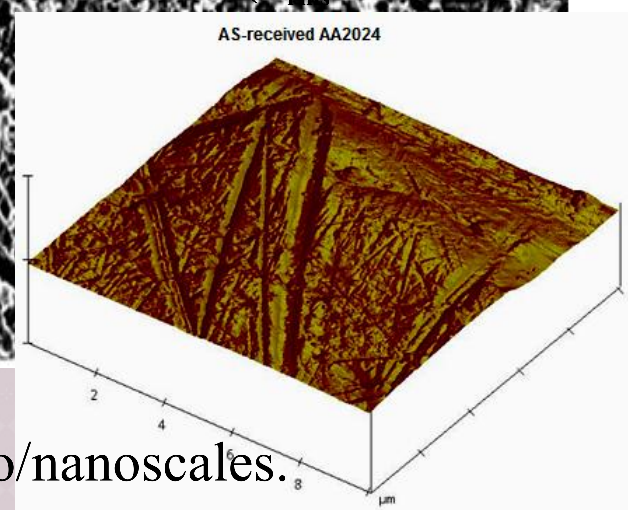


Rough sample coated with BTSE/ODTMS (R_{rms}: 418±12 nm, S_{sk}: 2.8±0.2 and S_{ku}: 12.5±3)

Flat sample coated with ODTMS (R_{rms}: ~25 nm)

A superhydrophobic surface with higher roughness *(more "spiky" peaks)* … demonstrated improved water repellency and therefore, lower CAH values!

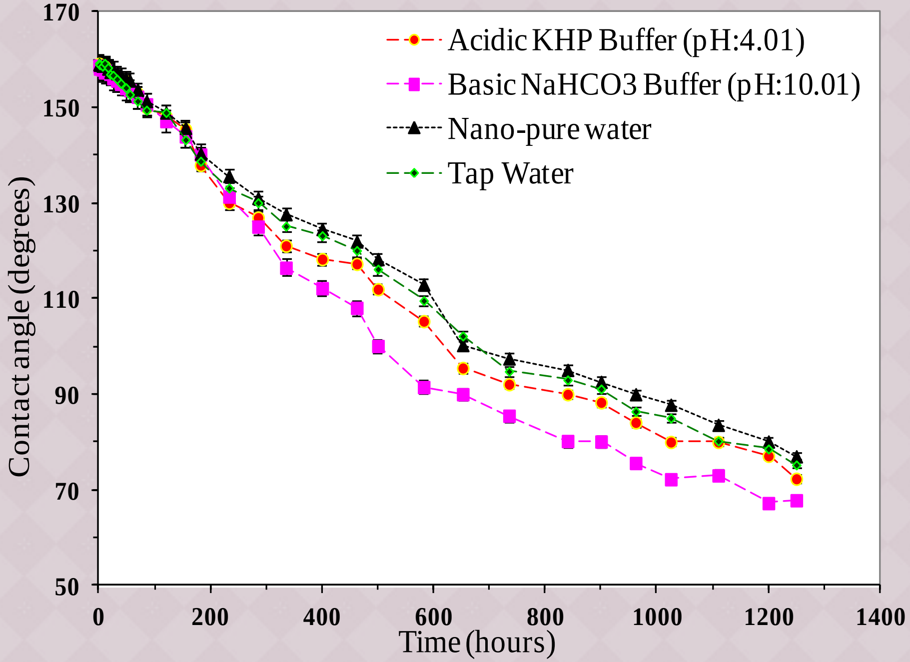


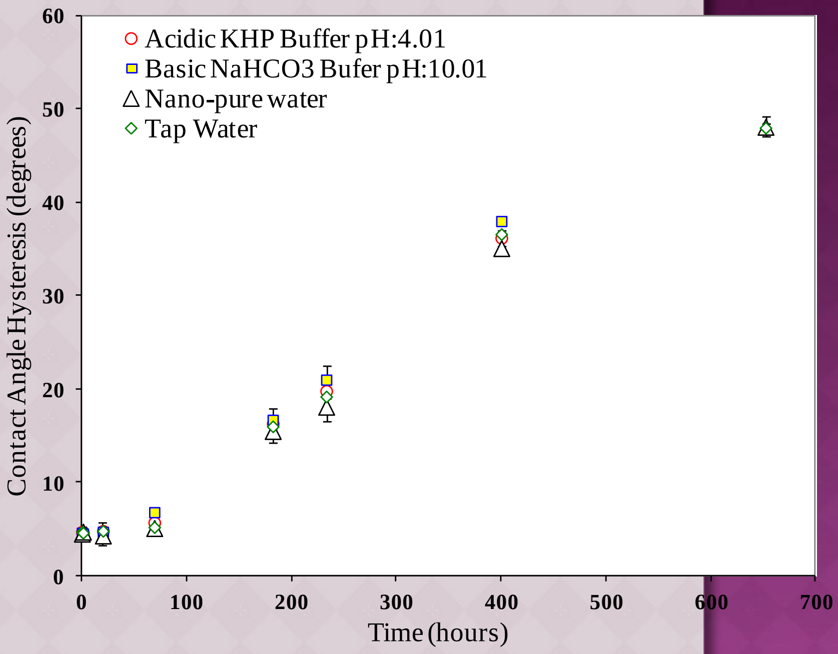


➢ Rough samples at micro/nanoscales.

As-received AA2024 (R_{rms}: ~ 109 nm)

Coating durability (different pH conditions)





- ❑ **Superhydrophobic samples (well-coated nano-structured surfaces)**
- ❑ **Gradually lose of superhydrophobicity (~720 to ~1000-h of immersion in basic and nano-pure media, respectively),**
- ❑ **Rupture of the Si-O-Si bond between the ODTMS (~10nm) and BTSE (~100nm) molecules due to bonds hydrolysis.**

Self-cleaning property of double layer coating on AA2024

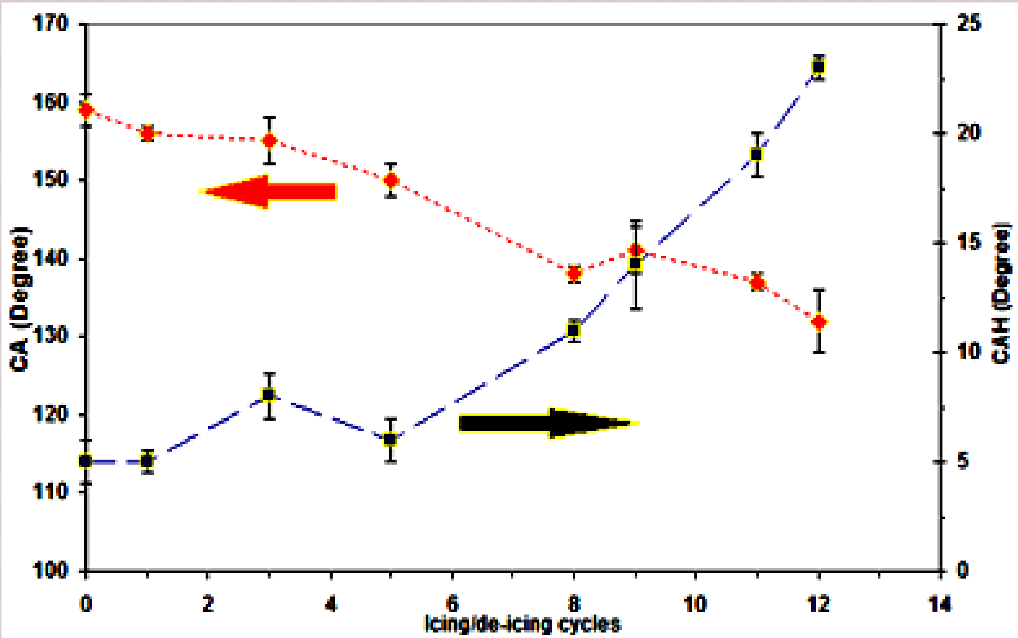
- Good self-cleaning property: soil mesh was easily carried away by water droplet while passing by.

- Small water-solid contact area [small CAH values (~4-6^{o}) and high CA values (>150^{o})]… characteristic of SH surfaces.

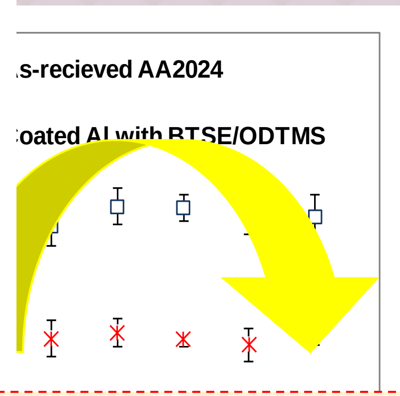
Ice-repellency of double layer coating AA2024

CA and CAH values vs. icing/de-icing cycles

- **Initial values of shear stress of ice detachment:**



S: reduced value of ~62 kPa

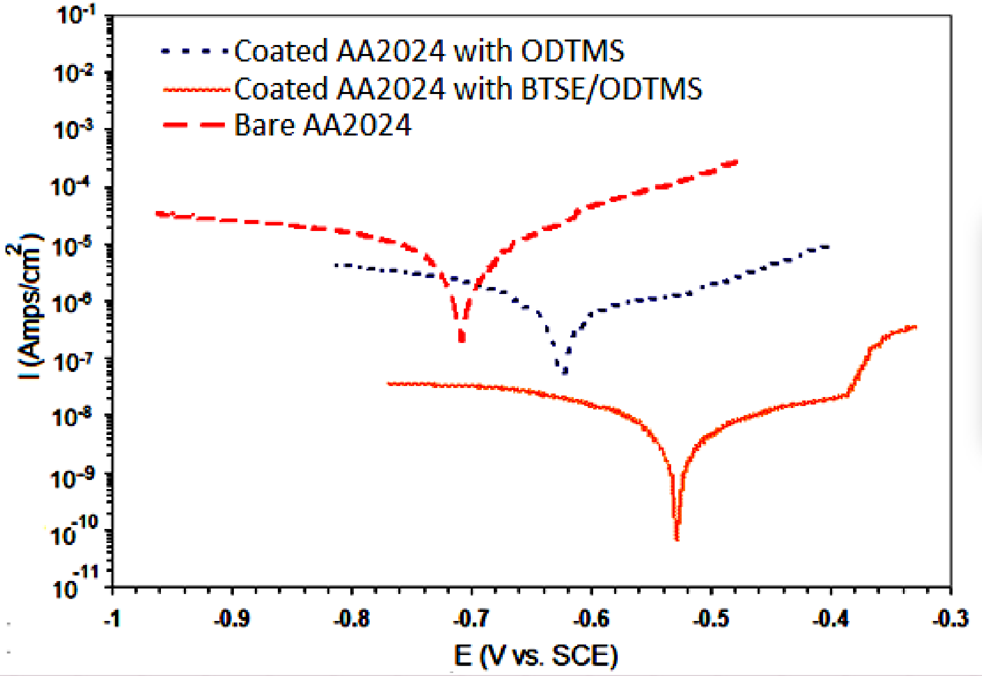


- Water-repellency gradually decreased over time (decrease of CA and increase in wetting hysteresis (CAH)).
- Water molecules attacked the R-Si-O- bond to hydrolyze it, resulting in hydrophilic –OH groups on the surface.
- Gradual damage of rough structures → partial switch of wetting regime from Cassie to a Wenzel-Cassie regime.

- Decay of ODTMS layer and larger ice-solid contact area after 12 icing/de-icing.

Potentiodynamic polarization curves

- **3.5% NaCl aerated solution (pH:7.9) *(Sea water)***
- **Corrosion potential positively increases.**
- **Corrosion current density of BTSE/ODTMS decreased (8.04E−9 Acm^{-2}) about:**
  a) <u>4 orders of magnitude</u> compared to bare Al (2.44E-5 Acm^{-2})
  b) <u>3 orders of magnitude</u> as compared to ODTMS (1.12-6 Acm^{-2}).

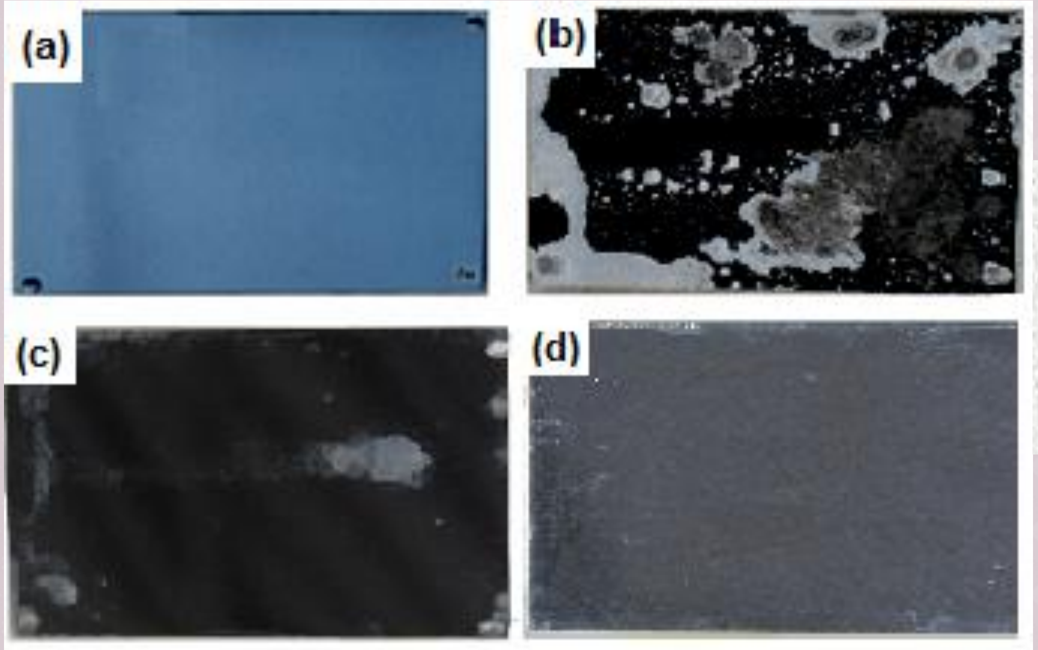


Sample	$E_{corr.}$ (V *vs.* SCE)	$j_{corr.}$ (μAcm^{-2})
Bare AA2024	-0.71±0.03	24.4
ODTMS Coating	-0.62±0.02	1.12
BTSE/ODTMS Coating	-0.53±0.02	0.008

- **Barrier property of the BTSE/ODTMS coated sample was improved significantly as compared to a bare or even single layer coated Al.**

Cyclic Corrosion Test

- **Bare Al ⇒ extensive corrosion after 8 cycles (appearance of localized corrosion).**
- **Increased size and density of black dots.**
- **Coated samples with single ODTMS layer ⇒ obvious corrosion products after 18 cycles.**
- **Coated samples with double layer BTSE/ODTMS layer ⇒ small traces of corrosion after 81 cycles ⇒ improved corrosion resistance.**



- Optical images of bare AA2024 before (a) and after (b) 18-cycle corrosion test for ODTMS coated AA2024 (c) and for BTSE/TMSOD coated alloy (d) after test

Conclusions

❶ *Alkyl-terminated nano-structured superhydrophobic surfaces were prepared by depositing layers of ODTMS on BTSE-grafted AA2024 or rough AA2024 substrate.*

❷ *Both samples demonstrated excellent superhydrophobic and self-cleaning properties.*

❸ *They were subjected to aggressive conditions (different pH), demonstrating gradually lose of superhydrophobicity after ~720 to ~1000-h of immersion in water, acidic or basic media (associated with decrease of water CA and increase of CAH).*

❹ *Their ice repellent performance were evaluated following successive icing/de-icing cycles, indicating reduced values of ice adhesion (~6 times lower than as-received Al. This reduction was attributed to the presence of micro-/nano-hierarchical surface structures and low surface energy layers.*

Conclusions

❺ ***Ice adhesion values gradually increased after 12 successive icing/de-icing cycles (decay of top layer and a larger ice-solid contact area).***

❻ ***The corrosion potential of the double layer coating increased significantly, and its corrosion current density decreased by 4 orders of magnitude as compared to those on bare Al.***

❼ ***Cyclic corrosion test showed that while bare Al exhibited extensive corrosion after 8 cycles, however, the earlier stage of corrosion was observed after 18 cycles for ODTMS and small traces of corrosion was observed after 81 cycles of exposure for BTSE/ODTMS coated samples.***

❽ ***These results showed that the BTSE under-layer provides particularly enhanced corrosion resistance*** *(an excellent approach to improving anti-corrosive performance of metallic surfaces for outdoor applications instead of the toxic chromate-based coatings currently in use).*

Thanks for Your Attention!