Role of nano-structured boehmite on anti-ice properties of super-hydrophobic hierarchical aluminum surfaces

M. Balordi[1], A. Cammi[1], C. Chemelli[1], G. Santucci de Magistris[2]

[1] *RSE- Ricerca sul Sistema Energetico, Milano, Italy*
[2] *Università degli Studi di Pavia, Dipartimento di Chimica, Pavia, Italy*

marcella.balordi@rse-web.it, andrea.cammi@rse-web.it, cristina.chemelli@rse-web.it, giorgio.santucci@rse-web.it

***Abstract*: Ice accretion on conductors can lead to extensive mechanical damage and consequent blackouts; strong wet-snowfall are the major cause of blackouts for the Italian overhead lines. Changing the wettability properties of the aluminum may represent a strategy to hinder the formation of snow-sleeve and lower the ice adhesion. In this work, several hydrophobic and super-hydrophobic surfaces were prepared on aluminum alloy by generating a flower-like pseudo-boehmite (AlO(OH)) nanostructured texture in a hydrothermal process and finally coating with fluorinated siloxane. Different immersion times (1-150 minutes) in boiling water were tested giving rise to a boehmite layer with different nano-roughness and porosity. The oxide growth was observed with EDX and FTIR. The hydrophobic behaviour of the samples was studied both at room and low temperatures (until -10°C) and compared with the water contact angles (WCA) of the coated no-boiled sample. All the boiled samples showed WCAs higher than the no-boiled sample, both at room and low temperatures. In some cases, very high WCAs were obtained, but the dependence on the duration of the treatment in boiling water is not linear. At low temperatures the WCA of the samples decreases, still maintaining fair hydrophobic properties. Contact angle hysteresis and roll off data at room and low temperature show similar dependence on treatment time. To evaluate the ice-phobicity, shear stress tests were carried out. Ice adhesion is lower in all the boiled samples, showing an interesting non-linear dependence on the boiling time. Repeated shear stress test gave a measure of the coating durability.**

Keywords — ***hydrophobicity; boehmite; water; contact angle; ice-phobicity; ice adhesion.***

I. INTRODUCTION

Over-head power lines are subjected to damages due to severe winter conditions and environmental pollutions. Ice and snow accretion on conductors can lead to extensive mechanical damage such as conductors weighted down to the ground with consequent blackouts.

The control of wettability properties of the surfaces of high and medium voltage aluminum conductors is a strategy to reduce the formation of snow-sleeve and to lower the ice adhesion during a snowfall event. Hydrophobic and super-hydrophobic coatings represent one of the strategies to avoid or limit ice accretion on overhead lines [1], [2], [3], even if a clear correlation between hydrophobicity and ice-phobicity is still to be fully understood [4], [5].

In this work, hydrophobic surfaces were obtained by imparting a nano-scaled roughness to the aluminum substrates and then by coating them with fluorinated alkyl silane (FAS). On such textured surfaces, the properties of wettability are described by two main models: Wenzel and Cassie-Baxter. According to Wenzel's model a homogeneous interface is described, in which liquid droplets are retained in contact with all the points of solid surface below them [6]. In Cassie-Baxter model liquid droplets don't conform to the topography of the surface and lay on the peaks of the solid texture in which air pockets are trapped, giving rise to a composite solid-liquid-air interface [7].

A simple and inexpensive method to obtain nano-scale roughness on aluminum and aluminum alloy surfaces is the immersion in boiling water. The oxidative process leads, in few minutes, to the growth on the surface of an aluminum oxyhydroxide layer with a boehmite crystalline structure (γ-AlO(OH)) with a well-defined grass-like nanostructure [8], [9], [10]. Density and porosity of this layer can be modified by varying the immersion time in boiling water [11], if the boiling time is increased a thicker, denser and less porous layer is obtained. Immersion times from 1 to 150 min were tested and the boehmite growth was observed with FE-SEM and with EDX and FTIR spectroscopies.

Hydrophobic behaviour was investigated by means of static and dynamic WCA at room and at low-temperature while ice-phobicity was evaluated with shear stress tests.

II. EXPERIMENTAL SECTION

Flat plates (20 x 70 x 2 mm) and bars (12 mm diameter x 100 mm length) of aluminum alloy (6082) were used as substrates. All the aluminum alloy specimens were cleaned with basic soap, rinsed in ultrasonic bath for 10 minutes with acetone and dried under nitrogen flux.

The cleaned samples were subjected to hydrothermal treatment in distilled water for the following periods: 1', 3', 5', 10', 15', 30', 45', 60', 90', 120' and 150'.

Boiled samples were dip-coated (dipping–withdrawing speed: 0.7 mm/s, permanence time: 120 s) with the commercial fluoro alkyl silane (FAS) coating Dynasylan® SIVO CLEAR EC purchased from Evonik. After dip-coating samples were cured at 70°C for 1 hour. For comparison purpose aluminum alloy plates and bars without previous hydrothermal treatment were also coated.

The morphologies and chemical compositions were examined using a TESCAN field emission scanning electron microscope (FESEM), equipped with Bruker EDX probe.

The FT-IR characterizations were conducted with the FT-IR Alpha 1 (Bruker) spectrometer with ATR apparatus (diamond was used as internal reflection element).

Wettability was evaluated at room and at low temperature using a Kruss DSA 30 drop shape analyzer with the method of the sessile drop, using a 2 µl volume of water. Measurements were replicated at least 5 times for each sample. Advancing and receding contact angles were measured increasing and decreasing the volume of a water drop. The WCA measurements at low temperatures were conducted by means of a Peltier chamber, decreasing the temperature in the range from 20°C to -10°C and depositing the drop on the cooled samples.

Roll-off angles (RO) were measured with a home-made tilting table equipped with a goniometric scale. To measure the roll-off angles at -2°C the tilting table was inserted in a climatic chamber. A volume of 20 µl of water was used to carry out the experiments.

Icing-thaw cycles were performed by cooling sample at -2°C, re-heating at 20 °C and by measuring WCAs with 2 µl sessile drops.

Ice adhesion was evaluated by shear stress analysis performed with a home-made apparatus, equipped on an electromechanical testing system INSTRON 4507. Alloy bars were used as test samples: they were frozen in 40 ml of deionized water at -19 °C for at least 8 hours in aluminum alloy moulds. After this period, the moulds were fixed into the machine and the samples were extracted from the ice with a speed of 4mm/min (Fig. 1). The force F needed to pull the sample off the ice was recorded. The ice adhesion strength (τ) in shear can be calculated by: $\tau = F/A$, where A is the surface of the bar in contact with the ice. The shear stresses were calculated as the average of 5 tests carried out on 5 different specimens for each treatment.

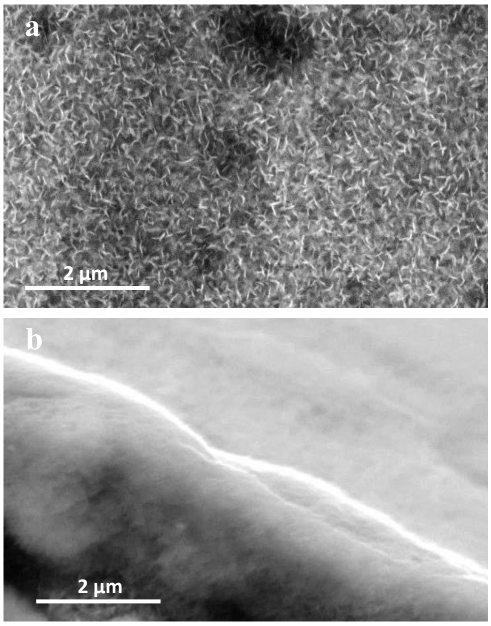

Fig. 1 FE-SEM images of aluminum alloy surfaces after a 30' treatment in boiling water (a) view from above (b) view from the side

The aluminium oxyhydroxide formation and growth are also confirmed by FTIR-ATR spectra. The signals at about 3200 cm^{-1} and at 1060 cm^{-1} are characteristic O-H stretching and bending, while the bands at about 730 cm^{-1} and 530 cm^{-1} are due to Al-O stretching. The intensity of FTIR-ATR signals increases in the spectra of samples boiled for longer times (fig. 2).

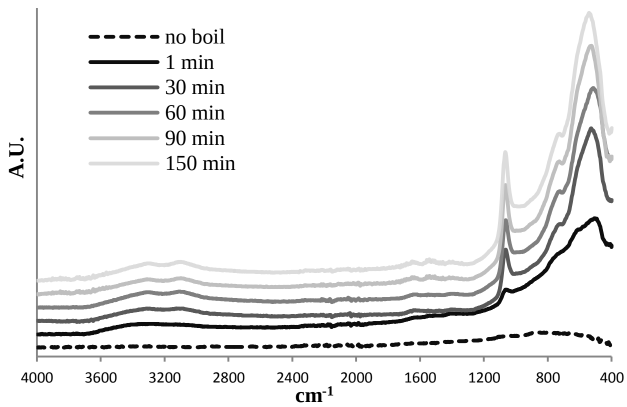

Fig. 2 FTIR-ATR spectra of aluminum alloy surfaces boiled for different periods. 3295 cm^{-1} and 3088 cm^{-1} O-H stretching; 1067 cm^{-1} O-H bending; 736 cm^{-1} Al-O stretching; 532 cm^{-1} Al-O stretching

III. RESULTS AND DISCUSSION

A. *Morphological and chemical evaluation*

FE-SEM images captured from above shows the formation of a layer acicular pseudo-boehmite on all the boiled sample (fig. 1 a) and the side view evidences its nano-grass structure.

SEM-EDX analysis evidences the presence of oxygen on aluminum surface confirming the formation of an oxide layer. Moreover, increasing the boiling time, the semi-quantitative analysis shows an increment in oxygen amount attributable to a thicker and denser oxide layer [12] (fig.3).

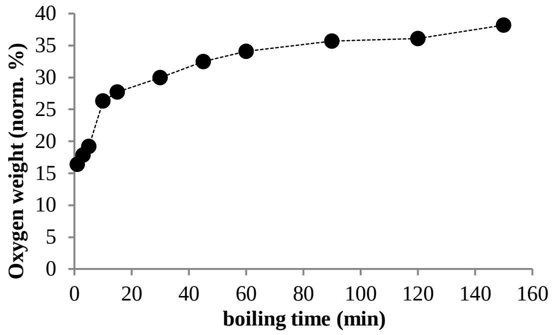

Fig. 3 normalized oxygen weight % found with EDX analysis on aluminum samples boiled for different times

The oxygen percent quickly increases in the first minutes of immersion. As reported in the literature [9], the film grows very rapidly in the first few minutes while subsequently thickness increasing and porosity decreasing contribute to slower the growth rate. Indeed, for longer time periods, the reaction rate is driven by the transport of soluble species through the hydroxide layer: a thicker and denser layer slows the further growth [9]. The duration of immersion in boiling water therefore produces significant modifications in the morphology of the nanostructured surfaces.

B. Hydrophobicity at room and at low temperature

All boiled aluminum plates coated with FAS showed hydrophobic properties: the combination of nano-roughness with a low energy coating leads to water repellent surfaces The WCA of the unboiled coated sample is 113°, while the WCAs of boiled and coated aluminum are higher than 140° (fig. 4). In particular, highest WCAs were found after boiling for 3 to 15 min: at room temperature WCAs significantly higher than 150° were measured. After 1 minute of immersion time the formation of the pseudo-boehmite pattern is not homogeneous on the surface and scattered WCAs are measured, with only a slight increase in average WCA with respect to untreated sample. For boiling time longer than 15 minutes (30 to 150 min), WCA significantly reduce with respect to the maximum values. This is due to the formation of a denser nanostructure with lower roughness, which reduces the formation of a composite solid-liquid-air interface below water droplets,.

At low temperature all WCAs decrease and the reduction is more appreciable for surfaces with higher WCAs at room temperature. When the nanostructured surfaces are exposed to temperatures lower than the dew point, condensed water arising from air humidity penetrates into the pores of coating forming a water layer. This water layer strongly increases the wettability of such surfaces resulting in lower WCAs. Nevertheless a certain hydrophobic behaviour is maintained.

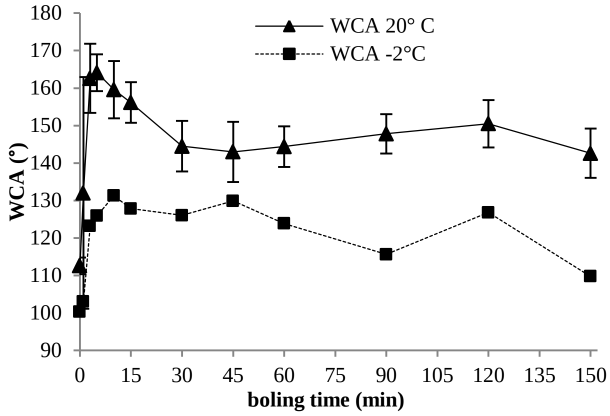

Fig. 4 static water contact angles measured at room and at low temperature vs. immersion time in boiling water

Contact angle hysteresis (CAH) and roll-off angles (RO) were also measured on some samples at 20°C and at -2°C (table I). All samples showed high CAH and RO both at room and at low temperature: these results are consistent with a Wenzel-like wetting regime. A clear relationship between CAH and boiling time was not found while RO measured at 20°C increase for longer immersion times.

TABLE I. HYSTERESIS AND ROLL-OFF ANGLES MEASURED AT ROOM AND AT LOW TEMPERATURE VS. IMMERSION TIME IN BOILING WATER

	RT		LT	
sample	**CAH (°)**	**RO (°)**	**CAH (°)**	**RO (°)**
not boil	68	>90	59	>90
5’	45	18	57	>90
30’	28	32	28	>90
60’	58	44	52	>90
150’	70	44	59	>90

C. Ice-phobicity

Ice adhesion tests were carried out on the Al 6082 alloy bars previously boiled and coated with FAS. All boiled and FAS coated samples show lower ice adhesion than no-boiled aluminum alloy (fig. 5).

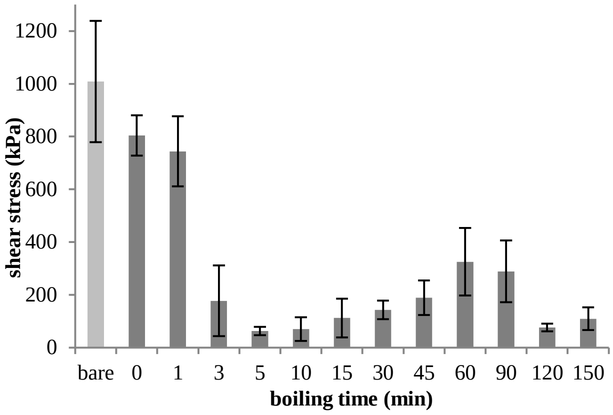

Fig. 5 shear stress vs. boiling time. For comparison purpose bare aluminum alloy sample is also reported

The minimum values are found for the samples boiled from 3 to 30 minutes. It is noteworthy the relationship between the static WCA and the ice adhesion: samples with higher WCAs show lower ice adhesion. Conversely to this trend, for 120’ and 150’ treatment times low ice adhesion values were found. The morphology of the nanotextured oxide seems to plays an important role also in this case: a layer with low density and high porosity, obtained after brief immersion times, ensures the lower ice adhesion.

D. Durability tests

The durability was assessed, in terms of hydrophobicity, by performing icing-thaw cycles on some of the prepared surfaces in order to evaluate their behaviour under simulated wintry conditions. The static WCAs measured after each icing-thaw cycle are reported in figure 6.

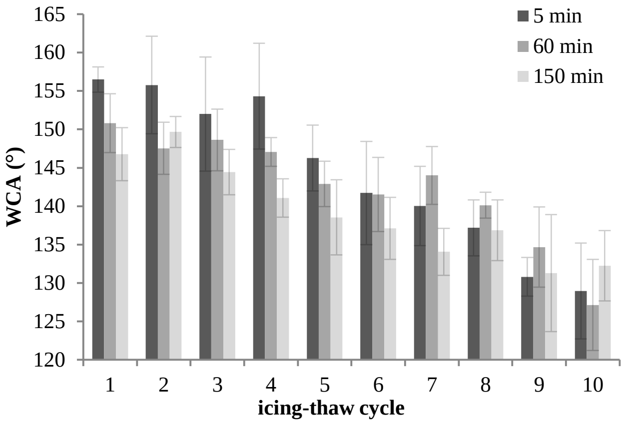

Fig. 6 static WCA trend after icing-thaw cycles on boiled surfaces

The WCAs measured on all the samples gradually drops as the cycles increase, and the values found are less homogenous. A similar trend is evidenced for every sample and no relevant differences are found among the different treatment times. Not even a thicker boehmite layer, obtained after longer treatment time, maintain appreciable hydrophobic properties.

In order to test the durability of ice-phobic properties of the sample, shear stress tests were conducted several times on the same bars: the variation of the strength needed to extract the samples from surrounding ice can give an indication of coating resistance.

TABLE II. SHEAR STRESS VALUES MEASURED ON SAMPLES AFTER REPEATED TESTS

	shear stress (kPa)			
sample	**after 1 test**	**after 2 tests**	**after 5 tests**	**after 10 tests**
5 min	64 ± 16	433 ± 308	428 ± 234	
60 min	326 ± 128	305 ± 59	343 ± 157	280 ± 152
150 min	109 ± 16	175 ± 60	247 ± 68	224 ± 175

The results (table II) in this case highlight remarkable differences between the samples. 5 minutes boiled sample, which had the lowest shear stress value after 1st test, dramatically increases ice adhesion after further extractions. The 60 minutes boiled sample doesn’t increase significantly ice adhesion even after 10 tests, and for 150 minutes sample only a moderate increase is observed. An effect of immersion time on the durability is thus observed in this case. The different morphologies of oxide layer in terms of density and thickness, generated with different boiling times, has a relevant effect on coating durability, even though it seems to be not sufficient to increase immersion time to ensure longer durability.

IV. CONCLUSIONS

In this study, we presented an economic and quick process to impart hydrophobic and anti-icing properties to aluminum alloy. A nanometric pattern was spontaneously generated on the surfaces by simple immersion of the specimens in boiling water. In all the boiled samples, the further coating with FAS gives rise to a significant enhancement of hydrophobic properties and to the lowering of ice adhesion. A study of the trend of these properties by applying different boiling times was performed and interesting results were obtained. Different morphologies of this nanometric pattern can be indeed obtained by varying boiling time. Best results both in terms of hydrophobicity and ice-phobicity were achieved for brief immersion times (3 to 15 minutes). The durability of these surfaces, which was found to be low, in terms of icephobicity, for short boiling times, must however be considered for the definition of best treatment time.

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