

Dropwise condensation over superhydrophobic aluminium surfaces

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Abstract. Superhydrophobic aluminum surfaces have been analyzed being a promising solution to promote dropwise condensation. Superhydrophobicity has been obtained on an aluminum substrate by etching it with two different reagents and by depositing a fluorosilane film over them to lower the surface energy. The samples are characterized by means of contact angle measurements and Scanning Electron Microscopy (SEM). Experimental tests of pure steam condensation have been carried out on the samples and DWC has been visualized. Images of the dropwise condensation have been captured with high speed camera and, furthermore, the phenomenon of the jumping droplets has been observed. A heat transfer coefficient higher than $50 \text{ kW m}^{-2} \text{ K}^{-1}$ has been measured over the samples.

1. Introduction

The improvement of the efficiency of two-phase heat transfer processes is increasingly relevant to many technical applications ranging from the chemical to the power industry. Furthermore, condensation of steam is a crucial process in many industries and any improvements in cycle efficiency would have a profound effect on global energy consumption. It is well-established that during film condensation (FWC) the liquid layer adjacent to the wall introduces a thermal resistance and adversely affects the thermal and mass transport. Dropwise condensation mode (DWC), instead of filmwise condensation, leads to higher thermal performance due to the lower interaction between the condensate and the surface. The surface properties, in particular the surface energy and the related phenomena, play a crucial role in determining the condensation mode. To this end, superhydrophobic surfaces, where a combination of low surface energy and surface texturing is used to enhance hydrophobicity, have recently been proposed as a promising approach to promote dropwise condensation. The sweeping and renewal mechanism present in the droplet growth process in dropwise condensation allows a facile mobility of the drops and thus could lead to a significant improvement in the heat transfer associated with the condensation process. The interaction between the solid and the liquid is described by the wettability. Wettability is defined by the contact angles of a water drop sitting on a surface. For a static drop, the equilibrium contact angle is taken into account while for moving drops the advancing (θ_a) and receding (θ_r) contact angles are taken as the reference. The difference between the last two gives the contact angle hysteresis ($\Delta\theta$). Superhydrophobic surfaces present high advancing contact angles, higher than 150° , and low contact angle hysteresis, lower than 10° . In this paper, superhydrophobic aluminum surfaces have been studied as promoters of dropwise condensation, since aluminum is not much studied in the DWC literature although it is widely utilized in the industry. Thus, two different surface morphologies are analyzed with the aim of understanding the main parameters in the process optimization.

2. Test surfaces

2.1 Preparation

Several techniques are available in the literature to modify the surface wettability [1–3] but they consist of two main phases. The two main steps necessary to create a superhydrophobic surface are: the etching



phase, which creates the proper surface roughness, and the functionalization step, where a hydrophobic layer is deposited to decrease the surface free energy. Hence, two etching reagents have been used in the present work to obtain two different surface morphologies and a fluorosilane film has been deposited to change the surface wettability. High purity (AW 1050, minimum Al quantity 99.50%) aluminum plates are first sanded using emery paper #1200 and then ultrasonically cleaned in isopropanol (IPA) for 15 minutes and dried in a nitrogen stream. The cleaned aluminum substrate is immersed in a NaOH (Sodium Hydroxide, Merck Dow Corning) aqueous solution (1% by weight) at ambient temperature for 15 minutes to remove the aluminum oxide that covers its surface. During the process the solution is constantly stirred by means of a sonication probe. The etching phase is carried out as follows for the two samples.

- IR etched sample. The sample is immersed in a FeCl_3 (Iron(III) Chloride, Sigma Aldrich) aqueous solution (1 mol L^{-1}) for 7.5 minutes. To avoid iron deposition on the surface the sample is taken out from the etching solution at the middle of the process (stopping the etching time count), ultrasonically cleaned in IPA for one minute, dried in N_2 and finally immersed again in the etchant for the remaining etching time. The cleaning process is also repeated at the end of the etching procedure.
- CO etched sample. The sample is immersed in 1 mol L^{-1} aqueous CuCl_2 (Copper (II) Chloride, Sigma Aldrich) solution at ambient temperature for about 8 seconds, to ensure a uniform deposition of a layer of Cu via a chemical substitution reaction. After immersion, the Al substrate is thoroughly rinsed with deionized water to eliminate any residual salt and subsequently dried in N_2 .

After this step the as-obtained surfaces are superhydrophilic and present a micro-structured morphology (figure 1). Thus, the micro-structured samples is immersed in a H_2O_2 (Hydrogen Peroxide ,35% w/w, Sigma Aldrich) solution for 30 minutes to form an oxide layer over the etched surfaces in order to enhance film adhesion over the substrates. The samples are then immersed in DI water for 15 minutes and dried with nitrogen. As regards the functionalization of the IR etched sample, the process consists of spin-coating a Hexane –FOTS mixture (5% by volume) (Hexane (anhydrous, 95%) and Trichloro(1H,1H,2H,2H-perfluorooctyl) silane (FOTS, 97%), Sigma Aldrich) onto the sample at 800 rpm for 30 seconds. After spin coating, the sample is baked at 150°C for 30 minutes for final solvent evaporation and film stabilization. The spin coating procedure is repeated twice to ensure FOTS homogenous distribution all over the surface. The CO etched sample is functionalized by another technique in order to improve the lifetime of the fluorosilane layer. Instead of spinning the hydrophobic layer, the dried substrate is introduced in a vial filled with a FOTS – hexane solution (5% by volume). Functionalization takes place at low temperature (7°C) for 5 hours. The sample is still rinsed in hexane and baked at 120°C for 45 minutes in air.

Table 1. Contact angles measurement for each specimen typology.

Sample	θ_a [°]	θ_r [°]	$\Delta\theta$ [°]
Untreated	85 ± 4	17 ± 4	67 ± 4
IR etched	155 ± 3	149 ± 3	7 ± 3
CO etched	158 ± 1	149 ± 5	9 ± 5

2.2 Surface characterization

Contact angles analysis. Contact angle measurements were performed using a compact CMOS camera (Thorlabs GmbH ® DCC1545M) combined with a Thorlabs GmbH ® MVL7000 zoom lens. Typical spatial and time resolution of the system are $5 \mu\text{m}/\text{pixel}$ and 30 fps respectively. Contact angles are measured using the standard sessile drop method, recording a water drop expanding and contracting quasi-statically over the horizontally oriented surface of interest. Advancing (θ_a) and receding (θ_r) contact angles are evaluated by post-processing the videos fitting with a circle the drop profile near the contact

point. Values of the contact angles reported in this paper are the average of at least six measurements for each sample in each condition, and the corresponding standard deviation is reported as experimental uncertainty. Table 1 reports values of the contact angles measured, at ambient conditions, for the untreated sample and after functionalization steps for the others specimens. The results in table 1 show that the as-received aluminum sample is slightly hydrophilic, with extremely reduced droplets mobility as shown by the high hysteresis $\Delta\theta=67^\circ \pm 4^\circ$. After the functionalization step, all the samples are superhydrophobic, since it is always verified $\theta_a > 150^\circ$ and $\Delta\theta < 10^\circ$.

SEM Analysis. Surface morphologies are visually characterized by Field Emission Scanning Electron Microscopy (SEM), having 0.1 – 30 keV beam energy and 1 – 1.7 nm resolution. In figure 1 SEM images of the samples IR and CO are shown. The samples have some common characteristics: the surfaces indeed are characterized by an evident degree of erosion which results in a non-homogeneous roughness of the substrate. Very dark areas can be noticed in the images a) and b), i.e. areas corresponding to holes of a certain depth, which could allow the stagnation of the condensate.

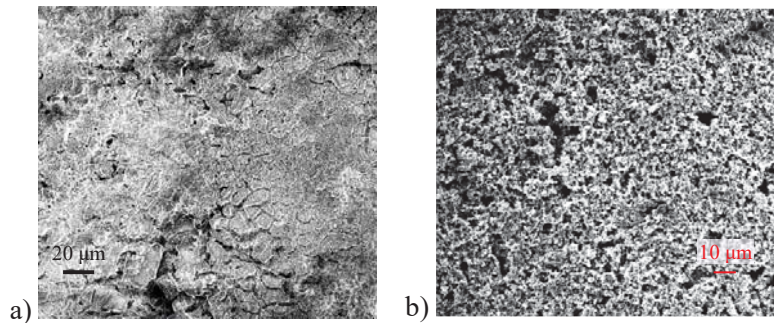


Figure 1. SEM images of: (a) IR etched specimen and (b) CO etched specimen.

3. Heat transfer measurements

The attitude of the superhydrophobic aluminum substrates to promote dropwise condensation has been tested in a two-phase thermosyphon loop during pure steam condensation (at different vapor velocities) over plain vertical surfaces. The system consists of four main components: the boiling chamber, the test section, the cooling water loop and the post-condenser. It is worthy to point out that, since even a small concentration of non-condensable gases (NCG) in the vapor could lead to a considerable modification of the dropwise condensation parameters [4], several actions have been undertaken to avoid it. The test section is designed for the measurement of the heat transfer coefficient over a metallic surface and for the simultaneous visualization of the condensation process. It is composed of several pieces realized in PEEK and glass. The test section basically consists of a rectangular channel grooved into a PEEK block; one side of the channel is covered by a double glass while the other is machined for accommodating the metallic substrate. The front side of the channel is in contact with the condensing vapor while the back one is in contact with the cold water, flowing inside the cooling channel, which is used for removing heat from the condensation process. The specimen is instrumented with four T-type thermocouples located at the inlet and at the outlet of the condensing surface, inside four 0.7 mm holes, at 1 mm and 2.75 mm depth below the front surface of the sample. More information about the experimental apparatus can be found in [5]. Since the coolant mass flow rate $\dot{m}_{COOL}$ is directly measured, along with the inlet coolant temperature $T_{IN,COOL}$ and the coolant temperature difference ΔT_{COOL} , the heat flow rate extracted by the cooling water from the condensing vapor can be obtained as

$$Q_{COOL} = \dot{m}_{COOL} c_{COOL} \Delta T_{COOL} \quad (1)$$

where c_{cool} is the specific heat capacity of the coolant evaluated at the mean temperature between the inlet and the outlet. Hence, the condensation heat flux q is given by

$$q = \frac{Q_{cool}}{A} \quad (2)$$

where A is the heat transfer area of the specimen (50 x 20 mm). Since the wall temperatures are measured with the thermocouples placed in the aluminum, 1 mm and 2.75 mm deep, the surface temperatures can be obtained from the measured values with the hypothesis of one-dimensional temperature distribution extrapolation, since the PEEK thermal conductivity is much lower in comparison to the aluminum sample. At the inlet and outlet of the aluminum sample the two surface temperatures are calculated as:

$$T_{WALL,IN} = T'_{IN} + (T'_{IN} - T''_{IN}) \frac{z_1}{z_2 - z_1} \quad (3), \quad T_{WALL,OUT} = T'_{OUT} + (T'_{OUT} - T''_{OUT}) \frac{z_1}{z_2 - z_1} \quad (4)$$

where T' are the inlet and outlet temperatures measured in the aluminum sample at $z_1 = 1$ mm and T'' are the inlet and outlet temperatures measured in the aluminum sample at $z_2 = 2.75$ mm. Finally, the condensation heat transfer coefficient is evaluated as:

$$HTC = \frac{q}{\Delta T_{ml}} \quad (5)$$

where ΔT_{ml} is the mean logarithmic temperature difference between the surface and the steam. The steam temperature is obtained from the pressure measurement at the inlet of the test section. The steam mass flow rate $\dot{m}_{steam}$ is obtained from Eq. (6), where Q_{BC} is the heat flow rate provided in the boiling chamber (measured from the electrical power supplied to the heaters), besides h_V and $h_{IN,BC}$ are the enthalpy values of the saturated steam and the subcooled liquid at the entrance of the boiling chamber, respectively.

$$\dot{m}_V = \frac{Q_{BC}}{h_V - h_{IN,BC}} \quad (6)$$

All the thermodynamic and transport properties of the steam are evaluated by means of NIST Refprop Version 9.1 [6] from temperature and pressure measurements. Once the mass flow rate is known, the mass velocity of the vapor flowing inside the test section can be calculated as

$$G_V = \frac{\dot{m}_V}{S} \quad (7)$$

where S is the cross section area of the channel. An uncertainty analysis is performed for the experimental parameters following the general rules reported in ISO Guide to the Expression of Uncertainty in Measurement [7]. The results of the uncertainty analysis lead to an expanded uncertainty of the heat transfer coefficient equal to a maximum of $\pm 25\%$ for a temperature difference between the saturated vapor and the surface equal to 4.41 K, while it is equal to a minimum of $\pm 7\%$ with $\Delta T = 17.64$ K. The mean HTC uncertainty calculated over all data points is equal to $\pm 14.5\%$.

4. Results and discussion

The experimental data acquired during condensation heat transfer over the treated aluminum surfaces are here presented. The tests have been carried out maintaining constant the steam mass flow rate, the saturation temperature ($\approx 103^\circ\text{C}$), the inlet cooling water temperature ($\approx 25^\circ\text{C}$) and the cooling mass flow rate ($\approx 0.11 \text{ kg s}^{-1}$). Since the surface properties may vary with time, the degradation of the superhydrophobic characteristic can be evaluated referring to the passing time. The vapor mass flow rate is maintained equal to $1.4 \text{ kg m}^{-2} \text{ s}^{-1}$ with the aim of minimizing the influence of the shear stress on the condensation phenomenon as compared to the gravity force [5]. As reported before, the experimental apparatus is not equipped with a circulating pump, thus the vapor takes some time to reach the aluminum sample and start to condensate over it. We need to define a zero time as the reference for the experimental points measured after the dropwise condensation is initiated. Since the dropwise condensation is a rather

homogenous phenomenon over the surface, the wall temperatures in the direction of the vapor flow must be roughly the same, i.e. isothermal curves are parallel to the condensing surface. Thus, the zero point is defined as the time when the temperatures difference measured at $z=0.001$ mm between the inlet and the outlet is lower than 5 K, at least for 20 seconds.

4.1 IR etched sample

In figure 2 all the four temperatures measured within the IR etched specimen are reported. The plotted measurements of wall temperature refer to two different test runs: the values on the left refer to a test run during dropwise condensation while the temperatures on the right are taken during a test run in filmwise condensation. For each test run, four values are plotted, two associated to the measured wall temperature at the inlet and two at the outlet, where the highest value corresponds to the thermocouple at 1 mm and the lowest is measured by the thermocouples at 2.75 mm from the surface.

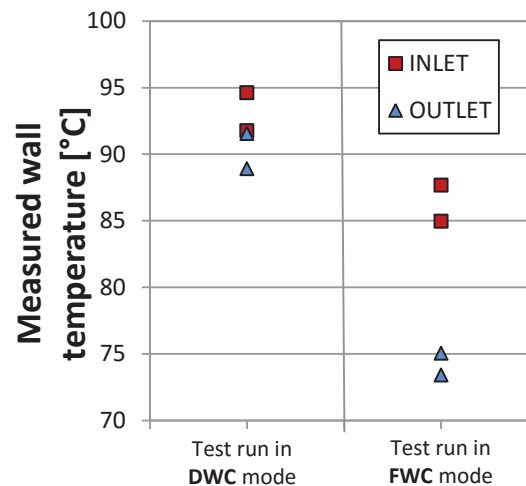


Figure 2. Wall temperatures measured during pure steam condensation over the IR etched sample.

For an ideal dropwise condensation case, T'_{inlet} and T'_{outlet} should be coincident since an homogenous droplet distribution should be achieved over the surface. In DWC case T'_{IN} and T'_{OUT} are not equal, even if they are much closer as compared to a filmwise condensation mode, and this result is clear in figure 2. When moving from the DWC test run to the FWC test run, the difference of wall temperatures between the inlet and the outlet greatly increases, meaning that the thermal resistance between saturated vapor and aluminum surface grows along the path of the steam, i.e. a water liquid film is present and its thickness increases between inlet and outlet. This is probably associated to the loss of the superhydrophobic characteristic due to the degradation of the fluorosilane layer, which involves the formation of the water film along the sample. Dropwise condensation visualizations have been performed using a Photron FASTCAM Mini UX100 high speed camera (CMOS sensor with Bayer color filter array) at 1280 by 606 pixel resolution and 2000 frames per second. The high speed camera has been coupled with a 100 mm Tokina macro lens. A LED illumination system is used as light source. Figure 3 shows the droplets behavior during pure dropwise condensation over an IR sample. Here, the departure radius is estimated equal to 1.23 ± 0.25 mm. It is possible to notice that different contact angles are displayed as a function of the droplet diameter, i.e. the smaller the diameter of the drop, the smaller is the advancing contact angle [8]. This phenomenon is reported in figure 3 (a) where a droplet with an $\theta_a > 90^\circ$ is highlighted by a red circle, and after the sweeping of it (figure 3 (b)) the new growing droplets present $\theta_a < 90^\circ$. Anyhow, the wetting mode achieved is the Wenzel state that leads to θ_a much lower respect to those reported in table 1. An interesting phenomenon has been captured by the high speed camera when the heat transfer rate was very low, i.e. the coolant mass flow rate was stopped. Randomly over the surface, some jumping droplets

were detected and they are shown in figure 4. A recent study [9] showed that when small droplets ($\sim 10\text{--}100\text{ }\mu\text{m}$) merge on superhydrophobic nanostructured surfaces, droplets can spontaneously eject via the release of excess surface energy irrespective of gravity. Droplet removal by this jumping mechanism is highly desirable due to the increased number of small droplets, which more efficiently transfer heat to the surface. An improved understanding will not only enhance heat transfer but prevent progressive surface flooding and extend high-performance condensation operational time due to the reduction in large pinned droplets on the condensing surface. In [8] a model framework to predict dropwise condensation heat transfer for micro/nanostructured superhydrophobic surfaces is developed and a specific morphology comes out to promote the jumping droplet phenomenon. Moreover a theoretical study on the mechanism of the phenomenon has been analyzed in [10]. In particular, it investigates how the coalescence of two or more droplets on ultralow adhesion surfaces leads to droplet jumping. At the basic level, droplet jumping is a process governed by the conversion of excess surface energy into kinetic energy when two or more droplets coalesce and involves a symmetry-breaking surface.

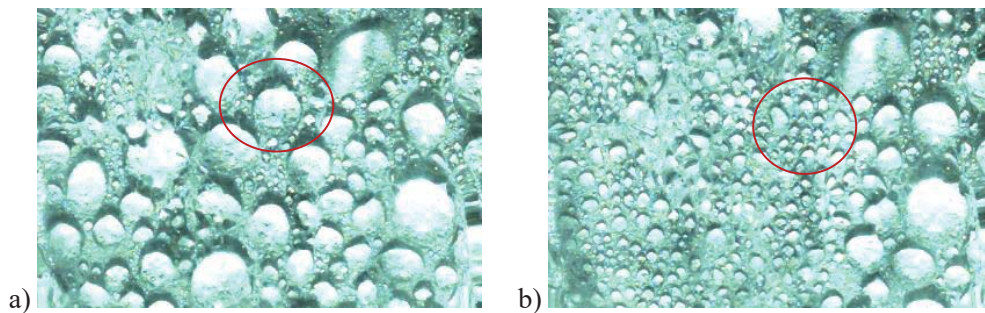


Figure 3. Time-lapse images of continuous saturated steam dropwise condensation over the IR etched sample.

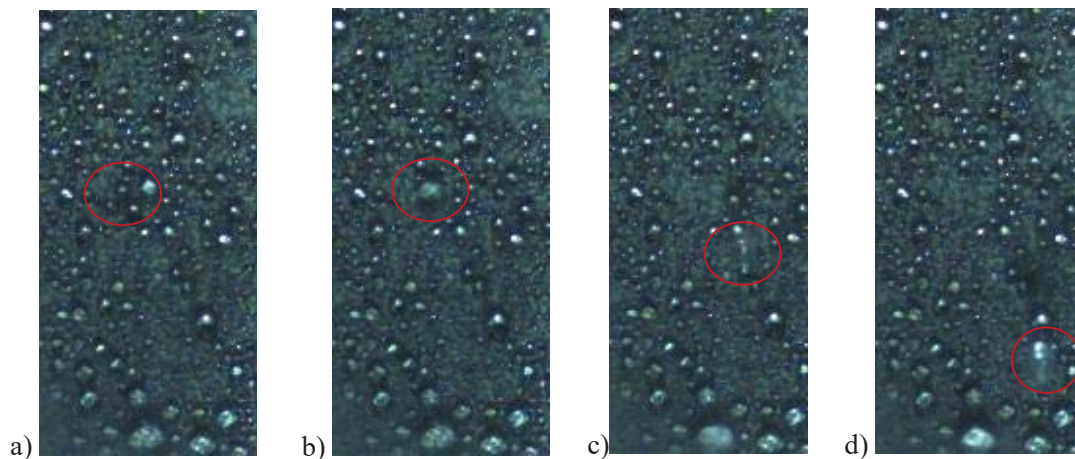


Figure 4. Jumping droplet phenomenon. The red circle highlights in (a) the four drops which will coalescence in one (b). In (c) the droplet jumps, since it does not clean the surface behind his path. These photos were taken after the cooling water was stopped.

However, the experimental results in [9] suggest that these surfaces cannot currently be used for high heat flux applications due to nucleation-density-mediated flooding of the surface. In our case, since the phenomenon requests specific morphological parameters, jumping droplets do not occur all over the surface, but only where those conditions are met.

Figure 5 reports the heat transfer coefficients measured over the IR etched sample during pure steam condensation. The first point corresponds to a pure DWC condition, while the second point presents the HTC measured after about 30 minutes. Even if there is not presence of droplets on the surface the coefficient is still higher as compared to the one obtained over an untreated surface. Instead, the third point displays a HTC comparable to those obtained over a superhydrophilic surface, thus all the hydrophobic layer has been eliminated from the surface. Data refers to a mean of 40 readings. For comparison, HTC measured over an untreated hydrophilic and over a superhydrophilic surface tested at the same conditions are reported: these data are taken from [5].

4.2 CO etched sample

In this section the data collected over the CO etched sample are presented. As it can be seen in figure 5 the heat transfer coefficients are comparable to those obtained over the IR etched sample. In the case of the CO etched sample the functionalization step was changed. The immersion method used in this case should allow a greatest amount of FOTS to bind to the surface structure, as compared to the spin coating technique and, in fact, the lifetime of the hydrophobic layer is extended, as can be seen in figure 5. Three points are reported in figure 5 regarding the CO specimen; the #1 corresponds to a pure DWC condition, the #2 and the #3 correspond to a hybrid condensation. During pure DWC (point #1 for both samples), the HTCs are almost the same, although the ΔT_{ml} of the IR etched sample is slightly higher. With the passing of time both specimens gradually lose their hydrophobic properties and consequently the HTC decreases. However the tendency lines display an extended life of about twice for the immersed treated sample.

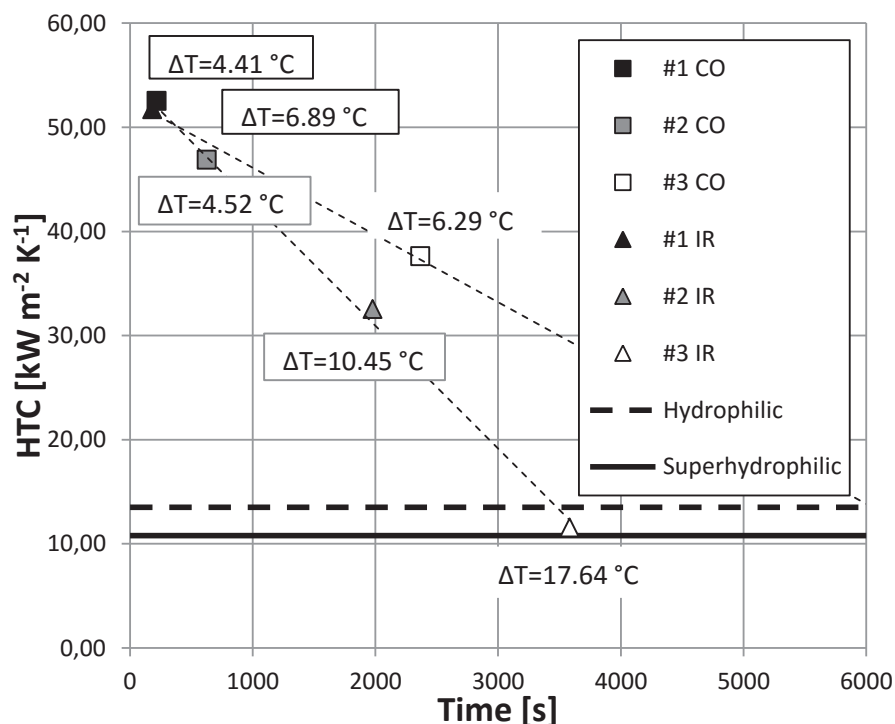


Figure 5. Heat transfer coefficient versus time during condensation over the CO etched and the IR etched sample. For each data point the mean logarithmic temperature difference between the saturated vapor and the surface is reported. For comparison, HTCs measured over hydrophilic and superhydrophilic surfaces are reported [5].

5. Conclusions

Condensation experiments on superhydrophobic aluminum surfaces are reported in this paper. Two wet-chemical fabrication processes were used to nanotexture the aluminum surface by forming different surface morphologies. Each chemical technique produced superhydrophobic samples, with high contact angle of about 156° and contact angle hysteresis lower than 10° at room temperature. Tests of pure steam flow condensation over the two superhydrophobic treated surfaces have been performed maintaining constant the input parameters, i.e. saturation temperature, vapor mass flow rate, cooling water inlet temperature and cooling water mass flow rate, in order to compare the condensation performance of the different specimens. Each substrate promoted dropwise condensation: in the saturated vapor environment the condensate droplets grow and move on the superhydrophobic surfaces in the Wenzel state. The heat transfer coefficient is similar for the two surfaces, reaching a maximum value of $52 \text{ kW m}^{-2} \text{ K}^{-1}$ which is about four times higher as compared to a hydrophilic untreated aluminum sample. Moreover, the phenomenon of jumping droplets has been captured by the high speed camera.

6. References

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