



Article Pool Boiling Performance of Water and Self-Rewetting Fluids on Hybrid Functionalized Aluminum Surfaces

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Abstract: The boiling performance of functionalized hybrid aluminum surfaces was experimentally investigated for water and self-rewetting mixtures of water and 1-butanol. Firstly, microstructured surfaces were produced via chemical etching in hydrochloric acid and the effect of the etching time on the surface morphology was evaluated. An etching time of 5 min was found to result in pitting corrosion and produced weakly hydrophilic microstructured surfaces with many microcavities. Observed cavity-mouth diameters between 3.6 and 32 µm are optimal for efficient nucleation and provided a superior boiling performance. Longer etching times of 10 and 15 min resulted in uniform corrosion and produced superhydrophilic surfaces with a micropeak structure, which lacked microcavities for efficient nucleation. In the second stage, hybrid surfaces combining lower surface energy and a modified surface microstructure were created by hydrophobization of etched aluminum surfaces using a silane agent. Hydrophobized surfaces were found to improve boiling heat transfer and their boiling curves exhibited a significantly lower superheat. Significant heat transfer enhancement was observed for hybrid microcavity surfaces with a low surface energy. These surfaces provided an early transition into nucleate boiling and promoted bubble nucleation. For a hydrophobized microcavity surface, heat transfer coefficients of up to 305 kW m⁻² K⁻¹ were recorded and an enhancement of 488% relative to the untreated reference surface was observed. The boiling of self-rewetting fluids on functionalized surfaces was also investigated, but a synergistic effect of developed surfaces and a selfrewetting working fluid was not observed. An improved critical heat flux was only obtained for the untreated surface, while a lower critical heat flux and lower heat transfer coefficients were measured on functionalized surfaces, whose properties were already tailored to promote nucleate boiling.

Keywords: pool boiling; nucleate boiling; surface modification; functionalized surfaces; heat transfer enhancement; self-rewetting fluids

1. Introduction

Pool boiling is utilized in diverse industrial applications, such as the cooling of electronic devices [1], heat exchangers [2], distillation [3], refrigeration [4] and others. Nucleate boiling is characterized by intensive heat transfer at relatively small temperature differences. Suitable techniques for the enhancement of heat transfer during boiling are highly required as miniaturization and increased power input demand more concentrated heat dissipation [5,6]. In this study, pool boiling experiments are performed on functionalized aluminum surfaces. Aluminum has a high thermal conductivity and is relatively cheap (approximately six-times cheaper compared with a similar volume of copper), lightweight and machinable, which makes it suitable for the mass production of functionalized boiling surfaces. It is also soft and can be easily roughened [7]. Furthermore, aluminum is prone to pitting corrosion [8], which is considered as beneficial for boiling applications as it might create additional nucleation sites and improve the heat transfer coefficient (HTC) [9]. Nanoscale structures can be easily created on aluminum surfaces. For example,



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). aluminum surfaces readily react with hot water and form a (super)hydrophilic nanostructure of aluminum oxide hydroxide called boehmite or pseudoboehmite [7,9,10]. A boehmite layer increases the wettability of the base aluminum [7] and significantly changes the boiling characteristics.

The chief methods to enhance boiling performance include modification of the boiling surface [11] or augmentation of the working fluid's properties [12,13]. Surface wettability and the presence of microstructures, which serve as preferential nucleation sites, are some of the most important characteristics of a boiling surface. The presence of vaportrapping cavities or similar defects on the micron and submicron scale is important to ensure an abundance of potentially active nucleation sites on the surface. The required size range for efficient nucleation can be determined using nucleation criteria such as Hsu's criterion [14]. A number of previous studies have shown that the presence of such microcavities importantly enhanced the heat transfer in the nucleate boiling regime and also grants an earlier transition into it [15–19]. Within this study, hybrid surfaces are defined as functionalized surfaces with a tailored microstructure and surface energy to promote nucleation and effective nucleate boiling. A stepwise approach to boiling heat transfer enhancement on hybrid functionalized surfaces is investigated by first changing the microstructure and morphology of flat aluminum surfaces, then reducing the surface energy of prospective surfaces through hydrophobization and, finally, by evaluating a possible further enhancement by using self-rewetting mixtures as the working fluid. The main factors and techniques used for the development of functionalized surfaces are briefly discussed in the following subsections, together with the employment of self-rewetting fluids for an enhanced pool boiling performance.

1.1. Surface Roughness and Topography

In recent decades, various techniques for surface modification have been proposed in the literature. A comprehensive review was recently published by Liang and Mudawar [11], who classify surface modifications into macroscale (>1 mm), microscale (from 1 to 1000 μ m) and nanoscale (<1 μ m) according to their size scale. A so-called hierarchical surface contains structures on multiple scales. The main, but mostly incompatible, goals of all surface modifications are as follows: (1) increase in the critical heat flux (CHF), (2) increase in the heat transfer coefficient, (3) decrease in surface superheat required for the onset of nucleate boiling (ONB) and (4) elimination of the boiling hysteresis [11]. A single modification induces topographical changes of the surface and, at the same time, modifies its wettability and wickability [20,21]. Surface modifications might not be stable, and their performance may change over time as they suffer from contamination, surface chemistry changes and degradation [22,23]. For instance, it is typical for hydrophilic surfaces characterized by their high surface energy to easily adsorb contaminants present in the boiling liquid or in the air [7,21,24].

Chemical etching represents a microscale method of surface modification mostly used for roughening a surface [11]. It is a cheap method of surface functionalization, simple to apply and suitable for various materials and geometries. Sankaran et al. [25] emphasize that low-cost, simple and straightforward methods for the manufacturing of micro- or nanoscaled textured surfaces for boiling applications with a scale-up potential are highly desired. Kim et al. [26] point out that microstructures are rarely applied in the industry due to the higher costs and need for special materials. However, no special equipment or tools are required for chemical etching [27]. Etching results in roughness generated directly on the base material. Surface structures are thus mostly stable and have similar properties as the base material [28]. During etching, pitting corrosion can occur and form micro-porous cavities, which might increase the entrapment of vapor or gas, increase the number of active nucleation sites and enhance the boiling HTC [8,9]. Rioux et al. [6] were able to lower the boiling superheat on an etched copper surface by 25% compared with a polished reference surface and increase the CHF by 28%. They obtained peaks and protrusions with sizes between 0.1 to 2 µm after etching. Li et al. [29] used chemical etching of stainless steel in hydrofluoric acid at 50 °C and etching times from 1.5 to 5 min to increase the roughness and enhance the wickability of the surface. While roughness monotonously increased with etching time, wickability did not and the roughest surface did not exhibit the highest wickability. Ferjančič and Golobič [30] measured an increase in CHF by 51% on etched steel and stainless-steel surfaces with respect to the sanded surface with the same roughness parameter, R_a . Vachon et al. [31] proposed that etching might be a cyclic process. With increasing time, cavities are broadened to large pits and the number of nucleation spots are reduced, but new cavities might be also created on the bottom of old erosions as the process continues. These cavities might be prone to contamination, chemistry changes and degradation, which decreases their longevity in use [21].

1.2. Surface Wettability

Micro- and nanoscale modifications of the boiling surface are able to induce topographical changes and modify its wettability [20,21]. The desired wettability might be achieved by proper selection of the surface modification technique [5]. Two wetting states with significant impact on the boiling process are typically discussed in the literature. The Wenzel state is often considered to be a *superwetting* state, in which cavities on the boiling surface are completely filled with liquid and liquid drops are strongly pinned to the surface due to the contact angle hysteresis [32]. On the other hand, the Cassie–Baxter state is characterized by a partial filling of the cavities on the surface. When in the Cassie–Baxter state, liquid drops roll off more easily from a hydrophobic surface and drag friction is reduced compared with the Wenzel state [20]. The Cassie–Baxter state is also characterized by the easiness of activation and the stability of active nucleation sites, which remain active even at significant drops in temperature [33]. Although the Cassie–Baxter state often occurs on superhydrophobic surfaces, it is metastable and might transition into the Wenzel state [32]. Furthermore, the Cassie–Baxter state should not be present on a properly degassed boiling surface when air or other non-condensable gasses entrapped in the surface's micro- or nanostructure are absent. In this sense, true superhydrophobicity does not exist on thoroughly degassed surfaces under boiling conditions. Intermediate states between the Cassie–Baxter and Wenzel states were observed as well [20].

It is usually accepted that the high wettability of a heating surface increases the CHF and simultaneously decreases the HTC. Superhydrophobic and hydrophobic surfaces are typically dismissed for boiling applications. Although they usually evince much higher HTCs and lower ONB compared with non-hydrophobic surfaces, their CHF is typically unacceptably low and more difficult to predict compared with non-hydrophobic surfaces [34]. Another problem related to these surfaces is the instantaneous coverage of superhydrophobic surfaces with a vapor film, either immediately after their immersion into liquid or at very low superheats. Boiling with this premature vapor film is characterized with extremely poor heat transfer performance [35]. However, Allred et al. [3] showed that when coated micro- and nanostructured superhydrophobic surfaces transition from the Cassie-Baxter state into the Wenzel state before boiling is initiated, they are able to reach comparable CHFs and much higher HTCs with respect to the hydrophilic surfaces. They proposed that boiling in the Wenzel state prevents vapor spreading due to strong contact-line pinning. According to them, the degassing procedure has a crucial role for superhydrophobic surfaces as it might bring the surface to the Wenzel state. According to Webb [22], hydrophobic coatings increase the radius of the liquid–vapor interface and, thus, decrease the superheat required for its existence. Consequently, a lower superheat is required for bubble growth on hydrophobic surfaces as the energy barrier for nucleation is smaller [35,36]. Webb [22] also speculates whether it is desirable to hydrophobize the whole surface, as it might lead to vapor blanketing at low superheats. However, vapor blanketing is likely the result of an inappropriate degassing procedure, as was discussed above. In general, the surface layer of the hydrophobizing agent should not affect the surface roughness [37] nor its topography [35] when it is thin enough, i.e., in the nanometer range.

1.3. Self-Rewetting Fluids

During the boiling of certain mixtures, a Marangoni flow appears, causing the liquid to spontaneously flow from cold to hot locations due to surface tension gradients, which are driven either by local changes of concentration (solutal flow) or temperature (thermal flow). For so-called self-rewetting fluids (SRFs), the solutal Marangoni flow is further enhanced by the thermal Marangoni flow, as their directions are aligned. This might be achieved in dilute mixtures of alcohols in water with four and more carbon atoms in their chains [38]. Such mixtures exhibit a positive surface tension gradient with an increasing temperature when heated close to their boiling point [39]. During the boiling of SRFs, an inflow of cold liquid from the bulk towards the hot boiling surface is supposed to rewet nucleation sites, prevent a boiling crisis and increase the CHF [40]. This was, indeed, observed during pool and flow boiling in confined spaces (heat pipes, microchannels, etc.) or during pool boiling in small boiling surfaces (wires, thin tubes and others) [12,40]. However, the conclusions of various studies seem to be contradictory and unpredictable for flat surfaces [40]. For instance, Ohta [41] discusses reduced CHF for mixtures of water and alcohols and concludes that, as the Marangoni flow supplies liquid from the macrolayer to the three-phase contact line, it also promotes local dryout of the microlayer, which leads to a CHF reduction. It was reported that SRFs promote a more rapid detachment of smaller bubbles at lower superheats and shorten bubble waiting periods, which induces stronger turbulence and intensifies heat flux [42–44].

In single-component fluids, the thermal Marangoni flow is negligible under common conditions [45]. For the saturated and even for the subcooled boiling of self-rewetting mixtures under common conditions, the effect of the thermal Marangoni flow was found to be insignificant relative to the intensity of the solutal Marangoni flow [45,46]. Hu et al. [45] used thermal and solutal Marangoni numbers to estimate the intensity of both Marangoni flows. They obtained thermal Marangoni numbers, which were two orders of magnitude lower compared with the solutal Marangoni numbers. Although the thermal Marangoni flow might be often neglected during the saturated boiling of self-rewetting fluids, it might outperform the solutal Marangoni flow under the following conditions: (1) when boiling is highly subcooled, (2) when a mixture has a narrow difference between the bubble point and the dew point or (3) when boiling occurs in microgravity [38].

1-butanol represents a primary alcohol that is miscible in water up to a 7.15% mass fraction of 1-butanol at 20 °C [39] and whose dilute aqueous mixtures evince self-rewetting properties [44]. Mixtures of water and 1-butanol become self-rewetting when they are heated above approximately 65 °C [39]. Although water has a lower boiling point than 1-butanol, vapor bubbles contain more butanol for dilute aqueous mixtures and the solutal Marangoni flow is induced from the alcohol-rich surrounding region to the water-rich region near the bubbles [38]. Shoji and Nishiguchi [47] confirmed this using gas chromatography during experiments with a water mixture of 1-butanol on a platinum wire. They also showed that CHF increases with an increasing 1-butanol concentration, but a significant scatter of the CHF values was recorded. According to Namura et al. [48], the strength of the thermal Marangoni flow does not depend on the concentration of butanol in the mixture. It was observed that small additions of butanol into water increase the CHF for wire heaters [45], lower both the contact angle and the surface tension [39,49], reduce the bubble departure diameters and prevent bubble coalescence [44]. Zhou et al. [44] also observed that bubbles tend to be repelled from each other in water-1-butanol mixtures and ascribe this to the self-rewetting properties of the mixture. Sitar et al. [49,50] showed that a higher surface superheat is necessary for the initiation of nucleation during the boiling of SRFs in silicon microchannels compared with pure water. However, they also show that using 1-butanol-based SRFs decreases average temperatures, which they attribute to the enhanced wettability due to a lower contact angle (and lower surface tension).

1.4. Boiling of SRFs on Modified Surfaces

The simultaneous use of modified surfaces and SRFs is poorly researched and is the topic of very few studies thus far, despite the potential for a synergistic effect of concomitant modifications of the boiling surface and the working fluid. Sahu et al. [43] studied the boiling of Novec 7300 and 1-heptanol-based SRF on a copper surface covered with coppercoated nanofibers and found that the simultaneous use of an SRF and a modified surface provides even better performance than either of the enhancement techniques on their own, although the enhancement was significant only at a very high heat flux. Hu et al. [42] evaluated the boiling of a 1-heptanol-based SRF on a titanium dioxide coated surface and found that both the CHF and HTC can be significantly enhanced using the SRF. Furthermore, a significant reduction in the bubble diameter was observed. Zhou et al. [51] investigated boiling enhancement using a combination of a copper foam and a 1-butanol-based SRF, finding that a very slight heat transfer intensification could be achieved using the densest foam in combination with the SRF. Sankaran et al. [25] covered copper surfaces with polymer nanofibers and found that using a 1-heptanol-based SRF on such surfaces can provide a small additional HTC enhancement but decreased the CHF values compared with the boiling of pure water. In general, the results of previous studies suggest that a small additional enhancement of boiling performance can be achieved using SRFs on modified surfaces, but no tests seem to have been performed on surfaces with hydrophobic properties.

1.5. Motivation of This Work

This work explores the enhancement of pool boiling performance via modification of the surface microstructure and morphology, lowering the surface (free) energy, and the use of a self-rewetting working fluid. These enhancement techniques are combined, and the resulting effect is investigated. A stepwise approach is followed for the gradual enhancement of, especially, the HTC and the CHF via a two-step functionalization of hybrid aluminum surfaces, followed by employment of the self-rewetting fluid. Flat aluminum surfaces are first subjected to chemical etching in hydrochloric acid. The etching is performed over different periods of time, which results in different surface morphologies. The saturated pool boiling tests are then performed on the resulting microstructured surfaces with water under atmospheric pressure. Based on the results of these tests, two surfaces with different morphologies and boiling characteristics are selected for hydrophobization, representing the second step of surface functionalization. After further water pool boiling tests, the best-performing surface is identified and the reasons for the differences between the performance of the studied surfaces are discussed. Finally, the best-performing surface is tested in both a hydrophobized and non-hydrophobized state alongside an untreated surface using water mixtures of 1-butanol, which exhibit self-rewetting behavior, with the goal of determining whether SRFs can be used to further enhance the boiling heat transfer on functionalized surfaces.

2. Materials and Methods

2.1. Surface Functionalization and Evaluation

The study was carried out on cylindrical aluminum samples (EN AW-6082; AlSi1MgMn). Functionalization and boiling experiments were performed on the flat face of cylindrical samples with a diameter of 14 mm. The geometry of the sample is shown schematically in Figure 1c and its installation in the boiling setup in Figure 1b. All samples were manufactured from the same stock rod and were subjected to identical pre-treatment prior to functionalization and boiling experiments. The face of the sample, later serving as the boiling surface, was sanded using P1200 and P2000 grit papers to achieve a near-mirror finish. Afterwards, the face was rinsed with 2-propanol and wiped clean with a lint-free wipe. This was the reference state of all samples and also the state in which the boiling performance of the sample without further treatment (REF) was evaluated.



Figure 1. Schematic diagram of the pool boiling experimental setup (**a**), cross section of the sample and the heating block (**b**) and dimensions of the sample including the placement of thermocouples (**c**).

The first step of surface functionalization was performed after the described pretreatment and cleaning procedure. The samples were etched in a 3 M solution of HCl for 5, 10 or 15 min. The etching was performed with the sample inserted into a PTFE holder and submerged into the etching solution face-down. The number in the name of each sample denotes the duration of etching in minutes (e.g., sample A5 was etched for 5 min), while A stands for aluminum. After the etching, the treated face of the sample was rinsed thoroughly with distilled water and submerged in a glass of fresh distilled water for 5 min for the reactions to stop and any traces of HCl to be diluted. Afterwards, the samples were dried in a convective oven at 80 $^{\circ}$ C for 15 min.

The second step of surface functionalization was performed on selected etched samples. Treated faces were hydrophobized after the etching using chemical vapor deposition (CVD) of a fluorinated silane. Hybrid surfaces with a modified microstructure and lowered surface energy were created this way. The hydrophobization was performed using a mixture of toluene (0.95 mL), 1,2-bis(triethoxysilyl)ethane (0.01 mL) and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (0.05 mL). The coating mixture in an open glass vial was placed into a plastic container together with the samples and the container was covered with aluminum foil. The container was then placed into a pre-heated convection oven at 90 °C, where the CVD process was carried out for 90 min. After the container cooled down, the now-hydrophobic samples were removed. The coating has a nanometric thickness of less than 5 nm, which prevents it from being observable in SEM images. Hydrophobized samples are denoted with the suffix "H" (e.g., A5H). After the hydrophobization, no further cleaning was performed prior to the boiling experiments. While aluminum typically exhibits hydrophilic behavior, etched surfaces might become superhydrophilic due to microstructures formed after etching [29]. Hydrophobic coating applied on etched aluminum surfaces should, therefore, enhance the boiling heat transfer and promote bubble nucleation at lower superheat values [37].

The wettability of the samples was analyzed using sessile droplet measurements performed on a goniometer. Five water droplets with a volume of 15–20 μ L were placed on various parts of each surface and their images were recorded. The images were processed using a custom script in a MathWorks MATLAB environment.

Surface morphology of select samples was analyzed using a scanning electron microscope (SEM) Carl Zeiss SUPRA 35 VP operating at an accelerating voltage of 1 kV and utilizing a secondary electron detector. SEM images of boiling surfaces were taken after boiling had taken place on them to avoid local changes of the surface properties due to their interaction with the electron beam.

All samples fabricated and evaluated within this study are listed in Table 1 alongside the measured contact angle (and its standard deviation) prior to exposure to boiling and specifics of the used fabrication method.

Sample Name	Treatment	Contact Angle before Boiling (°)
REF	none	$58^\circ\pm11^\circ$
A5	5 min etching	$68^\circ\pm8^\circ$
A10	10 min etching	<1°
A15	15 min etching	<1°
A5H	5 min etching + hydrophobization	$157^{\circ} \pm 3^{\circ}$
A15H	15 min etching + hydrophobization	$160^\circ\pm3^\circ$

 Table 1. Surface treatment and contact angles of samples used in the study.

2.2. Boiling Performance Evaluation

Boiling performance during pool boiling of water and self-rewetting fluids was evaluated using the setup shown in Figure 1a. The boiling chamber consists of a glass cylinder (inner diameter of 60 mm) between two stainless steel flanges, which is filled with 200 g of the working fluid during measurements. The sample is inserted through the bottom flange and is mounted onto a copper heater block, as shown in Figure 1b. Heat is supplied to the sample using three AC-powered cartridge heaters with a maximum power of 400 W each. The sample is surrounded by PEEK bushing, which is used to provide a seal and limit heat losses. Boiling on the side of the sample is prevented by a ring of flexible epoxy glue (Duralco 4538) around its edge. Further sealing is provided by a silicone O-ring, as shown in Figure 1b. The sample is mounted on the heater block and sealed with the epoxy resin after all surface functionalization steps have been carried out. An immersion heater is used to pre-heat and degas the working fluid and maintain saturation at low heat fluxes. Vaporized working fluid is condensed in a glass condenser and returned to the boiling chamber. The system was open to the environment and no pressure regulation was used. The measurements were therefore performed at ambient atmospheric pressure. Stability of the pressure was confirmed through stable saturation temperature of the working fluid.

The sample contains three type K thermocouples (Omega), which are used to measure the axial spatial temperature gradient along the direction of heat conduction towards the boiling surface, as shown in Figure 1c. The thermocouples are 5 mm apart from one another and the highest one is positioned 5.3 mm below the boiling surface. Another two sheathed type K thermocouples (Omega) are submerged into the boiling chamber at different heights to measure the temperature of the working fluid. Thermocouple signals are acquired using Dewesoft KRYPTONi-8xTh DAQ module. Temperatures are calculated based on recorded voltages using the NIST 9th degree polynomial for conversion. Offset based on the cold junction temperature of each input is made before the conversion. The cold junction temperature is measured internally using a Pt1000 probe on each input. Data are acquired using the Dewesoft X3 software at a frequency of 10 Hz. Visualization of the boiling process is performed using Photron FASTCAM Mini UX100 high-speed camera operating at 2000 fps.

An identical measurement protocol was followed during the evaluation of the boiling performance of all samples. After a sample was inserted, the boiling chamber was filled with 200 g of twice-distilled water and the immersion heater was turned on to bring the water to saturation. After degassing through vigorous boiling for 45 min, the cartridge heaters were turned on to ensure that boiling at approximately 200 kW m⁻² was established on the sample to further reduce the presence of entrapped non-condensable gasses on the boiling surface prior to measurements. After 15 min of boiling on the surface, all heaters were turned off and the water was left to cool down to below 90 °C to ensure the condensation of vapor residue on the surface. This subcooling protocol was also used in-between individual experimental runs on the same sample. Just before the start of each experimental run, the temperature of the water was brought back to saturation and data acquisition was started.

During each experimental run, the heat flux was increased slowly but continuously by increasing the voltage on the cartridge heaters. The heat flux increase rate was up to $0.2 \text{ kW} \text{ m}^{-2} \text{ s}^{-1}$ in the natural convection region and up to $2.5 \text{ kW} \text{ m}^{-2} \text{ s}^{-1}$ in the nucleate boiling region. This was already shown not to influence the results of the measurements in a previous study (see [16], including the Supporting Information). Additional validation of the dynamic measurement approach was carried out through finite volume simulations (see Supplementary Information, Section S1) and through experimental comparison of values measured under steady-state conditions and values obtained with the dynamic method (see Supplementary Information, Section S2). Deviations from steady-state results were generally found to be one order of magnitude smaller than the measurement uncertainty, confirming that the use of the dynamic method provides accurate boiling performance evaluation. Saturation of the working fluid was maintained during the measurement, with the immersion heater operating at a low power setting. When the onset of CHF and the transition toward film boiling were achieved, the cartridge heaters were turned off and the surface was left to cool down. Experiments were repeated for each tested surface until the position of the boiling curve stabilized and the surface was deemed stable under the given boiling conditions. The runs were performed one after another with spacing of approximately 40 min, which is the duration of a single measurement plus the time required for the setup and the sample to cool down to below saturation temperature. When all runs could not be completed within a single day, the surface was left submerged, the working fluid was allowed to cool down to room temperature and the measurements were finished on the following day.

Experiments using self-rewetting fluids (SRFs) were conducted by utilizing a mixture of water and 1-butanol (Honeywell Riedel-de Haën, \geq 99.5%) with different concentrations. To ensure the most accurate comparison between measurements performed with water and SRFs, the latter were used on the same surface after the boiling performance of water on the investigated surface had stabilized. Boiling curves obtained with SRFs were then compared with the stable water curves recorded on the same surface. After a stable state was reached with pure water, 1-butanol was added to the boiling chamber to bring the concentration to 1 wt.%. After the 1-butanol addition, boiling was initiated for 5–10 min to ensure the homogeneity of the mixture. Following the subcooling procedure, an experimental run was conducted using the same protocol as for pure water. After each run, the concentration of the mixture was increased by 1 wt.% until it reached 6 wt.%.

2.3. Data Reduction and Measurement Uncertainty

Temperature measurements were used to calculate the relevant heat transfer parameters, including heat flux, surface superheat and heat transfer coefficient. The methodology proposed in [52] was used to calculate the spatial temperature gradient between the uppermost and lowermost thermocouple using the following linear interpolation:

$$\frac{\Delta T}{\Delta x} = \frac{T_{s,3} - T_{s,1}}{2\Delta x_1}.$$
(1)

In Equation (1), Δx_1 corresponds to the distance between two adjacent thermocouples (5 mm). Heat flux was then calculated using Fourier law of one-dimensional thermal

conduction with the assumption that heat losses are insignificant, which is widely accepted for such experimental setups and warranted due to the insulation of the sample with a low-thermal-conductivity material (PEEK). The relevant equation accounts for the spatial temperature gradient and the thermal conductivity of the sample, as follows:

i

$$\eta = k_1 \frac{\Delta T}{\Delta x} \,. \tag{2}$$

A recent study [52] has shown that a temperature-dependent value of thermal conductivity should be used to ensure accurate calculation of the heat flux. Therefore, thermal conductivity of the sample (k_1) is evaluated at the arithmetic average of all three measured temperatures in the sample using the following equation:

$$k(T) = -0.0001165T^2 + 0.07486T + 198.81.$$
(3)

The latter equation was established based on the temperature-dependent thermal diffusivity measurements made using the laser flash method on the same type of aluminum utilized in this study and the literature-sourced values of temperature-dependent density and specific heat capacity. The temperatures are inserted into equation (3) in $^{\circ}$ C and the result is in W m⁻¹ K⁻¹.

To calculate the boiling surface's superheat, the surface temperature is extrapolated using the temperature recorded closest to the boiling surface, accounting for the distance to the surface $\Delta x_2 = 5.3$ mm. The thermal conductivity is first estimated at temperature $T_{s,1}$ and, after the calculation of the initial approximation of the surface temperature, at the mean temperature between the estimated surface temperature and $T_{s,1}$, yielding the value k_2 . This iteration allows a more accurate calculation of the surface superheat according to the following equation:

$$\Delta T_{\rm w} = T_{\rm w} - T_{\rm sat} = T_{\rm w} - \overline{T}_{\rm f} = T_{\rm s,1} - \frac{\dot{q}\Delta x_2}{k_2} - \frac{T_{\rm f,1} + T_{\rm f,2}}{2}.$$
(4)

The latter equation takes into account the arithmetic average of the two measured working fluid temperatures $T_{f,1}$ and $T_{f,2}$. Finally, the heat transfer coefficient is calculated as the ratio between the heat flux and the boiling surface superheat, as follows:

$$h = \frac{\dot{q}}{\Delta T_{\rm W}}.\tag{5}$$

The measurement uncertainty of heat transfer parameters was evaluated following the methodology proposed in [52]. Heat flux uncertainty results from the uncertainty of the distance between thermocouples ($u(\Delta x_1) = 0.16$ mm; evaluated experimentally), uncertainty of the thermal conductivity (1.5%; estimated based on thermal diffusivity measurement accuracy) and uncertainty of thermocouple calibration and measurements (u(T) = 0.191 K at 100 °C and u(T) = 0.301 K at 250 °C; evaluated experimentally). The expanded relative measurement uncertainty of the heat flux (coverage interval 95.45%) is highest at low heat flux values (12.2% at 100 kW m⁻²) and drops to approximately 4.5% at 1000 kW m⁻². The surface superheat uncertainty partially stems from the uncertainty of the distance between the uppermost thermocouple and the surface ($u(\Delta x_2) = 0.18$ mm; evaluated experimentally) and also depends on the thermal conductivity, heat flux and temperature uncertainty. The expanded surface superheat uncertainty is approximately 0.77 K at 100 kW m^{-2} and increases with the heat flux to 2.35 K at 1000 kW m⁻². Finally, the uncertainty of the heat transfer coefficient is based on the uncertainty of heat flux and surface superheat calculation. Its expanded relative value depends heavily on the boiling behavior of the surface and is lowest on the reference surface (approximately 11.7% at 500 kW m^{-2}) but can reach high values on the surfaces exhibiting extremely low superheat values, such as the A5H (approximately 43.5% at 500 kW m⁻² with the 95.45% coverage interval).

3. Surface Characteristics

The morphology of boiling surfaces was analyzed using SEM imaging after boiling had taken place on them and the results are shown in Figure 2. The untreated reference surface (REF) does not exhibit specific morphological features on the microscale, with the exception of a few shallow grooves, which resulted from surface pre-treatment by sanding. However, the morphological features in the form on nanoneedles appear on the submicron scale, as shown in the right-hand part of Figure 2b. The nanoneedles with a length of several hundred nanometers form due to the exposure of the aluminum surface to hot water and are composed of boehmite [53–55]. A similar natural modification of aluminum surfaces has been recorded by several previous studies [7,9,10,56].



Figure 2. SEM images of the untreated reference surface (**a**) and surfaces etched for 5 min (**b**), 10 min (**c**) or 15 min (**d**). Images were taken after boiling took place on the surfaces.

The effect of different etching durations is compared in Figure 2b–d, where the morphology of surfaces treated for 5 min [A5; Figure 2b], 10 min [A10; Figure 2c] or 15 min [A15; Figure 2d] are shown. A short etching time of 5 min results in local degradation of the naturally occurring passivation film on the aluminum surface and subsequent pitting corrosion [8,57]. The resulting main cavities have diameters between 3.6 and 32 μ m and are surrounded by additional smaller cavities with diameters between 1 and 4 μ m. The size range of the observed microcavities matches the optimal cavity diameters for efficient nucleation during the pool boiling of saturated water at atmospheric pressure, as predicted by Hsu's nucleation criterion [14]. The A5 surface exhibited slight hydrophilicity with a contact angle of approximately 68° before boiling tests were performed.

Longer etching times (10 min or more) result in a complete modification of the boiling surface due to the global penetration through the passivating film on the surface. Micropeaks are present on the surface, but specific features that would enhance the nucleation process (cavities or similar defects) are largely absent. The micropeak surface structure, therefore, seems to be unsuitable for vapor entrapment and the enhancement of bubble nucleation. However, the A10 and A15 surfaces exhibit strong capillary wicking and a contact angle < 1° before boiling, which indicates the superhydrophilicity and porosity of the surface. While surface porosity is generally favorable for achieving an enhanced heat transfer [58–61] (especially in the form of increased CHF values), hydrophobized porous surfaces might be prone to unwanted vapor spreading due to a higher affinity towards contact with the vapor phase opposed to the liquid phase.

Equivalent A5 and A15 surfaces were also tested in the superhydrophobic state after undergoing CVD hydrophobization and were denoted as A5H and A15H, respectively. The contact angle on both surfaces exceeded 150° before boiling and the roll-off angle was below 5°, which confirms the superhydrophobic behavior.

4. Boiling Performance Using Water

In the first stage of the discussed stepwise approach for the gradual enhancement of boiling performance, boiling tests were performed on etched surfaces and on the reference untreated surface. The effect of surface morphology resulting from different etching times on boiling performance was evaluated. In the second stage, two surfaces with different microstructures (microcavities and micropeaks) and different boiling behaviors were selected for hydrophobization. The results obtained with hydrophobized surfaces, their non-hydrophobized counterparts and the reference untreated surface were compared and the effect of hydrophobization on the enhancement of pool boiling performance was evaluated.

4.1. Effect of Surface Microstructure

The boiling heat transfer on etched surfaces with different treatment times was evaluated multiple times on each surface until a stable boiling curve was achieved. The evaluation is shown in Figure 3 for the untreated reference surface (REF; Figure 3a), surface etched for 5 min (A5, Figure 3b), surface etched for 10 min (A10, Figure 3c) and surface etched for 15 min (A15, Figure 3d). In all cases, the uppermost end of the boiling curve represents the onset of the CHF. For the reference surface, a gradual decrease in the CHF (from 1367 kW m⁻² during the first measurement to 898 kW m⁻² during the 10th measurement) was observed. However, the superheat also decreased slightly from 21.1 K at 800 kW m⁻² during the first measurement to 18.3 K at the same heat flux during the 10th measurement. A reduction in the wettability was observed after all of the runs with the contact angle increasing from 58° before the first run to 82° ($\pm 13^{\circ}$) after the last run. This is consistent with the observed small decrease in surface superheat, but the reduction in wettability cannot fully explain the lower CHF value. The reduction in wettability was likely caused by the aforementioned growth of boehmite (aluminum oxide hydroxide) and by changes of the surface chemistry and morphology due to high temperatures after the CHF onset. Može et al. [62] observed resembling wettability reduction for copper surfaces exposed to multiple instances of CHF incipience. Lee et al. [9] measured a 30% decrease in the heat transfer coefficient after five repeated boiling runs on an aluminum surface, which was attributed to the formation of aluminum hydroxide on the surface that resulted in increased thermal resistance and changes of surface morphology. Nikaido et al. [63] used electrolysis after boehmite treatment to make aluminum surfaces more corrosion resistant and pointed out that boehmite layers produced with the standard treatment, i.e., by using hot water or steam, are too thin and lack hardness and fine texture. Min and Webb [55] observed a loss of wettability due to detachment of the unstable boehmite layer from the surface. According to Godinez et al. [10], at temperatures higher than approximately 150 °C, diaspore structures might form and separate from the boehmite

structures. (Super)hydrophilic surfaces were also found to be more prone to contamination by impurities in the boiling liquid or in the air [21]. Jones and Garimella [64] observed a decreased heat transfer coefficient during the boiling of water on aluminum. Furthermore, they also noticed some deposits precipitated on the surface after the first experimental run and related the changes in the heat transfer coefficient to contamination and the level of oxidation of the surfaces.



Figure 3. Pure water boiling curves on the untreated reference surface (**a**) and surfaces etched for 5 min (**b**), 10 min (**c**) or 15 min (**d**).

The microcavity surface A5 exhibited the most stable behavior with insignificant deviations between consecutive measurements. Consequently, water measurements were discontinued after three runs. Even though the surrounding areas underwent the same changes as the untreated surface, no notable changes of the boiling performance were detected. A significantly enhanced boiling performance was observed on surface A5 and is attributed to microcavities serving as preferential active nucleation sites, which can be activated at low superheats. Since the nucleation process does not rely on submicron defects present on the untreated surface, the performance of the A5 surface does not change, even though the morphology and composition of the surrounding areas are affected by exposure to multiple instances of CHF incipience. From this, it can be concluded that the microcavities present on the surface A5 are the chief factor affecting nucleate boiling heat transfer, which is in agreement with previous studies, where microcavity surfaces were used to enhance the pool boiling heat transfer performance [15–19].

In contrast with the A5 surface, the micropeak surfaces A10 and A15, where the surface morphology was completely changed due to longer exposure to the etching process

and uniform corrosion, exhibited a very unstable boiling performance. Significant shifts of boiling curves towards higher superheats were observed during consecutive measurements. On surface A10, the curves shifted to approximately a 15 K higher superheat, while the CHF value decreased slightly. The changes were somewhat more pronounced on the A15 surface, where the boiling curves shifted roughly 17 K towards higher superheats. The initial instability of the surface is attributed to surface chemistry changes within the micropeak structure, where a boehmite layer in the form of nanoneedles grows due to exposure to hot water. Overall, these mostly negative changes of the heat transfer parameters (mainly the decrease in HTC) can be attributed to complex changes of micropeak structure formed during the etching process. The SEM images taken before boiling on A10 and A15 surfaces show noticeable surface transformations compared with the images taken after boiling. In Figure 4, an example is shown for surface A15 and its equivalent, which was not exposed to boiling. It is likely that the growth of boehmite nanoneedles in the pores alters the dynamics of wicking across the porous structure and also possibly raises the energy barrier for nucleation by reducing the number of open pores, which are able to form or entrap a vapor nucleus. Additionally, the formed surface layer of boehmite is possibly unstable, as discussed previously, which influences its heat transfer characteristics by increasing the heat transfer resistance inside the porous structure.



Figure 4. SEM images of the etched surface A15 before (a) and after boiling (b).

A comparison of the first and the last boiling curve recorded for each surface is shown in Figure 5. It is evident that long etching times, which completely change the morphology of the boiling surface, impact the heat transfer coefficients negatively since the boiling curves for surfaces A10 and A15 are shifted to the right relative to the untreated reference surface. This might be caused by surface superhydrophilicity, which is known to shift the boiling curve towards higher superheat values due to the higher energy barrier for nucleation. The shift is exacerbated due to the absence of preferential nucleation sites on the A10 and A15 surfaces. Consecutive experimental runs on the aforementioned surfaces shifted the boiling curves further towards higher superheats. On the other hand, surface A5 (fabricated using the shortest etching duration of 5 min) provided a significant enhancement of the HTC with both a significant increase in the CHF value and a considerable shift of the boiling curve towards lower superheats. On this surface, heat transfer coefficients of up to 137 kW m⁻² K⁻¹ were recorded, which marks a 165% improvement over the reference surface. The enhancement can be attributed to the microcavity structure characterized by an abundance of cavities with diameters in the micrometer range, which can serve as active nucleation sites for the pool boiling of pure water at atmospheric pressure, as

predicted by nucleation criteria [14]. Furthermore, the results agree with previous findings that an abundance of microcavities on the boiling surface provides many potentially active nucleation sites and, thus, greatly increases the heat transfer performance [14–16,18]. Additionally, no noticeable degradation and stable performance were recorded during consecutive experimental runs on the A5 surface.



Figure 5. First and last boiling curve recorded on each surface.

4.2. Effect of Hydrophobization

Two surfaces with different microstructures and boiling performances (A5 and A15) were tested in a hydrophobized state, in which they exhibit superhydrophobicity (outside of boiling conditions). These surfaces were denoted as A5H and A15H. The boiling performance of the said surfaces is compared with the performance of the untreated reference surface in Figure 6a. Both of the hydrophobized surfaces exhibited an enhanced heat transfer relative to the reference surface. Furthermore, the CHF on both surfaces remained largely the same as on the untreated surface, showing that the surfaces were properly degassed, which prevented an early formation of a vapor film, as recorded in certain other studies using poorly wettable boiling surfaces [3,65,66]. The comparison of three consecutive experimental runs on hydrophobized surfaces shows that the silane coating greatly limits the boiling performance's deterioration, which was significant for the hydrophilic surface A15. Hydrophobization of the untreated reference surface was not attempted since previous studies have shown that it has only a minor effect on the boiling heat transfer [16,56].

Figure 6b shows a comparison of the boiling performance of the hydrophobized surfaces with their hydrophilic counterparts and the untreated reference surface. The first experimental run is shown for all surfaces. The results indicate that the micropeak morphology, which is not tailored to promote nucleation and nucleate boiling through the presence of microcavities, does not enhance the boiling heat transfer in a superhydrophilic state (surface A15). After hydrophobization, a shift of the boiling curve towards lower superheats is achieved for surface A15H together with an earlier transition into the nucleate boiling regime, but the overall heat transfer enhancement is limited. The limited enhancement can also be attributed to the hydrophobized porous micropeak structure of the surface, which allows vapor spreading across the surface microstructure, which increases the heat transfer resistance. On the contrary, a significant boiling performance enhancement is achieved on surface A5 in a hydrophilic state since the surface is covered by many microcavities promoting nucleation at a low surface superheat. After hydrophobization, this enhancement is increased further, and exceptionally high values of the heat transfer coefficient are achieved on the A5H surface, together with the onset of nucleate

boiling at just 1.1 K of superheat. The CHF value is reduced for the A5H surface due to less intensive rewetting on the poorly wettable hydrophobized surface compared with both hydrophilic counterparts A5 and A15. This trend shows that a surface's microstructure and wettability have a concomitant effect on its boiling performance. Lower surface energy decreases the energy barrier for the onset of nucleation, which tends to shift the boiling curve towards lower surface superheat values, improving the heat transfer performance. However, this effect is limited if the surface morphology is not tailored to promote nucleation as well. When the surface morphology promotes nucleation and early onset of nucleate boiling is achieved, extreme heat transfer coefficients (over 300 kW m⁻² K⁻¹) can be achieved for specific experimental conditions.



Figure 6. Pure water boiling curves on hydrophobized surfaces A5H and A15H (**a**), comparison of the effect of microstructure change and hydrophobization on boiling performance (**b**) and comparison of the highest heat transfer coefficients recorded during boiling of pure water at selected heat fluxes (**c**).

A comparison of heat transfer coefficients at selected heat fluxes on both hydrophilic and hydrophobic surfaces is shown in Figure 6c. Furthermore, Table 2 lists the relative heat transfer coefficient enhancement compared with the untreated reference surface at the same heat flux values (e.g., A15 vs. REF) and also the relative enhancement achieved using hydrophobized surfaces compared with their hydrophilic counterparts (e.g., A15H vs. A15). In all cases, the performance comparison is made for the experimental run where the highest overall heat transfer coefficient on a given surface was recorded. At the lowest analyzed heat flux of 150 kW m⁻², both hydrophobized surfaces (A5H and A15H) have fully transitioned into the nucleate boiling regime and exhibit a much higher heat transfer coefficient compared with hydrophilic surfaces (A5, A15 and REF), which can also be attributed to high nucleation site density, as observed using high-speed imaging. The relative heat transfer coefficient enhancement provided at 150 kW m⁻² by hydrophobic surfaces compared with their hydrophilic counterparts is 179% and 327% for surfaces A15H and A5H, respectively. The hydrophobized microcavity surface A5H provides a heat transfer coefficient of 71 kW m⁻² K⁻¹ at 150 kW m⁻², which marks a 559% improvement over the untreated surfaces. The relative enhancement provided by surface A15H, which lacks the microcavity structure, decreases at higher heat fluxes. Above 500 kW m⁻², the hydrophilic microcavity surface A5 already outperforms the hydrophobized micropeak surface A15H. The overall highest heat transfer coefficient of $305 \text{ kW m}^{-2} \text{ K}^{-1}$ was achieved on the hybrid surface A5H near CHF incipience, which marks a 488% enhancement over the heat transfer coefficient recorded on the untreated reference surface at its respective CHF onset. Deviations from the average value of the heat transfer coefficient determined at the same heat fluxes from three consecutive experimental runs on surfaces with favorable stability (A5, A5H and A15H) were within the expanded measurement uncertainty of the heat transfer coefficient, demonstrating good repeatability of the results.

Table 2. Relative heat transfer coefficient enhancement achieved using functionalized surfaces at selected heat fluxes.

Heat Flux (kW m ⁻²)	A15 vs. REF	A15H vs. REF	A15H vs. A15	A5 vs. REF	A5H vs. REF	A5H vs. A5
150	+6%	+179%	+163%	+54%	+559%	+327%
500	-5%	+78%	+88%	+64%	+582%	+316%
1000	-5%	+34%	+41%	+90%	+583%	+260%
CHF	+5%	+12%	+7%	+165%	+488%	+122%

5. Boiling Performance Using Self-Rewetting Fluids

In this section, we present the investigation of the possible further enhancement of the boiling heat transfer of the functionalized aluminum surfaces using water-based mixtures of 1-butanol with mass fractions between 1 and 6 wt.%. This represents the third phase in our stepwise approach to boiling enhancement. Specifically, microcavity surfaces A5 and A5H, which exhibited the best performance using pure water, were evaluated alongside the untreated reference surface for comparison.

5.1. Effect of Self-Rewetting Fluid Concentration

As the boiling surfaces are rather prone to changes in their boiling behavior and performance, we performed experiments with SRFs on surfaces that were previously exposed to multiple instances of CHF incipience and exhibited stable boiling curves. The boiling curves recorded during two consecutive experimental runs using water (to ensure boiling curve stability) and using 1–6 wt.% of 1-butanol in water are shown in Figure 7a for the untreated reference surface, in Figure 7b for the hydrophilic surface A5 and in Figure 7c for the hydrophobic surface A5H.



Figure 7. Boiling curves for 1-butanol mixtures with 0–6 wt.% of butanol recorded on the untreated reference surface REF (**a**), etched hydrophilic surface A5 (**b**) and hydrophobized etched surface A5H (**c**).

In all cases, a shift of the boiling curves towards higher superheat values was recorded when using SRFs. A possible reason for this is the absence of surface defects (cavities) with suitable diameters for nucleation at lower superheats. Specifically, the addition of 1-butanol to water significantly reduces the surface tension of the mixture, which results in a reduced contact angle compared with water on the same surface. According to nucleation criteria, hydrophilic surfaces require smaller cavities (often in the submicron range) for nucleation at a low superheat and such cavities are mostly absent on the tested surfaces. Furthermore, the entrapment of vapor into cavities is less likely to occur when the (advancing) contact angle is very low, and the cavity is more likely to be wetted. An increased superheat resulted in a decreased heat transfer intensity, as evident from the lower HTCs. This is especially pronounced on the hybrid surface A5H, where very low superheat values achieved by an appropriate combination of surface microstructure and low surface energy are negated by the use of the low-surface-tension fluid, which increased the superheat by a factor of more than two at the highest tested concentrations. The use of SRFs also changed the CHF on all surfaces with reduced values being recorded on the functionalized surfaces A5 and A5H, but increased the values being observed on the untreated surface REF. Overall, the use of self-rewetting fluids shifted the boiling curves of the reference surface approximately 4 K towards higher superheats, where they reached a stable position at a concentration of 2 wt.% or more. On the other two surfaces, the increase in the concentration of 1-butanol in the mixture also resulted in the shift of the boiling curve towards higher superheat values, with surface A5 exhibiting a general shift between 2-6 K, while the boiling curves for surface A5H exhibited a gradual shift of 0.6–1.0 K for each wt.% of added 1-butanol.

The heat transfer coefficients for the boiling of pure water, 1 wt.% and 6 wt.% of 1-butanol at selected heat fluxes are compared in Figure 8a. On the untreated reference surface (blue group) the use of SRFs decreases the heat transfer coefficient for all analyzed heat flux levels except at CHF, which is due to the increase in the CHF value using SRFs, while the superheat at its incipience remains similar as for water. On both functionalized surfaces, the heat transfer coefficients steadily decreased with an increasing 1-butanol concentration, which is also noticeable from the shift of the boiling curves.



Figure 8. Comparison of heat transfer coefficients on surfaces REF, A5 and A5H for boiling of pure water, 1 wt.% or 6 wt.% 1-butanol mixture (**a**) and the relationship between the CHF value and mass concentration of 1-butanol for the same surfaces (**b**).

Figure 8b compares the CHF values on all three analyzed surfaces for all of the tested 1-butanol concentrations. The untreated surface exhibited a steady increase in the CHF with an increasing 1-butanol concentration and reached a steady value of approximately 1700–1750 kW m⁻² at 5 wt.%, marking an improvement of approximately 50% compared with the value for the boiling of pure water on the same surface. A significant decrease in the CHF (up to 300 kW m⁻²) was observed on functionalized surfaces A5 and A5H following the first addition of 1-butanol (1 wt.%). Further additions increased the CHF compared with the value for 1 wt. %, but the original CHF value for the boiling of pure water was not achieved, even at 6 wt.%. It is likely that a low concentration of 1-butanol does not provide strong-enough Marangoni flows, while the higher concentrations are able to provide a CHF value close to that for pure water, but at the expense of significantly higher superheat values due to a lower surface tension. Overall, the only recorded benefit of

using SRFs within this study is the increased CHF value on the untreated surface, while the heat transfer intensity was severely degraded on the functionalized surfaces A5 and A5H.

5.2. Comparison of Bubble Dynamics

Phenomena on and above the boiling surface during the boiling of pure water and SRFs were analyzed further using high-speed visualization. Figure 9 shows the bubble dynamics for the untreated reference surface, which was the only one positively influenced by the use of SRFs, at two different heat fluxes for pure water and two different concentrations of 1-butanol.



Figure 9. High speed snapshots of the boiling process on the untreated reference surface at two different heat fluxes during boiling of water (**left column**), 1 wt.% 1-butanol mixture (**middle column**) and 6 wt.% 1-butanol mixture (**right column**).

On this surface, morphological features, capable of promoting nucleation, are largely absent, resulting in relatively few active nucleation sites and greater bubble diameters. Big bubbles (diameter in excess of 6 mm during the boiling of pure water at 100 kW m⁻²) were also found to be more prone to coalescence on the untreated surface. Extensive horizontal coalescence leads to worse rewetting of dry parts of the surface [18,56] and eventually to vapor spreading over the surface and CHF incipience. The use of 1-butanol-based SRFs

significantly reduced the bubble departure diameters due to the lower surface tension and Marangoni flow, as is evident in the middle and the right column of Figure 9. Using a mixture with 1 wt.% 1-butanol content, the bubble diameters decreased to below 2.4 mm at 100 kW m⁻². At the highest tested concentration (6 wt.%), the bubble departure diameter was found to be below 0.6 mm at 100 kW m⁻². Figure 9 also shows that bubble coalescence becomes noticeably limited when SRFs are used as the working fluid. Therefore, it can be concluded that the observed CHF increase using SRFs on the untreated surface resulted from a lower bubble diameter and limited bubble coalescence compared with the boiling

from a lower bubble diameter and limited bubble coalescence compared with the boiling of pure water, where the bubbles were larger and prone to coalescence. The reduced coalescence and lower bubble diameters result from the lower surface tension of the SRFs compared with pure water and from the Marangoni flow induced by the surface tension gradient due to the preferential evaporation of the more volatile component.

Visualization of the boiling process and bubble dynamics on functionalized surfaces A5 and A5H is shown in Figures 10–12 for the boiling of pure water, 1 wt.% and 6 wt.% of 1-butanol. During the boiling of pure water (Figure 10), smaller vapor bubbles and a higher nucleation site density were observed for both functionalized surfaces compared with the untreated surface. Furthermore, both surfaces enter the nucleate boiling regime below 50 kW m⁻². Specifically, the bubble diameters of non-coalesced bubbles for the boiling of pure water at 100 kW m⁻² were measured to be below 2 mm and 0.8 mm on surface A5 and A5H, respectively.



Figure 10. High speed snapshots of the boiling process on the A5 (**left column**) and A5H (**right column**) surfaces at three different heat fluxes during boiling of water.

Using a 1 wt.% water mixture of 1-butanol, the bubble diameters were reduced significantly, which is evident from Figure 11. At this concentration, departure diameters of below 1.0 mm were recorded on surface A5 and below 0.3 mm on surface A5H at 100 kW m⁻². Additionally, bubble coalescence on and above the boiling surface was substantially reduced, as is evident from the comparison of Figures 10 and 11.

Finally, using a 6 wt.% water mixture of 1-butanol, the bubble diameters decreased further and reached values of below 0.5 mm on surface A5 and below 0.2 mm on hybrid surface A5H at 100 kW m⁻². This is depicted in Figure 12 at three different heat fluxes.



Figure 11. High speed snapshots of the boiling process on the A5 (**left column**) and A5H (**right column**) surfaces at three different heat fluxes during boiling of 1 wt.% 1-butanol mixture.



Figure 12. High speed snapshots of the boiling process on the A5 (**left column**) and A5H (**right column**) surfaces at three different heat fluxes during boiling of 6 wt.% 1-butanol mixture.

Based on the high-speed visualization, we can conclude that the observed trends of the CHF changes are a consequence of a complex combination of multiple effects of the surface microstructure, wettability and Marangoni flows on the boiling surface during bubble growth. SRFs only enhanced the CHF on the untreated surface, where a nucleation-promoting microstructure is absent and SRFs enhance boiling performance through decreased bubble departure diameters and limited coalescence. Even though the bubble diameters are decreased for SRFs, their values still remain considerably larger than on the functionalized surfaces A5 and A5H, where nucleation augmentation is already achieved by an etching-induced microstructure (both surfaces) and a lower surface energy due to hydrophobization (surface A5H). On surfaces A5 and A5H, the high nucleation site density and limited (i.e., smaller) bubble diameters are already evident during the boiling of pure water. Hence, the use of a low-surface-tension working fluid decreases the heat transfer intensity due to a further reduction in the bubble size, which limits the amount of energy removed by a single bubble. Furthermore, the several millimeters thick layer of non-coalesced bubbles above the surface (e.g., at 6 wt.% of 1-butanol on hybrid surface A5H as shown on the right side of Figure 12) limits the inflow of fresh liquid to the boiling surface [67], which reduces the rewetting intensity and potentially contributes to decreased CHF values.

A phenomenon, noticeable in Figures 9 and 12, was also observed when SRFs were used as the working fluid. On the untreated reference surface REF and hydrophilic surface A5, nucleation at high 1-butanol concentrations often only started on a part of the boiling surface and initially did not spread across the entire surface. This is especially noticeable in the left part of Figure 12 and was also identified to be the cause of a slight boiling curve inversion at a low heat flux, which is observable in Figure 7a,b for most 1-butanol concentrations. When a sufficiently high heat flux was reached (approximately 200–400 kW m⁻²), nucleation spread across the entire surface and the surface superheat decreased noticeably, since nucleate boiling was present on the whole surface. The improved heat transfer performance for the reference surface can also be attributed to the more intensive rewetting action, which limits the spreading of vapor across the surface.

Additionally, bubble nucleation frequencies were analyzed using the high-speed footage. The analysis was conducted at 100 kW m⁻² where all three analyzed surfaces (REF, A5 and A5H) have several activated nucleation sites, but the nucleate boiling was not yet too intense to identify individual bubbles prior to coalescence. The results are shown in Figure 13 as average frequencies of 4–8 active nucleation sites, together with the standard deviation of the measurements. For the boiling of pure water, both of the functionalized surfaces exhibit much higher bubble nucleation frequencies than the untreated reference surface. Specifically, a bubble nucleation frequency of 51 ± 15 Hz was observed on the untreated surface, while the hydrophilic microcavity surface A5 enhanced the frequency to 86 ± 40 Hz. Hydrophobized surface with microcavities A5H exhibited even higher bubble nucleation frequencies of 255 ± 54 Hz. The results agree with previous observations that smaller bubbles form on the functionalized surfaces with the low surface energy (hydrophobic) coating on the A5H surface further contributing to faster bubble growth cycles producing significantly smaller vapor bubbles. The use of a self-rewetting mixture of 1 wt.% 1-butanol in water increased the bubble nucleation frequencies on all analyzed surfaces with the most notable increase being observed on the A5 surface. Finally, the highest SRF concentration (6 wt.% of 1-butanol) further increased bubble nucleation frequencies on all surfaces. Nucleation frequency values of 379 ± 104 Hz were observed on the reference surface, marking a more than 600% increase compared to the boiling of pure water on the same surface. Even higher frequencies of more than 500 Hz were detected on the functionalized surfaces A5 and A5H, corresponding to extremely small bubbles forming at 6 wt.% 1-butanol concentration, as evident from Figure 12. Overall, the bubble nucleation frequency confirmed previous observations that (i) functionalized surfaces produce smaller vapor bubbles at a higher frequency and (ii) the use of SRFs further increases the bubble nucleation frequency, while the departure diameter decreases significantly. The observed trends can largely be attributed to the lower overall surface tension of the SRFs in comparison with pure water. It should be noted, however, that the analysis of high-speed footage is difficult due to the very large density of active nucleation sites and very small bubble diameters obscuring the identification and observation of individual bubbles, with

both effects arising when SRFs are used instead of pure water. Additionally, in some cases, the entire surface was not activated until high heat flux was reached (e.g., boiling of 6 wt.% 1-butanol mixture on the A5 surface at 100 kW m⁻², as observable in Figure 12).



Figure 13. Bubble nucleation frequencies at 100 kW m⁻² on three different surfaces for boiling of either pure water or a water mixture containing 1 wt.% or 6 wt.% 1-butanol.

The main reason why many articles report positive effects of SRFs in heat pipes and microchannels, but more rarely under pool boiling conditions, is the effect of the limited geometry in which boiling/evaporation takes place. Vapor bubbles in heat pipes and microchannels are mostly confined due to the geometry of the boiling vessel/surface, where the use of SRFs can provide a thin liquid film between the bubble and the heating wall, thus enhancing heat transfer. However, under pool boiling conditions, the bubbles are mostly unconstrained, which reduces the positive effects of SRF use. Furthermore, the lower surface tension of SRFs also lowers the bubble departure diameter. This reduces the area under and around the growing bubble that is under the influence of the Marangoni flow. If the bubble diameter is additionally decreased due to surface modification (as is the case with functionalized surfaces A5 and A5H), the positive effects of SRFs are diminished even further. Consequently, the CHF is not enhanced and the major effect of using SRFs on surfaces developed within this study is an increased surface superheat and a reduced heat transfer performance.

6. Conclusions

A stepwise approach to surface modification was successfully demonstrated through the development of hybrid functionalized surfaces. A short duration of a chemical etching treatment was found to induce pitting corrosion, generating microcavities with optimal diameters for nucleation under given boiling conditions. The evaluation of the boiling performance of developed etched surfaces using pure water revealed that surface functionalization using short etching times, resulting in the creation of microcavity surface morphology, is preferable to longer etching times, which create micropeak surface morphology lacking nucleation-promoting surface features (vapor-trapping cavities).

The hydrophobization of microcavity and micropeak surfaces showed that an additional enhancement of heat transfer performance can be achieved by lowering the surface energy. The highest boiling performance was recorded on a hydrophobized microcavity surface, where the heat transfer coefficient reached 305 kW m⁻² K⁻¹ (enhancement of 488% over the untreated surface), while the CHF values remained close to that of the untreated

reference surface. Furthermore, complete transition into nucleate boiling is achieved at a very low superheat (~1.1 K), allowing for efficient heat dissipation, even at low heat fluxes. The results on hydrophobized etched surfaces clearly show that tailoring both the surface microstructure to promote nucleation and the surface energy to lower the energy barrier for the onset of nucleate boiling has a concomitant positive effect on boiling performance.

The boiling of self-rewetting fluids on the untreated reference surface provided an increased CHF, reduced bubble diameters, increased nucleation frequencies and limited bubble coalescence compared with the boiling of water. However, for both tested functionalized surfaces, the heat transfer coefficient deteriorated, and the CHF decreased relative to the boiling performance obtained with pure water. The boiling of self-rewetting fluids, therefore, did not enhance heat transfer on developed surfaces, which were tailored to promote nucleate boiling, as bubble diameters and coalescence were already reduced through surface functionalization. An additional reduction in bubble diameter induced by the self-rewetting fluid, therefore, resulted in a lower heat transfer performance of both microcavity surfaces.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/pr9061058/s1; Section S1: Numerical validation of the dynamic measurement method; Section S2: Experimental validation of the dynamic measurement method.

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Nomenclature

Latin symbols

f	bubble nucleation frequency (Hz)	
h	heat transfer coefficient (W m ^{-2} K ^{-1})	
k	thermal conductivity (W m ^{-1} K ^{-1})	
ġ	heat flux (W m $^{-2}$)	
T	temperature (°C)	
и	uncertainty	
x	distance (m)	
Greek symbols		
Δ	difference	
Subscripts		
f	fluid	
s	sample	
sat	saturated	
W	wall	

Abbreviations	
Ax	aluminum surface etched for <i>x</i> minutes
AxH	aluminum surface etched for <i>x</i> minutes with subsequent hydrophobization
CHF	critical heat flux
CVD	chemical vapor deposition
HTC	heat transfer coefficient
ONB	onset of nucleate boiling
PEEK	polyether ether ketone
REF	untreated reference sample
SEM	scanning electron microscope
SRF	self-rewetting fluid

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