# Fabrication Optimization of Ultra-Scalable Nanostructured Aluminum-Alloy Surfaces

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ABSTRACT: Aluminum and its alloys are widely used in various industries. Aluminum plays an important role in heat transfer applications, where enhancing the overall system performance through surface nanostructuring is achieved. Combining optimized nanostructures with a conformal hydrophobic coating leads to superhydrophobicity, which enables coalescence induced droplet jumping, enhanced condensation heat transfer, and delayed frosting. Hence, the development of a rapid, energy-efficient, and highly scalable fabrication method for rendering aluminum superhydrophobic is crucial. Here, we employ a simple, ultrascalable fabrication method to create boehmite nanostructures on aluminum. We systematically explore the influence of fabrication conditions such as water immersion time and immersion temperature, on the created nanostructure morphology and resultant nanostructure length scale. We achieved optimized structures and fabrication procedures for best droplet jumping performance as measured by total manufacturing energy utilization, fabrication time, and total cost. The wettability of the nanostructures was studied using the modified Cassie-Baxter model. To better differentiate performance of the fabricated superhydrophobic surfaces, we quantify the role of the nanostructure morphology to corresponding condensation and antifrosting performance through study of droplet jumping behavior and frost propagation dynamics. The effect of aluminum substrate composition (alloy) on wettability, condensation and antifrosting performance was investigated, providing important directions for proper substrate selection. Our findings indicate that the presence of trace alloying elements play a previously unobserved and important role on wettability, condensation, and frosting behavior via the inclusion of defect sites on the surface that are difficult to remove and act as pinning locations to increase liquidsolid adhesion. Our work provides optimization strategies for the fabrication of ultrascalable aluminum and aluminum alloy superhydrophobic surfaces for a variety of applications.

KEYWORDS: superhydrophobic, boehmite, jumping droplet, frosting, nanofabrication, optimization, defect

## INTRODUCTION

The past two decades have seen a paradigm shift in superhydrophobic (SHP) surface utilization from an esoteric emerging research material to a rapidly increasing industrial presence with impact of multiple applications.<sup>1-4</sup> Superhydrophobic surfaces can be fabricated with single-tier or multitier micro/nanostructures coupled with a conformal hydrophobic (lowering surface energy) coating to trap air between the liquid–solid interfaces. The combined effects of surface roughness, hydrophobicity and air trapping on SHP

surface performance lead to apparent advancing contact angles  $(\theta_a^{app})$  and apparent receding contact angles  $(\theta_r^{app})$  of water droplets that exceed 150°, and contact angle hysteresis ( $\Delta \theta$  =

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**Figure 1.** Schematic of the fabrication procedure used to create superhydrophobic (SHP) aluminum (Al) surfaces through hot deionized (DI) water immersion. (a) Substrate cleaning. The polished Al alloy (Al-6061) substrates are cleaned with a standard degreasing procedure. For Al films on different substrate materials, high purity Al (99.999%, Hi-Al) is sputtered on a silicon wafer and used as-is after deposition. SEM images showing the cleaned sample surfaces for the Al-6061 (bottom left) and Hi-Al on Si (bottom right). Scale bars: 500 nm. (b) Nanostructuring. Cleaned samples are immersed in hot DI water for 1 min to create boehmite (AlO(OH)) nanostructures shown in the SEM images for Al-6061 (bottom left) and Hi-Al on Si (bottom right). Scale bars: 500 nm. (c) Functionalization. To render the substrates hydrophobic, a conformal SAM is deposited on top of the boehmite nanostructures through atmospheric pressure chemical vapor deposition (CVD). Resulting apparent advancing water contact angles approach  $165^{\circ}$  (bottom image). Scale bar: 100  $\mu$ m.

 $\theta_a^{app} - \theta_r^{app}$ ) below 10°.<sup>5</sup> These characteristics of SHP surfaces lead to unique interactions between liquid droplets and the surface, such as droplet bouncing,<sup>6,7</sup> directional droplet transport,<sup>8,9</sup> rapid shedding<sup>10</sup> and dropwise condensation,<sup>11</sup> to name a few. A particular phenomena of intense interest is coalescence-induced droplet jumping due to its potential to enhance the efficiency of multiple processes.<sup>11–15</sup>

When water vapor condenses on a cold, suitably designed SHP surface, two or multiple microscale droplets coalescence together and can jump away from the surface in the perpendicular direction and independent of gravity, due to surface-to-kinetic energy transfer.<sup>16,17</sup> Jumping droplet condensation is a recently discovered mode of condensation which can be harnessed to remove micro/nanoscale condensed water droplets passively to enhance condensation heat transfer when compared with state-of-the-art dropwise condensation. A second attractive application of jumping droplet condensation is its delay of frost and ice formation on the surfaces.<sup>18-21</sup> Specifically, coalescence induced droplet jumping delays heterogeneous ice nucleation as well as ice bridge propagation via the synergistic combination of coalescence-induced droplet jumping and frost halo formation.<sup>21,22</sup> Past work had shown that the propagation of interdrop frost fronts on suitably developed SHP surfaces can be reduced by up to 70% when compared to smooth hydrophobic surfaces due to the reduced droplet size distribution stemming from droplet jumping as well as small droplet evaporation caused by vapor pressure gradients.<sup>21,23</sup>

Aluminum and its alloys are widely used in various applications such as heat exchangers, structural components, and framing materials due to their combination of low density compared to alternatives such as copper and steel, high specific strength, high thermal conductivity, and low cost. Hence, the development of optimized structures on aluminum surfaces in

a rapid, energy effective, and highly scalable fashion that ensure jumping-droplet phenomena offers great potential energy related applications. Until now, a variety of fabrication methods have been used to create micro/nanoscale roughness to create superhydrophobicity on aluminum surfaces, such as spray coating,<sup>24,25</sup> chemical etching,<sup>26–28</sup> oxidation,<sup>29–32</sup> drop casting,<sup>33,34</sup> electrochemical deposition,<sup>35,36</sup> anodization,<sup>37–39</sup> and sol-gel coating.<sup>30,31,40</sup> Although SHP aluminum surfaces have clearly been identified as an emerging method to enhance the efficiency of various applications, the majority of developed micro/nanostructured SHP surfaces have been fabricated using expensive techniques, time-consuming methods, processes having poor scalability. These methods present a barrier to the implementation of SHP surfaces in real applications.<sup>41-43</sup> The aluminum hot water immersion method has potential for scale-up which is a key point to enable SHP surface technology to penetrate to real world applications. The hot water immersion method depends only on the fabrication infrastructure (i.e., immersion bath size). It is well-known that the reaction product of aluminum and hot water is boehmite.<sup>43–49</sup> In the past, research has focused on creating a boehmite layer on aluminum to act as a barrier to corrosion or as a bonding enhancement medium.  $^{46,50-52}$  Recently, researchers have noted the fabrication simplicity and high scalability of the hot water immersion method, especially boehmite based structured surfaces.<sup>53</sup> This has led to the use of boehmite nanostructures for a wide range of interfacial engineering applications, such as boiling,<sup>54,55</sup> liquid infused surface fabrication (LIS),<sup>56,57</sup> and anticorrosion.<sup>3</sup>

Although significant progress in the scalable fabrication of boehmite structures has been achieved, fundamental questions remain pertaining to the ability to achieve high-performance metal-based SHP surfaces for applications using jumping droplet condensation. These include identifying the optimum surface morphology and structure length scale, understanding the effect of structure order versus disorder, and how to best characterize structures and harness them to achieve jumpingdroplet performance on industrially relevant pure metals and metal alloys. Hence, to enable the penetration of jumping droplet SHP aluminum surfaces to real-world applications, indepth theoretical understanding bridging the nanostructure morphology and jumping droplet phenomena as well as advanced mass production methods for scalable, reliable and cost-effective fabrication approaches are needed.

In this study, we systematically study the simple and ultrascalable fabrication of boehmite ( $\gamma$ -AlO(OH)) nanostructures on a range of aluminum substrates (Figure 1) through hot water immersion to achieve optimized jumping droplet condensation and antifrosting performance. We rigorously explore the influence of fabrication conditions such as water immersion time and immersion temperature, on the created nanostructure morphology and boehmite nanostructure length scale. We achieve optimized structures and fabrication procedures for best performance considering a multitude of parameters such as total energy utilization during manufacturing, fabrication time, and total cost. The nanostructured aluminum surfaces are functionalized with thin and conformal hydrophobic self-assembled monolayer (SAM) coatings to enable superhydrophobicity and characterized using water contact angle microgoniometry. Nanostructure morphology and length scales were characterized through image processing of SEM results, followed by theoretical validation using the modified Cassie-Baxter model. To better differentiate performance of the fabricated surfaces, we evaluated jumping droplet condensation and antifrosting performance through microscopic phase change visualization experiments. We connect the nanoscale structure morphology to corresponding condensation and antifrosting performance, thus, enabling the identification of optimized fabrication process conditions. Furthermore, the effect of aluminum substrate composition (aluminum alloy type) on wettability, condensation and antifrosting performance is investigated to provide direction to proper substrate selection guidelines. Our findings indicate that the presence of trace alloving elements play a previously unidentified role on wettability, jumping droplet condensation, and frosting behavior via the inclusion of defects on the surface that are difficult to remove and which act as pinning locations to increase liquid-solid adhesion. Our work provides optimization strategies to fabricate ultrascalable aluminumbased SHP surfaces for a variety of energy and water applications.

#### METHODS

Aluminum Alloy Surface Fabrication. Mirror-like-polished aluminum 6061 alloy (Al-6061, 1655T1, McMaster-Carr) were chosen as the main substrate of interest due to its low native roughness and the prevalent use of 6061 alloy. The as-received alloy sheet with thickness of 0.81 mm was cut into 25.4 mm × 25.4 mm coupon sizes. Before conducting the standard cleaning process, the protective film on the polished side of the Al-6061 samples were peeled off and the residual adhesive on the surfaces were removed by applying a commercial grease remover (Orange Blast, Greased Lightning). Briefly, the adhesive cleaner was sprayed on each sample generously, followed by rubbing of the sample surface with a clean sponge and rinsing in warm tap water. Complete removal of the adhesive residue was confirmed by characterization of the apparent contact angle, which transitioned from nonwetting ( $\theta \approx 90^\circ$ ) prior to cleaning, to completely wetting ( $\theta \approx 0^\circ$ ) after cleaning. A thin layer of

grease remover remains on the sample surface after the adhesive residue removal process, thus making the aluminum surface completely wetting. The grease remover residue is subsequently removed by the following the standard cleaning process.

After removing the adhesive, all coupons were cleaned through a standard cleaning process (Figure 1a). The samples were first sonicated (Branson 2800 Ultrasonic Bath, Branson) in acetone (CAS No. 67–64–1, Sigma-Aldrich), followed by isopropyl alcohol (IPA, 67–63–0, Sigma-Aldrich), and followed by ethanol (CAS No. 64–17–5, Sigma-Aldrich) for 5 min each. After sonication, the samples were rinsed with deionized (DI) water (CAS No. 7732–18–5, Sigma-Aldrich). All samples were dried in a clean nitrogen (N<sub>2</sub>) gas stream.

To create boehmite nanostructures on the Al-6061 surfaces, cleaned sample coupons were immersed into hot water bath (Figure 1b). The water temperature in the bath is controlled by a hot plate (C-MAG HS 7, IKA) and an electronic contact thermometer (ETS-D5, IKA). To eliminate bubbles during sample immersion, a magnetic stirrer is used with 800 rpm. The samples were immersed in the water bath right after the target temperature is reached and maintained for a target immersion time for each sample. After immersion, the sample coupons were rinsed in DI water followed by drying under a clean N<sub>2</sub> gas stream. SEM images of the typical boehmite nanostructure created on an Al-6061 surface is shown in Figure 1(b).

To functionalize the surfaces, (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) Trimethoxysilane (HTMS, CAS No. 83048-65-1, SIH5841.5, Gelest) was deposited via chemical vapor deposition (CVD, Figure 1c). If there was no trimethoxysilane coating, because the boehmite surface is naturally hydrophilic, the whole boehmite surface would show liquid wicking properties and thus the surface would be superhydrophilic. The nanostructured samples were placed in a beaker container with a vial of 1 mL of HTMS-toluene mixture solution (5% v/v). An aluminum foil lid was placed on top to seal the beaker, followed by heating in an atmospheric pressure oven (Thermo Scientific BF51732C-1) at  $85 \pm 1$  °C for 3 h. To investigate effect of deposition time on wettability, we also ranged the HTMS SAM coating time from 1 min to 4 h. This process allowed for a highly conformal coating on the structured surfaces. The thickness of the HTMS layer was measured to be 2.1  $\pm$  0.1 nm using spectroscopic ellipsometry (J.A. Woollam VASE), which is close to the theoretical chain length of a fully extended HTMS monomer (~2 nm). The measurement was performed on an HTMS-coated polished silicon wafer with a native oxide layer (P-type, 2 in., <100> orientation, 0-100  $\Omega$ -cm, University Wafer). HTMS thickness measurement details are included in Supporting Information (SI) Figure S1.

In order to explore the effect of elemental composition of the aluminum alloy, six different types of aluminum alloys: Al-1100 (88685K91, McMaster-Carr), Al-2024 (88835K12, McMaster-Carr), Al-3003 (8973K304, McMaster-Carr), Al-5052 (88895K102, McMaster-Carr), Al-6061 (89015K11, McMaster-Carr) and Al-7075 (89015K11, McMaster-Carr) were selected with a general roughness which is different from the aforementioned polished Al-6061 samples. All Al alloy samples were treated with the same cleaning, nanostructuring and functionalization process discussed above.

**High Purity Aluminum Sample Fabrication.** To create high purity Al, a thin Al (99.999%, Hi-Al, Figure 1) layer was deposited on a smooth silicon wafer ( $\langle 100 \rangle$ , 350  $\mu$ m, 444, University Wafer) in a sputtering system (AJA Orion-8 Magnetron) with RF power of 200 W. The base pressure of the sputter system was maintained at 3 mTorr and Argon gas was introduced to generate plasma with mass flow rate of 30 sccm. These conditions gave a uniform deposition rate of 0.7 Å/s. The thickness of the deposited Al layer was controlled by monitoring the sputtering time. SEM images in Figure 1a show the surface morphology of the as-deposited Al film on the silicon wafer surface. The as deposited sample was nanostructured and functionalized without cleanings. The typical boehmite nanostructure created on the high purity Al film is shown in Figure 1(b) and is denoted as Hi-Al herein.

Scanning Electron Microscopy (SEM). SEM analysis of the fabricated samples was conducted with a Hitachi S4700 scanning electron microscope with imaging voltage of 10 kV or 15 kV. Since



**Figure 2.** SEM images of boehmite nanostructures on Al-6061 surfaces with varying (a) hot DI water immersion time (fixed water temperature at  $T_i = 90$  °C) and (b) hot DI water temperature (fixed immersion time of  $t_i = 10$  min). See SI Figure S4 for full data set.

boehmite nanostructures are nonconductive, a thin layer (<3 nm) of gold–palladium (Au–Pd) was sputtered on to the samples prior to imaging to avoid charging and image distortion.

**Energy-Dispersive X-ray Spectroscopy (EDS).** EDS analysis of the fabricated samples was conducted on the Hitachi S4700 SEM. To study the chemical composition on the Al alloy surfaces, wide band EDS point and line scans were performed on a single microscale defect before and after nanostructuring.

Contact Angle Measurement. The surface wettability (contact angle) of all structured surfaces was characterized immediately after functionalized with the SAM. Contact angle measurements of  $\approx 100$ nL droplets on all samples were performed using a microgoniometer (MCA-3, Kyowa Interface Science Co., Ltd.). A piezoelectric dispenser was set 5-10 mm above the sample surface and the dispenser would dispense microscale droplets on the surface, allowing droplets to accumulate into a larger droplet to measure apparent advancing contact angle ( $heta_a^{\mathrm{app}}$ ). To measure apparent receding contact angle  $(\theta_r^{app})$ , the dispenser was shut off for allowing the water droplet to evaporate. Then, the evaporating droplet images were recorded continuously until the droplet evaporated completely. At the initial evaporation stage, the water droplet is pinned on the surface with a constant base and a decreasing contact angle. The  $\theta_r^{app}$  was determined as the minimum contact angle before the base of the water droplet began to shrink (recede).<sup>59</sup> At least five measurements were performed on spatially varying location of each sample surface. All contact angle data were analyzed using the image processing software (FAMAS software, Kyowa Interface Science Co., Ltd.) with the circle fitting method which is implemented in it.

Condensation and Frosting Experiments. Condensation and frosting experiments were performed on a customized top-view optical microscopy setup implemented with a temperature controllable cold-stage. A high-speed camera (Phantom v711, Vision Research) and a high-resolution camera (DS-Qi2, Nikon) were attached to the upright microscope (Eclipse LV100, Nikon) for topview analysis of jumping droplet dynamics and frost propagation dynamics. Imaging was performed with a 20× (TU Plan Fluor EPI, Nikon) objective. Test samples were horizontally attached on a coldstage (PE-120, Linkam) and the sample surface temperature was set to  $T_{\rm w}$  = 1.0 ± 0.5 °C for condensation experiments and  $T_{\rm w}$  = 15.0 ± 0.5 °C for frosting experiments. All the experiments were performed in ambient laboratory temperature of  $T_{air}$  = 23 ± 1 °C and relative humidity ( $\Phi$ ) of  $\Phi$  = 40–60%, which were recorded and logged by a temperature and relative humidity transmitter (HX93BDV0, Omega). The supersaturation  $(S = \Phi P_{sat} (T_{air})/P_{sat}(T_w))$  of the condensation and frosting experiments correspond to 2.0 to 8.5.

The minimum departing droplet size during jumping  $(D_{\min})$  was measured by applying the breath figure method. The breath figure method was applied on the low temperature  $T_{\rm w} = 1.0 \pm 0.5$  °C) sample surface in a short time (~1 s) period. The breath figure method gave high supersaturation condition which could initiate high nucleation density, thus reducing the mean separation distance between nucleation sites to observe droplet jumping of small droplets. Exhaled human breath is composed of CO<sub>2</sub> and saturated water vapor at  $\approx$ 36 °C which corresponds to  $T_{\rm air} \approx$  35 °C,  $\Phi \approx$  100%, and supersaturation degree  $S = \Phi P_{sat} (T_{air})/P_{sat}(T_w) \approx 8.56$ . After applying breath figures on the sample surface, the high-speed camera captured jumping dynamics at 1000 frames per second (fps). The rate of jumping (N) was acquired by counting the jumping rate in the observation area with a steady jumping condensation time period for 10 min under ambient laboratory temperature conditions. Subsequently, the data was converted to calculate the jumping rate per unit area using the sample surface area and recording time. To measure the frost velocity during frosting experiments  $(V_{\text{frost}})$ , a fixed observation point on all samples was used to eliminate the possible uncertainties due to edge effects. In the meantime, the average  $V_{\rm frost}$ was quantified by calculating the ratio of the average width of the field-of-view (square root of observed field view area, (264  $\mu$ m × 176  $\mu$ m)<sup>0.5</sup> = 215.6  $\mu$ m) to the time duration for the frost to propagate the entire field of view.

## RESULTS AND DISCUSSION

Nanoscale Surface Morphology and Wettability Characterization. The boehmite on the aluminum substrate was produced in situ during the hot water immersion process. Aluminum and Al alloys are very active and form very thin layers of amorphous oxide and hydroxide on the free surface (see SI Figure S2 for XPS characterization results). When the Al or Al alloy is immersed in hot deionized water with the temperature higher than room temperature, the oxide film is first hydrolyzed. Subsequently, the film dissolves to yield a soluble species which either remains in solution or precipitates as a porous hydroxide having an extremely small particle size. Then the Al or Al alloy substrate starts to react with the water to form the observed boehmite nanostructures. During the reaction, Al ions diffuse to the free interface to react and the oxygen and hydrogen is supplied from the water in contact with the free interface. After the reaction is complete and approximately 150 nm of boehmite is formed owing to the 2 h of reaction time, the oxidation reaction stops and the boehmite layer ceases to grow (see SI Figure S3). Figure 2a shows SEM images of boehmite nanostructures on Al-6061 surfaces with varying hot DI water immersion time  $(t_i)$  at a fixed immersion water temperature  $(T_i)$  of 90 °C. The immersion time was varied from 5 s to 120 min (see Methods for fabrication details). At short immersion times  $(t_i < 20 \text{ s})$ , the surface



**Figure 3.** Effect of (a) immersion time (fixed  $T_i = 90$  °C) and (b) immersion DI water temperature (fixed  $t_i = 10$  min) on apparent advancing contact angle ( $\theta_a^{\text{app}}$ ) for Al-6061 samples. (c) Effect of DI water immersion time and (d) DI water immersion temperature on average boehmite nanostructure length scale (l) and surface solid fraction ( $\phi_s$ ). The l and  $\phi_s$  are calculated through image processing from multiple SEM images taken for each sample (SI Figures S4 and S5).

remained as smooth as the bare Al. When the immersion time exceeded 20 s, discrete boehmite nanostructures began to appear on the surface (see SI Figure S4). The delayed formation confirms that before the Al substrate reacts with the hot water to create boehmite nanostructures, the smooth amorphous oxide film needs to be removed by the hydration process in order to promote the Al-water reaction. With increasing immersion time, the morphology changed to an intersected platelet structure with denser nanostructures. To investigate the effect of immersion temperature on nanostructure formation, we fixed immersion time at  $t_i = 10$  min and varied immersion temperature from 40 °C <  $T_i$  < 90 °C. As shown in Figure 2b, the nanostructures started to appear on surface when the temperature exceeded 60 °C and grew denser as well. After functionalization of the surface with a thin hydrophobic SAM (see Methods), the wetting properties of each fabricated surface was characterized through microgoniometry (see Methods). Note, the silane monolayer has a thickness of a few nanometers and it is negligible when compared to the length scale of boehmite nanostructures (hundreds nanometer thick). Hence, when viewing the structures in SEM images before and after coating, there is no discernible difference between the two roughness morphologies. Figure 3a,b show the effect of immersion time (fixed  $T_i = 90$  °C) and immersion temperature (fixed  $t_i = 10$ min) on the apparent advancing contact angle  $(\theta_a^{app})$  and contact angle hysteresis ( $\Delta \theta$ ), respectively. The  $\theta_a^{app}$  increased to  $\approx 165^{\circ}$  when  $t_i > 40$  s and  $T_i > 70 \,^{\circ}$ C. The first increment of  $\theta_a^{app}$  resulted from the formation of discrete boehmite structures which act to increase surface roughness (see SEM images with  $t_i = 20$  and 40 s in SI Figure S4). The results indicate that droplets begin to reside in the Cassie-Baxter

(CB) wetting state when the immersion time exceeds 40 s, whereas droplet prefer the Wenzel wetting state when the surfaces were processed for shorter times which resulted in discrete and low-roughness nanostructures.<sup>5</sup> In contrast,  $\Delta\theta$  decreased to a minimum value ( $\approx$ 5°) when the  $t_i = 5$  and 10 min, after which  $\Delta\theta$  began to increase reaching values as high as  $\Delta\theta\approx 25^{\circ}$  at  $t_i = 120$  min. This nonlinear variation of apparent water contact angle is attributed mainly to the dependence of the surface wetting properties on the created boehmite nanostructure morphology on the aluminum alloy surface at different processing conditions.

To quantify the surface morphology on each sample and establish a quantifiable connection between the surface morphology and wetting properties, SEM images for each surface were processed to extract two typical parameters: apparent nanostructure length scale (1) and apparent surface solid fraction ( $\phi_s$ ). The characteristic *l* represents the averaged top-view line width of nanostructures, while  $\phi_s$  represents the apparent fraction of total top-view area of nanostructures normalized by the total surface area (see SI Figure S6 and S8). Although the solid fraction of surface structures is rigorously defined as the wetted area of the superhydrophobic nanostructures normalized by the total surface area, we approximate the apparent solid fraction by the top-view area of nanostructures due to the low amount of liquid penetration into structures during droplet condensation within structures and growth on top of structures.<sup>11</sup> As shown in Figure 3c,d, both of l and  $\phi_s$  increase gradually with increasing DI water immersion time  $(t_i)$  and DI water immersion temperature  $(T_i)$ , respectively. Specifically, *l* increased from ~12 nm ( $t_i = 20$  s) to ~30 nm ( $t_i$  = 120 min) which resulted in increment of  $\phi_s$ from ~0.05 to ~0.3, respectively. The variation of nanostruc-



**Figure 4.** Top-view time-lapse optical microscopy of condensed water droplets on the Al-6061 surfaces processed with immersion temperature of  $T_i = 90$  °C (Figure 1b) and immersion time of (a)  $t_i = 20$  s, (b) 10 min, and (c) 120 min. Sample surface temperature and relative humidity were set to 1 °C and 50 ± 0.5% for all condensation experiments. At relatively short immersion time (a), condensed droplets coalesced to become larger droplet without jumping (green dashed box). When the sample immersion time increased (b), condensed droplets coalesced and jumped from the surface (gold dashed box). When the immersion time increased (c), we observed droplet jumping with the presence of coalescence without jumping (white dashed box). Top-view time-lapse optical microscopy of frost propagation dynamics on Al-6061 surfaces processed with (d)  $t_i = 10$  min and (e) 120 min with  $T_i = 90$  °C. Sample surface temperature and relative humidity were set to -15 °C and  $50 \pm 0.5\%$  for all frosting experiments. The frost propagates with droplet jumping (green and gold dashed box) for  $t_i = 10$  min. However, for  $t_i = 120$  min, less jumping occurs and the frost propagated 3× faster when compared to the uniform boehmite surface. Scale bars are 50  $\mu$ m and each time lapse image represents a 264  $\mu$ m × 176  $\mu$ m field of view.

ture length scale and solid fraction results in corresponding wettability variation. The higher solid fraction lead to stronger pinning of the triple phase contact line on the surface.<sup>60</sup> For a solid surface having an equilibrium intrinsic contact angle  $\theta_1$ , the apparent contact angle ( $\theta^{CB}$ ) of a textured, rough surface can be determined via<sup>60,61</sup>

$$\cos\theta^{\rm CB} = r\phi_{\rm s}\cos\theta_1 + (1 - \phi_{\rm s})\cos\theta_2 \tag{1}$$

where  $\theta_2$  is the equilibrium contact angle on air, r is the boehmite roughness factor defined as the total wetted nanostructure surface area normalized by the projected total

surface area,  $\phi_s$  is the surface solid fraction, and  $(1-\phi_s)$  is area ratio of the liquid—air interface (see SI Figure S8). Generally, the classic CB equation predicts only a single value of static apparent contact angle. Hence, debate exists regarding the applicability of the classic CB equation to arbitrary surfaces and capability of predicting droplet dynamics.<sup>60,62–67</sup> For example, the contact angle hysteresis ( $\Delta\theta$ ) is a parameter used to represent the dynamic behavior of a droplet on the surface, that is, droplet impacting, sliding and jumping. However,  $\Delta\theta$ cannot be predicted using the classical CB eq (eq 1). To overcome this challenge, numerous modifications to the CB



**Figure 5.** Minimum jumping droplet diameter  $(D_{min})$ , droplet jumping rate per unit area (N) and frost propagation velocity ( $V_{frost}$ ) on Al-6061 as a function of (a–c) DI water immersion time and (d–f) immersion temperature. The hot DI water immersion temperature was fixed at 90 °C to investigate the effect of immersion times shown in (a–c). The DI water immersion time was fixed at 10 min to investigate effect of hot DI water immersion temperature shown in (d–f). During the condensation and frosting experiments, the sample surface temperatures were set to  $1 \pm 0.5$  °C and  $-15 \pm 1$  °C, respectively. The relative humidity was  $50 \pm 5\%$  for all experiments. The results for  $D_{min}$ , N, and  $V_{frost}$  show local optima near DI water immersion times of 10 min. All areas left of the vertical black dashed line in (a), (b), (d), and (e) are left blank because no jumping was observed at these fabrication conditions.

equation have been developed.<sup>60,68–79</sup> Using local differentials of the energy minimization and the differential area model, successful prediction of receding contact angles for various textures is possible using<sup>60</sup>

$$\cos \theta_{\rm r}^{\rm CB} = r_{\phi} \phi_{\rm d,r} \cos \theta_{\rm 1,r} + (1 - \phi_{\rm d,r}) \cos \theta_2 \tag{2}$$

Here,  $\phi_{d,r}$  is a differential parameter of surface solid fraction which deviates considerably from the global solid fraction  $\phi_s$  when the triple phase contact line recedes infinitesimally on a nanostructured surface (i.e., boehmite structures in this study). The relation between  $\phi_{d,r}$  and  $\phi_s$  is strongly dependent on the surface topology. The SEM images and atomic force microscopy (AFM) results show that boehmite structures have morphology analogous to intersected platelets which could be simplified into nanopore arrays or inversed hoodoo structures.<sup>14</sup> In this case, the differential parameter for the receding contact angle is  $\phi_{d,r} = 1 - \sqrt{1 - \phi_s}$  and  $\theta_2 = 180^{\circ}$ .<sup>60</sup> The roughness factor,  $r_{\phi}$ , was acquired from AFM scanning (SI Figures S9 and S10). Equation 2 simplifies to

$$\cos\theta_{\rm r}^{\rm CB} = r_{\phi} \cos\theta_{\rm l,r} (1 - \sqrt{1 - \phi_{\rm s}}) - \sqrt{1 - \phi_{\rm s}}$$
(3)

where  $\theta_{1,r}$  is the intrinsic receding contact angle measured on a smooth boehmite surface  $(t_i = 5 \text{ s})$ . As observed in Figures 3c,d, the measured  $\theta_r^{\text{app}}$  matches well with  $\cos \theta_r^{\text{CB}}$  calculated using eq 3. Hence, the CB regime  $(t_i = 1 \text{ min } \sim 60 \text{ min and } T_i = 80-90 \text{ °C})$  of the fabricated surface structures can be predicted using the modified CB model. It is important to

note, even if  $\theta_a^{\rm app}$  on surfaces having immersion time of 40 s and 120 min can reach ~165°, the  $\Delta\theta$  on these surfaces is relatively high (>10°), indicating that they represent a transition regime between Wenzel and CB preferred wetting states (same as the  $T_i = 70$  °C case). It means that the modified CB model is unable to predict the measured contact angle at the transition region and Wenzel wetting state because of the formation of sparse nanostructures rather than dense nanostructures.

Condensation and Anti-Frosting Performance. To evaluate condensation and antifrosting performance, microscopic condensation and frosting dynamic studies were carried out in ambient environmental conditions. The use of condensation and frosting is important to differentiate the performance of the SHP Al surfaces due to the convergent properties with minimal differentiation in equilibrium wetting properties using conventional microgoniometry (Figure 3). Droplet nucleation, growth, coalescence and removal behavior were recorded under a customized microscope setup (see Methods). Figure 4a-c show top-view time-lapse optical microscopy images of condensed water droplet dynamics on the Al-6061 surfaces processed with immersion DI water temperature of  $T_i = 90$  °C and sample immersion time of  $t_i =$ 20 s, 10 min, and 120 min, respectively. With relatively short immersion time (Figure 4a,  $t_i = 20$  s), condensed droplets grew and coalesced to become larger stationary droplets, identical to dropwise condensation on smooth hydrophobic surfaces.<sup>81</sup> Given the SEM images (SI Figure S4) and contact angle data (Figure 3), the insufficient reaction time between DI water and



**Figure 6.** Top-view optical microscopy of polished Al-6061 for DI water immersion times of 0 min (bare), 10 min, and 60 min. The density of defects (black spots) increases with longer immersion times. (b) EDS of a clean polished Al-6061 sample. Spot A demarks the defect observed during EDS, while spot B represents a clean polished Al-6061 surface which has a native oxide. (c) Elemental composition of the analyzed spots demarked by A and B in (b).

Al created discrete boehmite nanostructures which result in high contact angle hysteresis and droplet-surface adhesion (Wenzel wetting state). When the immersion time increased to  $t_i = 10 \text{ min (Figure 4b)}, \text{ uniform and dense boehmite}$ nanostructures were created and the droplet-surface adhesion decreased. This was made clear via the observation of continual condensation and droplet jumping, enabled by the low-adhesion Cassie-Baxter wetting state.<sup>81</sup> The observation of droplet jumping enables us to infer that air trapping beneath the droplets within the boehmite structures occurs. Past experimental and theoretical work has developed extensive understanding of the effect that nanoscale structure solid fraction and morphology and wetting state on droplet jumping,<sup>16</sup> showing that limiting the liquid-surface adhesion in the composite wetting state (via air trapping) during droplet growth is key to predicting jumping(see SI Figure S11). When the immersion time increased further to  $t_i = 120 \text{ min}$  (Figure 4c), we observed droplet jumping with the additional presence of coalescence without jumping. As shown in the time lapse images, the droplet initially nucleated on a microscale defect (black spot inside the white dashed box) and coalesced with droplets surrounding it while maintaining pinning to the defect. This observation indicates that a secondary factor affects condensation dynamics other than boehmite nanostructure length scale.

The frosting performance of each surface was evaluated at subzero surface temperature conditions (see Methods). Macroscopically, frost nucleated from the edge of square sample surface followed by inward propagation through interdroplet bridging until complete coverage of the surface was achieved. The initial onset of droplet freezing at the surface edge was attributed to the presence of enough physical and chemical defects which could activate heterogeneous droplet freezing.<sup>21</sup> Prior to frost propagation into field of view, continuous subcooled droplet jumping was observed. As the continuous jumping minimized the averaged subcooled droplet size on the surface, the frost wave on the SHP surface was delayed when compared to bare and smooth hydrophobic Al-

6061 surfaces. Once droplet freezing was detected ( $t_f = 0$  s in Figure 4d,e), the frost front swept through the entire field of view. Figures 4d,e show the condensation frosting propagation behavior on the surfaces with immersion time of  $t_i = 10$  and 120 min, respectively. The time period for the frost front to sweep the entire field-of-the-view for the  $t_i = 10$  min surface was more than three times longer when compared to the  $t_i = 120$  min surface. Although both surfaces showed droplet jumping, the condensation and antifrosting performance had large differences depending on the surface structure morphology and wetting characteristics.

To quantify the condensation and antifrosting performance, we measured minimum jumping droplet diameter  $(D_{\min})$ , droplet jumping rate per unit area (N) and frost propagation velocity  $(V_{\text{frost}})$  on each surface (Figure 5, see Methods for quantification explanation). Removal of condensate at smaller length scales leads to a reduction in the time-averaged droplet size distribution, which results in a decreasing total thermal resistance condensed droplets. In part,  $D_{\min}$  is governed by the surface structure length scale and morphology, which can be characterized by the initial droplet wetting state (CB mode or Wenzel mode), the apparent advancing contact angle  $(\theta_a^{app})$ , and the contact angle hysteresis ( $\Delta \theta$ ). Figure 4a,d show the effect of DI water immersion time and immersion temperature on  $D_{\min}$ . Droplet jumping was observed when immersion time and immersion temperature exceeded 40 s and 70 °C, respectively. By varying immersion time, we demonstrate an optimum  $D_{\min}$ (smallest value) when  $t_i = 10$  min. In general, for a fixed immersion time, D<sub>min</sub> increased with increasing immersion temperature. The variation of  $D_{\min}$  as a function of immersion time and immersion temperature correlate well with the  $\theta_a^{app}$  and  $\Delta \theta$  trends presented in Figure 3, which indicates that  $D_{\min}$  is a sensitive function of surface morphology and corresponding surface wetting properties. Figure 5b, e show the change of droplet jumping rate (N) on each surface. The results indicate that the droplet jumping rate is also affected by the nanostructure morphology. For example, the number of droplets jumping on the surface with immersion



**Figure 7.** SEM images of (a) microscale defects on a 60 min immersed sample with corresponding (b) high magnification image of a typical defect (intermetallic particle) as outlined in (a) with the orange dotted box. (c) EDS line scan of a partially created boehmite layer on a defect. The red dotted line represents the scan line on the surface. (d) EDS line scan results for intensity of major elements on the defect. All *x*-axes in (d) represent scan length with *y*-axis representing intensity in arbitrary units.

time of  $t_i = 120$  min is less than 30% of that on the surface with immersion times of  $t_i = 5$  and 10 min. If we compare the results for  $D_{\min}$  (Figure 5a,d) and N (Figure 5b,e), a clear correlation is observed between the optimized surface structure length scale and enhanced condensation performance, represented as minimized  $D_{\min}$  and maximized N (i.e., surface with  $t_i = 10$  min at  $T_i = 70$  °C). The optimized surface morphology also results in an enhanced antifrosting performance as shown in Figure 5c,f. On a surface with optimized nanostructures ( $t_i = 10$  min), the frost propagation is suppressed more than 1 order of magnitude when compared to a smooth hydrophobic surface or a nonoptimized Al SHP surface ( $t_i = 120$  min).

**Microscale Alloying Element Defects.** As shown in Figure 4c, we observed coalescence-only behavior when the droplet nucleates on a defect site (black spot) and interacts with droplets nearby. The droplets were observed to show preferential nucleation on the microscale defects, and to grow and remain pinned on these defect sites. This behavior indicates that the surface morphology of these sites is entirely different the from boehmite nanostructures which could induce droplet jumping. Figure 6a shows top-view optical microscopy images of a polished Al-6061 surface for

DI water immersion times of 0 min (bare), 10 min, and 60 min, respectively. The bare surface is relatively smooth, however, with increasing immersion time, we could observe more microscale defect sites which are shown as black spots. To investigate these defects, Energy-dispersive X-ray spectroscopy (EDS, see Methods) analysis was conducted on both defect site and smooth area (Figure 6b). Spot A demarks the microscale defect observed during EDS analysis, while spot B

represents a clean polished Al-6061 surface which has a native oxide layer. The concentration of Al at spot A (63.55%) is significantly lower than at spot B (91.57%) (Figure 6c). In the contrast, the concentration of other metal elements is higher at spot A than spot B, especially magnesium (Mg), silicon (Si), and iron (Fe), which are the main chemical elements in the Al-6061 alloy.

To show the details of the localized microscopic morphology after hot water treatment, the SEM images of microscale defects on a 60 min DI water immersed sample with corresponding high magnification image of a typical single microscale defect (intermetallic particle) were taken and are shown in Figure 7a,b, respectively. The typical intermetallic particle size was about 5  $\mu$ m and the surrounding areas were free from boehmite nanostructure. The lack of boehmite originates from the low aluminum composition as well as continuous bubble nucleation at the particle site during hot water immersion. We also found that some of the intermetallic particles could be partially covered by the boehmite (Figure 7c) which depended on the processing conditions such as the local temperature difference and steam vapor pressure.<sup>82</sup> However, EDS line scan results on the partially created boehmite layer confirmed that the Al intensity decreases at the microscale defect, and Fe and Si signals increase, indicating that boehmite was created on top of an intermetallic particle (Figure 7d). In our study, the maximum immersion temperature and immersion time were set at 90 °C and 120 min. However, most of the elements in the Al alloys react water slowly (such as Cu, Cr, Ni, ti >2 h) or did not react at all with



**Figure 8.** (a) Optical image of a sputtered Hi-Al surface (50 nm initial Al thickness and 60 min immersion time) and (b) high magnification image of the region demarked with the orange dotted box in (a) demonstrating the uniformity of the boehmite nanostructure. (c) SEM images of boehmite nanostructures on sputtered Hi-Al surfaces with DI water immersion times of 5, 30, and 120 min. For more SEM images, see SI Figure S7. (d) Apparent advancing contact angle  $(\theta_a^{\text{pp}})$  and contact angle hysteresis ( $\Delta \theta = \theta_a^{\text{app}} - \theta_r^{\text{app}}$ ) of Al-6061 (hollow sphere symbols) and sputtered Hi-Al (hollow square symbols) surfaces (50 nm initial Al thickness) as a function of DI water immersion time. Although  $\theta_a^{\text{app}}$  was nearly identical for both substrates,  $\Delta \theta$  increased on Al-6061 surfaces with increasing DI water immersion time, in addition to having a higher magnitude compared to the Hi-Al surfaces. (e) Frost velocity ( $V_{\text{frost}}$ ) comparison between Al-6061 and Hi-Al surfaces with varying thickness of 10 nm (red), 50 nm (blue), 250 nm (green). The solid and patterned color bars represent surfaces fabricated with DI water immersion times of 10 and 60 min, respectively.

hot water.<sup>53</sup> The reacting elements, such as Mg and Fe, create nanostructures with similar morphology of boehmite.

To confirm the effect of microscale defect on the performance of boehmite Al SHP surfaces, we compared Al-6061 SHP surfaces with SHP surfaces fabricated from high purity Al (Hi-Al, 99.999%, see Methods). Figure 8a,b show optical microscopy images of boehmite nanostructured surfaces fabricated on sputtered Hi-Al on a silicon wafer. Even with long water immersion times (120 min, Figure 8c), ultrauniform boehmite nanostructures was created and the surface was free of defects, extremely smooth and conformal, in contrast with the microscale defects observed on the Al-6061 surfaces. Figure 8d shows the wettability comparison between Hi-Al (50 nm initial Al thickness) and Al-6061 surfaces as a function of DI water immersion time. Although the measured  $\theta_a^{\text{app}}$  values were nearly identical for both substrates,  $\Delta \theta$ increased on Al-6061 surfaces with increasing DI water immersion time, in addition to having a higher magnitude compared to the Hi-Al surfaces. The higher and increasing  $\Delta \theta$ originates from a combination of increased solid fraction and microscale defect exposure with longer DI water immersion time. The higher defect density results in higher surface adhesion and pinning on Al-6061 surfaces, which is the main reason for reduction in frosting performance as showed in Figure 4. The pined microsclae water droplets prefer to nucleate and they works as a frost propagation initiator. Figure 8e shows a comparison of  $V_{\text{frost}}$  between the Al-6061 and Hi-Al SHP surfaces for varying Al film thickness of 10 nm, 50 nm, 250 nm, respectively. On the Al-6061 surfaces, a 60 min DI water immersion time resulted in nearly three times faster frost propagation speed when compared with the 10 min DI water

immersion time. However, on the Hi-Al surfaces,  $V_{\rm frost}$  was demonstrated to be independent of DI water immersion time. Furthermore, we also found that the original Al film thickness does not have a direct effect on  $V_{\rm frost}$  indicating that boehmite conformality is independent of the Al film thickness studied here.

Effect of Aluminum Alloy grade. Aluminum alloys consist of a chemical composition where other elements are added to pure Al in order to enhance its properties, primarily to increase its strength, formability, electrical conductivity, and corrosion resistance. Based on the application, different grades of Al are used and the effect of intermetallic particles on the surface wetting performance is different. The intermetallic particles present within the Al alloy lead to microscale defects after the hot DI water immersion process due to the inability of the alloying element to react with the water. During the Al alloy fabrication processes, segregation of certain alloying elements ensues to form a heterogeneous microstructure. This segregation results in the formation of relatively large (micron sized) intermetallic phases. The microscale defects induced by intermetallic particles degrade condensation and antifrosting performance.

To provide a comprehensive analysis, we selected six commercial Al alloys and investigated their antifrosting performance. Previous studies have shown that most of the elements in Al alloys react with water slowly (such as Cu, Cr, Ni,  $t_i > 2$  h) or do not react at all (Si) with hot water. Reacting elements, such as Mg and Fe, create nanostructures with similar morphologies as those observed for boehmite.<sup>53</sup> Figure 9a shows top-view optical microscopy images of the surface morphology for the different Al alloy grades with DI water



**Figure 9.** (a) Top-view optical microscopy images showing the surface morphology for the different Al grades when sing a DI water immersion time of 60 min and DI water immersion temperature of 90 °C. (b) Aluminum elemental composition of the selected Al grades (data obtained from manufacturers). (c) Frost propagation velocity ( $V_{\text{frost}}$ ) comparison for selected grades of Al alloys. The Al-1100 samples, which have the highest Al composition (>99.0%), showed the lowest value for  $V_{\text{frost}}$  compared to other alloys.

immersion time of 60 min and DI water immersion temperature of 90 °C). The reason we choose this specific processing parameter is to maximize the number of microscale intermetallic defects on the superhydrophobic surface in order to show the effect of Al grade on the antifrosting performance. The optical images showed that all of the Al grades consisted of a high number of microscale defects on the surfaces after the boehmite formation process (Figure 9b). Evaluation of the frosting results revealed that the antifrosting performance on Al-1100 samples, which have the highest Al composition (>99.0%) and lowest intermetallic phase content, had the lowest frost propagation speed ( $V_{\rm frost}$ ) when compared to the other alloys, especially when compared to alloys having the lowest Al composition (Al-2024 and Al-7075, Figure 9c).

**Fabrication Optimization for Superhydrophobic Aluminum Production.** The hot water immersion method used here presents an environment-friendly process which has the potential to be applied at scale during SHP Al surface production. However, because of the need to maintain the immersion water temperature and to control immersion time, the whole process has the potential to be energy intensive. Reducing the immersion and CVD times will lead to a significant reduction in the coating cost of manufacturing.

In order to optimize the fabrication process, we conducted a parametric study with the Hi-Al sample (50 nm aluminum thickness) in order to eliminate the effects of impurities as well as to study the effect of processing parameters on the surface wettability only. Figure 10a,b show experimentally measured  $\theta_{a}^{app}$  and  $\Delta \theta$  as a function of DI water immersion time and DI water temperature for the Hi-Al surfaces. With immersion water temperatures of 90  $^{\circ}\mathrm{C}$  and 1 min DI water immersion times,  $\theta_a^{app}$  and  $\Delta\theta$  reach >165° and <5°, respectively, which represent ideal behavior for superhydrophobicity. In contrast, when the immersion water temperature was fixed at 50 °C, to achieve ideal boehmite nanostructures, the surface needed to be immersed for more than 30 min. This result means that an optimized processing condition exists such that lower energy usage is attained, and hence a higher fabrication efficiency is achieved. Figure 10c shows the total thermal energy input during fabrication. The total thermal energy is the summation of the specific heating of the aluminum substrate to reach the target temperature and the required energy to maintain the target DI water temperature during the fixed immersion time.



**Figure 10.** Contour plots of experimentally measured (a)  $\theta_a^{app}$  and (b)  $\Delta\theta$  as a function of DI water immersion time and DI water temperature on Hi-Al surfaces. With immersion water temperatures of 90 °C,  $\theta_a^{app}$  and  $\Delta\theta$  reach >165° and <5° (ideal region), respectively even for 1 min DI water immersion time. (c) Contour plot of the total energy input, defined as the specific heating of water to reach the target temperature and required energy to maintain the target temperature during the immersion time, required to create the required nanostructures on the surfaces. The ideal region is the overlap from the optimized  $\theta_a^{app}$  and  $\Delta\theta$  in (a) and (b). The upper left region in (c) outlined with the orange dotted line is optimized for a fast fabrication and low energy consumption. (d) Experimentally measured  $\theta_a^{app}$  and  $\Delta\theta$  as a function of SAM vapor deposition time at 85 °C for Hi-Al surfaces. (e) Specific energy input as a function of production rate for creating SHP Al at the optimized  $\theta_a^{app}$  and  $\Delta\theta$  for different immersion temperatures. Inset: Zoomed in view of the dotted rectangular region. (f) Production rate and specific energy comparison for different Al substrate immersion areas. Red bars are for the right axis, while black bars are for the left axis.

The total energy is a function of the processing condition used to create the required nanostructures on the surfaces. See the Supporting Information for calculation details and assumptions used. Note, the specific heating of water to reach the target DI water immersion temperature was not included in the calculation as that is part of system startup, and represents a minimal energy component when considering continuous production. The optimized fabrication region is the area of overlap between the optimized  $\theta_a^{app}$  and  $\Delta\theta$  results shown in Figure 10a,b. The upper left region is optimized for faster fabrication times with lower energy input during fabrication. The optimal fabrication process can be selected for Al SHP mass production based on the trade-off between time and energy consumption.

In addition to the DI water immersion, CVD of the hydrophobic SAM also consumes energy. Optimization can be achieved through control of the CVD process parameters with a fixed deposition temperature. Figure 10d shows the experimentally measured  $\theta_a^{\text{app}}$  and  $\Delta \theta$  as a function of SAM vapor deposition time at an oven temperature of 85 °C on Hi-Al boehmite nanostructured surfaces. The result shows SAM deposition times do not need to exceed 10 min to achieve high quality superhydrophobic surfaces.

Figure 10e shows the calculated relation between the required specific energy input (per 1 m<sup>2</sup> Al surface area) and production rate for SHP Al surfaces. The results show that the highest production rate does not have a corresponding high energy input which is in agreement with results presented in Figure 10c. In fact, the lowest production rate has the highest energy input due to the requirement for long immersion times (i.e., immersion temperature of 90 °C). The results indicate that it is important to choose the proper fabrication conditions based on the production efficiency needs such as rate and cost. It is important to note that the production rate in Figure 10e was predicted in the basis of a surface immersion area of  $1 \text{ m}^2$ . In order to achieve higher production rates (i.e., >1000 m<sup>2</sup>/ hour), scaled up immersion facilities and more efficient hydrothermal treatment methods (i.e., impingement with hot steam) are required.<sup>83</sup> Figure 10f shows the comparison of the production rate and specific energy input for different immersion areas of the Al substrate. The Al SHP production rate increases linearly with increasing immersion area. However, the specific energy input gradually decreases with increasing immersion area due to the nonlinear scaling of sample area and required immersion tank volume for production.

## DISCUSSION

In this study, we optimize the fabrication process of ultrascalable boehmite to enable SHP Al surface production. We investigated the effect of fabrication conditions and Al alloy composition on the resulting nanostructure morphology and surface wetting properties, which are both crucial for the successful enhancement of condensation and frost reduction performance. Furthermore, analysis was conducted on the energy consumptions and sample production rate during fabrication.

Although our results develop comprehensive guidelines and strategies for the mass fabrication of SHP Al surfaces, certain caveats must be considered. First, our work may not be the global optimum for all conditions to fabricate boehmite nanostructures, however, the proposed evaluation methods using modified CB model, condensation droplet dynamics and frost propagation provide an avenue to develop optimized nanostructures for phase change heat transfer applications. In the future, additional experimental work is needed to test all possible permutations of fabrication conditions in case a global optimum exists within. Second, consideration of when the functionalization takes place, with respect to the manufacturing process, is paramount. For example, when finned Al heat exchangers are made, functionalization could take place on a full assembled and joined heat exchanger,<sup>84</sup> or on the fin stock material prior to stamping and assembly. This process flow position introduces other variables which need consideration such as potential coating degradation during handling and brazing.<sup>8</sup> <sup>87</sup> In this case, as long as the SHP surface survives the fabrication and assembly processes, the SHP surfaces on the Al heat exchangers plane surfaces are rarely damaged by external mechanical impact (i.e., mechanical abrasion) due to their internal nature after assembly (shielding by adjacent fins). With regards to the durability of hydrophobic coating material on the SHP surface, other than the interaction of frost/ice with the SHP surface (mechanical durability), the adhesion of the functional hydrophobic material with the nanostructure layer, conformality of the coating, as well as the moisture reactivity of the hydrophobic material needs to be considered.<sup>88</sup> Third, the

effect of Al alloy (aluminum purity and element type) on the SHP coating performance needs to be considered. Our results show that the surface wetting and antifrosting performance strongly depend on the Al alloy composition, which presents a potential reason for previously observed manufacturer-dependent antifrosting heat exchanger performance. Industrial Al heat exchangers use different Al alloy grades for the fin material depending on the application. For example, air side heat exchangers in marine applications use more corrosion resistive Al alloys, however, for building applications, high purity Al alloys are preferred due to their better heat transfer performance stemming from their higher thermal conductivity.

The orientation and size of the alloy metal crystalline grains is another factor that may affect nanostructure morphology, especially after etching treatment with acid or anodization (see SI Figure S12 for an example of grain boundary etching results with acid). In our hot water immersion process, we did not find a significant effect of grain boundaries on the formation of boehmite nanostructures and total microscale roughness of the resulting surface. Instead, the boehmite nanostructures were created on the surface uniformly. In the future, controlling the grain size and orientation may enable more efficient directional droplet shedding on hierarchical structures with boehmite nanostructures which are combined with microscale etched grains.

Finally, although we calculate the energy input for the DI water immersion process based on small scale samples with low thermal mass (*i.e.* One m<sup>2</sup> substrate area and 0.2 mm thickness for typical heat exchanger fins), when real fabrication processes are scaled up for mass production, the effect of metal heat capacity and thermal mass on the hot water temperature needs greater consideration to achieve an accurate calculation of the total energy consumption. High throughput processes such as fin stock material coating as well as large volume/mass parts such as assembled heat changers, stand to significantly cool down the DI water bath temperature during production, which will require energy compensation to maintain temperature control.

## CONCLUSIONS

In conclusion, we systematically investigated the effects of processing conditions and alloy composition of Al substrates for the ultrascalable formation of boehmite SHP surfaces fabricated by hot water immersion. Our work shows that the resulting nanoscale surface morphology, nanostructure length scale, as well as previously unidentified microscale defects are the main factors influencing surface wettability. These effects in turn control jumping droplet condensation and antifrosting characteristics of SHP Al surfaces. We elucidate the observed wetting mechanisms by connecting the fabricated nanostructure morphology and length scales with a modified Cassie-Baxter model. The model enables theoretical prediction for optimized SHP Al surface design. A full parametric study of water immersion conditions showed that the immersion time can be as short as 10 min (with 90 °C water temperature) to create optimum boehmite nanostructures. Furthermore, we found that previously unidentified microscale defects, which originate from intermetallic phases in the Al alloy, play an important role on wetting and decrease SHP performance. Our investigation showed that higher purity Al alloys lead to fewer microscale defects formed as a result of intermetallic phases, and more uniform boehmite nanostructures after water immersion. Finally, we optimize the entire fabrication process,

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including water immersion time and temperature, along with CVD hydrophobic coating functionalization for high purity Al surfaces. We provide a fabrication regime map based on energy consumption and fabrication throughput. Our work provides design guidelines for the efficient water-immersion-based ultrascalable fabrication of SHP Al surfaces which are key to the success of a plethora of applications.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c08051.

Additional SEM images, XPS results, spectroscopic ellipsometry results, calculation details of energy input for fabrication process, AFM scanning results and relation of roughness factor and rms surface roughness with treatment time (PDF)

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#### Notes

The authors declare no competing financial interest.

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