Tunable Hierarchical Nanostructures on Micro-Conical Arrays of Laser Textured TC4 Substrate by Hydrothermal Treatment for Enhanced Anti-Icing Property

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Abstract: In this work, an anti-icing structured surface was fabricated by combining laser ablation with hydrothermal treatment. A micro-patterned surface on a Ti alloy (TC4) substrate was easily fabricated by a highly effective nanosecond pulsed laser ablation. It was observed that titania (TiO₂) nanostructures were formed by hydrothermal treatment in aqueous alkali on the laser ablated TC4 substrate to obtain the micro/nano-hierarchical structures. The growth mechanism of the tunable nanoarrays was discussed by the adjustment of hydrothermal temperature. The as-prepared samples exhibited excellent superhydrophobicity with contact angles greater than 160°. It was found that optimized hydrothermal treatment on laser-processed TC4 substrates could further enhance surface anti-icing property. The results showed that the delay time (DT) had been extended by achieving over 90 min for the water droplets to freeze on the as-prepared structured surfaces, providing great potential in various anti-icing applications.

Keywords: laser ablation; hydrothermal treatment; micro/nano-hierarchical structures; wetting model; anti-icing

1. Introduction

Icing and ice accretion on aircraft structural material surfaces such as titanium alloys, typically of TC4 (Ti–6Al–4V) with good mechanical properties and high corrosion resistance, cause serious consequences such as freezing the wings, impairing sensing, and even ceasing operation [1,2]. There are a series of active solutions to solve aircraft icing such as thermal treatment and mechanical breaking. However, these methods incur plenty of energy waste and cause undesired damage to the main body. Hence, an alternative passive solution is in high demand so that ice will be prevented from accumulating on the anti-icing surfaces, which is advantageous in terms of energy and cost savings. With the fast development of nanotechnology and biomimetics, there have been many studies indicating that superhydrophobicity has positive effects on anti-icing property [3–5], although debates on the
underlying mechanism are still unclear [6,7]. Additionally, no studies have clarified the comprehension of whether superhydrophobicity really suits icephobic applications by considering the durability issue of anti-icing property on a superhydrophobic surface due to the degradation of the coating materials [8,9]. Therefore, scientists have placed much attention on the surface structural properties of bulk materials and designing their superhydrophobic surface to reduce the possibility of surface icing.

Surface structure and surface energy are the two main factors affecting surface hydrophobicity. A large number of creatures in nature exhibit excellent hydrophobicity such as the micro-conical structure of the surface of pansy petals, which shows excellent hydrophobicity [10–12]. Furthermore, Herminghuas et al. found that hierarchical structures could make the surface wettability more significant [13]. In the past, researchers have successfully prepared superhydrophobic surfaces via fabricating surface structures through various methods [14] such as sandblasting [8], the anodization method [15], microwave irradiation [16], the sol-gel technique [17], chemical vapor deposition [18], and chemical etching [19]. However, it is quite hard to produce controllable biomimetic micro-array structures by these methods, generating harmful by-products for the environment. Instead, laser ablation is deemed as one of the most promising techniques to produce a periodic micro-array structure due to its high accuracy, environmental-friendly, controllability, and high efficiency in large-area manufacturing [20–25]. However, it was found that there are different sizes and disordered nanoparticles on the surfaces after laser ablation. These disordered nanostructures may cause defects, possibly weakening the de-wetting capability. Therefore, it is important to prepare tunable nanostructures on laser-induced microstructures. The hydrothermal reaction has been proposed as an excellent method to manufacture a large number of nanostructures. Moreover, it has been widely reported that nanostructures fabricated by hydrothermal reaction can be easily tuned by adjusting the hydrothermal temperature, leading to the formation of nanobelts, nanopetals, nanoneedles, and nanotubes [26–29]. However, the rational synthesis of a TiO$_2$ nanostructure on a laser ablated Ti alloy sheet by using the hydrothermal method has seldom been reported. This provided us with the inspiration to use nanosecond laser ablation to texture micron-scale structures on the surface and then hydrothermally grow nanoscale structures on the micron-scale structures, thereby constructing multiple hierarchical structures to enhance surface hydrophobicity.

In this work, laser processing was applied to fabricate the micro-conical array structure on a titanium alloy sheet, while hydrothermal treatment was adopted as a post-treatment process to grow and tune the nanoscale structure. After the surface texturing, the surface was modified by fluorosilane to obtain the superhydrophobic surfaces. The characteristics of the anti-icing properties are discussed for the as-prepared samples to reveal the underlying mechanisms. The results showed that the selected surfaces fabricated with the method above-mentioned could be equipped with enhanced anti-icing property compared to the sample only processed by laser or hydrothermal treatment. It is expected that this method will allow a bright future in designing better anti-icing surfaces.

2. Materials and Methods

2.1. Materials

TC4 Ti alloy sheets (Ti–6Al–4V, Shenzhen Hongwang Mold Co. Ltd., Shenzhen, China) with an area of 10 mm × 10 mm and a thickness of 1 mm were used as substrates. A Teflon-lined autoclave with 50 mL was used as the hydrothermal reaction container. Deionized water, ethanol, 1.0 mol/L NaOH solution, 0.8 mol/L HCl solution, and heptadecafluoroxytrimethoxysilane (FAS-17, Qufu Jiaye Chemical New Material Co. Ltd., Qufu, China) were used for the following syntheses.

2.2. Sample Preparation

In this work, we used a Nd:YAG pulsed laser with a wavelength of 1064 nm and a pulse width of 100 ns. The spot size of the laser was 0.1 mm. The scanning speed, average laser power, and repetition frequency were set at 500 mm/s, 15 W, and 20 kHz, respectively, during the process. Prior to the laser
texturing, the Ti alloy sheets were cleaned with ethanol and deionized water in an ultrasonic bath for 10 min sequentially and dried in air. Then, the Ti alloy sheets ablated by laser were transferred into a Teflon-lined autoclave containing 1.0 mol/L NaOH solution with 40 mL for hydrothermal treatment and the temperatures were set as 150, 170, 190, and 210 °C, respectively. After the hydrothermal reaction for 24 h, the obtained samples were immersed in a 0.8 mol/L HCl solution for 2 h by ion exchange reaction. Subsequently, the Ti alloy sheets were rinsed with deionized water and dried entirely. Then, the samples were subjected to annealing treatment at 300 °C for 3 h for the purpose of dehydration and annealing. Finally, to achieve the superhydrophobic surfaces, all samples were modified with 2 wt % solution of FAS-17/ethanol at ambient temperature for 6 h and well dried. A schematic diagram of the entire sample preparation process is shown in Figure 1. In addition, control samples were prepared. Control sample 1 is the substrate that was only processed by laser. Control sample 2 is the substrate without pre-treatment of laser ablation, which was only treated by hydrothermal reaction, ion exchange reaction, and annealing treatment with the same process. All control samples were covered with FAS-17.

Figure 1. Schematic illustration of the fabrication process for the superhydrophobic Ti alloy.

2.3. Characterization

The as-prepared samples were observed with a Supra 55 scanning electron microscope (SEM, Carl Zeiss, Jena, Germany) for their surface morphologies and characterized with X-ray diffraction (XRD, Shimadzu, Kyoto, Japan) for possible phase and crystalline structure variations. The surface contact angle (CA) measurement was carried out in air at room temperature by a contact angle goniometer (KRUSS DSA-25, Hamburg, Germany) using the sessile drop method and 4 µL deionized water droplets. The CA for each sample was measured five times and the average value was adopted [22]. The surface water droplet adhesion test was carried out by using 6 µL of deionized water droplets.

2.4. Anti-Icing Property

The in-house anti-icing testing platform was established and included a temperature control platform, camera, and a computer. The surface temperature of the experimental platform could be tuned and stabilized at −5 °C under ambient conditions, fully supporting the characterization of anti-icing property. First, the as-prepared sample was fixed with heat-conducting silicone grease on the experimental plate horizontally. Second, deionized water droplets with the volume of 6 µL were dropped onto the surfaces. Then, the temperature of the experimental platform was decreased from room temperature to −5 °C with a decreasing rate of 1 °C/s by a temperature controller. The temperature
of the plate could be in-situ monitored by a digital temperature measuring instrument and fed back to the temperature controller, ensuring that the temperature stabilizes at \(-5\,^\circ\text{C}\) throughout the experiment. The time recording starts when the plate temperature reaches \(-5\,^\circ\text{C}\). Meanwhile, the icing process is monitored and recorded by the camera. The delay time, \(DT\) (i.e., the time taken for the deionized water droplets to freeze), is recorded by observing the non-transparency of the droplets on the surface at \(-5\,^\circ\text{C}\). In this work, \(DT\) is the measurement of the sample's anti-icing property \[30\]. The anti-icing characterization for all samples were measured five times. Since the desired micro-conical arrays do not exist for control sample 2 without pre-treatment of laser ablation, the control experiment of anti-icing characterization was only carried out on control sample 1, which was only processed by laser.

3. Results and Discussion

The large-area SEM images of the surfaces of the micro/nano-hierarchical structures with micro-conical arrays synthesized by the combination of laser process and hydrothermal reaction at 150 \(^\circ\text{C}\) are shown in Figure 2a–c. It can be seen that a large number of small micro-conical array structures with the same sizes were evenly located on the as-prepared sample surface (Figure 2a), and those cones were similar to the micro-structure pattern of the surface of the pansy petal \[12\]. A closer examination revealed that micro-cones were vertically located in the as-prepared substrate with diameters of about 200 \(\mu\text{m}\) at the bottom. The micro-conical array structure was produced by laser ablation. When the nanosecond pulsed laser hits the surface of the target material, a large number of photons are absorbed by the electrons of the TC4 substrate and transferred to the crystal lattice in a short time (~picosecond level), causing thermal diffusion and raising the temperature of the target material, leading to heating, melting, and evaporation \[31\]. The heat-affected zone can change the surface morphology by recasting and formation of burrs. In laser ablation, compressive forces can be created by the vapor and plasma plume at the focus point, leading to the expulsion of a molten pool of materials \[32\]. A portion of the liquefied material is resolidified after pressed out of the ablation zone, and accumulates and covers the surrounding non-processed areas, eventually forming a conical structure. Figure 2b is the top-view SEM image of the micro-conical structure. With further investigation, it can be observed that the surface was covered by many nanoscale flocculent structures, as shown in Figure 2c. These flocculent structures are synthesized by the hydrothermal reaction and are composed of layered unit cells. The crystalline structure of the flocs can be described with a representative \(\text{TiO}_6\) octahedral. During the alkali-hydrothermal process, the laser processed titanium alloy reacts with the NaOH solution at 150 \(^\circ\text{C}\) in the autoclave, where some of the Ti–O–Ti bonds are broken and form the six-coordinated monomer \([\text{Ti(OH)}_6]^2^-\), which can form polynuclear complexes by olation or oxolation, depending on the concentration of the solution at different temperatures.

Under the hydrothermal process, the solution is in a saturated state; hence, the \([\text{Ti(OH)}_6]^2^-\) is unstable and tends to combine via oxolation or olation, forming original nuclei \[33,34\]. As these nuclei grow and exceed the critical nuclei size, they become stable. Small and thin flocs can be formed when the growth continues \[33\]. Eventually, it can be observed that the micro/nano-hierarchical structures were successfully fabricated on the Ti alloy sheet surface. The surface of the Ti alloy is initially hydrophilic since the Ti alloy is a kind of material with high surface energy. According to the surface structural influence on the surface wettability, the surface structure can make a hydrophilic surface more hydrophilic, and a hydrophobic surface more hydrophobic. Thus, the surface of the Ti alloy with micro/nano-hierarchical structures becomes a superhydrophilic surface. Micro-structure and low surface energy are both prerequisites to achieve surface superhydrophobicity \[35\]. Therefore, in order to obtain superhydrophobic surfaces, samples were immersed inside the FAS-17 solution for low surface energy modification. After the treatment, the water droplet exhibited a spherical shape on the sample surface with a contact angle of approximately 160° ± 2°, as illustrated in Figure 2e. Furthermore, the as-prepared surface was very slippery and it was easy for the water droplets to slide off with an inclination angle of less than 1°, which is shown in Figure 2f. This indicates that the
solid–liquid wetting model between the water droplet and the sample surface is in Cassie–Baxter state, as shown as Figure 2d.

![Figure 2](image)

**Figure 2.** Scanning electron microscopy (SEM) images of the as-prepared surface with different magnifications: (a) 100x; (b) 500x; (c) 5000x; (d) Cassie–Baxter state; (e) Optical micrograph of water droplets; (f) Water droplets slide off the surface. Hydrothermal temperature is 150 °C.

In this work, the micro-conical structures of TiO₂ were first created on the TC4 substrates by laser ablation. The secondary nanostructure was then fabricated by imposing a hydrothermal treatment at different temperatures. According to the XRD pattern shown in Figure 3a, after the hydrothermal reaction, the samples exhibited the strong peaks of the (110), (211), (121), and (431) planes, indicating that Na₂TiO₃ nanostructures had been successfully synthesized during the alkali-hydrothermal process, corresponding to Equation (1).

\[
\text{TiO}_2 + 2\text{NaOH} = \text{Na}_2\text{TiO}_3 + \text{H}_2\text{O} \quad (1)
\]

By increasing the temperature from 150 to 210 °C, the intensities of the (110) and (121) peaks increased, indicating the gradual enhancement in the crystallinity of the as-prepared Na₂TiO₃ nanostructures. After soaking and washing in HCl solution, the Na⁺ ions were replaced by H⁺ ions to produce H₂TiO₃ nanostructures, corresponding to Equation (2).

\[
\text{Na}_2\text{TiO}_3 + 2\text{HCl} = \text{H}_2\text{TiO}_3 + 2\text{NaCl} \quad \text{(ion exchange reaction)} \quad (2)
\]

Finally, a calcination process was used for the dehydration of H₂TiO₃ to obtain crystalline TiO₂ nanostructures, corresponding to Equation (3).

\[
\text{H}_2\text{TiO}_3 = \text{TiO}_2 + \text{H}_2\text{O(g)} \quad \text{(annealing treatment)} \quad (3)
\]

The XRD patterns of the calcined samples are shown in Figure 3b. The diffraction peaks of the (101), (110), and (112) planes can be well indexed as TiO₂. By increasing the temperature from 150 to 210 °C, the intensities of the diffraction peaks increased, indicating that the crystallinity of the as-prepared TiO₂ nanostructures gradually enhanced.
when the hydrothermal temperature was 150 °C, the nanostructures became filamentous. At a sufficiently high temperature, the nanostructures became filamentous.

By further raising the hydrothermal temperature to 210 °C, it can be observed that the wire structures after hydrothermal treatment. This may be due to the easier growth of nanostructured crystals by hydrothermal processes on TiO₂ obtained after laser ablation. At the beginning of the hydrothermal reaction, TiO₂ reacted with the NaOH aqueous solution and many TiO₆ octahedral ions were created. Then, the TiO₆ octahedral ions electrostatically combined with Na⁺ ions and OH⁻ ions to form Na₂TiO₃ crystal nuclei. During the hydrothermal reaction, the nucleus are randomly distributed on the surface of the laser-treated titanium alloy substrate and grow to form nanostructures. The images of Figure 4a–d correspond to hydrothermal temperatures of 150, 170, 190, and 210 °C, respectively. As shown in Figure 4a, when the hydrothermal temperature was 150 °C, Surf 1 was covered by flocculent nanostructures with poor crystallinity. Many crystal dislocations/defects could be produced, existing at the crystal boundary during the hydrothermal growth process. When the hydrothermal temperature increased, the number of crystal nuclei generated by the hydrothermal reaction increased, and the rate of crystal growth also increased. The crystalline growth in the cross-sectional direction was inhibited due to the competitive growth from a large number of crystals simultaneously, leading to the inner stress in the radial direction. While increasing the temperature up to 170 °C, the inner stress could suppress the crystal to form nanofloc. The nanostructures began to grow vertically on the substrate through a dissolution–recrystallization process, where needle-like nanostructures appeared on the surface of the sample (as shown in Figure 4b, Surf 2). When the hydrothermal temperature reached 190 °C, the length of the nanoneedles could be increased by elevating the reaction temperature, contributing to the formation of filamentous structures on the surface of the sample (Figure 4c, Surf 3). By further raising the hydrothermal temperature to 210 °C, it can be observed that the wire structured crystal could be achieved (Figure 4d, Surf 4). In this study, it was found that at a low reaction temperature, the nanostructures were mainly short and flat nanofloc. When the temperature increased, the nanosheets not only elongated, but are also shrank in the cross direction. At a sufficiently high temperature, the nanostructures became filamentous.

As shown in Figure 4, it can be observed that the nanostructures on the micro-conical array produced by the hydrothermal treatment could be tuned by adjusting the hydrothermal temperature. The laser-ablated surface of the sample can form small needles or filamentous structures after hydrothermal treatment. This method can produce ideal micro-nano-hierarchical structures. The images of Figure 4a–d correspond to hydrothermal reactions at 150, 170, 190, and 210 °C, respectively. As shown in Figure 4a, when the hydrothermal temperature was 150 °C, Surf 1 was covered by flocculent nanostructures with poor crystallinity. Many crystal dislocations/defects could be produced, existing at the crystal boundary during the hydrothermal growth process. When the hydrothermal temperature increased, the number of crystal nuclei generated by the hydrothermal reaction increased, and the rate of crystal growth also increased. The crystalline growth in the cross-sectional direction was inhibited due to the competitive growth from a large number of crystals simultaneously, leading to the inner stress in the radial direction. While increasing the temperature up to 170 °C, the inner stress could suppress the crystal to form nanofloc. The nanostructures began to grow vertically on the substrate through a dissolution–recrystallization process, where needle-like nanostructures appeared on the surface of the sample (as shown in Figure 4b, Surf 2). When the hydrothermal temperature reached 190 °C, the length of the nanoneedles could be increased by elevating the reaction temperature, contributing to the formation of filamentous structures on the surface of the sample (Figure 4c, Surf 3). By further raising the hydrothermal temperature to 210 °C, it can be observed that the wire structured crystal could be achieved (Figure 4d, Surf 4). In this study, it was found that at a low reaction temperature, the nanostructures were mainly short and flat nanofloc. When the temperature increased, the nanosheets not only elongated, but are also shrank in the cross direction. At a sufficiently high temperature, the nanostructures became filamentous.

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Figure 3. X-ray diffraction (XRD) patterns with different hydrothermal temperatures of micro/nano-hierarchical structures: (i) Surf 1: 150 °C; (ii) Surf 2: 170 °C; (iii) Surf 3: 190 °C; (iv) Surf 4: 210 °C. (a) After hydrothermal reaction; (b) After annealing treatment at 300 °C for 3 h.
Figure 4. Control sample 1 is the sample only treated by laser processing. Control sample 2 is the sample only treated by hydrothermal treatment, where the hydrothermal temperature was 190 °C. (a–d) SEM images of the hydrothermal reaction Ti alloy surfaces after laser ablation with a magnification of 500x. The hydrothermal temperature is (a) Surf 1: 150 °C; (b) Surf 2: 170 °C; (c) Surf 3: 190 °C; (d) Surf 4: 210 °C. Inset images is at the magnification of 5000x.

Table 1 summarizes the water contact angles (WCA) of all samples with micro/nano-hierarchical surfaces, which were modified by FAS-17. The WCAs of all surfaces exceeded 160° in their natural state at room temperature and ambient pressure, indicating the superhydrophobic surfaces. It is well-known that there are two classic models widely used to explain the hydrophobicity of rough surfaces: the Cassie–Baxter state and the Wenzel state [37]. When water droplets cannot penetrate into the structure, the solid–liquid contact state can be assumed as the Cassie–Baxter state. In this condition, the air trapped in the structured gaps can block the contact between the liquid and the surface, resulting in the water droplets easily rolling off from the surface without sticking. It also promotes a reduction in the contact area between the droplet and the sample surface. When the solid–liquid wetting model is in the Wenzel state, the surface still exhibits a large contact angle, however, water droplets are significantly infiltrated into the surface structure, so the water droplets adhere on the sample and it is hard to roll off them from the surface. Therefore, the solid–liquid contact state could only be determined by the combination of static contact angle measurement and the adhesion test of the surface to water droplets in the case of superhydrophobicity. Figure 5 shows the adhesion test of water droplets on the sample surface. The water droplet bumped on all surfaces and then left off. It can be found that the water droplets did not adhere onto the surfaces, which means that these micro/nano-hierarchical structured patterns can perform a Cassie–Baxter state when they make contact with the water droplets, leading to the blocking of water droplets to penetrate into the pattern and be suspended on the as-prepared surfaces [38–40].
When the temperature of a water droplet decreases below the freezing point, the molecules of water tend to bond in an orderly arrangement to form an ice nucleus and be frozen. During the anti-icing characterization, the water droplet loses heat to the samples’ surface. According to the analysis of structural characteristics, the nanostructures synthesized by hydrothermal treatment take up a part of the surface layer and a lot of air is trapped in the nanostructure to form air bags [38,39]. Thus, the water droplet is suspended up onto the micro-cone with nanostructures to decrease the wetting contact with the solid surface. These air bags rarely occur on surfaces with only micro-structures. Therefore, on the surface of the micro/nano-hierarchical structure, the water droplets isolated by the air bags find it more difficult to transfer the heat to the surface of the sample, resulting in the prolonged freezing time of water droplets.

**Table 1.** Water contact angle of all micro/nano-hierarchical surfaces.

| Hydrothermal Temperature/°C | 150  | 170  | 190  | 210  |
|-----------------------------|------|------|------|------|
| Samples                     | Surf 1 | Surf 2 | Surf 3 | Surf 4 |
| WCA/°                        | 161.2 ± 1.3 | 161.9 ± 1.3 | 161.7 ± 1.1 | 161.9 ± 0.4 |

**Figure 5.** Surface water droplet adhesion test corresponding to different hydrothermal temperatures of micro/nano-hierarchical structures: (i) Surf 1: 150 °C; (ii) Surf 2: 170 °C; (iii) Surf 3: 190 °C; (iv) Surf 4: 210 °C.

4. Anti-Icing Property

The anti-icing property of the as-prepared surfaces was investigated by the in-house platform. Figure 6a shows the photographs of the icing process of deionized water droplets on the as-prepared surfaces. Surf 0 is the control sample 1 where the surface was only processed by laser. Initially, the reference droplets on all surfaces were transparent (Frame 1). Then, it was observed that the droplet on Surf 4 became non-transparent after ~17 min (frame 2), which indicated that the droplet was frozen. After ~34 min (frame 3), the droplet on Surf 0 became non-transparent. In contrast, the droplets on other textured surfaces were still transparent. Then, after ~95 min (Frames 5 and 6), all the water droplets on the rest of surfaces were frozen. This implies that these surfaces (e.g., Surf 1, Surf 2, and Surf 3) had a relatively long time to resist the water freezing. Obviously, the micro/nano-hierarchical structure synthesized by the collaborative effect of laser processing and hydrothermal treatment at a suitable temperature can effectively enhance the surface anti-icing property, in comparison with the sample processed only by laser. Water droplets need to lose heat to be frozen. When the temperature of a water droplet decreases below the freezing point, the molecules of water tend to bond in an orderly arrangement to form an ice nucleus and be frozen.
After multiple measurements of anti-icing characterization, it can be observed that, when the hydrothermal temperature is 150, 170 and 190 °C, the anti-icing property can be really enhanced via tunable hierarchical nanostructures on micro-conical arrays of laser ablated substrates by hydrothermal treatment. However, it is interestingly that the DT of Surf 4 was much shorter than that of other surfaces, which means that the anti-icing property of Surf 4 becomes worse, as shown in Figure 6b. As known, the process of icing is mainly affected by the heat transfer between water and the medium. In terms of thermodynamics, the icing of water droplets needs to transfer heat to air and the substrate material under the temperature gradient. In this work, the water droplets were suspended over the as-prepared superhydrophobic surfaces and the solid–liquid–air three-phase interfaces existed, providing the droplet with the routes to gain or lose heat. For example, while decreasing the temperature of the anti-icing characterization platform, the water droplet loses heat to the cold as-prepared surfaces through contact heat conduction and thermal radiation between the droplet and the surface. On the other hand, the water droplets gain heat from air in the form of thermal radiation [41]. From the aspect of energy equilibrium, it can be quantitatively described as Equation (4) on the cold as-prepared surfaces:

\[ Q_d = Q_o + Q_g + Q_l, \]

where \( Q_d \) is the heat energy of droplet, which corresponds to its enthalpy; \( Q_o \) is the original heat energy of droplet; \( Q_g \) is the heat energy gains from air; and \( Q_l \) is the heat energy loss by thermal radiation between the droplet and the surface. The droplet is hypothesized to be stable in a spherical shape and the heat transfer from any point around the water droplet is homogeneous. The description of the heat transfer between the droplet and ambient air is as per Equation (5):

\[ Q_g = \alpha S_d (T_a - T_d), \]

where \( \alpha \) is the radiant heat-transfer coefficient; \( S_d \) is the surface area of the droplet; \( T_a \) is the temperature of ambient air; and \( T_d \) is the temperature of the droplet. Fourier’s law is also introduced to describe the heat transfer \( (Q_l) \) between the droplet and surface as Equation (6):

\[ Q_l = \int_{T_1}^{T_2} KS_c dT, \]

where \( T_1 \) is the temperature of the droplet; \( T_2 \) is the temperature of the sample surface, which is controlled by the temperature control platform; \( K \) is the heat-transfer coefficient; and \( S_c \) is the
solid–liquid contact area. Combining Equations (4)–(6), the heat transfer equation is derived as Equation (7):

$$Q_d = Q_o + \alpha S_d (T_a - T_d) + \int_{T_1}^{T_2} KS_d dT,$$

(7)

Assuming that the water droplet on the as-prepared surfaces lose the same amount of heat to air, the contact heat conduction from water droplets to the sample surfaces is the key factor affecting the DT of droplets. Thus, the solid–liquid contact area is the key factor affecting the contact heat conduction, influencing the DT of droplets. The effect of different morphologies on the solid–liquid contact area is further investigated by observing the contact states of various surfaces with water droplets after cooling. After placing all the micro/nano-hierarchical structure samples at −5 °C for 3 min, it was observed that the water droplet on Surf 4 was firmly adhered to the surface, but the water droplets on other surfaces easily rolled off, as shown in Figure 7a, indicating that the superhydrophobic state of Surf 4 may change from a Cassie–Baxter state to a Wenzel state in 3 min, while Surf 1–3 still maintained a Cassie–Baxter state. This may be due to the condensation of the humidity on the surface, which occurred at low temperature. Surf 4 seems to have a much larger surface area than the other samples (because it was covered with numerous nanowires, as shown in Figure 4), which increased the number of van der Waals interactions between the vapor phase molecules inside the confined spaces and is more exposed to the water capillary condensation phenomenon that leads to the loss of the Cassie–Baxter state, allowing water droplets to penetrate into the surface and forming “sticky” drops. When Surf 4 was subsequently tilted, the droplet remained adhered without rolling-off behavior [42]. This greatly increased the solid–liquid contact area $S_c$ (as shown in Figure 7b), enhancing the heat dissipation efficiency of the liquid and causing the water droplets on the surface to freeze more easily. Accordingly, it was observed that $t_{surf \ 4} < t_{surf \ 0} < t_{surf \ 3} < t_{surf \ 1} < t_{surf \ 2}$, where $\ t$ is the duration to sustain the Cassie–Baxter state before state transition at low temperature, resulting in $DT_{surf \ 4} < DT_{surf \ 0} < DT_{surf \ 3} < DT_{surf \ 1} < DT_{surf \ 2}$, as shown in Figure 6b. Consequently, the structural differences of the superhydrophobic surface can significantly impact delayed freezing time. The capability of the as-prepared surfaces to maintain the superhydrophobic Cassie–Baxter state determines the delayed freezing time. Although the micro/nano-hierarchical structures can effectively delay the freezing time, water droplets are more likely to penetrate into the structure and accelerate freezing while the nanowire structure dominates the surface morphology.

![Figure 7.](image-url)

Figure 7. (a) Water droplet adhesion test after 3 min at a temperature of −5 °C; (b) The abridged general view of transformation from the Cassie–Baxter state to the Wenzel state by decreasing the ambient temperature.
5. Conclusions

Superhydrophobic surfaces with hierarchical nanostructures on micro-conical arrays have been successfully fabricated on Ti alloy substrates through a combination of laser ablation and hydrothermal treatment. The nanostructures, transforming from flocs to filamentous, can be tuned by adjusting the hydrothermal temperature. Moreover, the constructed superhydrophobic surfaces with a micro/nano-hierarchical structure can efficiently delay the freezing of water droplets, which is mainly attributed to the fact that the structure hindered the contact of the water droplets with the solids, reducing the heat loss efficiency of the water droplets and enabling the resistance of water droplets for a longer time without freezing. It was also found that denser nanowire structures are likely to trap the water droplets and convert the solid–liquid wetting model from the Cassie-Baxter to Wenzel states by decreasing the ambient temperature, which shortens the delay time of the water droplet freezing. It is expected that micro/nano-hierarchical structures with nanoneedles on micro-conical arrays promise an achievable future for developing a surface anti-icing strategy.

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