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**Nickel-based Coatings and Structures for
Hydrophobic/Icephobic Applications**

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Abstract

Ice accretion often causes severe hazards and results in performance degradation to outdoor facilities and infrastructures ranging from aviation systems to energy constructions and so on, leading to huge economic loss or even catastrophic failures. Ice protection systems, typically in the form of icephobic coatings, have been receiving intensive attention in recent years due to the increasing requirement in relevant application areas. However, the design and creation of icephobic coatings for practical applications in severer environmental conditions (e.g. rain erosion) remains a big challenge, especially the limited service life and poor mechanical durability of icephobic coatings in long-time service.

This study aims to develop effective hydrophobic/icephobic coatings and structures with high durability because high durability could ensure the service life in long-time service. To start, the feasibility of metallic based coatings for hydrophobic/icephobic applications was investigated based on Ni-Cu-P ternary coatings due to its high mechanical properties and good anti-corrosion resistance. The time-dependent wettability phenomenon has been verified. The effect of time-dependent wettability and surface gaseous adsorption on the coating icephobicity was also studied for the first time. A new construction of durable icephobic layer structures using porous Ni foam skeletons and polydimethylsiloxane (PDMS) fillings was proposed, which demonstrated good mechanical durability and icephobic performance.

First, Ni-Cu-P ternary coatings with hierarchical cauli-flower structures were prepared using an electrodeposition method on 304 stainless steel (SS) substrates and the optimised preparation parameters were also investigated. The adsorption of airborne hydrocarbon molecules and decrease of lattice oxygen groups would alter the surface free energy and introduce more hydrophobic groups onto the coating surface, resulting in the changes of wetting behaviour from hydrophilic state to hydrophobic state, and

causing the observed time-dependent surface wettability.

To better investigate the time-dependent wettability phenomenon, a comparison study using different surfaces and coatings including electroless deposited Ni-Cu-P coatings, 304 SS, CeO₂ and PDMS polymeric coatings has been carried out and help with the understanding of the mechanism. The results showed that the main reason for the time-dependent wettability among the studied systems could be similar to that of Ni-Cu-P coatings, which is ascribed to the adsorption of airborne hydrocarbons and the change of lattice oxygen on the coating surface. The stable hydrophobicity of PDMS layer that does not show any time-dependent wettability also verified the significant role of the surface gaseous adsorption.

The effect of time-dependent wettability on icing behaviour has also been studied using Ni-Cu-P ternary coatings. The results showed that the icing time of water droplets on the Ni-Cu-P coatings in hydrophilic state was decreased significantly, and the ice adhesion strength suffered a sharp increase. The ice removal efficiency with electro-thermal heating also deteriorated in the hydrophilic state, accompanied by a significantly increased energy input and longer detachment duration and higher detachment temperature. Due to the spontaneous surface adsorption of gaseous species (mainly hydrocarbon groups) during the ageing process in ambient air, the coating could recover back to the hydrophobic state, and the increased icephobicity is also regained. The adsorbed hydrocarbon species would promote the formation of air pockets between the ice-coating interfaces, which could effectively reduce the interfacial contact of the formed ice with the coating. When the adsorbed hydrocarbon species were removed by plasma cleaning, water droplets tended to have more direct contact with the coatings prior to icing, leading to the formation of interlocked ice, which significantly increased the ice adhesion on the surface. In-situ water condensation and ice formation process observed by environmental scanning electron microscopy (ESEM) confirmed the role of air pockets and the presence of interlocked ice. The variation of surface icephobicity could also be attributed to the changes in surface energy due to the surface adsorption.

The results indicated that the surface gaseous adsorption in air played an important role in determining the surface icing behaviour and the icephobicity of the materials.

A new design concept of combining robust porous metallic skeletons and icephobic filling was then proposed to construct a two-phase layer structure with good anti-icing and de-icing performance, as well as excellent mechanical durability. Nickel/PDMS layers with small surface cavities were prepared using porous Ni foam skeletons (phase I) impregnated with PDMS (phase II) as the filling material by a two-step method (vacuum impregnation and spinning coating). The surface topographies, wettability and icing process were studied. Excellent icephobicity and mechanical durability of the two-phase Ni foam/PDMS icephobic layers have been verified. Under an external force, micro-cracks could be easily initiated at the Ni foam/PDMS interface region due to the small surface cavities and elastic modulus difference between Ni and PDMS, which would promote the fracture at the ice/solid interface and thus significantly lower the ice adhesion strength. Electro-thermal heating tests also confirmed the good thermal transfer efficiency of Ni foam/PDMS layers. The surface morphology and icephobicity remained unchanged after the water-sand erosion test, showing the good mechanical durability. ESEM was also used to study the in-situ icing process on the samples. The icing and de-icing cycle supported the low ice adhesion of the two-phase layer structures. By combining the advantages of mechanical durability of porous Ni skeleton and icephobicity of PDMS matrix, the Ni foam/PDMS layer demonstrates great potential for ice protection with long-term service time.

List of Publications

Journal paper:

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List of Abbreviations

Adv	– Advancing water contact angle
AFM	– Atomic force microscope
BE	– Binding energy
BSE	– Backscattered electron
CA	– Contact angle
CAH	– Contact angle hysteresis
CNT	– Carbon nanotube
CVD	– Chemical vapour deposition
DC	– Direct current
DLC	– Diamond-like carbon
DVB	– Divinyl benzene
EDX	– Energy dispersive X-ray spectroscopy
EHD	– Electrohydrodynamic
ESEM	– Environmental scanning electron microscopy
FAS-17	– Fluoroalkylsilane
fcc	– Face centred cubic
FE	– Finite element
GNR	– Graphene nanoribbon
GSED	– Gaseous secondary electron detector
KE	– Kinetic energy
LDPE	– Low-density polyethylene
LIT	– Low-interfacial toughness
MAGSS	– Magnetic slippery surface
MD	– Molecular dynamic
MN	– Micro- and nanoscale
MS	– Micrometer-scale pit surface
Ni	– Nickel

NS – Nanowire structured surface

NTSB – National Transportation Safety Board

PDF – Powder diffraction file

PDMS – Polydimethylsiloxane

PECVD – Plasma enhanced chemical vapour deposition

PFA – Polyfluoroacrylates

PFDA – 1H, 1H, 2H, 2H-perfluorodecyl acrylate

POSS – Polyhedral oligomeric silsesquioxane

POTS – 1H,1H,2H,2H-perfluorooctyltriethoxysilane

PP – Polypropylene

PTFE – Polytetrafluoroethylene

R – Thermal resistance

Ra – Surface roughness

Rec – Receding water contact angle

REO – Rare earth oxide

RF – Radio frequency

RPM – Revolutions per minute

SA – Sliding angle

SDS – Sodium dodecyl sulfate

SEM – Scanning electron microscope

SHS – Superhydrophobic surface

SLIPS – Slippery liquid-infused porous surfaces

SLWL – Self-lubricating liquid water layer

SPS – Suspension plasma spraying

SS – Stainless steel

TPG – Tripropylene glycol

TSU – Thermosetting polyurethane

UV – Ultraviolet

WCA – Water contact angle

XPS – X-ray photoelectron spectroscopy

List of Abbreviations

XRD – X-ray diffraction

2D – Two dimension

3D – Three dimension

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Chapter 1 Introduction

1.1 Background and Motivation

Undesirable icing phenomena including formation, accretion, and adhesion of ice, snow, frost, glaze, rime or their mixtures could cause severe socio-economic impacts in daily life and could even lead to catastrophic failures in certain situations such as transportation systems, infrastructure, wind turbine and many other areas [1-3]. Therefore, it is of great significance to mitigate the icing problem on certain surfaces. Over the last decade, intensive attention from researchers all over the world has been put into the area [4, 5].

Hydrophobic surface is defined as a solid surface with a static water contact angle (WCA) higher than 90° and tends to repel water droplets. High WCA on hydrophobic surfaces would decrease the contact area and thermal transmission between the water droplet and surface, which could help to minimize the ice accretion and delay the icing phenomenon. There are two key factors influencing the surface hydrophobicity: surface topography, e.g. hierarchical micro/nanostructure [6] and surface energy determined by the material composition [7]. The hierarchical structures and low surface energy could introduce high energy barrier and thermal barrier for ice formation [8, 9].

Inspired by the hydrophobic concepts, some reports suggest that surface hydrophobicity could be applied to design the icephobic coatings due to the capability of water repellency and freezing delay [9, 10]. Zheng et al. fabricated superhydrophobic aluminium surface with hierarchical micro/nano structures by anodization method which has a water contact angle of 156° , exhibiting a delay in ice formation and low ice adhesion strength of 40 kPa [11]. Wang et al. reported that superhydrophobic steel surface prepared by chemical etching process demonstrated excellent anti-icing

properties [12]. It is widely believed that the hydrophobic surface would help to repel water droplets and delay or prevent ice nucleation and play the dominant role.

For icephobic coatings, they should meet the following characteristics: firstly, the condensed water droplets in supercooled state could roll off easily and quickly from the coating surface before ice solidifies; secondly, the coating surface could prohibit or introduce delay effect to the ice nucleation process of the supercooled water droplets; thirdly, once supercooled water droplets become ice, the icephobic coatings could bring effective reduction to the ice adhesion strength between the interfaces [13]. Many new concepts have been proposed to design and develop new icephobic coatings and surfaces. For instance, enlightened by the slippery pitcher plant that repels liquid and solid, slippery liquid infused porous surfaces (SLIPS) has been intensively reported for its icephobic capacity and application recently [14, 15]. The low ice adhesion strength of SLIPS proves its potential in icephobic surfaces. Various types of oils have been chosen as lubricants and applied on different substrates to fabricate SLIPS. For example, Kim et al. prepared SLIPS-coated Al surface by infusing a water-immiscible liquid into a chemically functionalized nanostructured surface, which suppressed ice/frost accretion and provided lower ice adhesion compared to reference materials [16]. Irajizad et al. studied magnetic slippery surfaces (MAGSS) by exploiting the magnetic volumetric force to exclude the role of solid-liquid interface in ice formation and induce a liquid-liquid interface [17]. The magnetic liquid-liquid interface with low surface energy could help to shift the ice nucleation towards the homogeneous nucleation limit. These surfaces show extreme icephobicity with ice adhesion strength of 2 Pa and 2-3 orders of magnitude extended ice formation time. Another inspiration is the crack-initiation design concept, He et al. [18] obtained a sandwich-like PDMS sponge with a sugar-made template. The reduced apparent elastic modulus and macroscopic crack initiators at the ice-solid interface helped with the super-low ice adhesion strength as low as 0.9 kPa. The durable performance had also been verified by the remaining constant icephobic adhesion after 25 icing and de-icing cycles.

Among current mainstream hydrophobic/icephobic coatings, various polymeric coating systems have been developed intensively and it could be found that polymeric coatings form a very important and large part of current research [15, 19, 20]. A myriad of reports has been published on polymeric icephobic coating systems or using the polymer modification. But the limited durability of these polymeric coatings remains the biggest challenge [21], as they cannot survive long-termly in a harsh environment, which is a major restriction for their practical applications [22, 23]. The stability in long-term service would inevitably be limited by their poor durability. The depletion of the lubricants remains a serious problem during icing/de-icing cycles [24-26]. It is essential for icephobic surfaces to maintain long-term durability during their service when exposed to severe mechanical, and erosive environmental conditions.

The current development for durable and reliable icephobic surfaces still remains elusive. A range of research has been carried out to address the remaining challenge. For example, Irajizad et al. fabricated a new type of icephobic material composed of silicone elastomer matrix with high shear modulus and highly dispersible silicon-based gel, having low shear modulus [32]. The surface shows fairly low ice adhesion that is derived from the crack initiation based on the stress-localization concepts. However, a durable icephobic surface with good erosion resistance in long-time harsh service environments still remains deficient.

In recent years, metallic-based surface and coatings have been attracting significant interests due to their outstanding mechanical durability and possible multifunctionalities. For example, Wei et al. prepared a Fe-based composite surface using electro-brush plating which exhibited excellent hydrophobicity, anti-corrosion performance and abrasion resistance [27]. Khorsand et al. fabricated super-hydrophobic Ni-Co coatings that exhibited good chemical stability and long-term durability as well as the self-cleaning effect [28]. Vorobyev et al. reported a hydrophobic multifunctional metal surface showing combined effects of self-cleaning, anti-biofouling, and self-sanitation by producing a hierarchical nano- and micro- structures with femtosecond

laser pulses [29].

Among the metallic coatings, Ni-Cu-P ternary coating system is a promising candidate for practical hydrophobic applications because of its high mechanical properties, showing good mechanical strength with hardness of 8.5 GPa and modulus of 175 GPa [30] and anti-corrosion performance [31]. The anti-corrosion performance of Ni-Cu-P coatings is superior to common Ni-based coatings, which mainly come from the absence of the defects, corrosion current decrease from amorphous phosphorus and free energy reduction effect from the incorporation of Cu [32]. Ni-Cu-P coatings also possess improved anti-friction and anti-wear performance, as compared with ordinary Ni-based coatings [33, 34]. So in this work, Ni-Cu-P ternary coatings with hierarchical structure by different methods will be prepared to investigate the feasibility as hydrophobic/icephobic coatings. New durable Ni-based structures will also be developed with the design concept of using Ni foam as porous skeleton and Polydimethylsiloxane (PDMS) as the filling material, to provide alternatives for designing durable icephobic surfaces.

Another main priority is that the influencing factors on material icephobicity have not been well identified. There are many factors that could affect surface icephobicity. In certain circumstances, the hierarchical surface that is necessary for hydrophobicity could increase the ice adhesion strength which is contradictory for icephobic applications [35]. The icephobicity of materials surface often refers to the capability of delaying the ice nucleation and growth [16], as well as the “non-stick” feature - low ice adhesion [36]. It is believed that the icephobicity of a material surface is affected by many factors: surface condition, relative humidity of atmosphere [37], liquid water content [38], and mechanical adhesion [39], etc. Among them, the surface condition could be one of the dominating factors. Some recent work demonstrates that the surface gaseous adsorption on the material surface could have significant impacts on surface condition, reflected by the change of wettability [40, 41]. Feng et al. reported a reversible conversion of surface wettability on aligned ZnO nanorod films caused by

the adsorption and desorption of surface hydroxyl groups using ultraviolet (UV) illumination and dark storage, respectively [42]. Archana et al. found that plasma-treated CuO/Cu(OH)_2 exhibited reversible wettability transition due to the surface adsorption [43].

It has been noticed by some researchers that the unusual time-dependent wettability phenomenon may bring effects on coating hydrophobicity and icephobicity [44, 45]. However, there is a lack of direct investigation on the effect of time-dependent wettability on the material icephobicity. The unusual feature of time-dependent wettability has not been disclosed and the detailed surface wetting and icing mechanism have yet to be studied. In this work, the time-dependent wettability of coatings will be investigated, the common principle and the practicability of the phenomenon in both metallic system, ceramic system and polymer system will also be studied. The relationship between time-dependent wettability and coating icephobicity will also be studied in detail. The study could help to establish universal and repeatable testing standards when evaluating the material icephobicity, which is also a critical issue for the development of icephobic coatings and surfaces.

1.2 Project Aims and Objectives

Based on the background information, it is known that the undesirable icing phenomenon has become a severe problem and brings many hazards to the industries. To address the existing icing problems, huge attention has been paid to the relevant area. Great progress has already been made, but there are still many unsettled problems for current icephobic coating development: the ice accretion between hierarchical structures under high humidity environment, the de-icing energy efficiency, and the limited mechanical durability under harsh environment. Many new physical concepts and coating designs have been put forward successively for addressing these problems. However, a durable icephobic surface with good erosion resistance in long-time harsh

service environments is still unavailable.

The main aim of this research is to develop new types of reliable and durable icephobic coatings for potential ice protection applications, mainly on nickel-based coatings and structures. The underlying hydrophobic/icephobic mechanisms will be studied, including the time-dependent wettability and its effect on coating icephobicity.

To achieve the above aims, several objectives have been defined as below:

- The feasibility study using nickel-based coatings as hydrophobic/icephobic applications will be attempted. The Ni-Cu-P ternary coatings and the metallic skeleton promoted two-phase layer structures using Ni foam and polymer fillings will be developed.
- Different fabrication techniques including electro-deposition, electroless deposition, vacuum impregnation and spin coating methods will be used to prepare the hydrophobic/icephobic coatings with different surface structures and properties. The optimised preparation parameters will also be investigated simultaneously.
- Multiple characterisation techniques will be adopted to characterise the surface morphologies, phase composition, surface chemistry variation. The relationship between these structural features and experimental conditions will be investigated and discussed.
- Surface wettability and icephobicity evaluation including standard and home-made facilities will be conducted to study the overall performance of coating samples. The icephobicity will be assessed from both anti-icing and de-icing aspects in terms of icing delay, ice adhesion strength and ice removal efficiency, etc.

- The specific relationship between the time-dependent wettability and coating icephobic behaviour will be established based on the wettability characterisation and relevant icephobicity results in different coating systems.

1.3 Scope of Thesis

This thesis will be divided into seven chapters:

Chapter 1 briefly introduces the main task of this study and the importance of the applications of ice protection systems in various aspects of daily life and industries. The basic background, research motivation, project aims and objectives of the research have been further outlined. The scope of the thesis is also outlined in this chapter.

Chapter 2 presents the literature review of this project, which mainly consists of the significance of ice protection system, principles and basic theories of hydrophobicity and icephobicity, research progress and current challenges and solutions towards hydrophobic/icephobic surface. Chapter 2 specifically reviews the fundamental literature related to icephobic mechanisms and the most up-to-date progress in relevant fields.

Detailed methodologies including applied substrates, coating preparations, icephobicity and durability tests, and related characterisation are presented in Chapter 3. The preparation process of Ni-Cu-P coating and Ni foam/PDMS layer structures and other experimental details are provided. The fundamentals of microscopic, spectroscopic and icephobic characterisation techniques employed in this study will also be introduced in this chapter.

Chapter 4 focuses on the fabrication and optimization process of electrodeposited Ni-Cu-P coatings. Primary investigations and characterisations including the scanning

electron microscopy (SEM), Energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), X-ray photoelectrons spectroscopy (XPS), 3D topography and environmental scanning electron microscopy (ESEM) observation have also been carried out. The good mechanical durability of Ni-Cu-P coatings and the wettability evolution of as-deposited coating during ageing process has also been confirmed. The surface variation along with the changing wettability will also be investigated to explain the phenomenon.

The detailed mechanisms of time-dependent wettability will be investigated systematically using different material systems. The main causing factors of this phenomenon could be the adsorption of airborne hydrocarbon and the change of lattice oxygen on the coating surface. While for polymeric system, it is chemically inert and cannot bond easily to airborne hydrocarbon groups, so the time-dependent wettability does not exist in the polymeric system. It also proves that the surface gaseous adsorption could be the significant resulting factor of the phenomenon. Multiple icephobicity evaluation methods focusing on anti-icing and de-icing aspects and in-situ ESEM observation of water condensation and icing formation will also be applied to evaluate the icephobic performance of samples with different wettability. The underlying relationship between coating icephobicity and time-dependent wettability will be studied and discussed in detail in Chapter 5.

Chapter 6 introduces a new design concept of combining robust porous metallic skeletons and icephobic filling to construct a two-phase layer structure. The two-phase Ni foam/PDMS layer structures with fine surface cavities have been prepared. The icephobicity of the layer structures could also be improved by the icephobic PDMS layer, the micro-crack initiation mechanism and improved energy use efficiency will also be studied and discussed. The mechanical durability could be significantly promoted with the use of Ni foam skeleton. The reduction and adsorption effect of Ni foam skeleton regarding shock and vibration energy from the water-sand impinging erosion tests will also be demonstrated. The two-phase Ni foam/PDMS layers will perform well at icephobic applications and remain stable under severe water-sand

impinging test.

Finally, the conclusions of the study are refined and summarised in Chapter 7. New design strategies for icephobic coatings are proposed based on the investigation of relevant hydrophobic/icephobic mechanisms and coating feasibility in this study. Recommendations for future work are also provided at the end of this chapter.

Chapter 2 Literature Review

Icing, a term used to describe the process of ice or wet snow growth on a structure exposed to the atmosphere, has become a serious issue to various industries and daily lives such as disturbing the aviation industry, downing the power cables, freezing the roads, and perturbing the operation of wind-turbine blades, etc [46, 47], as shown in Figure 2.1. Icing in electricity transmission systems can lead to collapse of poles and towers and rupture of conductors. Icing in cooling systems significantly drops the heat transfer rate leading to their inefficient operation [48]. According to Lawrence Berkeley Laboratory, ice storms account for 10% of power transmission outages in United States [49]. Among them, flight safety is undoubtedly the most important. The accretion of ice on aircraft could cause severe aerodynamic and flight mechanical effects due to disrupted aerodynamics or lead to disastrous general aviation accidents [50, 51]. For example, a 1.2 mm ice layer accreted on the aircraft could cause up to 25% reduction to the lift force and lead to difficulty in handling the aircraft [52, 53]. Consequently, the performance of aircraft are hugely affected by ice accretion and disasters may happen. The adherence and accretion of snow and ice could also result in far more inconvenience to the daily lives, bringing about enormous economic loss [54, 55]. So it is very important to take measures for addressing such factors. In order to efficiently prevent or suppress ice build-up, a lot of studies focused on freezing physicochemical mechanisms and ice protection strategies has been gaining extensive attention from researchers all over the world. Researchers and engineers are trying to create effective technologies that could minimize the hazard of ice formation and accelerate the de-icing process.



Figure 2.1 The icing problems in a broad spectrum of systems including transportation systems, power systems, and energy systems [48].

2.1 Ice Protection System

2.1.1 Aircraft icing

The phenomenon of ice adhesion and accretion could cause adverse impacts on both safety and performance. Especially the build-up of ice could be a huge threat to the aviation industry. When a plane is in the sky, ice formation could take place at high altitude. When icing occurs, the performance of the aircraft will be hugely influenced which may lead to disasters. The adherence of snow and ice to the airframe also has a significant impact on operation, particularly during take-off and landing. In the aviation industry, icing-related accidents account for more than 15% of aircraft crashes [56].

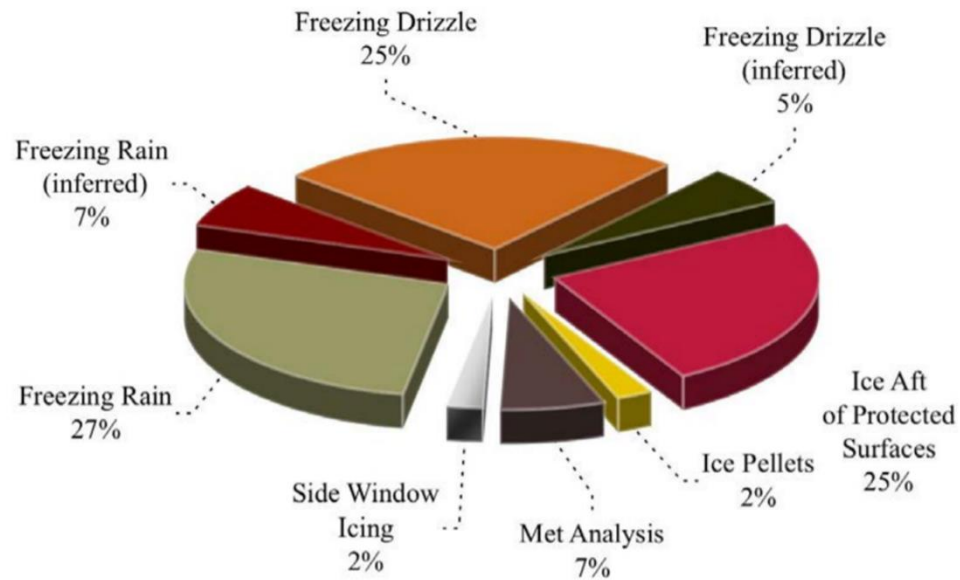


Figure 2.2 Different inflight icing conditions from National Technical Information Services (NTIS) [57].

As shown in Figure 2.2 which is derived from the Meteorological Aerodrome Report, there are different common Inflight icing conditions, including the freezing rain, freezing drizzle, and other ice related problems such as ice pellets, ice aft of protected surfaces and so on [57]. Based on a study from 2009 to 2014, 65 aircraft incidents were categorized as Loss of Control In-flight (LOC-I), as demonstrated in Figure 2.3, the data comes from the Annual Safety Review 2014 (European Aviation Safety Agency, 2015) [58]. Icing conditions were found to be related to six accidents (most severe scenario), two serious incidents, and not related to incidents (least severe scenario). Icing problems are among the top contributing factors for most severe accidents jeopardizing aircraft safety.

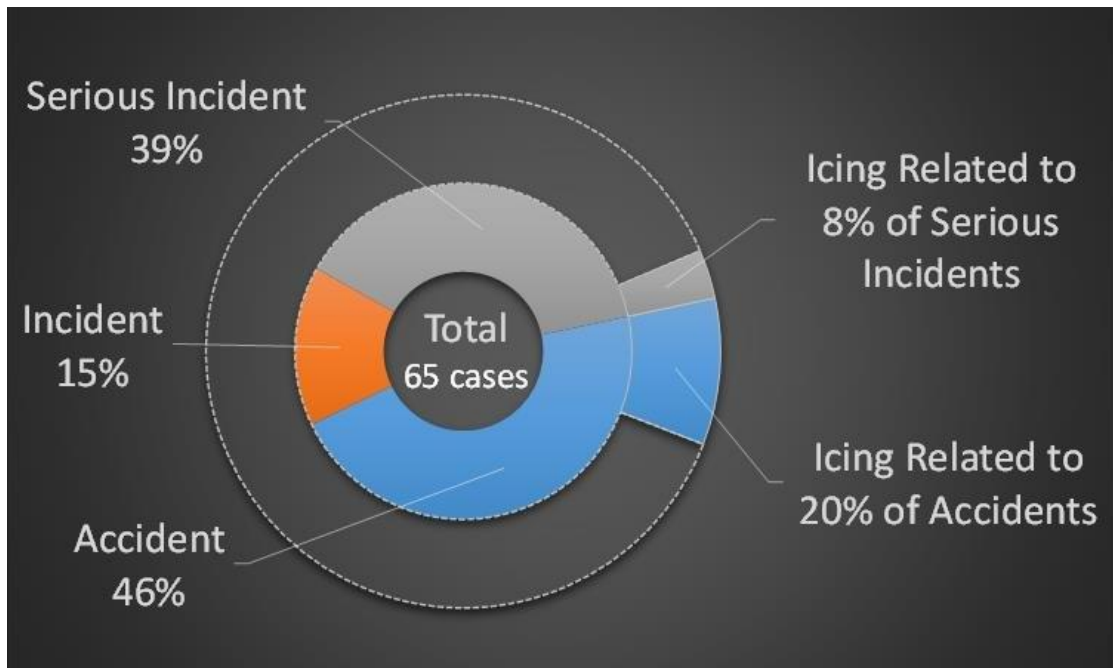


Figure 2.3 Distribution of icing related Loss of Control In-flight aircraft incidents [58].

The icing phenomenon on aircraft is normally affected by the shape and metrological conditions of engineering parts [59]. Ice is more likely to construct on prominent parts of the aircraft, including the windward surfaces of the wings, tails, windscreen, engine inlets, blades, airspeed tubes, and antennas. The shape of the leading edges of the engineering parts could also have significant effects on the ice accretion.

Figure 2.4 shows that the icing phenomenon on aircraft could be categorized into the following types according to the degree of hazard, including glaze ice, glaze and rime ice, and rime ice [60]. For glaze ice, it generally occurs in the temperature between 0 °C to -10 °C. Normally, the most dangerous icing conditions are surfaces with formed smooth, transparent, and strong glaze ice. The glaze and rime ice is also relatively rough and often occurs in the temperature range from -10 °C to -20 °C. While for rime ice, it often generally appears when aircraft suffer significant temperature change. The formed undesirable ice on airplane wings would change the shape of the wings, making it difficult to maneuver or even lead to a crash. If the engine air intake is frozen, the airflow would then change, leading to the reduction of engine efficiency and even sudden stop.

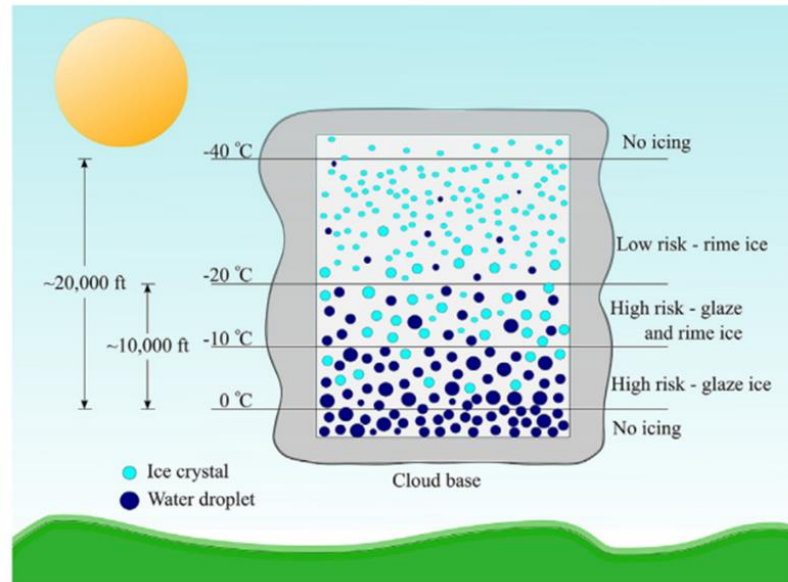


Figure 2.4 Ice formation within a cloud and the resulting probability of aircraft icing [60].

Because of the various shapes, the icing phenomenon could be unavoidable on many sensors of the aircraft. Ice accretion on engine blade or impact from fallen ice could also lead to engine failure. For example, a crash could easily occur if one of the parts including the airspeed tube, elevation sensor, temperature sensor, atmospheric data sensor fail. Besides, the formed ice on the windshield of the aircraft could also obstruct the pilot's vision seriously, which raises risks on the safe operation. The icing phenomenon including ice accumulation and ice accretion on radome and other parts will also increase the overall weight, making the aircraft difficult to manipulate even lead to a crash, causing serious incalculable consequences [61]. So it is very important to take measures for addressing such problems. Ice protection systems have now been widely applied to solve the icing problem.

2.1.2 Current ice protection methods

At the current stage, the de-icing fluid, a chemical mix of glycol and water is most commonly used as active de-icing methods to remove the formed snow and ice on aircraft or prevent the formation of ice by lowering the freezing point of water and preventing the bonds between ice and paved surfaces before the aircraft take off [62].

The fluid is usually heated and sprayed on an airplane with pressure in order to remove the existing ice and snowflake. The main two types include propylene glycol and ethylene glycol. But de-icing fluid has limitations in preventing further ice formation. If ice precipitation falls, it is very important to remove them and stop ice from forming again before take-off [63]. What is more, the usage of de-icing fluid is also not eco-friendly, the discharge and improper handling of the chemicals could lower the oxygen levels in waterways and prevent fish and other aquatic creatures from breathing, the chemicals that end up in nearby waterways could slowly create waterways that would not support life [64].

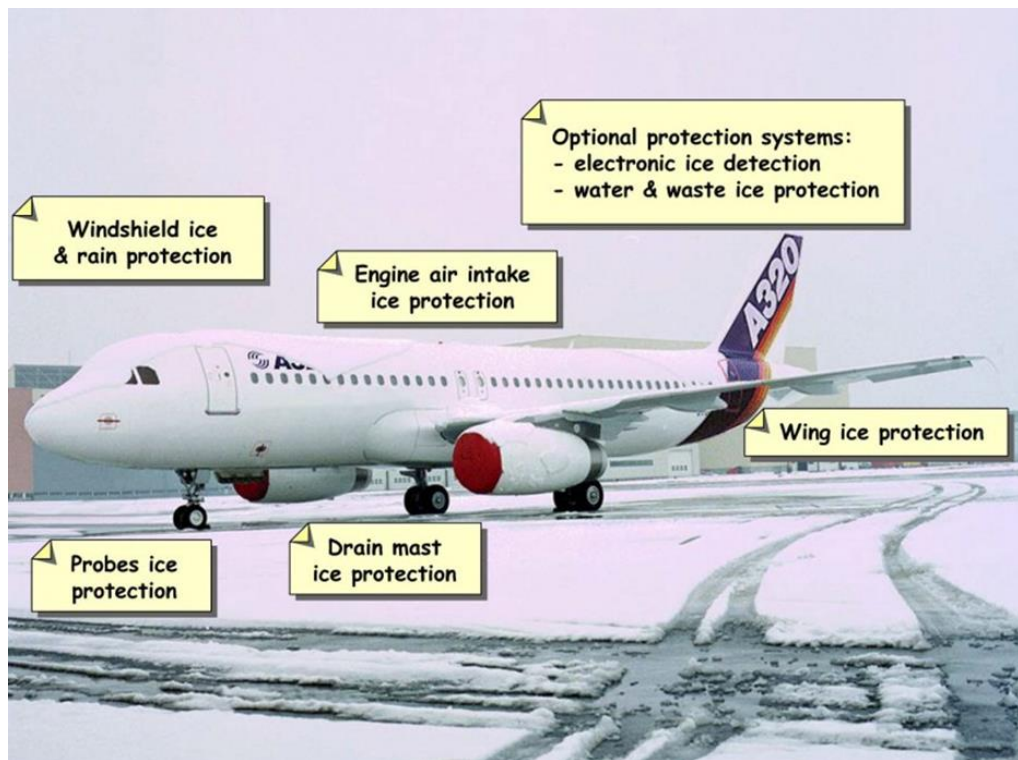


Figure 2.5 Schematic of aircraft ice protection system [46].

Apart from the de-icing fluid, as such, there have been great efforts devoted to the development of strategies for ice protection systems. So far, there are many anti-icing/de-icing methods, which could be summarized into two schemes. The active de-icing and passive anti-icing are the two main strategies used in industries [65]. Typically, the mainstream strategy to remove formed ice in aircraft systems is active de-icing,

which could be classified into chemical methods such as spraying anti-icing agents or de-icing liquids and physical methods (mechanical de-icing and de-icing with heat input). Using the exhaust hot air from the engines (vapour heating), which is oriented through piping onto the wings, engine openings, and other engineering parts, as indicated in Figure 2.5. The surfaces could be heated using the exhaust and the icing phenomenon could be delayed and eliminated. Besides, the electro-thermal melting and mechanical vibration methods are also widely used as ice removal approaches. So far, the ice prevention on aircraft wings mainly includes two parts, anti-icing and de-icing: anti-icing focuses on preventing water droplets from freezing on the surface, and the purpose of de-icing is to remove the formed ice from the surface, let the ice melt or fall off.

The aforementioned methods could be categorized into active de-icing methods. To date, the active ice protection methods mainly include: (1) pneumatic de-icing boots, it is mainly proper for low and medium speed aircraft [66]; (2) bleed air, it is mainly used to keep flight surfaces above the freezing temperature by directing the hot air from the jet engine into piccolo tubes routed through the engineering parts [67]; (3) mechanical de-icing: mechanical force is used to knock the ice off the flight surface, the actuator located underneath the skin of the structure is moved to induce a shock wave in the protected surface to dislodge/remove the ice, as indicated by Electro-mechanical Expulsion Deicing Systems (EMEDS) [68]; (4) thermal de-icing: use resistive circuits buried in the airframe structure to generate heat intermittently to shed ice as it accretes on key surfaces, the Thermawing system in Boeing 787 Dreamliner could be a good example [69, 70].

However, the technologies referred above are usually energy-intensive and high cost, relying on continuous heating or intermittent vibration, which would increase the weight of aircraft structure and control system as well as energy consumption. Hence the passive anti-icing/de-icing method is considered to be more appealing than active methods and a universal strategy for mitigating the icing problem. Passive de-icing

refers to the construction of surfaces or coatings with anti-icing/de-icing performance. On the one hand, the surface/coating could make it difficult for incoming water droplets to infiltrate the surface of the component and could be easily separated from the surface. The icing duration could be prolonged and the formed ice could be reduced. On the other hand, the formed ice could be shed away from the surface with a minimal applied force due to the low adhesion between the surface and ice. With the above two aspects, the aim of passive ice protection is then achieved. Material with excellent hydrophobic/icephobic performance could serve as a passive anti-icing agent to repel supercooled droplets, and thus less ice would form or adhere to the surfaces. In this way, the purpose of anti-icing could be achieved and the dependence on or even replacing the above-mentioned active de-icing methods could be reduced. For engineering surfaces, it could also decrease both the ice quantity and the adhesion of accreted ice [1].

In recent years, with more new types of coatings developing, more and more academic and engineering attention has been gained on the ice protection system due to their superior ice protection performance. Research on developing ice protection system is of great scientific and practical values. The advantages of less energy consumption and more eco-friendly than traditional methods make it a very economical supplementary way for aircraft system ice protection.

As shown in Figure 2.6, the ideal mechanism of ice protection system could be reflected in the following three aspects: firstly, it could help the water droplets in a supercooled state to roll off the surface quickly before the ice solidifies; secondly, the crystallization process of supercooled water droplets could be delayed; thirdly, once supercooled water droplets have frozen into ice, the ice protection system could bring effective reduction to the ice adhesion strength between the interfaces [13].

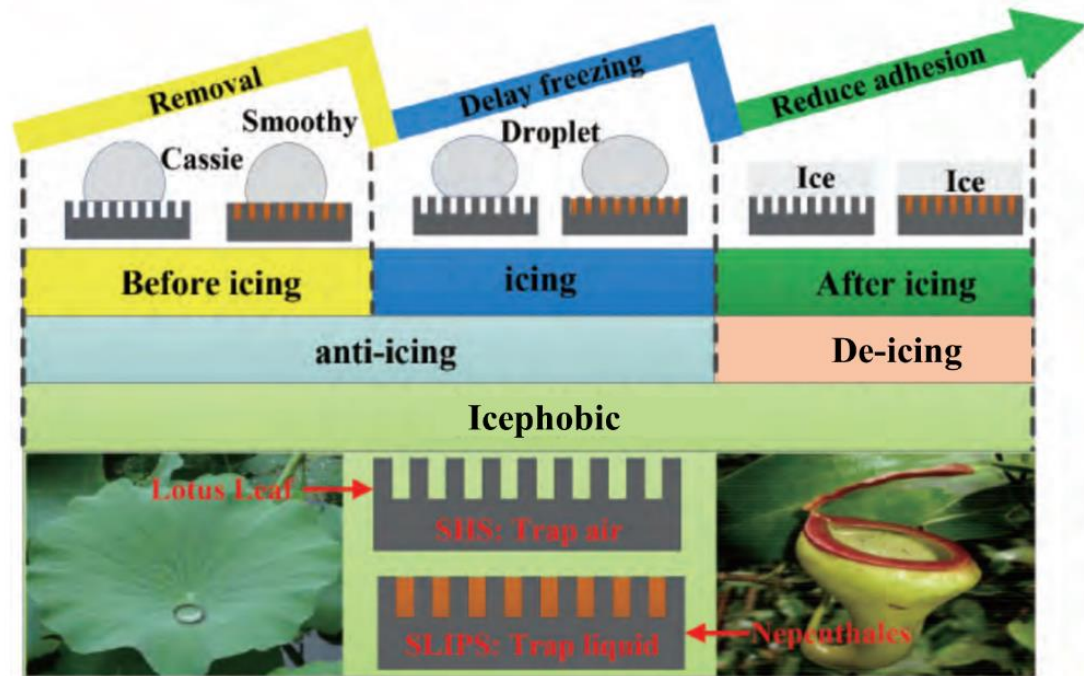


Figure 2.6 Schematics of ice protection systems (anti-icing/de-icing) [13].

2.2 Principles of Hydrophobicity and Hydrophobic Surfaces

It is suggested that surface hydrophobicity can be applied to design the icephobic coatings due to the capability of water repellency and freezing delay effect [9]. Some scholars have identified that hydrophobic surfaces could be used as potential candidates for icephobic applications [71]. The assumption behind this is that mechanisms of icephobicity and hydrophobicity are similar. By designing hydrophobic surface with large water contact angle or low surface energy, one can achieve weak adhesion between the surface and ice, the icephobic surface could be obtained. Here, the detailed mechanisms of wettability and icephobicity are explained in detail.

2.2.1 Basic wetting theory

Wetting behaviour is one of the most important characteristics of solid surface, and wettability at a static state is the result of the equilibrium of three phases (solid, liquid, and vapour) at the interfaces. When leaving a water droplet on a solid surface, the

droplet will not spread out entirely but keep part of the droplet shape and stay on the surface. It also forms a certain angle with the solid surface. As the water droplets under thermodynamic equilibrium state between the boundaries of solid, liquid, gas phase make tangent of solid-liquid interface and gas-liquid interface, the angle between the two tangents inside the droplets is called water contact angle. WCA is the balance of the three kinds of surface tensions between solid, gas, and liquid phase interfaces. The thermodynamic equilibrium state tries to make the overall system energy of the droplet be the minimum value. So droplets on solid surfaces always remain in stable state [72]. The advancing water contact angle (Adv) is determined for an increase in the contact area between the liquid and the solid, it corresponds to a dynamic on a completely dry substrate. The receding contact angle of water (Rec) corresponds to a decreasing contact area, a retraction on a wet substrate [73]. While for contact angle hysteresis (CAH), it is the difference between advancing and receding angles. It arises from the chemical and topographical heterogeneity of the surface, or swelling, rearrangement or alteration of the surface by the solvent. CAH cannot be measured directly but through the measurement of advancing and receding contact angles [74].

The wettability of solid surface could be characterised by WCA. The larger the WCA, the more difficult the surface to be wetted. Surface with WCA higher than 90 ° is called hydrophobic surface. Surface with WCA $\geq 150^\circ$ and contact angle hysteresis (CAH) $\leq 10^\circ$ is called superhydrophobic surface. The WCA is determined by the surface/interface free energy (or surface tensions) and could be explained by the classic Young's equation (2.1) [75]:

$$\cos \theta_y = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} \quad (2.1)$$

where γ_{sv} , γ_{sl} , and γ_{lv} are the surface tensions of solid-gas interface, solid-liquid interface, and liquid-gas interface, respectively. θ_y is the WCA of solid, liquid, and gas phase equilibrium, namely the intrinsic contact angle with solid surface, which is only

associated with the chemical composition of solid surface materials.

The Young's equation is the quantitative theoretical basis to investigate the wettability of solid surface and could only be applied to a smooth, ideal homogeneous solid surface [76]. However, the solid surface is often rough and uneven in real life. The surface wettability is not only related with the surface chemical composition, but also have important relations with surface roughness [77]. Normally, solid surfaces always have certain surface roughness. It is the rough structure that leads to the very big difference between the apparent WCA and the intrinsic WCA of the solid surface. In order to better analyse the wettability of real surfaces, two kinds of mathematical models Wenzel model and Cassie model were proposed to evaluate the wettability [78].

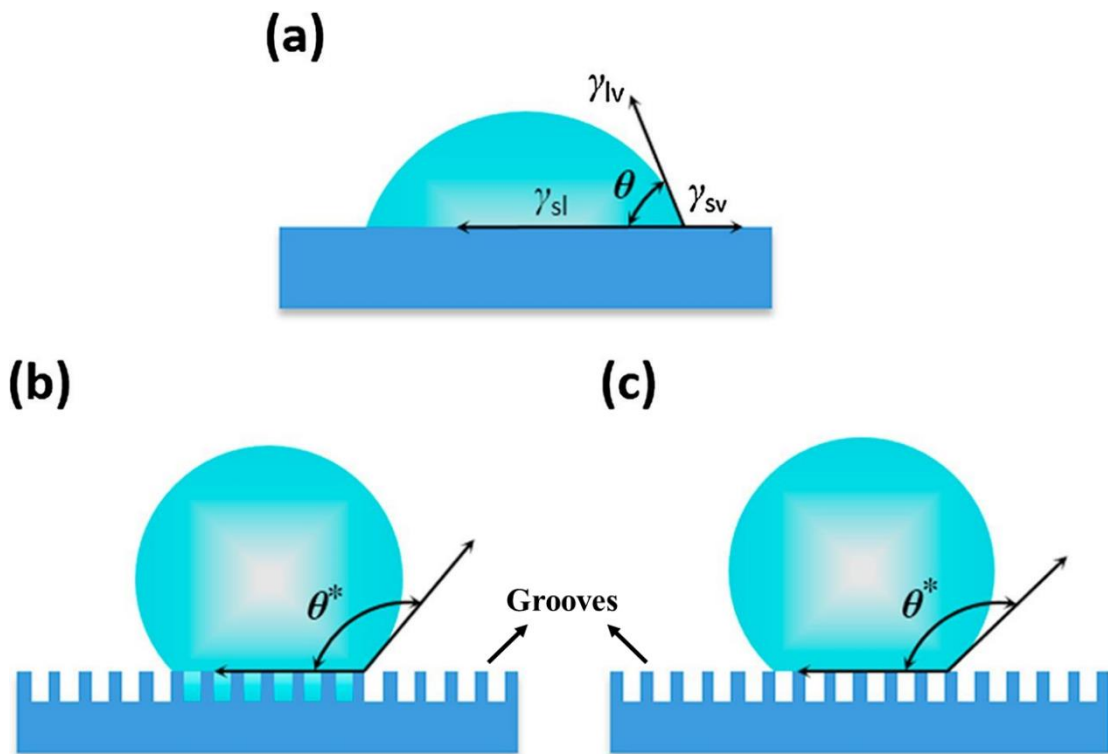


Figure 2.7 Typical wetting mechanisms (a) Young's contact mode on a flat surface (b) Wenzel mode on a rough surface (c) Cassie-Baxter mode on a rough surface with air trapping [79].

In 1936, Wenzel first referenced roughness correction factor to amend Young's equation. It was argued that because of the existence of solid surface rough structure, it increases

the real surface area. It makes the actual solid-liquid contact area much larger than the apparent geometry contact area. Surface roughness directly changes the contribution of solid-gas interfacial tension and solid-liquid interfacial tension to the system energy. This assumption model could be named as Wenzel model. According to the model, the WCA on solid rough surface could fit Wenzel equation [80] and is described as equation (2.2):

$$\gamma_{lv} \cos \theta_w = R_f (\gamma_{sv} - \gamma_{sl}) \quad (2.2)$$

where θ_w is the equilibrium water contact angle of Wenzel model, known as the apparent WCA of Wenzel model. R_f means roughness factor of solid surface, which is defined as the ratio of actual solid/liquid contact area over the nominal interface contact area. γ_{sv} , γ_{sl} and γ_{lv} are the surface tension of solid-gas interface, solid-liquid interface and liquid-gas interface, respectively.

When the wetting behaviour of the water droplets on solid surface fit the Wenzel model, the liquid could completely fit into the grooves, as shown in Figure 2.7. The movement of water droplets on the solid surface needs to overcome a series of potential barrier caused by the rough structure. If the vibration of water droplets cannot overcome these barriers, they would not scroll.

In 1944, Cassie and Baxter made further amendments to Wenzel's theory. They thought the rough structure of the solid surface as a composite surface. It is assumed that the water droplets cannot seep into the groove of a solid surface. There are some available air bubbles stranded by the grooves, leading the non-direct contact of water droplets with the solid surface. Direct contact only occurs between some parts of water droplets and solid surfaces. The other parts are water droplets in contact with the air inside the groove. The Cassie-Baxter equation [81] which is applied to the composite surface was obtained according to the thermodynamics analysis using equation (2.3):

$$\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2.3)$$

where θ_c is equilibrium water contact angle in the Cassie model, referred to the apparent WCA of Cassie model. θ_1 , θ_2 are both intrinsic WCA when droplet stands on the medium surface. f_1 and f_2 are the percentage of two interfaces to the total contact area, respectively. Equation (2.3) can be applied to any composite contact surface. For hydrophobic surface, the two mediums in contact with the water droplets are solid itself and the air inside the groove on the surface.

It is worth mentioning that the water droplet on the solid surface only needs to overcome smaller barrier if the water droplet seems to suspend on the rough structure when the wetting behaviour of water droplet on the solid surface fits well with Cassie model. So in the Cassie model, water droplets always show smaller WCA hysteresis and rolling angle when rolling on solid surfaces.

Besides, there is another criterion for hydrophobic performance, namely, contact angle hysteresis, as shown in equation (2.4) [74]:

$$CAH = \theta_a - \theta_r \quad (2.4)$$

where θ_a is the forward angle and θ_r is the backward angle, as shown in Figure 2.8. Due to the larger contact area between liquid and solid surface in Wenzel's Model and the anchoring effect between liquid and rough surface, the CAH of liquid in this state becomes larger and its value is much higher than that of smooth surface. In the Cassie-Baxter state, the liquid underside is in the composite contacting state, with both solids and gases, so the liquid-solid contact area decreases and the droplets "hover" on the surface. In this way, CAH would be very small, the water droplets are easy to fall off, with a good hydrophobic effect.

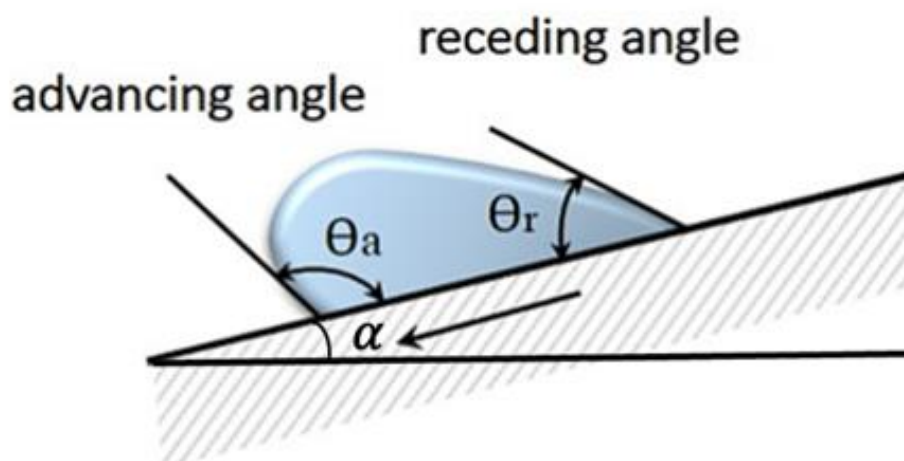


Figure 2.8 Schematic view of contact angle hysteresis [74].

Wenzel and Cassie both carried out thorough study on the impact of surface roughness to contact angle, respectively. They have established two kinds of mathematical models: Wenzel's model [80] and Cassie's model [81]. Wenzel's model and Cassie's model represent two different types of superhydrophobic states, respectively. The two states are not completely isolated. When the droplets are squeezed, the transformation between the models may take place on solid-liquid contact surfaces. Relevant studies on transformation between the two models have been reported. Patanka et al. [82] thought the Wenzel model and Cassie model are two different energy states of the water droplets on rough surface. The energy that water possesses in Cassie state and Wenzel state is not the same even for the same surface. The mutual transformation could be realized between the two states if the corresponding energy barrier could be overcome.

The two models can explain the action mechanism of surface textures on enhancing the wettability, yet some difference exists. Wenzel wetting model could lead to robust adhesion on the solid surface due to the enlarged actual contact between the solid and liquid phases. While for Cassie-Baxter wetting model, it would result in low adhesion with smaller actual contacting areas. Therefore, from the view of repelling water and anti-icing, icephobic surfaces are expected to possess the microscopic structures that conform to the requirement of Cassie-Baxter wetting regime, which could reduce the

solid-liquid contact between the interfaces.

2.2.2 From hydrophobicity to icephobicity

Icephobicity and hydrophobicity are considered closely related and many icephobic coatings are in fact derived from hydrophobic coatings and surface processing methods. Hydrophobic surfaces are commonly designed to have topography on the micro/nanoscale that enables the entrapment of air between the surface textures and the overlying liquid, which is more aligned with Cassie's model. These surfaces naturally offer the potential for icephobic applications in that they could offer the advantage of reducing ice adhesion or accretion from supercooled water sprayed or poured onto the surface [83], as indicated in Figure 2.9. During the icing process, trapped air between the rough surface structures could form air pocket and help to bounce off or of "trampolining" the impacting and condensed water droplets before the icing phenomenon takes place [84]. It has come out that for icephobic surfaces, one of the important directions is to extend the freezing time of water droplets in a supercooling state, and the other is easy to remove the supercooled water droplet out of the surface before its solidification using external force [85]. The other aspects focus on de-icing purposes. The surface also has low ice adhesion strength and the formed ice could easily slide off or be removed.

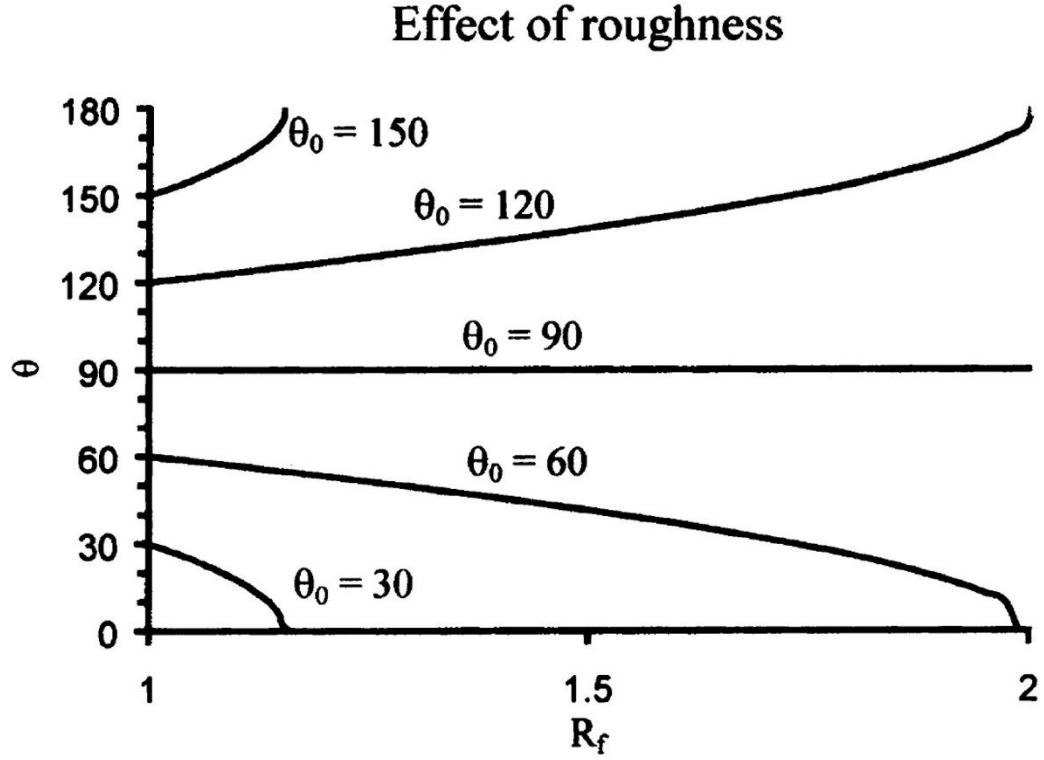


Figure 2.9 Contact angle as a function of roughness factor (R_f = actual surface area/geometric surface area) for different smooth surfaces of different CA [86].

When the radius of ice crystals is larger than the r_c , (the critical ice nucleation radius which is the critical size that an ice crystal must reach for freezing to occur [87]), the ice nucleation would trigger and ice would grow on the substrate. The water droplets need to overcome the barrier - Gibbs Free Energy Difference (ΔG_C) when changing from liquid to stable solid state, as shown in equation (2.5) [88]. There is a positive correlation between $f(\theta)$ and θ inferred from equation (2.6), where θ means WCA. Hence, increasing θ could help to enlarge the barrier of water solidification process and extend the freezing time on the substrate.

$$\Delta G_C = \frac{4}{3} \pi \cdot r_c^2 \cdot \sigma_{IV} \cdot f(\theta) \quad (2.5)$$

$$f(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \quad (2.6)$$

Derived from the above formulas, the rough structure of the substrate could slow down

the water solidification process by increasing the WCA and reducing the heat loss of water droplets through impeding effect in the rough structure [16]. So it is an effective way to help with freezing delay and icing extension by designing coating structure that could ensure the radius of the formed ice crystal on it is lower than r_c [89].

But superhydrophobic surfaces are not always icephobic, the mechanisms of water and ice adhesion are different [90]. Wetting state transition could take place when ice forms, impinging water droplets with high kinetic energy or moisture condensation from the ambient atmosphere within micro/nanoscale texture of the substrate would also affect the icephobic performance [91]. Because the contacting area between the ice and substrate would be reduced in Cassie ice state, this could help with low ice adhesion strength. As a comparison, the contact area in Wenzel ice state would increase due to surface roughness and leading to the increasing ice adhesion strength.

The thermodynamic stability of surface hydrophobicity under common engineering applications, involving high-velocity water droplet impact, high humidity, or variable temperatures, have also raised significant challenges in the field of icephobicity. For example, it has been shown that superhydrophobic surfaces with low surface energy and hierarchical surface morphologies can only inhibit ice formation in a frost-free environment [16]. The icephobicity of certain surfaces not only depends on the intrinsic surface properties, but also on the ice formation conditions. Therefore, to better link the icephobicity with hydrophobicity, it needs to be discussed carefully under specific icephobic definition and characteristic testing conditions. In the following sections, explanation based on definitions of icephobicity and characteristic measures will be given and elucidate the differences.

2.3 Fundamentals of Icephobicity and Icephobic Surfaces

For the definition of icephobicity, some reports define it as low ice adhesion shear

strength [36, 92]. The icephobicity is also defined as the ability to delay and prevent ice nucleation and formation on surfaces, induced either by pouring super-cooled water on the substrate (below the normal freezing temperature of 0 °C) or decreasing the substrate temperature after placing a water droplet on the surface [93]. The different definitions of icephobicity correspond to different related properties of anti-icing and de-icing surfaces. Related discussion and contents have been unfolded below for the aim to study and comprehend the proper strategies for developing icephobic surfaces.

2.3.1 Definition of icephobicity

In general, the definitions of icephobicity normally consist of three parts: (1) the ability to prevent or delay water condensation ice on surfaces, (2) preventing or delaying the freezing of incoming water, (3) the easy removal of formed ice which corresponds to low ice adhesion strength.

The first two parts could be explained by the anti-icing prospect. To understand ice nucleation on surfaces, the nucleation theory is demonstrated. The simplest case of nucleation or the growth of new phase is homogeneous nucleation. Homogeneous nucleation theory describes how nucleation occurs in a homogeneous medium. The free energy ΔG of a budding nucleus could be described as equation (2.7):

$$\Delta G = \frac{4}{3}\pi r^3 \cdot G_v + 4\pi r^2 \sigma \quad (2.7)$$

where r means the radius of the nucleus, G_v is the energy per volume liberated during formation (a negative quantity). σ is the surface tension of the newly formed interface [84]. In other words, with the formation of the nucleus, energy would release. But it gains energy with the newly formed interface. Therefore ΔG would increase as the size of the nucleus increases up to a certain critical radius where $dG/dr = 0$. Increasing the size of the molecule from then on will only release energy. The critical radius (r^*) is easily calculated to be in equation (2.8):

$$r^* = -\frac{2\sigma}{G_v} \quad (2.8)$$

Homogeneous nucleation is not common in nature and daily lives. However, since heterogeneous nucleation occurs much more easily on certain surface, nucleation at surfaces could be described as equation (2.9):

$$\Delta G_{heterogeneous} = \Delta G_{homogeneous} \times f(\theta) \quad (2.9)$$

where $f(\theta)$ is a factor between 0 and one that depends on the properties of the surface.

The icephobicity could also be defined from the de-icing aspect: an icephobic surface should also possess weak ice adhesion strength with the formed ice (the threshold of 100 kPa can be suggested, although the value is somewhat arbitrary [94]), so that the ice could be easily shed from the surface by action of wind, gravity or vibration. It is also important to take the wetting state transition during ice formation into consideration when discussing ice adhesion strength. The Cassie-Baxter's state could transfer into Wenzel's state in a high humidity environment on a rough surface. Furthermore, if icing phenomenon takes place under this condition, the oversaturated supercooled droplets would heavily condense between the hierarchical structures of the former superhydrophobic surface, the condensed water would then replace the existing air pockets and fill the structure. Serious mechanical interlock could occur. In this way, the ice adhesion strength on the rough substrate would be much higher than that on smooth substrate.

Another aspect that needs to be considered for defining icephobicity is based on the specific characteristic testing conditions for icephobicity evaluation. Considering the common engineering applications of icephobic coatings, it often involves high velocity water droplet impact, high humidity or variable temperatures. This could pose significant challenges to the thermodynamic stability of surface icephobicity. Therefore,

the icephobic performance of certain surfaces needs to be studied carefully based on different characteristic testing conditions.

For example, some studies indicate that for hydrophobic surfaces with rough asperities and low surface free energy, the ice formation could be prevented only in a frost-free environment. Because under high humidity conditions, the hierarchical structures could increase nucleation site density and easily induce ice nucleation at a faster speed than that on smooth surfaces due to their high specific surface area [16]. Under some circumstances, the hydrophobic surfaces could even fail in environments without bulk super-saturation because the water droplets increase the humidity of local related environment [95]. The source of discrepancy lies in the difference of ice adhesion strength measurement (in either shear or tension or mixed mode fracture). Some researchers tend to use rotating horizontal beams in a centrifugal apparatus to carry out ice adhesion test [96], while other groups measure the ice adhesion strength by propelling ice off from the substrate [97], or calculate the shear strength for detached ice formed between cylindrical pin and cylindrical mould [93]. Based on this, it is important to consider the environmental conditions and evaluation methods when doing tests on these surfaces. Because of the absence of uniform and standard definition for icephobicity and icephobic surfaces and a variety of icephobicity test conditions, the icephobicity based on different characteristic test methods and definitions of icephobicity would be discussed in the following sections.

2.3.2 Ice nucleation mechanism and icing delay

An icephobic material should have the ability to delay ice nucleation in terms of temperature (under continuous cooling) or time (under a constant temperature). The ability to prevent or delay ice nucleation on surfaces depends on whether water droplets in supercooled state (below 0 °C) could freeze at the interface and the delay effect it brings to the heterogeneous ice nucleation. The process is governed by ice nucleation and growth, which is consistent with the classical nucleation and crystal growth theories

in material science [98].

Schutz et al. [99] concluded that the nucleation temperature is relatively insensitive to surface roughness when surfaces only have a fraction of area occupied with nanoscale pits below $10 r_c$ (critical radius). The energy barrier for ice nucleus formation could be increased (which further retards the icing process) by keeping the curvature radius between the rough structures and water droplets on certain surfaces smaller than the critical radius to keep the formed ice nuclei stable. Hydrophobicity and icephobicity could be linked together when using enhanced surface morphology to increase the solid-air fraction of the surface to fulfill the delay effect in ice nucleation. The change in surface roughness and surface topography could lead to the decrease of wetted area fraction between the interfaces. This could further affect the heat transfer and the probability of heterogeneous nucleation at the water-solid interface [100].

According to the analysis of the classical nucleation theory, two different theories could be categorized: nucleation theories on homogenous and heterogeneous surfaces. For homogeneous ice nucleation, the reduction of system Gibbs free energy would occur spontaneously with the icing process. Under the thermodynamic driving force, the ice nucleation could take place once a large amount of relatively long-lived hydrogen bonds at the same location to form a compact nucleus [101]. Afterwards, the formed nucleus would keep changing the shape and size until it has reached a stage that allows the rapid expansion and crystallization of the whole system [102]. The three essential conditions of ice nucleation consist of supercooling, structure fluctuation, and energy fluctuation, which has been emphasized by the molecular dynamics (MD) simulation. The ice nucleation on homogeneous surfaces could also be regulated by controlling the essential conditions to achieve anti-icing [103]. The critical nucleus radius r_c could be obtained using the classical nucleation theory on a continuum scale:

$$r_c = \frac{2\gamma_{IW}}{\Delta G} \quad (2.10)$$

where γ_{IW} is the water/ice interfacial energy and ΔG is the free energy barrier of bulk ice vs bulk liquid, which conforms to the Gibbs-Helmholtz equation [104]:

$$\Delta G = \frac{\Delta H (T_m - T)}{T_m} \quad (2.11)$$

Furthermore, ΔH is the water volumetric enthalpy of fusion, and T_m is the ice melting temperature at 1 atm. Combining equation (2.10) and equation (2.11), the critical ice nucleus radius r_c could be calculated. This could be a good supplement to discussion parts in Section 2.2.2.

For heterogeneous ice nucleation, it is more easily to be triggered with lower nucleation free energy on solid surfaces in a practical situation due to the reduction of the energy barrier. On the other side, the ice nucleation could also be delayed if the surface roughness is smaller than the critical nucleus size on a very low surface energy surface.

In the heterogeneous nucleation between solid/liquid interface, the free energy barrier $\Delta G_c'$ is reduced by a geometric factor $f(\theta)$ compared with the free energy barrier ΔG_c for homogeneous ice nucleation, and the relationship is well given through the classical nucleation theory, as shown in equation (2.12) [79]:

$$\frac{\Delta G_c'}{\Delta G_c} = f(\theta) = \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \leq 1 \quad (2.12)$$

If the heterogeneous ice nucleation takes place on the perfectly flat surface, it is only related to the CA (θ), and the variation of geometric factor $f(\theta)$ with CA is shown in Figure 2.10.

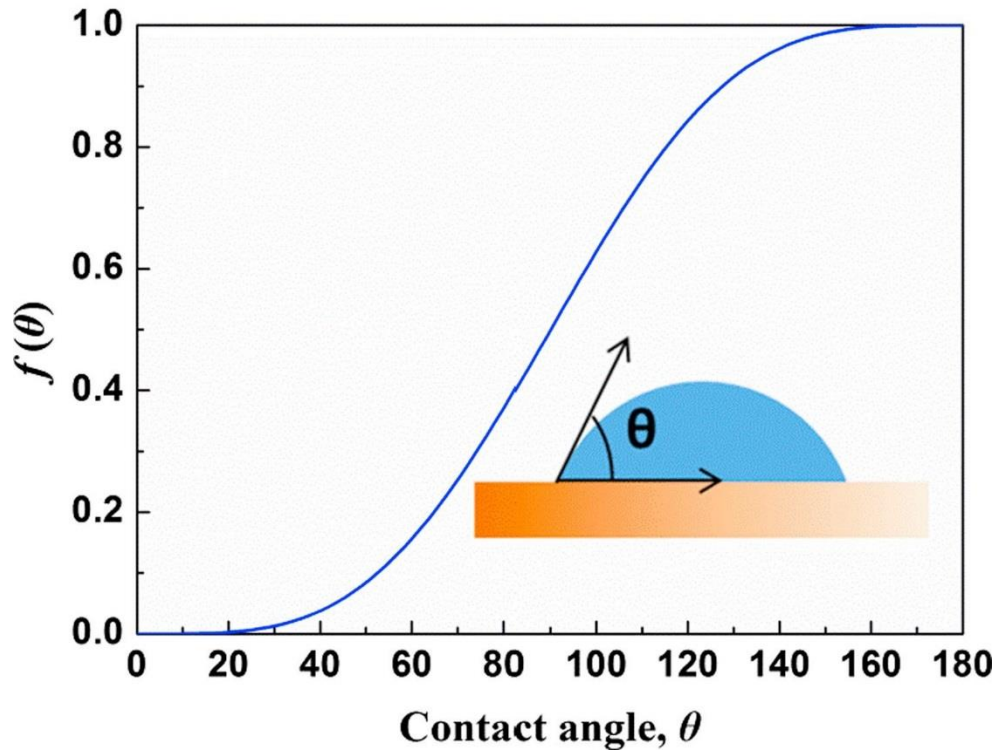


Figure 2.10 Geometric factor $f(\theta)$ for a heterogeneous ice nucleation as a function of contact angle θ on a flat surface [79].

Alizadeh et al. have figured out the nucleation rates (including homogeneous and heterogeneous) with different icing conditions as a function of surface wettability [105]. The delay effect for ice nucleation derived from the reduced water-solid contact area is more effective at moderate supercooling state. The nucleation effects in both bulk and the air-water interface become equally important. Icephobic surface with a relatively long icing delay effect could be designed upon the aforementioned principles. It is also suggested that rational design frameworks could be used to develop and design icephobic surfaces focusing on preventing heterogeneous nucleation and prolonging icing delay [106].

2.3.3 Interaction at ice/solid interface

Understanding the interaction between the formed ice and surface is very important for designing new and feasible icephobic coatings. Vapour-liquid-solid or condensation followed by freezing and direct liquid-solid freezing could be the two main pathways

of solid ice formation [38]. The phase diagram in Figure 2.11 also indicates the different types of ice solid formation (the other one is vapour-solid desublimation or deposition). They involve different interaction mechanisms between the ice and solid during the icing process.

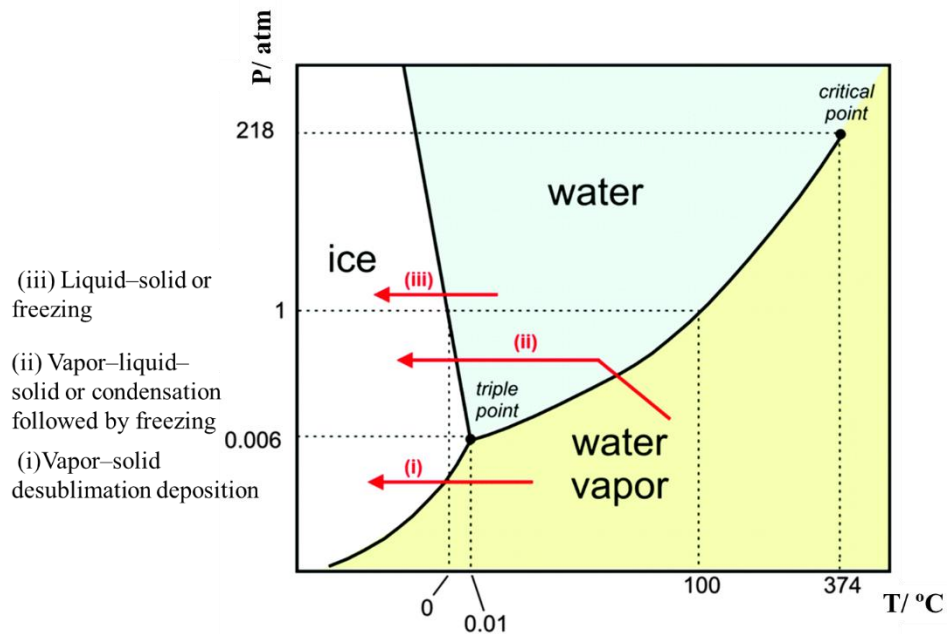


Figure 2.11 Phase diagram for water indicating three different pathways for formation of water-based solid by changes in temperature and/or pressure of water [38].

The intrinsic atomistic interactions between ice and substrate are a combination of electrostatic forces, hydrogen bonding, van der Waals forces, and mechanical adhesion. They always exist between ice and its adhering surface and cannot be avoided in any attempts to create low ice adhesion surface [39]. The short-range interactions include covalent bond, ionic bond, metallic bond and interaction and dipole interactions (hydrogen bond interaction and van der Waals forces) at the atomic or molecular levels [107]. The mechanical interlock between the hierarchical structures could contribute to mechanical adhesion at the interface between the two materials. It is very important to lower the adhesion between the formed ice and the coating surface because this would make the formed ice easy to shed from the surface by an external force such as action of wind, gravity, or vibration. It is noted that the condensed water droplet would not

replace the air pocket if only the water vapour from the environment condenses heavily inside the micro/nanostructure of a hydrophobic surface under fully oversaturated conditions. Chen et al. [108] have shown that ice adhesion on textured hydrophobic surfaces was also as large as that on hydrophilic surfaces because of the existence of mechanical interlock between the formed ice and the surface structure when the replacement of air pockets occur under high humidity environment.

A series of studies show that the ice adhesion strength correlates well with the work of adhesion between liquid droplet and substrate [36]. As shown in equation (2.13), the work of adhesion could be calculated with the Young-Dupre 'equation as suggested by Gao and McCarthy [109]:

$$W_{adh} = \gamma_{LV} (1 + \cos \theta_R) \quad (2.13)$$

where θ_R is the receding contact angle of water and γ_{LV} is its surface tension in the air. The relation has also been verified by Nosonovsky et al. [90]. The role of the initial size of interfacial cracks has been considered additionally. It is concluded that surfaces with very high Rec might have strong adhesion with ice if the size of the cracks is small. Among these studies, icephobicity implies a reduction in the normal and/or shear adhesion strength of ice through surface coating and/or texturing. It means reduced ice adhesion strength to a solid surface in shear or tensile adhesion experiments.

Nosonovsky et al. studied the detailed mechanisms of low ice adhesion strength using micro-/nano- structured superhydrophobic surfaces. They found that the trapped air pockets would change into air voids if the formed ice on certain surfaces conforming to Cassie-Baxter mode, and it could act as stress concentrators and lead to ice adhesion strength reduction with shear loading, as shown in Figure 2.12 [90]. If it is under normal loading, the contact area at the interface could be reduced by the generated air voids, which results in a lower tensile ice adhesion strength [110].

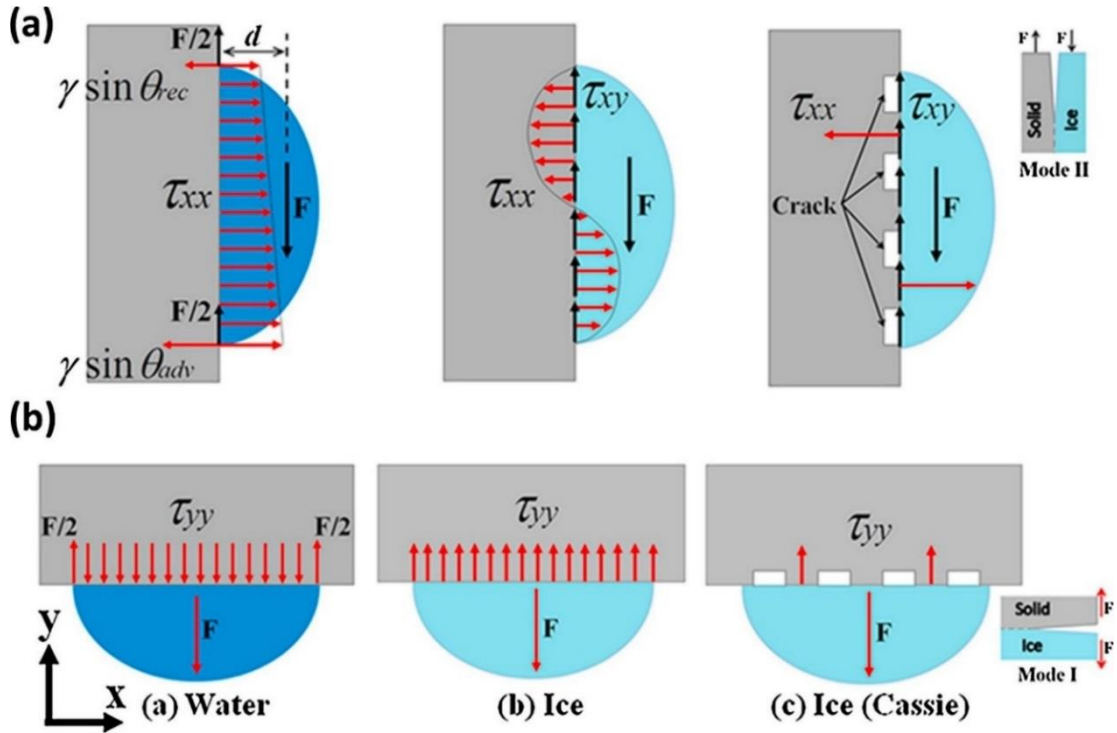


Figure 2.12 (a) Shear loading and (b) normal loading regimes of water droplet and ice frozen droplet on the flat and texture surfaces [90].

Based on the aforementioned aspects of icephobicity, icephobic coatings could be designed from the matrix compositions and surface topologies to achieve the following functions: (1) Detachment or removal of water droplets from a coated surface (supercooled droplets could roll off before icing); (2) Prevention or delay of icing by decreasing heat transfer between supercooled droplets and coating surface so that ice crystallization is delayed; (3) Minimization or reduction of energy/force input for de-icing derived from the low ice adhesion strength of the surface. Developing a single unifying icephobic surface structure or treatment to fully address the icing problem is still a great challenge. Therefore, it is suggested that specific application-based approaches and clear definitions are required when designing icephobic surfaces.

2.4 Progress of Hydrophobic/Icephobic Surfaces

In the previous sections, the multiplicity of icephobicity definitions and related

mechanisms on ice nucleation, icing delay, and ice/solid interaction have been demonstrated. The present part will focus on the discussion of the current progress of mainstream icephobic surfaces.

During the last few decades, studies on preparing hydrophobic/icephobic surfaces have caused great interest all over the world [111]. There are a variety of icephobic surfaces developed and they could be classified into the following categories based on their chemical compositions, surface topographies and application methods, such as: (1) Polymeric coating system which could be further divided into fluoropolymers based coatings [112], polysiloxane based coatings [113], polymer coating based on cross-link density and interfacial lubricant [4], etc; (2) Metallic based coatings [87]; (3) Bio-inspired icephobic coatings [114]; (4) Coatings with surface texturing and topography modifications, including laser texturing [115], multi-tiered surface structuring [116]; and other coating systems [117]. Some icephobic studies have been conducted, but considering the different evaluation methodologies and testing parameters, they may not be directly comparable.

2.4.1 Polymeric coatings

Among the researches toward icephobic surfaces, it could be found that polymeric coatings form a very important and large part of the current research. These surfaces possess the virtue of having a very large WCA and exhibiting little sticking to formed ice. A myriad of reports have been published on polymeric icephobic coatings which could be classified into the following categories.

2.4.1.1 Fluoropolymers based coatings

The fluoropolymer is a fluorocarbon-based polymer with multiple carbon-fluorine bonds. It has the advantage of high resistance to solvents, acids, and bases. The most famous fluoropolymer should be polytetrafluoroethylene (PTFE, commercially known as Teflon). PTFE films and other fluorinated silicone rubber/polyurethane coatings

were widely applied to achieve icephobic applications.

For example, Jafari et al. [118] deposited PTFE coating by Radio Frequency (RF) sputtering method onto the anodised substrate with a microstructured aluminium oxide underlayer. Coating with high WCA of 165.0 ° and CAH of 3.0 ° was obtained. The PTFE coatings under atmospheric icing conditions showed an ice-adhesion strength 3.5 times lower than polished aluminium surface due to the presence of CF₃ groups. In another study, the polyfluoroacrylates (PFA) emulsions coatings were prepared on aluminium 1050 plates via spin coating process. The WCA could reach up to 121 ° with low ice adhesion strength. The ice adhesion strength of the coatings also reduced with the increase of fluorine content, the chain structures of the synthesized co-polymer is also shown in Figure 2.13 [119]. Besides, Grimmer et al. [120] reported that thin, hydrophobic fluorocarbon films were coated on differently shaped microstructures by plasma enhanced chemical vapour deposition (PECVD) process. The coatings with advancing water contact angle of 150 ° and CAH of lower than 3 ° showed a reduced ice adhesion of below 200 kPa for the functional surfaces. The above examples suggested that the fluoropolymers based coatings materials could provide both hydrophobic and icephobic capabilities. The aluminium alloy 6061 underlayer that was produced by anodisation and further improved with colloidal PTFE particle impregnation possessed reduced ice adhesion by almost 2.5 times compared to other bare substrates. The coatings showed that the impregnation of polymer composition and the creation of 3D structure were promising methods to fulfill hydrophobicity/icephobicity [121].

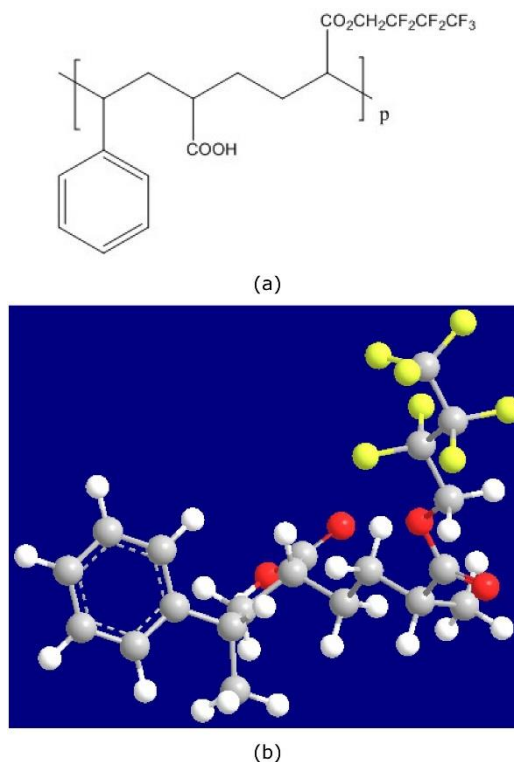


Figure 2.13 (a) 2D and (b) 3D chain structures of the synthesized polyfluoroacrylates polymer [119]

2.4.1.2 Polysiloxane based coatings

This class of polymeric coatings is normally on the basis of viscoelastic silicones. Silicones are polymers made of repeating units of siloxane along with functional constituents such as methyl, phenyl or trifluoropropyl. The low surface energy of the functional groups that bond to the siloxane chain in combination with the low elastic modulus enables them to be icephobic [4]. Many hydrophobic/icephobic coatings have been developed to make use of the viscoelastic dimethylsiloxane polymeric materials recently.

For example, Zhang et al. [122] designed the PDMS coatings with three patterns of hollow sub-surface structure prepared by spin coating. The low ice adhesion strength mainly comes from the crack initiation mechanism. The roles of hollow sub-surface structure geometry in reducing ice adhesion strength have also been studied. He et al. [18] obtained sandwich-like PDMS sponge with sugar-made template by a facile low-

cost preparation method, as shown in Figure 2.14. The reduced elastic modulus, lowered surface energy and macroscopic crack initiators at the ice-solid interface are helped with the super-low ice adhesion strength as low as 0.9 kPa as well as the durable icephobic adhesion performance (remaining constant after 25 icing and de-icing cycles).

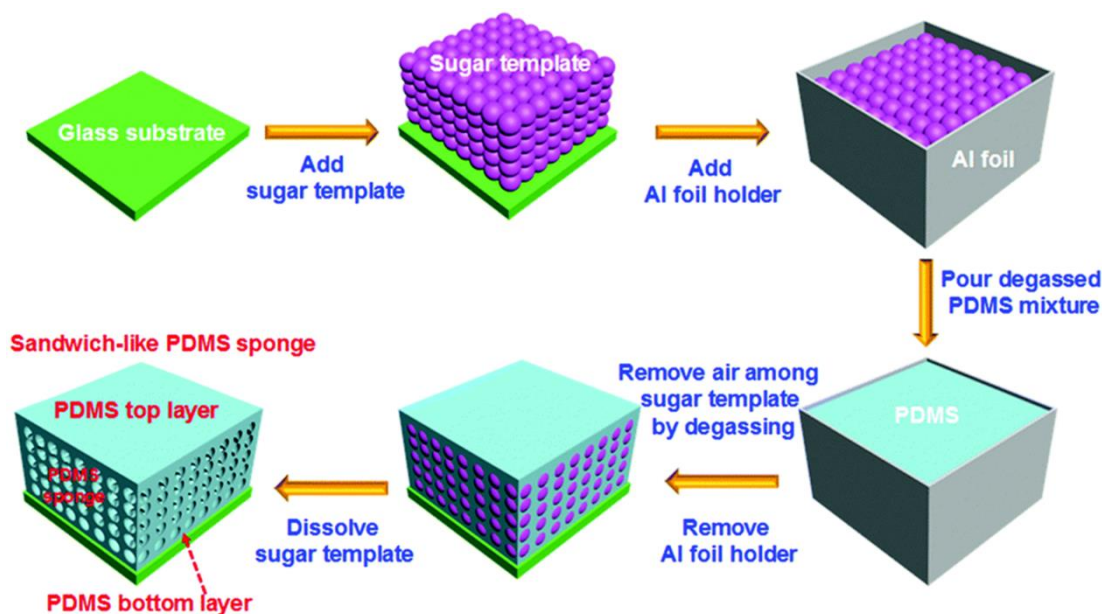


Figure 2.14 Schematic overview of facile preparation of the sandwich-like sponge [18].

2.4.1.3 Polymer coating based on cross-link density and interfacial lubricant

Another new strategy for icephobic polymeric coating could be the design that enables polymer chain mobility within an elastomer matrix and create a slip boundary condition between the ice/solid interface [4]. The reduction of ice adhesion strength could be achieved by (1) using a polymer with low cross-link density and (2) the addition of miscible lubricant to enable interfacial slippage. For example, using the first method, Donadei et al. [123] reported that the LDPE (low-density polyethylene) polymer icephobic coatings with ice adhesion of only 32 ± 3 kPa were produced with flame spraying method. The study also showed that the thermal stability of the coating is necessary for further icephobic performance. With the addition of interfacial lubricants into the polymer structure, the icephobic effect could be further improved. Vogel et al. prepared a honeycomb-like patterned superhydrophobic surface through

fluorosilanzation using vapour-phase deposition and further lubrication on colloidal monolayers, as indicated in Figure 2.15. The surface structure has a measured ice adhesion strength of as low as 10 kPa and it remained stable after several severe mechanical stability tests [124].

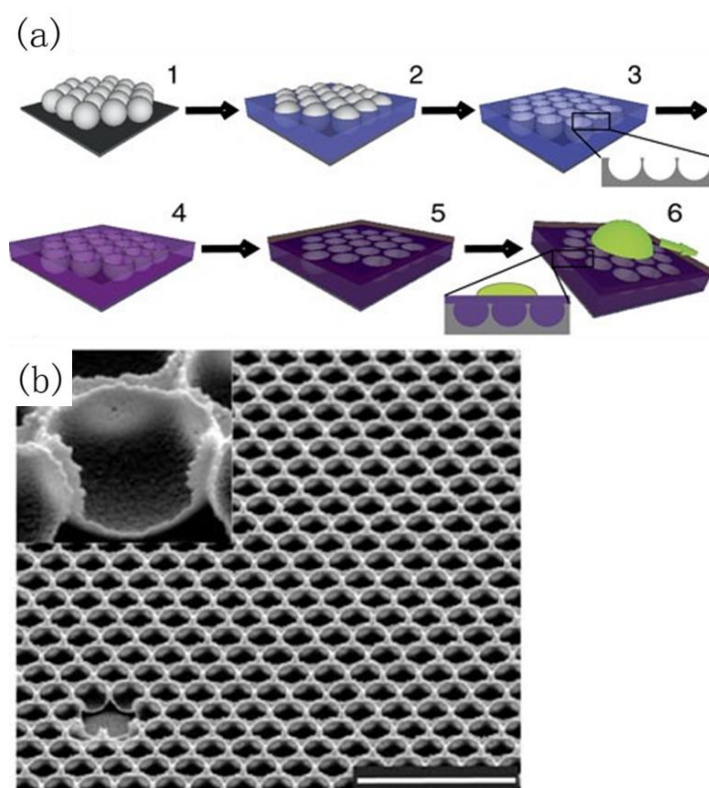


Figure 2.15 (a) Schematic diagram of the construction scheme of the honeycomb-like patterned surface, (b) SEM image taken at an angle of 45° showing high regularity and structural details of the nanopore arrays. The scale bar in (b) is $5\ \mu\text{m}$ (adapted from Ref [124]).

2.4.2 Metallic based coatings

Erosion from rain, sand, and dust particles is a critical issue for icephobic surfaces in the operating environment. So it is essential for icephobic coatings to possess sufficient erosion resistance and durability to survive a long term. Metallic-based coatings with good robustness and icephobicity have become of interest. For example, Ruan et al. reported that superhydrophobic surface with WCA of 159.1° and CAH of 4.0° were prepared on aluminium alloy substrate by a chemical etching process, which

demonstrated excellent anti-icing properties [12]. Zheng et al. fabricated a superhydrophobic Al surface with hierarchical micro/nano structure by anodisation method which has a WCA of 156° and sliding angle (SA) of 2.5° (which is the tilt angle at which the movement of the drop across the surface begins [125]), exhibiting a delay in ice formation and temperature, as well as low ice adhesion strength of 40 kPa. The optical images of the icing process comparison between bare Al surface and SHS Al are shown in Figure 2.16. The as-prepared coating shows good mechanical stability against sand erosion and chemical durability in a series of solutions [11]. Brassard et al. [126] prepared the nano-micro structured superhydrophobic zinc coating on stainless steel (SS) substrate via electrodeposition method and further silicone functionalization treatment. The as-prepared superhydrophobic surface showed both corrosion resistance and reduced ice adhesion (6.3 times lower than bare steel). The zinc coatings have promising applications in offshore environment and ice detachment aspects.

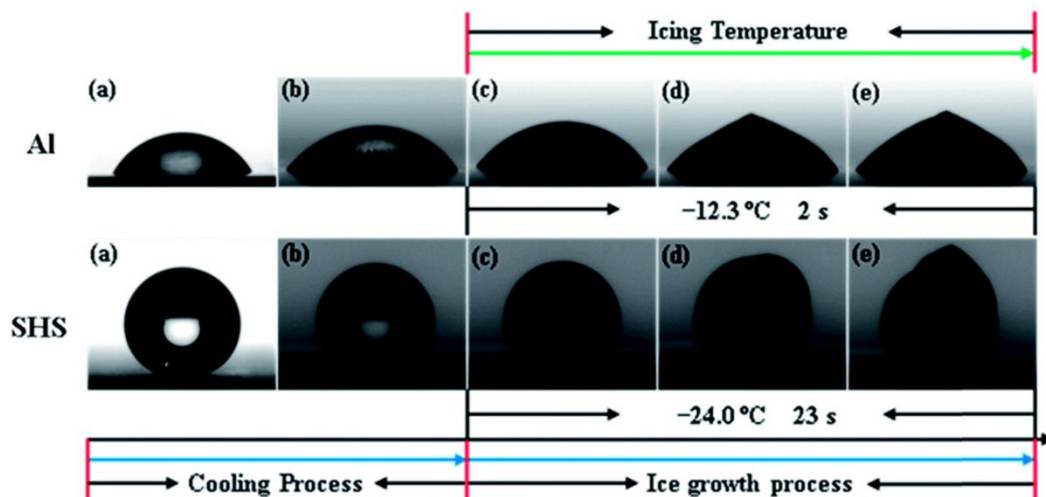


Figure 2.16 Optical images of the icing process comparison between bare Al surface and SHS Al [11].

2.4.3 Bio-inspired icephobic coatings

Recent studies have also provided new insights into the icing phenomenon and shed light on some promising bio-inspired anti-icing strategies. One direction is preparing coatings which can help with the inhibition of ice nucleation or timely removal of the

incoming water droplets before freezing take place. Another is that coating which can reduce the ice adhesion after ice forms by using organic liquid lubricating layer and aqueous lubricating layer [127].

The hydrophobic surfaces have the characteristic of inhibiting ice nucleation and removing incoming supercooled water droplets. By mimicking lotus leaves and water strider legs, the hydrophobic surfaces usually have micro-/nano- structure with air trapped inside the surface textures. For example, Jiang et al. prepared a superhydrophobic polystyrene film consisting of porous microspheres and nanofibres by versatile electrohydrodynamics (EHD) methods. The water droplet on the film stays at a nonwetting Cassie-Baxter state, possesses WCA of $162.1 \pm 1.1^\circ$, small contact area with the solid surface and minimized interaction between water and solid surface [128]. The unique characteristic of hydrophobic surfaces could also result in the complete retraction and elastic rebound of impacting water droplets [129]. Mishchenko et al. presented a detailed study on dynamic droplet freezing on structured surfaces with different wettability. The nano- and micro- structured fluorinated Si surfaces would completely retract and timely rebound off before the freezing process take place, as demonstrated in Figure 2.17 [130].

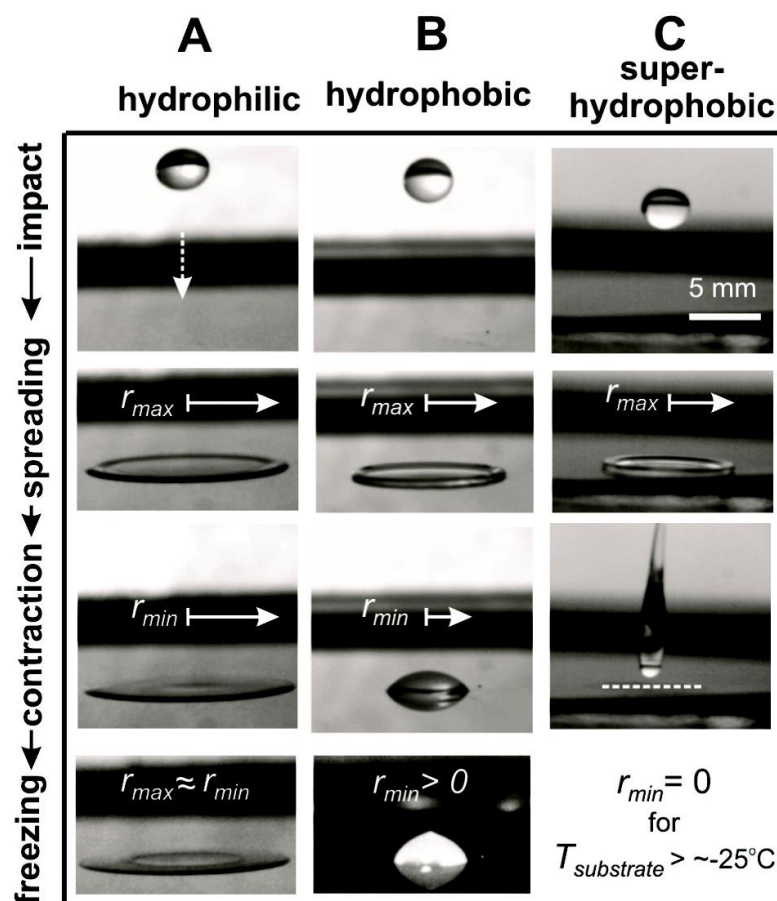


Figure 2.17 Sequential images of the dynamic behaviour of droplets impacting on comparison samples (a) hydrophilic (b) smooth hydrophobic surfaces and (c) microstructured fluorinated Si surfaces [130].

If ice is already formed on certain surfaces, trapping liquid as a lubricant between the substrate surface and formed ice enables substantial weakening of the interaction between the ice and the solid surface, which can reduce the ice adhesion significantly. For example, Wong et al. reported the self-healing surface textures with a water-immiscible lubricating organic liquid trapped inside, maintaining low CAH of 2.5° , as shown in Figure 2.18. The trapped organic liquid acts as an intermediary lubricating layer to prevent the penetration of frost/ice into the surface textures and lead to an extremely low ice adhesion strength [14].

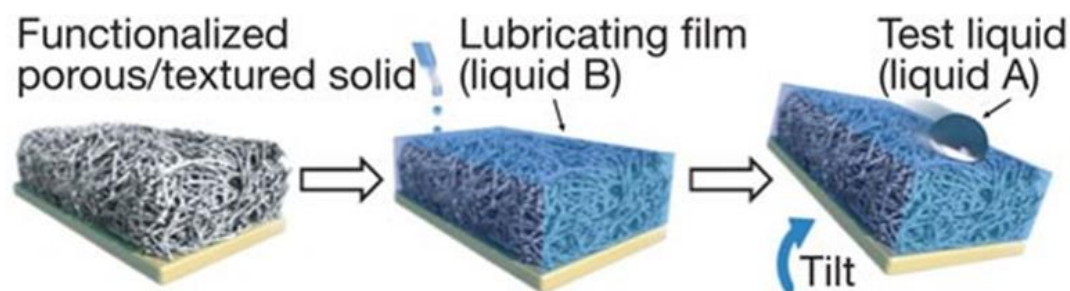


Figure 2.18 Schematic diagram of the fabrication process of icephobic coating with trapped organic liquid [14].

2.4.4 Coatings with surface texturing and topography modifications

It is suggested that further reduction on ice adhesion lower than 150 kPa could be achieved by polymer molecular engineering or surface topology changes [4]. The main focuses of the aforementioned parts are on surface chemistry engineering, the surface texturing could be another direction. Based on the observations, roughened surfaces that could trap air pockets between their surface structures have also been proposed as an approach to lower ice adhesion.

2.4.4.1 Multi-tiered surface structuring

With multi-tiered surface structuring work, several new icephobic alternatives have been developed. For example, Barthwal et al. prepared the dual geometric architectures with micro- and nanoscale (MN) structures on aluminium plate using the combining method of chemical etching and anodisation, which is shown in Figure 2.19. The MN-structured surface showed good mechanical stability and good potential in icephobic applications [131]. Ruan et al. reported that rough micro/nano alumina coatings with WCA of 157.6° were prepared through sol-gel approach combined with further surface modification. The ice adhesion strength on prepared samples was about 1.5-2.0 times lower than that on uncoated aluminium plates [132].

Hou et al. [133] fabricated surfaces with a series of micro-cubic arrays using plasma etching method. The micro-cubic arrays with micro-spacing distance of $70\text{ }\mu\text{m}$ could

entrap more air pockets underneath the water droplets and lead to lower actual solid/liquid contact areal fraction and larger heat transfer barrier. The surfaces with ice adhesion of only 16 kPa also greatly delayed the icing process for up to 1295 s (two orders of magnitude comparing with that on the substrate surface).

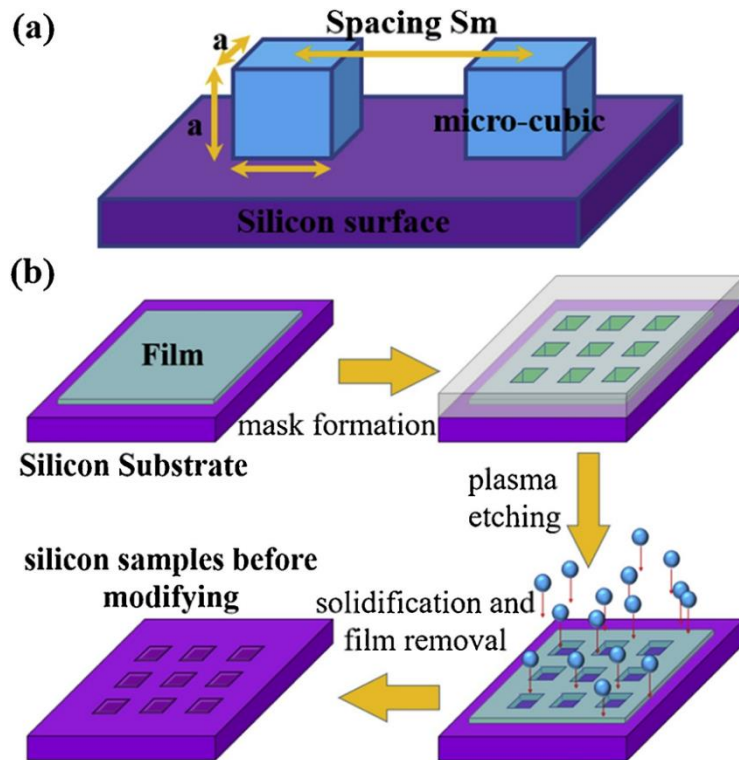


Figure 2.19 (a) Sketch image of the designed micro-cubic array structures (b) plasma etching process of silicon micro-cubic structures [133].

2.4.4.2 Laser texturing

Laser treatment has also been applied to micromachine different surfaces. With the wide spread use of lasers in processing and potentially in additive manufacturing, the use of laser profiling to construct icephobic surfaces is appealing from the perspective of manufacturability and durability. For example, Arnaldo's work showed that laser texturing could help to impart icephobicity to both metal substrates and diamond-like carbon (DLC) coatings [134]. Boinovich et al. [135] prepared the wear and chemically resistant fluorooxysilane coatings on laser-treated aluminium-magnesium alloy by chemical vapour deposition (CVD) method. Their results show that the combination of

chemical modification and micro- and nano- texturing of materials surface layer using nanosecond laser processing could be a reliable method of surface treatments for coating design.

2.4.4.3 Textured surface with further modification

By tailoring the chemical composition through the rough structured surface using chemical or physical methods could also be a general scheme. Shen et al. [136] reported the icephobic/anti-icing potential of $\text{Ti}_6\text{Al}_4\text{V}$ surfaces with hierarchical textures via combination of modifying micro-nanostructures (constructed by the combination of sand blasting and hydrothermal treatment) and later fluoroalkylsilane (FAS-17) treatment, as observed in Figure 2.21. The surface displayed excellent non-wettability with apparent contact angle of 161° and sliding angle of 3° . By trapping a large amount of air under the droplet within the micro-nanostructures, it could result in the low efficiency of heat conduction between water droplet and cold solid surfaces. This process seemed to directly help with the long icing-delay time (750.4 s) and low ice adhesion strength (80 kPa) at -10°C .

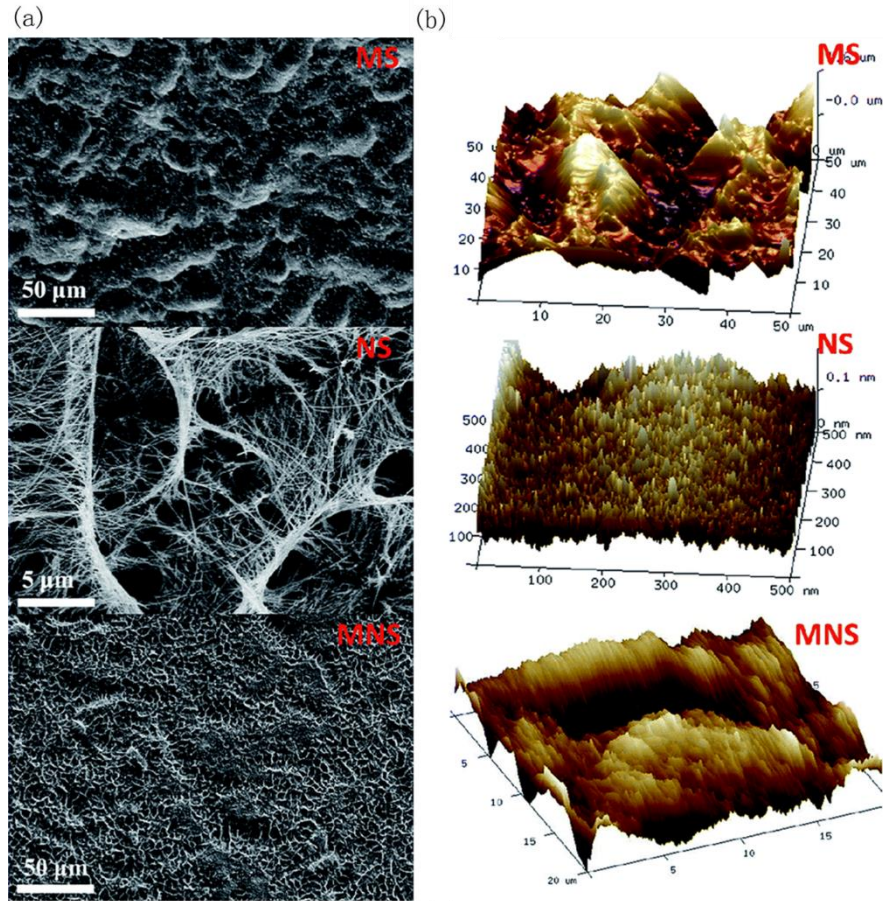


Figure 2.20 Images of hierarchical morphologies of surfaces with different scale patterning (a) SEM and (b) Atomic force microscope (AFM) images of micrometer-scale pit surface (MS) and nanowire structured surface (NS) (adapted from Ref [136]).

Sharifi et al. [137] studied the anti-icing and de-icing performances of micro-textured TiO_2 coating prepared by suspension plasma spraying (SPS) with further stearic acid treatment. The WCA is 170° with SA of 1° and CAH of 4° . The SPS coatings show a positive effect in decreasing the ice accretion and required electrical energy input to maintain ice-free surface. Liu et al. [138] prepared hydrophobic/icephobic coatings using thermal sprayed MCrAlY (M=Ni, Co) layers with further functionalization of 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS) deposition onto the rough surface of MCrAlY. The WCA could reach 135° and the lower ice adhesion strength could facilitate ice removal obviously. The coating also possesses reduced energy consumption in de-icing process.

2.4.5 Other icephobic coatings

Apart from the displayed categories of coatings, the icephobicity could also be inspired from other aspects, there are still many different types of icephobic coatings, which have obtained a wide interest in recent years due to their multi-functions and versatility. For example, the design of superomniphobic surfaces could have wide prospects for icephobic applications. Pan et al. [139] prepared a hierarchical structured superomniphobic coating with re-entrant curvature method using cross-linked PDMS and fluorodecyl polyhedral oligomeric silsesquioxane (POSS) on SS substrate. The low surface energy and significantly reduced solid-liquid contact area help to achieve the high WCA, low CAH and low roll-off angles with virtually different liquids. It is well understood that low surface energy and re-entrant structures are beneficial to icephobic applications.

In another study, the template method could be used to construct relatively complex icephobic surfaces with hierarchical structures. Yang et al. [140] developed a highly hydrophobic two-component TSU (thermosetting polyurethane) surfaces with sandpaper templates and modified nano-silica. The nanocomposite surface showed excellent water repellency with a contact angle of $152 \pm 2^\circ$.

Ayres et al. [141] prepared a titanium alkoxide sol-gel coating system for anti-icing purposes. The size and distribution of the phase domains within the coating ensured that each water droplet that came in contact with the surface would be directly exposed to the hydrophobic matrix. This limits the contact area of the droplet with the surface structure. It also ensured that the sol-gel domains which slowly released tripropylene glycol (TPG) and glycerol could prevent ice adhesion and nucleation.

Besides, the carbon nanotube (CNT) and graphene could provide the required physical/mechanical properties considering the durability and electrical properties required for potential aircraft applications. It offers a feasible way to impart

hydrophobicity and perhaps icephobicity. For example, Raji et al. fabricated a conductive composite of graphene nanoribbon (GNR) stacks and epoxy matrix to effect Joule-heating of composite structures for de-icing applications. The tuneable conductivity of the GNR epoxy composites and low GNR content required make this an attractive method to use in aircraft composites, as shown in Figure 2.21 [142]. The use of nanotubes or graphene in coatings could provide an opportunity to incorporate electro-thermal heating into the surface for de-icing and anti-icing purposes.

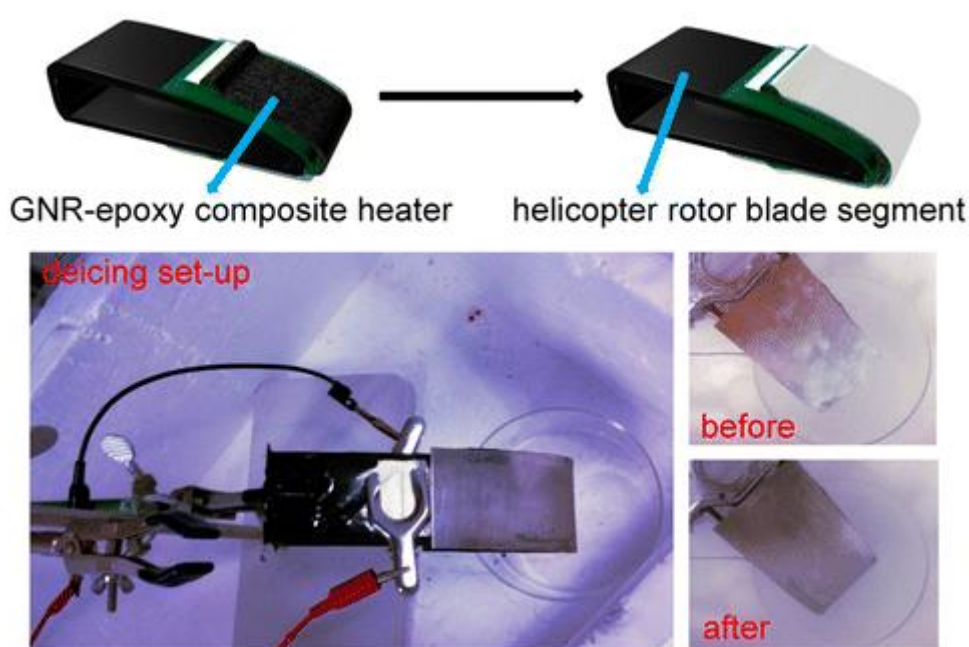


Figure 2.21 Schematic of GNR-epoxy composite heater and the heating de-icing process [142].

2.4.6 Newly developed concepts of icephobic surface and design

Up to now, research progress on icephobic surfaces has developed rapidly due to the advancement of nanomaterials, coating fabrication methods and biomimetics, and more in-depth understanding of ice nucleation and ice adhesion mechanisms. Many new designs and concepts have also been proposed and promoted the development of icephobic surfaces. For example, Golovin et al. [4] discussed that irrespective of material chemistry, it is possible to systematically design coatings with extremely low ice adhesion either by tailoring the cross-link density of different elastomeric coatings or by enabling interfacial slippage. They verified that the interfacial slippage makes the

biggest impact on the ice adhesion strength of low cross-link density elastomers. Relevant icephobic coatings could be designed and fabricated using this understanding. Wang et al. [143] reported that robust superhydrophobicity can be realized by structuring surfaces at two different length scales with a nanostructure design to provide water repellency and a microstructure design to provide durability. The interconnected surface frame could act as “armour” and house the mechanically fragile and hydrophobic nanostructures. Another example is that recently, Irajizad et al. [17] introduced the new concept of MAGSS by exploiting magnetic force to induce a liquid-liquid interface, as shown in Figure 2.22. These surfaces show extremely good icephobicity with ice adhesion of only 2 Pa and 2-3 orders of magnitude higher ice formation delay time. These newly developed surfaces supply a new paradigm for developing icephobic surfaces.

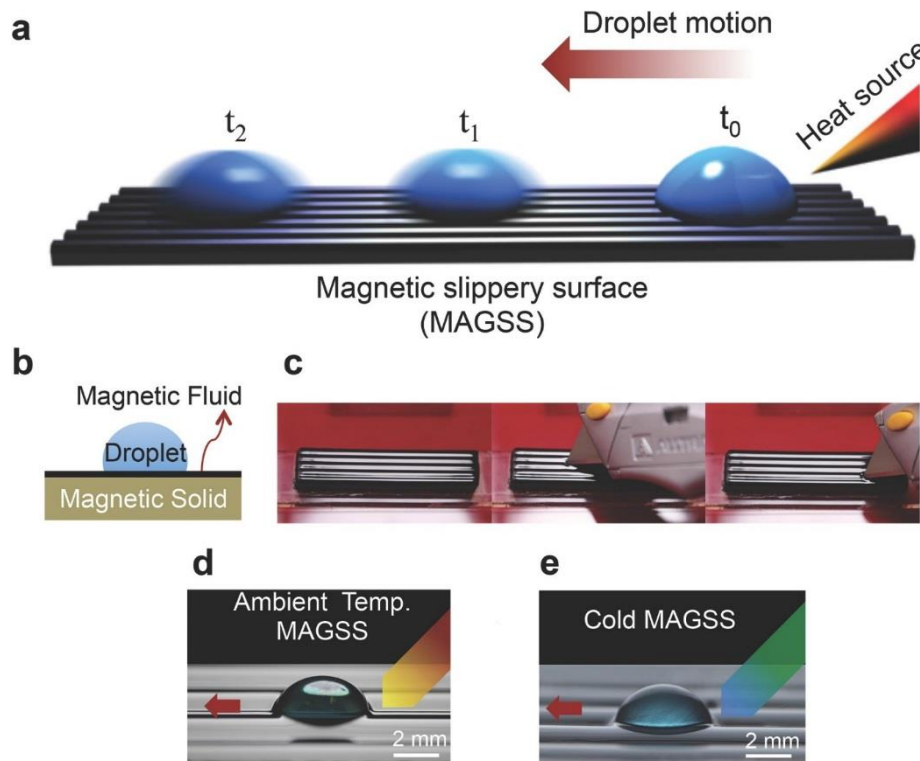


Figure 2.22 (a) Schematic of noncontact motion of droplet on MAGSS; (b) Thin ferrofluid film is locked on the surface by the imposed magnetic force; (c) The self-healing characteristics of MAGSS; (d) Motion of a droplet on MAGSS at room temperature; (e) Easy movement of droplet in case of cold MAGSS [17].

Inspired by the slippery pitcher plant that repels liquid and solid, the nano/microstructured porous material infused with lubricating fluid, named SLIPS, creates exceptionally repellent and robust self-cleaning surfaces on metals, plastics, optics, textiles, and ceramics. It has been widely used in the coating industry and medical surfaces. It has also been discussed for its icephobic capacity. Because of the infused low surface energy lubricant that poses a higher free energy barrier, SLIPS is proposed by using the smooth nature of a liquid surface to enhance icephobicity.

The liquid is trapped in the pores of the rough surface by capillarity, forming a smooth and homogeneous surface on which the CAH is extremely small. In addition to the low CAH value, SLIPS also exhibit anti-wetting behaviour to almost all fluids and show extreme temperature and pressure stability. The liquid-like transition layer at the surface could reduce the pinning effect of water droplets. The lubricating layer could lower the ice adhesion strength. At lower temperatures, there would be a change in the molecular configuration of the transition film, it would increase the ice adhesion to a very large scale [97]. So keeping a non-frozen liquid-like layer on the surface could help the surface with low ice adhesion strength. Various types of oils have been chosen as lubricants and deposited on substrates with different types of material to fabricate SLIPS. These surfaces are all lubricant-impregnated with an extremely small water droplet sliding angle.

For example, Guo et al. [144] analysed the lubricant-impregnated surface by molecular dynamics simulations and found that a proper increase in the lubricant thickness might increase the sliding velocity for the encapsulated state of nanostructures. Chen et al. [97] fabricated a robust prototypical anti-icing coating with a self-lubricating liquid water layer (SLWL) via grafting cross-linked hygroscopic polymers inside the micropores of silicon wafer surfaces. The surface with self-lubricating liquid water layer exhibits excellent capability of self-healing and abrasion resistance. Kim et al. [16] also reported a radically different type of SLIPS by infusing a water-immiscible liquid into a chemically functionalized nanostructured surface on Al surfaces, as indicated in

Figure 2.23. They demonstrated that the SLIPS-coated Al surfaces not only suppress ice/frost accretion but also exhibit at least an order of magnitude lower ice adhesion than state-of-the-art materials.

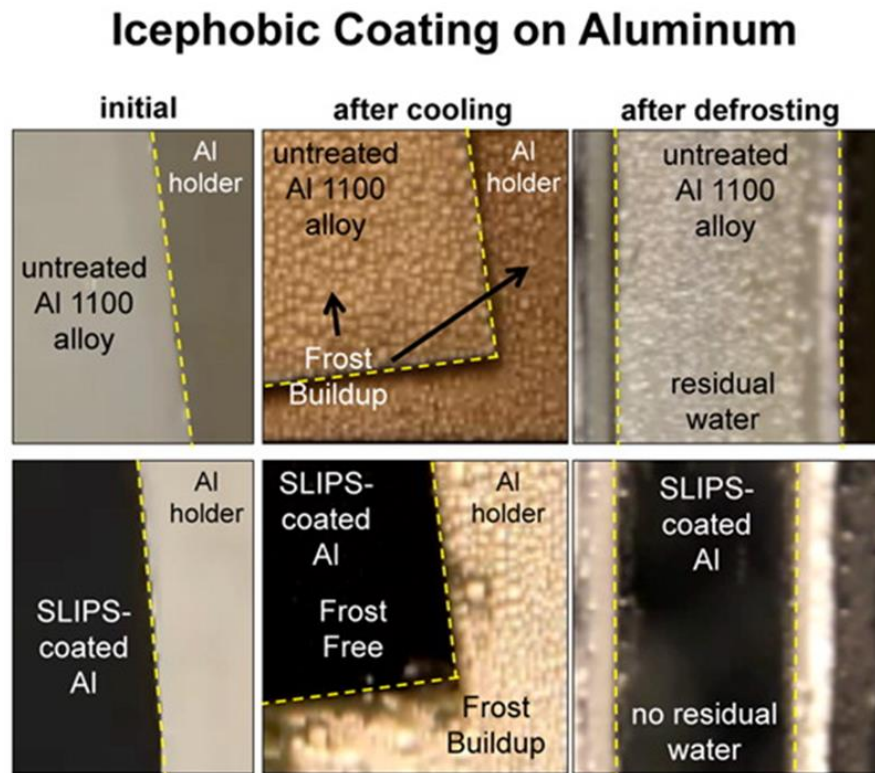


Figure 2.23 Icephobic coating on aluminium: frost buildup and residual water distribution on coatings with different states: initial, after cooling, and after defrosting states [16].

2.5 Current Challenges and Solutions towards Icephobic Surfaces

2.5.1 Durability issues of icephobic surfaces and coatings

While the main research driving forces remain preventing ice nucleation and icing delay, reducing the ice adhesion strength and preventing frost formation, the service life and limited mechanical durability of icephobic surfaces in long-time service under harsh environmental conditions remain a big challenge. Specially, the micro/nano surface structures could fail upon mechanical impact (in the forms of scratches, abrasions or

high speed impacts) [145], the chemical structure could also possibly decompose by some portion of the solar spectrum (for example, the infused liquid would decrease) [146]. The durability of the surface can be defined as the ability for the surface to maintain its surface topography and low surface energy under practical working conditions. The long-term durability when exposed to severe mechanical, chemical, and environmental conditions could be one of the main expected figures of merit in practical use.

Notwithstanding significant theoretical and experimental progress in icephobic coating systems, challenges remain here. First and foremost, there are concerns on issues of robustness and surface fragility, both thermodynamic and mechanical [22], especially on the polymeric coatings. Erosion from rain, sand, and dust particles is a critical issue for icephobic surfaces in the operating environment. There have been numerous reports on the non-durability, aiming to analyse the cause and design durable coatings [24, 25], foreseeing the immediate, worldwide applications of such extremely durable, icephobic coatings across various industrial sectors, academic disciplines and engineering endeavours.

The practicality of these polymeric surfaces is hampered by the poor mechanical stability of the microscopic surface topography that is essential for good icephobicity [26, 147]. The fragile micro- and nano- hierarchical structures are prone to be destroyed after a slight scratch, abrasion, impacting, and even finger touch [148], to say nothing of peeling with adhesive tape or the abrasion by the sandpaper. This could be a major restriction for practical applications as they cannot survive long-termly in harsh environment conditions (e.g. wings of aircraft, wind turbines, solar panels, power lines, automobiles, and roofs of any structures). UV-durability and anti-corrosion properties are equally crucial for practical outdoor use, which mainly depends on the surface chemical composition and surface structures [149].

2.5.2 Strategies for durable icephobic surfaces

Based on the current progress towards icephobic coatings, many strategies aiming to solve the durability issues have been proposed and developed in recent years:

1. Enhancing mechanical durability by grafting and/or crosslinking. Grafting and/or crosslinking methods are generally used to enhance the mechanical durability of icephobic surfaces (which has been discussed in Section 2.4.1). For example, Sojoudi et al. [150] constructed smooth bilayer structures using divinyl benzene (DVB) and 1H, 1H, 2H, 2H-perfluorodecyl acrylate (PFDA) with the crosslinked DVB network grafted directly to the silicon substrate. The surface maintains its low ice adhesion strength after repetitious icing cycles. The result of nanoscratch tests verifies the significant role of in situ grafting in reducing the possibility of coating delamination.

2. Create damage-tolerant, protective icephobic surfaces that are self-repairable upon mechanical damage or other external force. It is desirable to design icephobic surfaces with self-repairing (or self-healing) capabilities because of the progressive loss of hydrophobicity and potential icephobicity upon prolonged wear conditions is unavoidable. Chen et al. prepared all-water-based self-repairing superhydrophobic coatings using UV-responsive microcapsules by Pickering emulsion polymerization. The coatings could regenerate superhydrophobicity and self-cleaning ability under UV light, as indicated in Figure 2.24, mimicking the outdoor environment, after they are mechanically damaged or contaminated with organics [146].

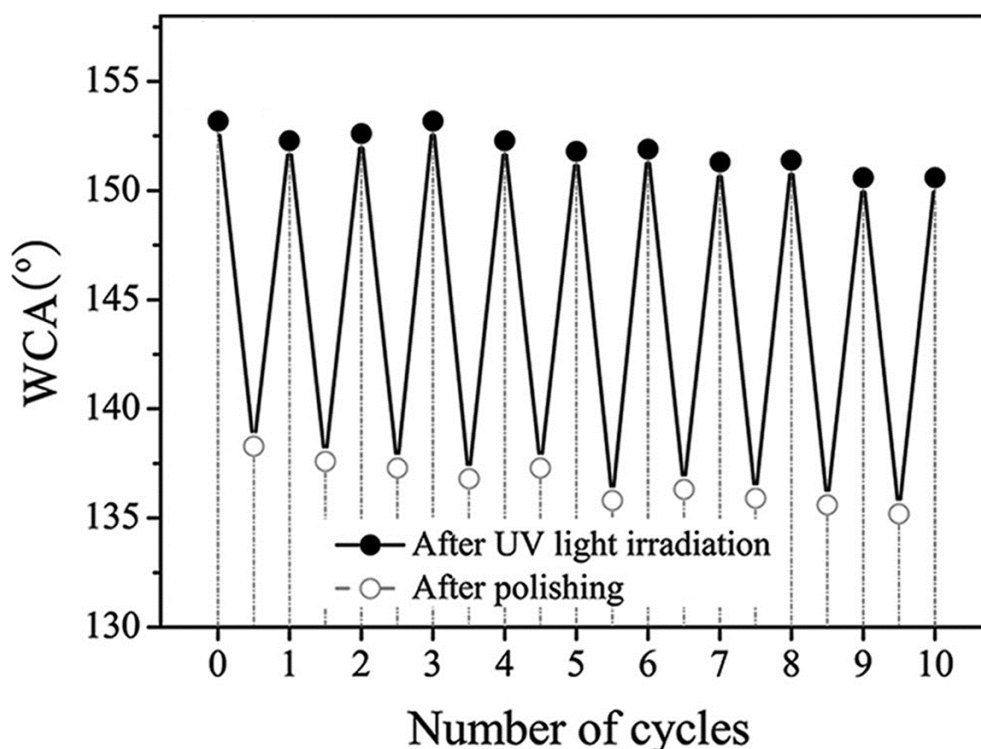


Figure 2.24 Change of WCA for the self-repairing superhydrophobic coatings as a function of repeated polishing and accelerated weathering cycles [146].

3. Icephobic surfaces with protective pillars. This is a unique research direction that aims to isolate hierarchical structures from compression or abrasion forces by constructing protective pillars. As shown in Figure 2.25, Huovinen et al. prepared a polypropylene (PP) based surface with protective pillars using template method with WCA of 150 ° and sliding angle of 10 °. With the protection of pillars, the WCA and SA remained unchanged under 30 cycles of abrasion tests at loads up to 120 kPa [151].

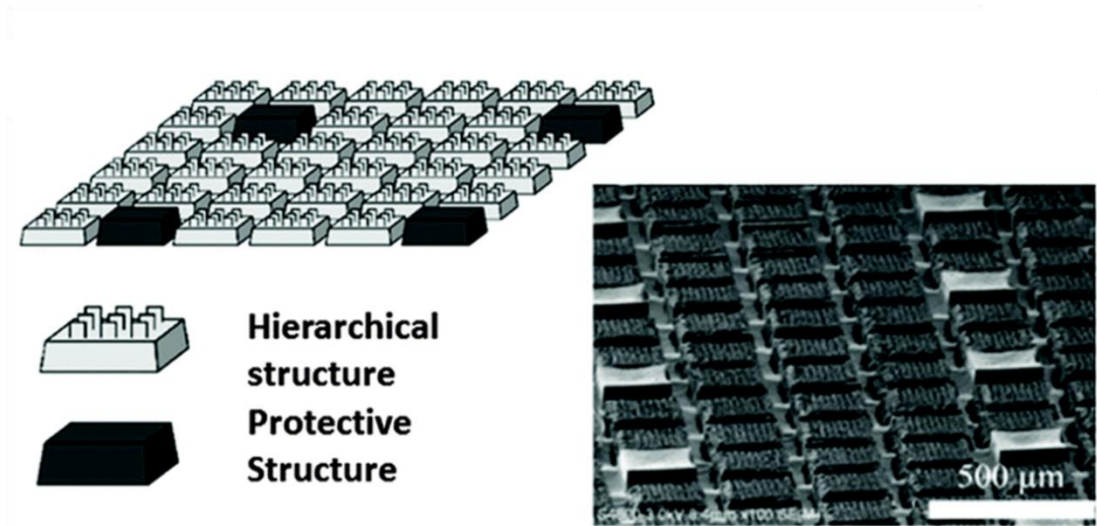


Figure 2.25 Hierarchical micro and nano structures with protective pillars [151].

4. Create mechanically-durable structures and employed low surface energy materials onto them. For example, machine abrading the surface to create robust microstructures and followed by fluorinating the micro/nanostructures [38]. These surfaces retained their anti-icing properties after the ice formation/melting process was repeated for at least 20 times, indicating the durability of the surfaces.

2.5.3 Consideration on coating durability

Besides the aforementioned durable strategies, designed surfaces and metallic-based coating systems combined with low surface energy layer could also be a good choice. In recent years, metallic-based coating systems have been attracting significant interests due to their outstanding mechanical durability and possible multi-functionalities. For example, Wei et al. prepared a Fe-based composite surface using electro-brush plating which exhibited excellent hydrophobicity, anti-corrosion performance, and abrasion resistance [27]. Khorsand et al. fabricated superhydrophobic Ni-Co coatings that exhibited good chemical stability and long-time durability as well as the self-cleaning effect [28]. Vorobyev et al. reported a hydrophobic multifunctional metal surface showing combined effects of self-cleaning, anti-biofouling, and self-sanitation by producing hierarchical nano- and micro- structures with femtosecond laser pulses [29]. Metallic-based coating systems combined with low surface energy layer could ensure

the good mechanical and environmental durability derived from the metallic-based system and good hydrophobic/icephobic performance with the deposited low surface energy layer. Boinovich et al. reported a multimodal roughness textured SS surface modified with 2D polymer network of fluorooxysilane showing good icephobicity and remained stable after 100 icing/de-icing cycles accompanied with mechanical stresses [152]. Zheng et al. fabricated superhydrophobic Al surface with hierarchical micro/nano structure by anodisation method which had a water contact angle of 156° ; exhibiting a delay in ice formation and low ice adhesion strength of 40 kPa [11]. Ruan et al. reported that superhydrophobic steel surface prepared by chemical etching process demonstrated excellent anti-icing properties [12].

Therefore, to obtain long-time mechanical, chemical and environmental durability, the metallic-based coating systems could be considered, it is one of the most promising research directions and is of great significance to be widely studied. The non-wetting, liquid-infused and hydrated surfaces have also inspired routes for development of icephobic surfaces. For example, Irajizad et al. [153] reported the physical concept named stress-localization with the implementation of elastomers to minimize the solid adhesion on certain surfaces. Icephobic surfaces with low ice adhesion have been developed. The new form of icephobic surface is composed of a matrix with high shear modulus as phase I and a highly dispersed phase II with low shear modulus. The schematics are shown in Figure 2.26. Phase I is a silicon elastomer and phase II is a silicon-based organogel. To ensure the major role of the matrix in long-term mechanical durability, it is very important to choose an elastomer (phase I) with high shear modulus. For the aim to form a homogenous material, compatibility of the matrix and the dispersed phase II is also very important. Phase II would be responsible for cavitation and crack initiation at the interface. Stress-localization leads to a shear force at the interface. The interfacial cracks could then formed at the coordinate of phase II, which easily detaches the ice from the material.

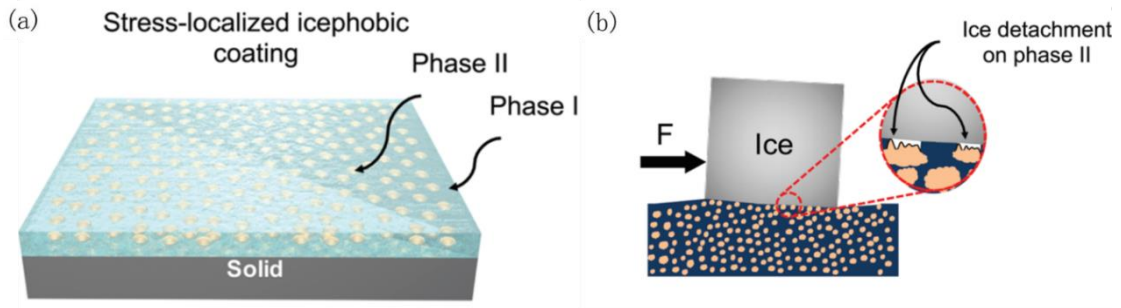


Figure 2.26 (a) Stress-localized icephobic surfaces (b) schematic of formation of crack at the coordinate of phase II with minimal forces [153].

Another significant example is the low-interfacial toughness materials used for effective large-scale de-icing with good mechanical durability [154]. The concept that the force needed to remove an ice layer reaches an asymptotic value if the interface is long enough has been verified in this paper. Materials (mainly polymers) that exhibit low-interfacial toughness (LIT) with ice could lead to the low forces that are required to remove large areas of ice from systems and is independent of the iced area, as indicated in Figure 2.27. The reasons could be ascribed to: (1) The low bonding energy between the ice and coating, a lower bound on this energy could be 0.1 J/m^2 , corresponding to van der Waals interactions [39]; (2) Another could come from localized losses within the coating, associated with the high-stress region at the crack tip. The research describes a class of materials that are made of such low-interfacial toughness that allows ice to be shed readily from large areas merely by self-weight.

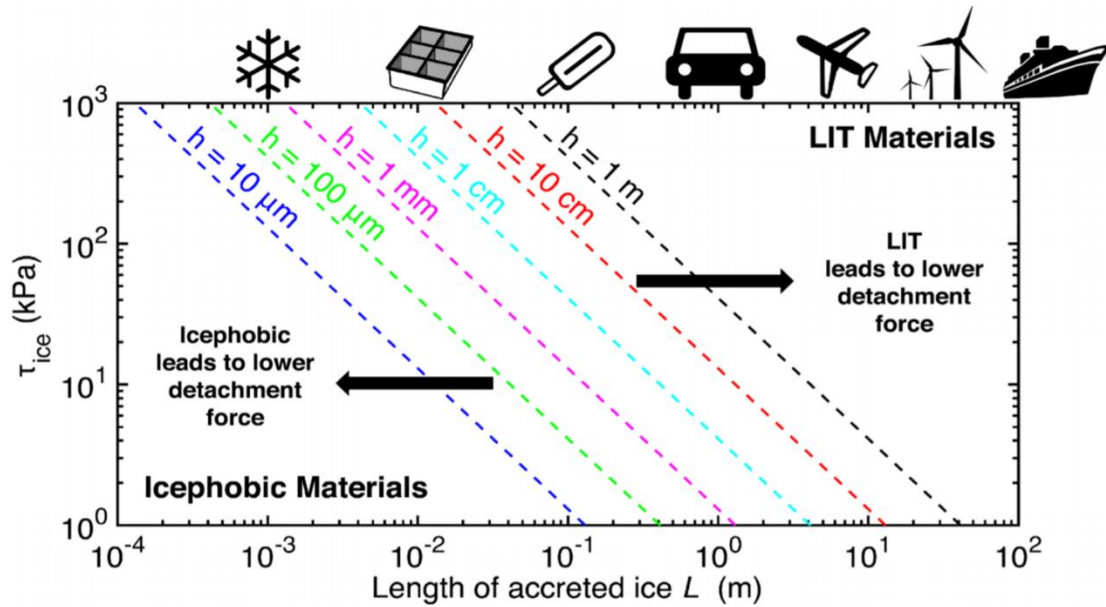


Figure 2.27 Significance of the length of accreted ice. The length of accreted ice determines if an icephobic material or a LIT material should be used for a given application [154].

The developed concept of stress-localization and LIT could be implemented in a broad range of material systems to minimize adhesion of any solid, including bio-species, salt, dust and gas hydrates, and on surfaces with no compromise in mechanical properties. New icephobic coating design could be developed towards the inspiration of the displayed concepts. It is envisioned that newly designed and developed surfaces could help with a wide range of applications including aviation systems, oceanic sciences, energy systems and bio-sciences.

2.6 Summary

In this chapter, the requirement of the ice protection systems has been demonstrated. The ice protection system is mainly used to minimize the hazard of icing phenomenon in daily life and industry. The active de-icing and passive anti-icing are the two widely used strategies.

After a short introduction, the principles and basic theory of hydrophobicity and hydrophobic coatings were demonstrated systematically by taking the relationship between icephobicity and hydrophobicity into consideration. A detailed demonstration of the definitions and mechanisms including WCA, Young's equation, Wenzel's and Cassie's modes, and so on have also been carried out. The fundamentals of icephobicity including the specific definition of icephobicity, detailed mechanisms on ice nucleation, and icing delay and interaction between the ice/solid interfaces have also been discussed to give a full and better understanding.

Then the current progress toward hydrophobic/icephobic surfaces has been categorized according to the chemical compositions, surface topographies, and application methods, which mainly consist of polymeric coatings, metallic coatings, bio-inspired coatings and coatings with topography modifications. They cover the most scalable approaches towards the fabrication of hydrophobic/icephobic surfaces, which build a full understanding.

Lastly, the state of art of development on icephobic surface has also been reviewed. Some of the new and promising design concepts were illustrated and discussed. The remaining challenge and some urgent issues facing further development towards current icephobic surfaces have been forwarded. The limited durability remains a big problem and needs to be addressed when designing icephobic surfaces. The mainstream solutions were also attached. Research work in this study is expected to answer the problem and help to address the remaining challenge towards this area. Study on hydrophobic/icephobic surfaces using Ni based coatings and further modification with PDMS layer will be carried out in the work.

Chapter 3 Methodologies

3.1 Substrate Preparation and Raw Materials

3.1.1 Substrate preparation

Two types of metallic samples have been used in this project, including: (1) 304 stainless steel, (GoodFellow Cambridge Ltd, Huntingdon, UK), the detailed chemical composition is also listed in Table 3.1; (2) Nickel (Ni) foam was obtained from TMAX Battery Equipment Ltd (Xiamen, China), with the extensibility of lengthwise $\geq 5\%$, widthwise $\geq 12\%$, tensile strength lengthwise ≥ 1.25 N/mm², widthwise ≥ 1.00 N/mm². All substrates were machined into proper shape for coating preparation according to their as-received form. The 304 SS was machined into 50 mm $\times$ 20 mm $\times$ 1 mm rectangle plates. The Ni foam was cut into 50 mm $\times$ 20 mm $\times$ 0.3 mm rectangle plates.

Table 3.1 Chemical compositions of 304 SS substrate.

304 Elements	C	Mn	P	S	Si	Cr	Ni
Wt (%)	≤ 0.08	≤ 2.0	≤ 0.04	≤ 0.03	≤ 1.0	18.0-20.0	8.0-11.0

3.1.2 Details of involved chemicals

All of the involved chemicals in this study have been displayed in Table 3.2. The features, origins, and states of the participating chemicals have also been supplied.

Table 3.2 Lists of involved chemicals.

Items	Features	Origin	States	Other Info
Nickel sulfate hexahydrate (NiSO ₄ 6H ₂ O)	Pure solid	Sigma-Aldrich	As-received	Metallic salt
Copper sulfate pentahydrate (CuSO ₄ 5H ₂ O)	Pure solid	Sigma-Aldrich	As-received	Metallic salt
Sodium dihydrogen phosphate (NaH ₂ PO ₂)	Pure solid	Sigma-Aldrich	As-received	Reducing agent
Sodium sulfate (Na₂SO₄)	Pure solid	Sigma-Aldrich	As-received	Metallic salt
Sodium dodecyl sulfate (SDS)	Powder	Sigma-Aldrich	As-received	Help to disperse the ions
Citric acid (C₆H₈O₇)	Pure solid	Sigma-Aldrich	As-received	Buffering agent
Sodium citrate dehydrate (C ₆ H ₅ Na ₃ O ₇ 2H ₂ O)	Pure solid	Sigma-Aldrich	As-received	Ligand
Ammonium chloride (NH₄Cl)	Pure solid	Sigma-Aldrich	As-received	Inorganic salt
Succinic acid	Pure solid	Sigma-Aldrich	As-received	Inorganic salt
Sodium acetate	Pure solid	Sigma-Aldrich	As-received	Metallic salt
Sodium molybdate (Na₂MoO₄)	Powder	Sigma-Aldrich	As-received	Stabiliser
Tin chloride (SnCl₂)	Pure solid	Sigma-Aldrich	As-received	Metallic salt
Palladium chloride (PdCl₂)	Pure solid	Sigma-Aldrich	As-received	Metallic salt
Hydrochloric acid (HCl)	Pure liquid	Sigma-Aldrich	Diluted	pH adjustment and washing
Sodium hydroxide (NaOH)	Pure solid	Sigma-Aldrich	As-received	pH adjustment
Ammonium hydroxide (NH ₄ OH)	Pure solid	Sigma-Aldrich	As-received	Inorganic salt
PDMS Silicone R2180	Colloid	NuSil Technology	As-received	Two parts
Xylene	Pure liquid	Fisher Scientific	As-received	Solvent
Deionised water	Pure liquid	Self-produced in Lab	As-prepared	Solvent

3.2 Preparation of Ni-Cu-P Coatings

For the preparation of Ni-Cu-P coatings, the SS was used as the substrate due to its wide application and good physical property. To ensure the comparability, all substrates were manually sandblasted to an average roughness (Guyson Formula 1200 cabinet using F220 with alumina, average size 68 μm) with the following parameters: gas pressure of 7.3 bar, distance between the nozzle and the specimen of about 5 cm and duration of 30 s. The sandblasted samples were treated by diluted hydrochloric acid for 2 min to remove the surface oxide and oil contamination later, then cleaned by deionised water, handle them with compressed air and ready for experiments. Deionised water with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ was used in the process of coating preparation.

3.2.1 Electrodeposition of Ni-Cu-P ternary coatings

Electrodeposition is a versatile coating technique with a high degree of control over deposition thickness. It focuses on preparing in situ metallic coatings by action of an electric current on conductive material immersed in a solution containing metal salt to be deposited. Electrodeposition is a convenient method to create micro/nanostructures metallic coatings which could be readily controlled by adjusting deposition parameters. Many metals could be electrodeposited from aqueous baths [155].

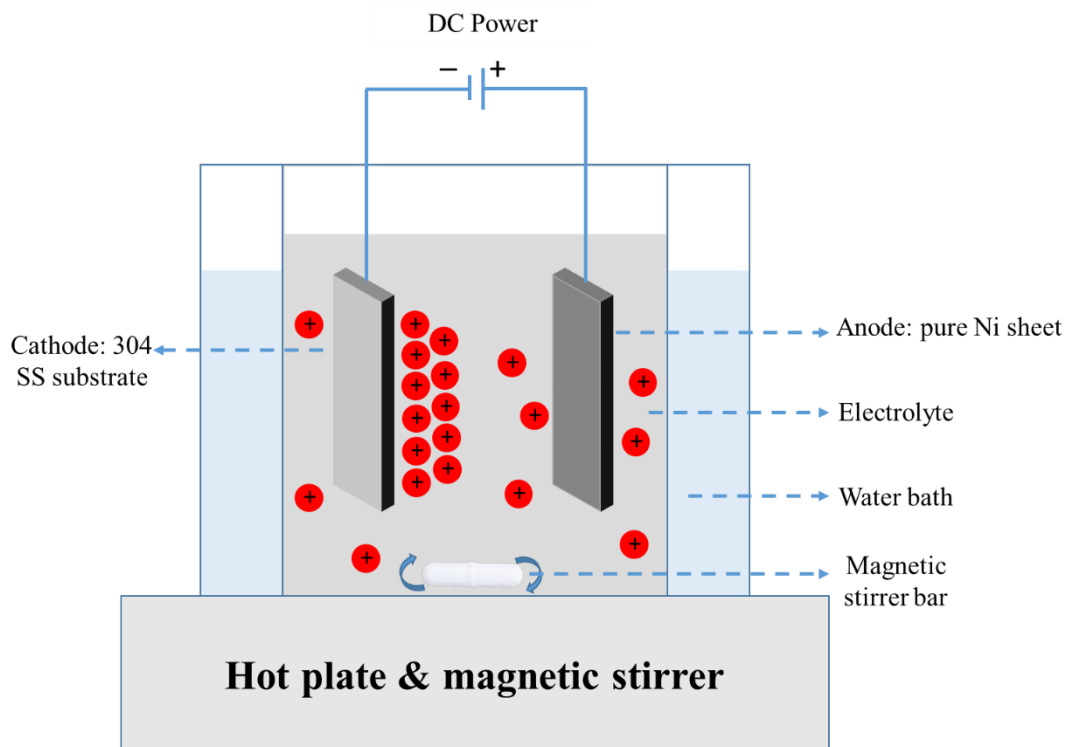


Figure 3.1 Schematic diagram of electro-deposition setup.

The facility was made up of direct current (DC) power supply, anode, cathode, and electrolyte, as indicated in Figure 3.1. During the experiment, deposit is formed on cathode that is negatively charged as cations, while 304 SS substrate were used as cathode. Positively charged anode may be inert or allow dissolution of metal ions. In this experiment, the pure Ni foil was selected as anode and the dimension was the same as the cathode because same reaction area contributes to good coating uniformity. In the bulk solution, movement of ions, conduction and diffusion, agitation or flow (hydrodynamics) helped to minimise concentration gradients and reduced the thickness of diffusion layer. Reducing the thickness of the diffusion layer increased the limiting current density for deposition and raised the plating efficiency.

The electrolyte of the electrodeposition consists of 0.125 mol/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 0.005 mol/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.026 mol/L NaH_2PO_2 , 0.05 mol/L citric acid and 0.12 g/L sodium dodecyl sulfate (SDS). 0.5 mol/L Na_2SO_4 was added to the electrolyte to enhance the solution ion strength. For the electrolyte preparation, the chemicals were measured by

an analytical balance with a precision of 0.0001 g, while the deionised water was determined by a measuring cylinder (precision: 0.2 ml) combined with micro-pipettor (precision: 0.001 ml). All of the electrolytes were prepared using analytical grade reagents and deionised water. Figure 3.2 shows the process flow chart of the electrodeposition process of the Ni-Cu-P ternary coating. The pH value was adjusted to 5.5 by ammonia hydroxide (the precision of the pH meter (FiveEasy Plus pH meter FP20-Std-Kit, Mettler-Toledo Ltd, UK) is 0.01). The deposition temperature was kept at 25 °C and the current density was set to 50 mA/cm². Magnetic stirring was utilized to maintain the uniformity of electrolyte. A magnet stirrer was applied for the agitation at around 100 revolutions per minute (rpm). The whole electrodeposition process had a duration of 30 min. Then the samples were taken out, washed with deionised water, dried with compressed air and stored in ambient air for further study.

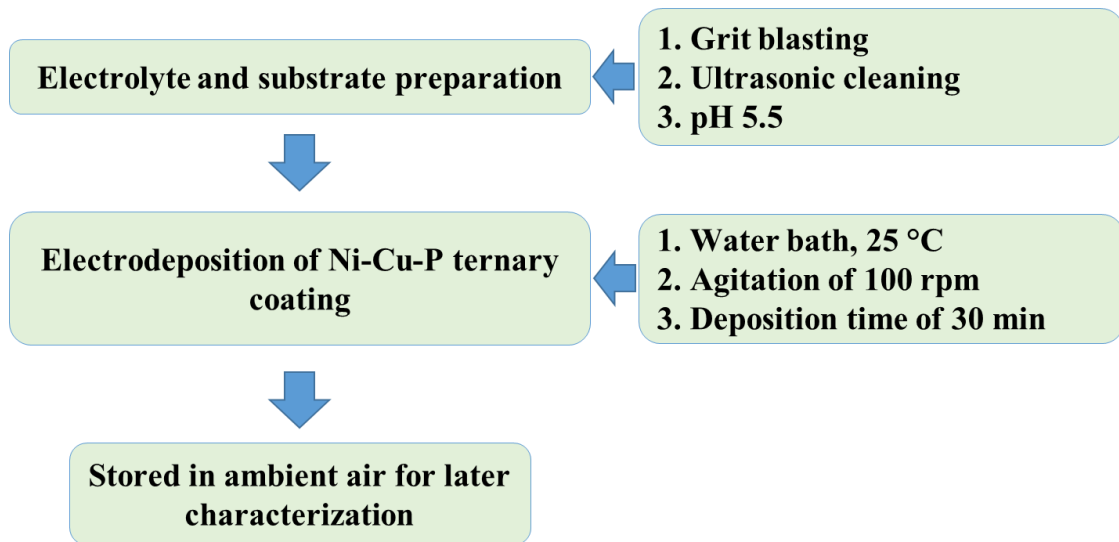


Figure 3.2 Process flow chart of the electrodeposition process of Ni-Cu-P ternary coating.

3.2.2 Electroless-deposition of Ni-Cu-P ternary coatings

Electroless deposition was also used to deposit Ni-Cu-P coating due to the processing advantages including more consistent thickness (uniformity in both edges, corners and holes), lower operating costs (no applied voltage needed), and wide applicability on complicated and irregular shape artifacts (can be used on non-electrical conducting

surface) [156, 157]. Electroless deposition is defined as a controlled autocatalytic deposition of a continuous layer on a catalytic surface by the reaction of a complex compound and a chemical reducing agent, where the substrate develops potential in a plating bath containing metallic ions, reducing agent, complexing agent, stabiliser and other components. The method allows easy preparation of coatings using simple equipment and any type of support with low thickness, no DC power supply is needed to drive the process. It could be applied to both metallic and non-metallic substrates. It also ensures uniform plating thickness on complex part geometries. The detailed process is shown in equation (3.1):

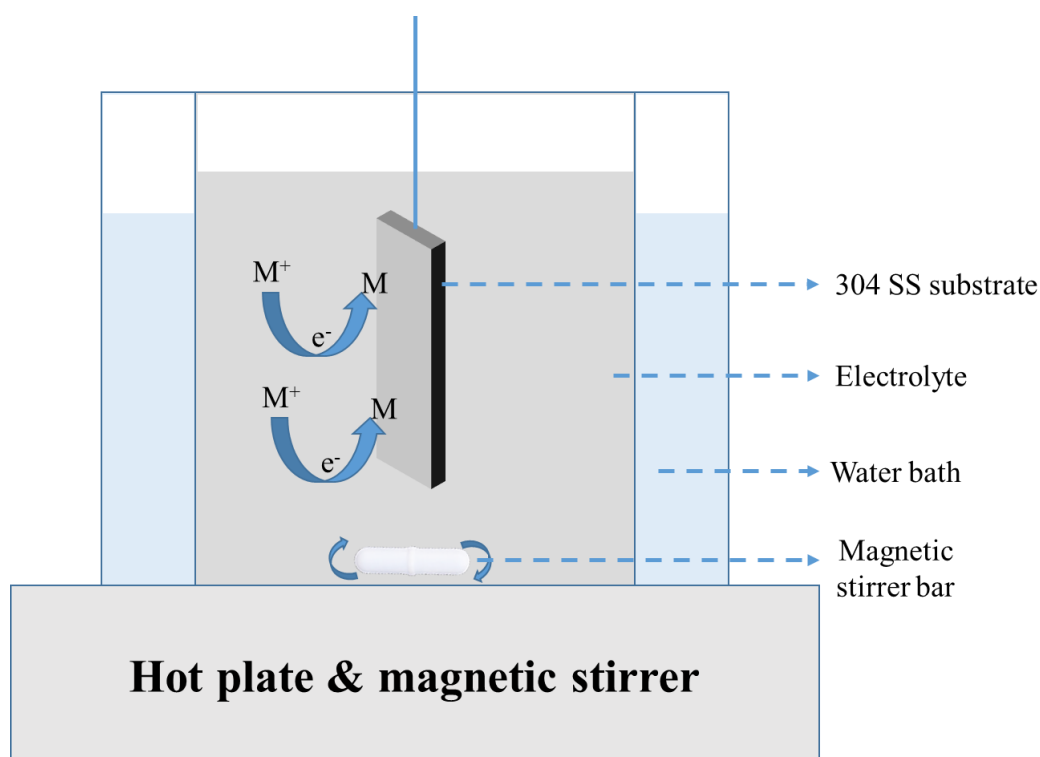


Figure 3.3 Schematic diagram of electroless deposition setup.

The stability of the deposition process fully depends on the substrate material, the pre-treatment process, the type of electrolyte, and the pH and temperature. So 304 SS was selected as the substrate due to its chemical activity, the electrolyte was also selected based on the mature craft [158]. The pH and deposition temperature were also strictly

controlled. The schematic view is shown in Figure 3.3. A two-step pre-treatments were performed before the electroless deposition process to form catalytic seeds. The substrates were immersed in 0.1 mol/L SnCl_2 and 0.1 mol/L HCl solution at room temperature for 30 min followed by deionised water washing. After that, they were immersed in a mixture of 0.0014 mol/L PdCl_2 and 0.25 mol/L HCl solution for another 30 min at room temperature. Then the substrates were cleaned in the ultrasonic bath with deionised water for 10 min.

The electrolyte for electroless deposition consists of 22.6 g/L NiSO_4 , 0.5 g/L CuSO_4 , 26.1 g/L sodium citrate dihydrate, 40 g/L NH_4Cl , 5 g/L succinic acid, 5 g/L sodium acetate and 5×10^{-6} g/L Na_2MoO_4 . For the pretreatment solution and electrolyte preparations, the chemicals were measured by an analytical balance with a precision of 0.0001 g, while the deionised water was determined by a measuring cylinder (precision: 0.2 ml) combined with micro-pipettor (precision: 0.001 ml). The pH value was maintained at around 5.0~5.3. The deposition temperature was controlled by a hot plate at around 90 °C. Magnetic stirring was utilized for the agitation at 100 rpm to maintain the uniformity of electrolyte. The whole electroless deposition process had a duration of 30 min. The ageing process of the coating was then carried out in ambient air with room temperature and humidity. The coatings prepared by electroless deposition and electrodeposition methods were designated as ELD and ED, respectively. The samples prepared with 0.5 g/L, 1.0 g/L, and 1.5 g/L CuSO_4 addition were designated as ELD-0.5, ELD-1, and ELD-1.5, respectively. The whole process could be summarized from the flow chart below, as shown in Figure 3.4.

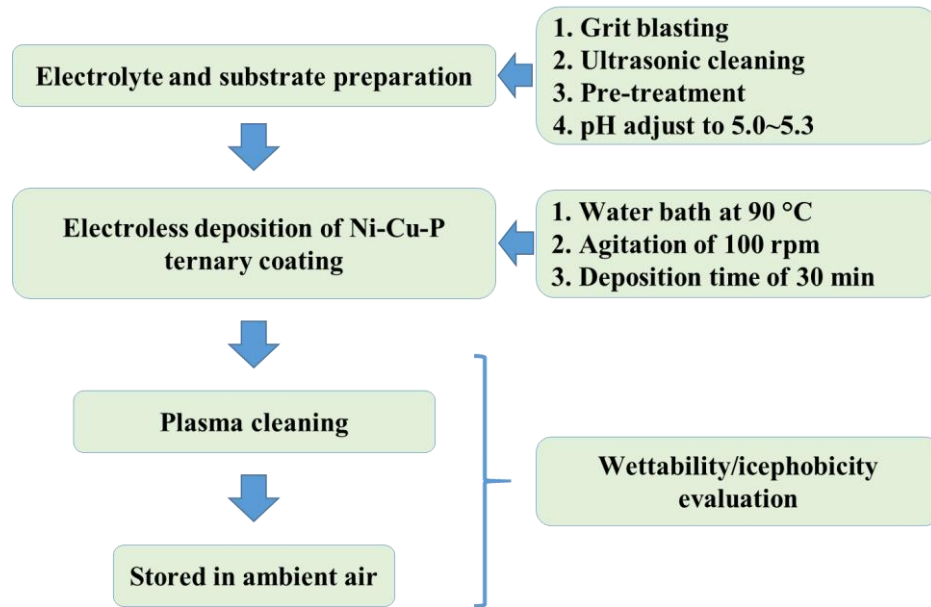


Figure 3.4 Process flow chart of the electroless deposition of Ni-Cu-P ternary coating.

3.3 Preparation of Two-Phase Ni foam/PDMS Layers

The substrates (Ni foam and 304 SS) were cut into 50 mm × 20 mm × 0.3 mm rectangular plates. The substrates were cleaned thrice using acetone and deionised water with ultrasonic bath and then dried with compressed air. For 304 SS substrate, sandblasting treatment needs to be conducted prior to the coating preparation.

PDMS (Silicone R-2180: two-part silicone elastomer dispersed in xylene) was purchased from NuSil Technology (High Wycombe, UK). Xylene was purchased from Fisher Scientific UK Ltd (Loughborough, UK). Silicone R-2180 is a two-part elastomer that is designed to have low surface adhesion when in contact with ice. Part A of the mixture contains the platinum catalyst required for curing inside of a silicone base and Part B is made up of crosslinker and inhibitor in the xylene. It contains silica as a reinforcing filler which enhances the van der Waals forces of the cured polymer and the hydrogen bonds are formed between the hydroxyl groups and the surface of the silica particles. The detailed physical properties are shown in Table 3.3. The R-2180 would be useful for coating small parts that could fit in and withstand the temperatures in an

oven. All of the chemicals were analytical grade reagents and used as received. The two individual components are thoroughly stirred prior to mixing to ensure homogeneity. The two medium viscosity parts then blend easily in a convenient 1:1 ratio (Part A:B).

Table 3.3 Typical physical properties of PDMS [159].

Uncured	
Viscosity	3600 cP
Work time	> 72 hr
Cured (30 min at 25 °C; 45 min at 75 °C; 135 min at 150 °C)	
40 Durometer, Type A	40
Tensile strength	1700 psi
Elongation	1050%
Tear strength	300 ppi
Stress at 100% strain	150 psi

3.3.1 Preparation for Ni/PDMS-A

For Ni/PDMS-A, the detailed preparation process is shown in Figure 3.5. The two parts of the PDMS prepolymer were mixed in xylene separately with a 1:1 ratio and magnetically stirred for 3 h. One more hour magnetic stirring was carried out after mixing the two solutions. The resulting mixture of silicone R-2180 was viscous. The Ni-foam substrates were put into the mixture to make it fully immersed. Then it was transferred into the low-vacuum oven (Vacutherm, Vacuum Heating and Drying Ovens, ThermoFisher, Waltham, MA USA) (0.05 bar) for 30 min to degas the existing air bubbles among the porous structure, followed by post-baking treatment at 75 °C for 45 min (to remove solvent) and 150 °C for 135 min (elevated curing temperature). The degassing process could help to decrease the number of air bubbles generated during the curing process effectively.

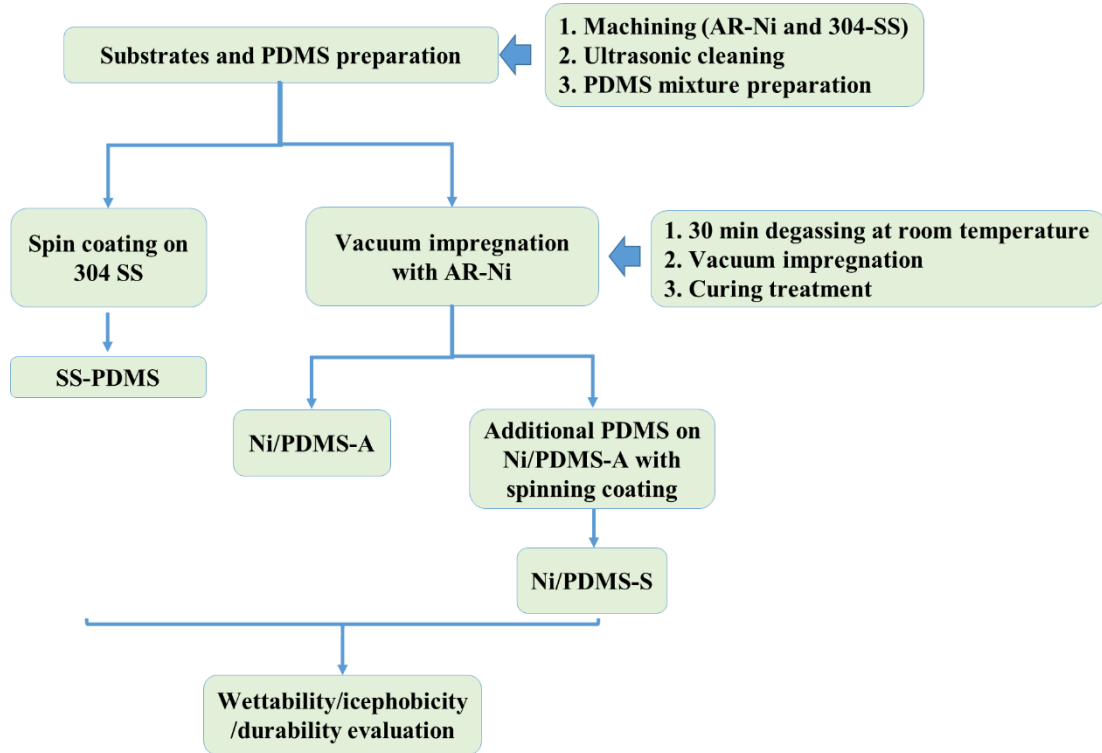


Figure 3.5 Process flow chart of the deposition process of two-phase Ni foam/PDMS layers.

3.3.2 Preparation for Ni/PDMS-S

Ni/PDMS-S was further fabricated based on the formerly prepared Ni/PDMS-A. After the impregnation and curing, additional PDMS was applied onto the sample surface using the same mixture solution and spin-coated (KW-4A, Chemat Group, Northridge, CA, USA) at a speed of 1500 rpm for 1 min. Here, the spinning coating is mainly used to prepare uniform thin films in the thickness range of micrometer to nanometer. It consists of several stages, such as fluid dispense, spin up, stable fluid outflow, spin off, and evaporation, respectively [160]. The samples were then heated in the vacuum oven for similar post-baking treatments. For further comparison purposes, a PDMS layer was coated onto sandblasted 304 SS substrates using spin coating with the same coating and post-baking treatment conditions.

There are four different kinds of samples prepared in this series of experiment: pristine as-received Ni foam substrate (AR-Ni); Ni foam/PDMS samples were designated as

Ni/PDMS-S; the sample immediately after impregnation and curing without the additional spinning process was abbreviated as Ni/PDMS-A; and PDMS coating on 304 SS substrate was designated as SS-PDMS.

3.4 Methods Utilized to Investigate Wettability Evolution

3.4.1 Ageing process

Due to the observation of wettability change of as-deposited samples after storage in ambient air, relevant ageing process needs to be conducted. The as-prepared samples are stored indoor in ambient air condition for certain time as further treatment, named ageing process. No other measure will be taken. The ageing duration for different samples is based on the experiment requirement. The relative humidity was monitored at around $45 \pm 10\%$, and the ambient temperature was $20 \pm 3\text{ }^{\circ}\text{C}$.

3.4.2 Plasma cleaning treatment

Plasma cleaning is a proven, effective, economical, and environmentally safe method for critical surface preparation. Plasma cleaning with oxygen plasma eliminates natural and technical oils & grease at the nanoscale & reduces contamination up to six-fold when compared with traditional wet cleaning methods, including solvent cleaning residues themselves. Plasma cleaning produces a pristine surface, ready for bonding or further processing, without any harmful waste material. The schematic view of the plasma cleaning process is shown in Figure 3.6.

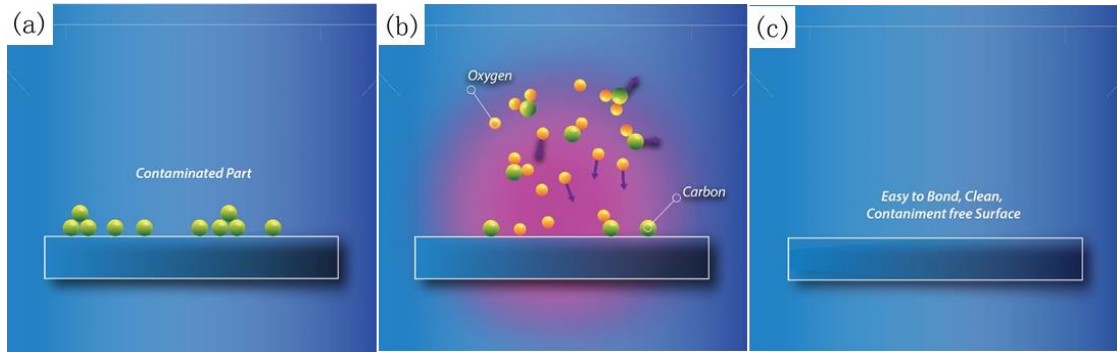


Figure 3.6 Plasma cleaning process (a) before plasma treatment (b) during plasma treatment (c) after plasma treatment [161].

In this study, plasma cleaning treatment was carried out for a duration of 8 min using the Plasma Cleaner (Model 1020, Fischione) to quickly remove adsorbed substances on the coating surface with a gas mixture of 25 vol% oxygen and 75 vol% argon. The relevant change in performance and microstructure will also be monitored.

3.4.3 Boiling water treatment

The plasma treatment might have surface activation effect to polymer by attaching polar or functional groups to the polymer surface, as indicated in Figure 3.7. Plasma surface activation renders many polymers receptive to bonding agents and coatings. The treated parts will remain active for a few minutes up to several months, depending on the particular material that has been plasma treated. To avoid the surface activation effect on polymer surface, another simple and easy way to remove the adsorbed airborne gaseous groups could be applied to the samples - hot water boiling treatment. The boiling treatment will not introduce any surface activation effect to the surfaces, it also does no damage to the surface morphology.

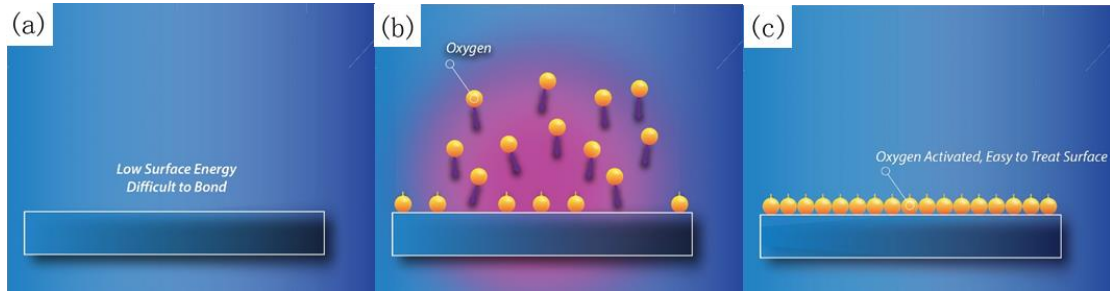


Figure 3.7 Plasma surface activation (a) before plasma treatment (b) during plasma treatment (c) after plasma treatment [161].

3.5 Microstructure Characterisation Methods

3.5.1 Scanning electron microscopy (SEM)

The surface morphologies of the samples were characterised by JEOL-6490LV SEM. The cross-section parts were also characterised. Samples were sectioned for microstructure characterisation after the coating fabrication. The microstructure characterisation was conducted on a JEOL-6490LV SEM operated with 20 kV voltage. The working distance was maintained at 10 mm. The spot size of the electron beam was adjusted to a proper scale in order to reduce the deadtime (the period of time that the EDX detector is effectively switched off) when performing energy dispersive X-ray analysis. Backscattered electron (BSE) mode was also utilized to image the cross-sectional areas of the samples.

An ATM Brilliant 220 cutting machine was used to cut the samples into small pieces for mounting using a BUEHLER AcuThin Abrasive Cut-off wheel. The cutting speed was set to 0.005 m/s in order to keep the minimum damage to coating cross-sectional areas. Normally, the sectioned samples were mounted using conductive epoxy resin for SEM characterisation. All of the mounted samples were ground by 240 p, 400 p, 800 p and 1200 p grit abrasive papers and polished by 6 μm and 1 μm diamond paste for further SEM characterisation.

3.5.2 Energy dispersive X-ray analysis (EDX)

An EDX (INCA, Oxford Instrument Link ISIS-3000) was used to help with the elemental analysis in the coatings, combined within the SEM. X-rays emitted from different elements in the coating were examined by an EDX detector. When performing the area detection, a minimum of $2\ \mu\text{m} \times 2\ \mu\text{m}$ area was examined to give accurate results due to the precision of the detector. For some smaller areas on the coatings, i.e. precipitates, a point scan would be performed, and the influence of other elements in nearby areas would also be considered. In general, the EDX detector was operated at 20 kV.

3.5.3 X-ray diffraction (XRD)

The prepared coatings were characterised by a Siemens D-500 X-ray diffractometer to determine the formed phases. The instrument was operated at 25 mA and 40 kV using a wavelength of Cu $K\alpha$ radiation with a scanning range of 2-theta (2θ) from 10° to 80° and a scanning step of 0.02° . The XRD results were analysed using the Jade software to determine the crystalline phases.

3.5.4 X-ray photoelectron spectroscopy (XPS) and CasaXPS software

XPS is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the very low range that exists within certain material. It could measure the X-ray photon radiation emitted by the surface when the photoelectron and auger electron energy is distributed by electron spectrometer, which is shown in Figure 3.8. It could be used for qualitative analysis and semi-quantitative analysis. XPS can be used to analyse the surface chemistry of material in its as-received state, or after some treatment. Generally, the element composition and chemical state of sample surface and the information such as molecular structure could be obtained from XPS spectrum peak position and peak shape. The surface elements or concentration could also be acquired from the peak intensity, as shown in equation (3.2):

$$E_{binding} = E_{photon} - E_{kinetic} - \phi \quad (3.2)$$

where $E_{binding}$ is the binding energy (BE) of the electron, E_{photon} is the energy of the X-ray photons being used, $E_{kinetic}$ is the kinetic energy (KE) of the electron as measured by the instrument and ϕ is the work function dependent on both the spectrometer and the material. This equation is essentially a conservation of energy equation.

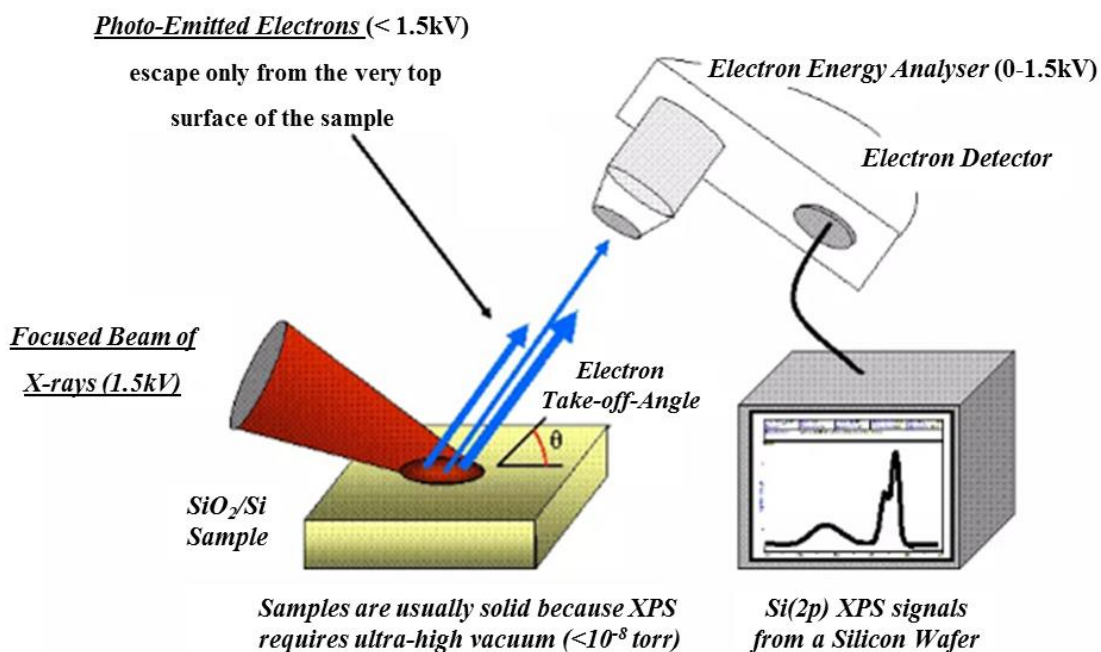


Figure 3.8 Schematic of X-ray Photoelectron Spectroscopy (adapted from Ref [162]).

The binding energies of elements were characterised by an XPS (ESCALAB Mark II, VG Scientific, Waltham, MA, USA) using Al K α X-ray as the radiation source with wavelength of 1486.6 eV. CasaXPS software has been utilized to deal with the XPS data [163]. CasaXPS processing software offers powerful analysis techniques for both spectral and imaging data. The system originally designed for XPS data offers features including full quantification including transmission correction and generates configurable quantification reports.

3.5.5 Surface roughness (3D topography)

The surface roughness is a component of surface texture, which is the most commonly used parameter to describe surface microstructure in mechanical processing. It reflects the surface micro-geometry shape error. More generally, a surface profile measurement is made with a profilometer. These can be the contact variety (typically a diamond stylus) or optical types (e.g. a white light interferometer or laser scanning confocal microscope).

In this study, the non-contact optical profiler (Zeta-20, KLA-Tencor) was applied to measure the sample surface roughness. The measurement system is designed for critical analysis of high precision applications. It delivers an in-depth understanding of characteristics such as radius, form, surface smoothness, contour, and dominant wavelength, providing important feedback for improvements in design and production [164]. During the measurements, an area of $350\text{ }\mu\text{m} \times 250\text{ }\mu\text{m}$ is selected by the instrument, the interference microscopes of the profilometer are used to accurately measure the three-dimensional height variations of the selected area. The 3D topography images are then acquired. The surface roughness, which is the arithmetical mean height of the selected area, could be calculated and obtained by the instrument. It expresses, as an absolute value, the difference in height of each point compared to the arithmetical mean of the surface. The values of surface roughness could be determined by the averages of several measurements to increase the data confidence. For each tested sample, several separate measurements are carried out. A set of examples showing the multi-measurements on certain sample is also shown here: (i) $0.5132\text{ }\mu\text{m}$, (ii) $0.4821\text{ }\mu\text{m}$, (iii) $0.5312\text{ }\mu\text{m}$, (iv) $0.5018\text{ }\mu\text{m}$, (v) $0.4779\text{ }\mu\text{m}$. They also indicate the good reproducibility of the measurements.

3.6 Evaluation of Coating Performance

3.6.1 Wettability evaluation

The wettability of the surfaces was characterised using a contact angle goniometer (FTA200, First Ten Angstroms, Inc., Portsmouth, VA, USA) with pumping out rate of 1 $\mu\text{L/s}$ and droplet of fixed volume 5 μL using micro-pipettor at room temperature and humidity condition. It includes static WCA, Adv θ_A , Rec θ_R , and CAH. The existing errors during the wettability evaluation include: the difference of surface structure between selected areas, the volume difference of the input droplet, the inherent error of the contact angle goniometer. An injection syringe with steady controlled pumping out and pumping in rates was used to ensure the droplet volume consistency. Several repeating measurements were conducted on the same sample to increase the data confidence considering the surface morphology difference during multi-measurement.

The equilibrium contact angle described by the Young's equation (Eq 2.1) is measured from a static state. A given substrate-liquid-vapour combination yields a continuous range of contact angle values in practice. It represents that how a liquid stay on a solid substrate spreads out or the ability of liquids to form boundary surfaces within solid states. As shown in Figure 3.9, it shows a typical WCA measurement, a water droplet of fixed volume is staying on the sample surface. The baseline (showing as blue, the one between water droplet and sample surface) needs to be confirmed. Then the tangent line (showing as red) between the water droplet and air also needs to be confirmed. With the two lines confirmed, the static water contact angle of the sample could be obtained with suitable fitting. In this way, the water contact angle on certain tested sample could be determined.

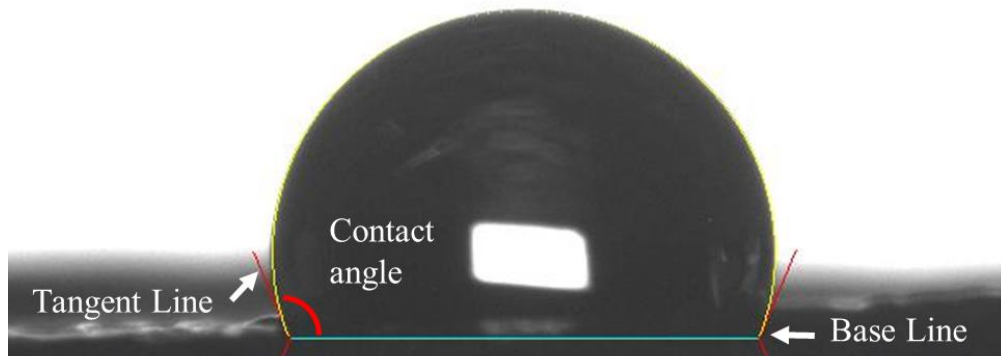


Figure 3.9 Example of static water contact angle measurement (including base line, tangent line and contact angle labels)

The advancing contact angle can be described as a measure of the liquid-solid cohesion while the receding contact angle is a measure of liquid-solid adhesion. The advancing and receding contact angles are measured from dynamic experiments where droplets or liquid bridges are in movement [73]. The detailed measurement process could be shown in Figure 3.10 and Figure 3.11. In Figure 3.10, a pumping out rate of $1 \mu\text{L/s}$ was applied to prepare the water droplet. The whole process is monitored by the camera of the goniometer with an image every 0.5 s. All of the WCA during the measurement process could be obtained. It is clear to see that from Figure 3.10 (b) to (d), there is no obvious change in the water droplet shape, it just becomes larger. The WCA did not change obviously within the duration. Although the liquid is in movement, the WCA could maintain at a steady level. In this way, the advancing angle could be furthered determined with the data within this period (from $t=20 \text{ s}$ to $t=46 \text{ s}$). For receding angle, it is clear to see from Figure 3.11 (a) to (d), the water droplet is keeping becoming smaller while its shape does not change, the WCA also remain at around the level. So the receding angle could also be determined by the data within this period (from $t=0 \text{ s}$ to $t=81 \text{ s}$).

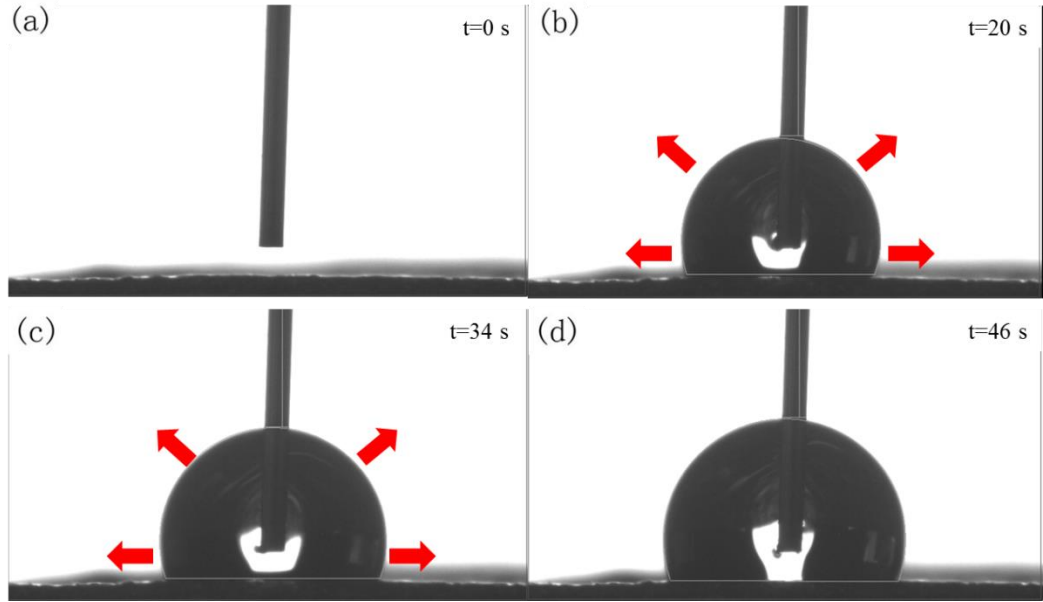


Figure 3.10 Optical images showing water droplet movement process during advancing angle measurement ((a) $t=0$ s; (b) $t=20$ s; (c) $t=34$ s; (d) $t=46$ s).

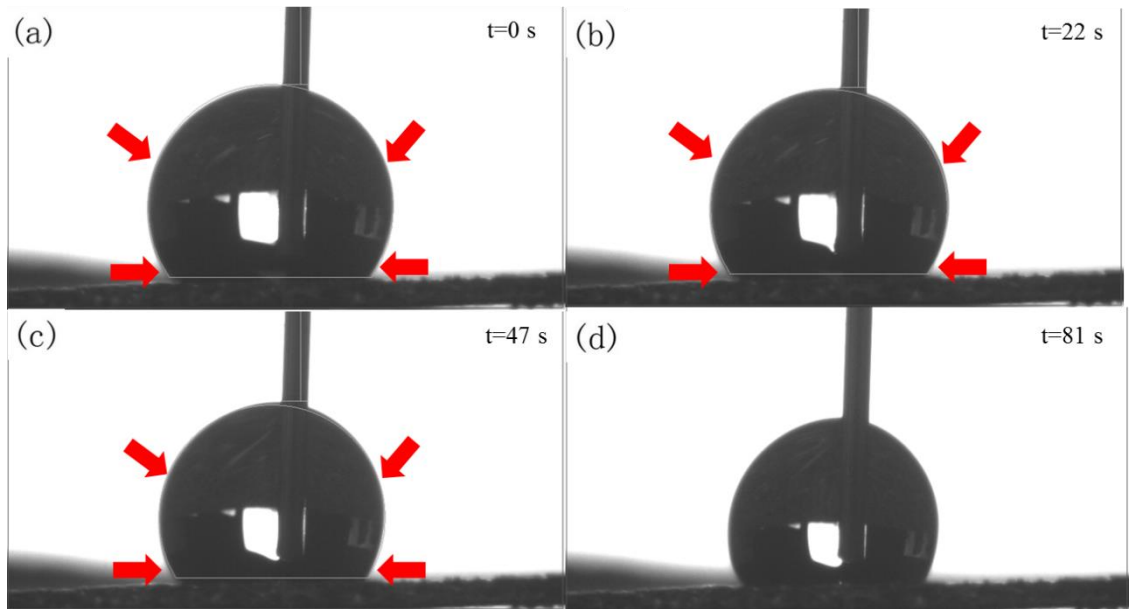


Figure 3.11 Optical images showing water droplet movement process during receding angle measurement ((a) $t=0$ s; (b) $t=22$ s; (c) $t=47$ s; (d) $t=81$ s).

After the advancing angle and receding angle have been confirmed, CAH could then be calculated by the subtraction between advancing angle and receding angle. It could be inferred that the adhesion energy varies locally according to the Young-Dupr é equation (Eq 2.13). Thus, the liquid has to overcome local energy barriers in order to wet the

surface. One consequence of these barriers is CAH: the extent of wetting, and therefore the observed contact angle (averaged along the contact line), depends on whether the liquid is staying in advancing state or receding state on the surface.

3.6.2 Coating durability tests

3.6.2.1 Water impinging test

To evaluate the durability, an erosion test rig (as shown in Figure 3.12) under pressurized pneumatic water impinging with gas pressure of 1.03 bar, velocity of 37 m/s, and liquid flow rate of 72 mL/min were set up. An anemometer (Skywatch Xplorer 3) is used to measure the airflow velocity that locates at the same position of the tested sample (4 cm distance away from the nozzle). The distance between the nozzle (with a diameter of 2 mm) and the tested sample was kept at 4 cm. Pressurized water droplets were sprayed onto the coated samples for a duration of 90 min.

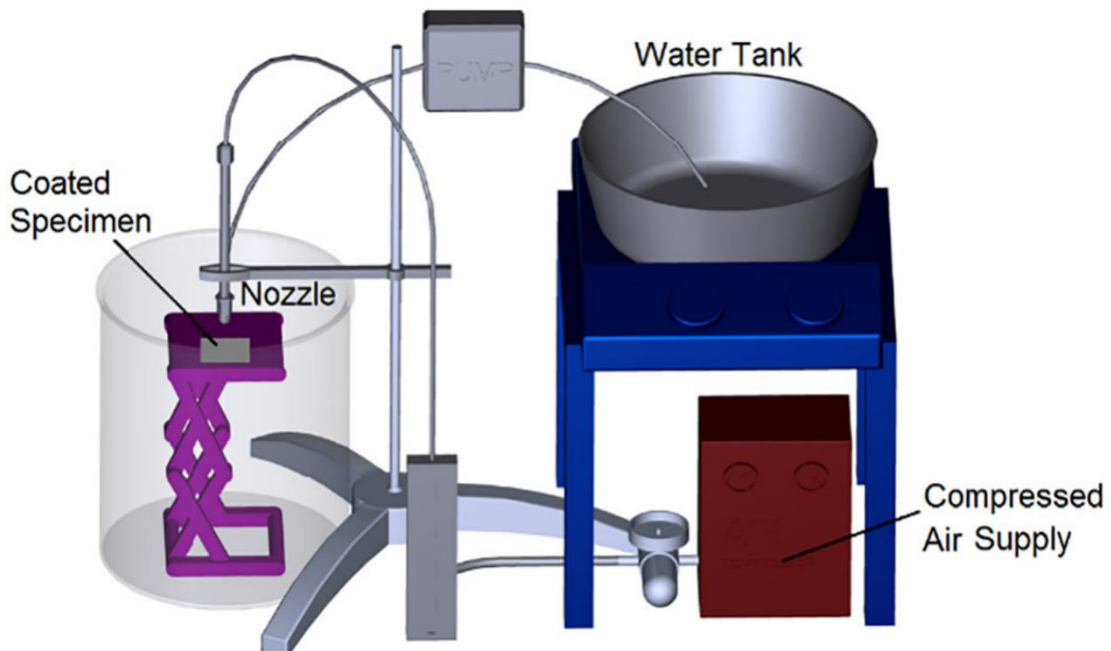


Figure 3.12 Schematic diagram of the water impinging test [10].

3.6.2.2 Water-sand erosion test

To increase the erosion rate of the tests, some improvement has been made. During the

test, water droplets with uniformly stirred micron size SiC (SC224, Silicon Carbide 600 Finer powder, average size 65 μm , Simba Materials Ltd, Doncaster, UK) sand under compressed gas were sprayed onto the coated specimen from the nozzle connected with the water tank using the following parameters including: gas pressure of 1.03 bar, velocity of up to 37 m/s, liquid flow rate of 72 mL/min, distance between the nozzle and the specimen of 4 cm and duration of 90 min. The surface morphology, wetting behaviour and icephobicity were monitored before and after the water impinging test.

3.6.3 Tests of icephobicity

In general, icephobicity could be defined as both anti-icing and de-icing performance. Anti-icing includes the ability of surfaces to prevent and delay ice nucleation and formation and adherence. De-icing includes low adhesion strength between ice and solid surface and easy detachment of formed ice from certain surfaces.

3.6.3.1 Droplet icing delay

The ice formation time is an important parameter for icephobicity evaluation because it reflects the nucleation and growth of ice on certain surfaces [165]. Longer icing time means longer ice formation delay and a better anti-icing performance. So the ice formation tests were carried out to better evaluate the anti-icing property of different samples.

The cold plate was utilized to provide an icing environment, the plate was set at $-10\text{ }^{\circ}\text{C}$, as shown in Figure 3.13. The errors often lie in these factors below: the effect from the ambient air; the volume difference of the input droplet, the difference of surface structure between selected areas. An injection syringe with steady controlled pumping out rate was used to ensure the droplet volume consistency. To avoid the effect from room temperature and humidity, the cold plate is airtight and the transparent plastic sheet is easy to observe the experiment procedure. The samples were put inside the cold plate in advance for pre-cooling to ensure the same starting condition. Droplet icing test

was carried out by determining the duration of ice formation from water droplets with a volume of 4 μL using micro-pipettor on five different points on the coated samples to minimize the existing error including surface morphology difference and environment influence. The substrates were also tested for comparison.

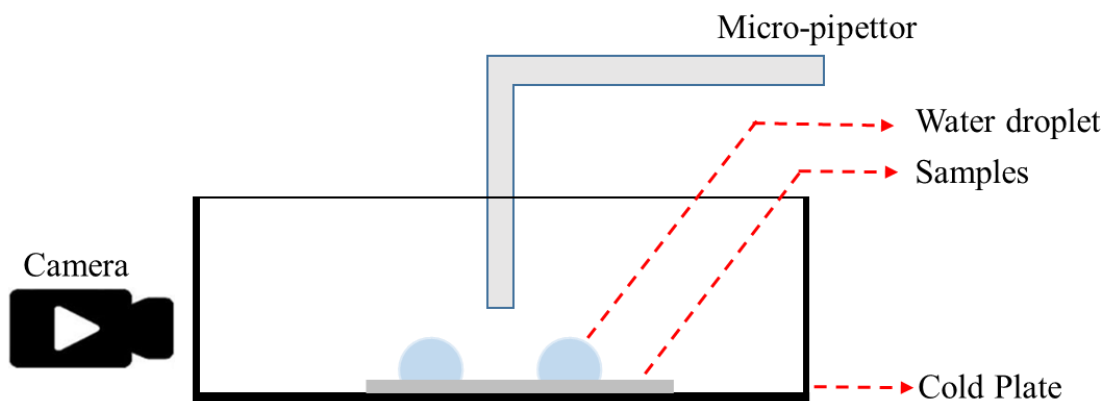


Figure 3.13 Schematic diagram of droplet icing test.

By video recording the icing process of water droplets, the icing formation time could be calculated from observation of the video, the icing times of the coatings were then obtained. The optical images showing the whole icing process of water droplet on tested sample are displayed in Figure 3.14. A stop watch was also used combined with the video to determine the time nodes and confirm the whole icing duration. The icing duration was calculated to evaluate the anti-icing performance.

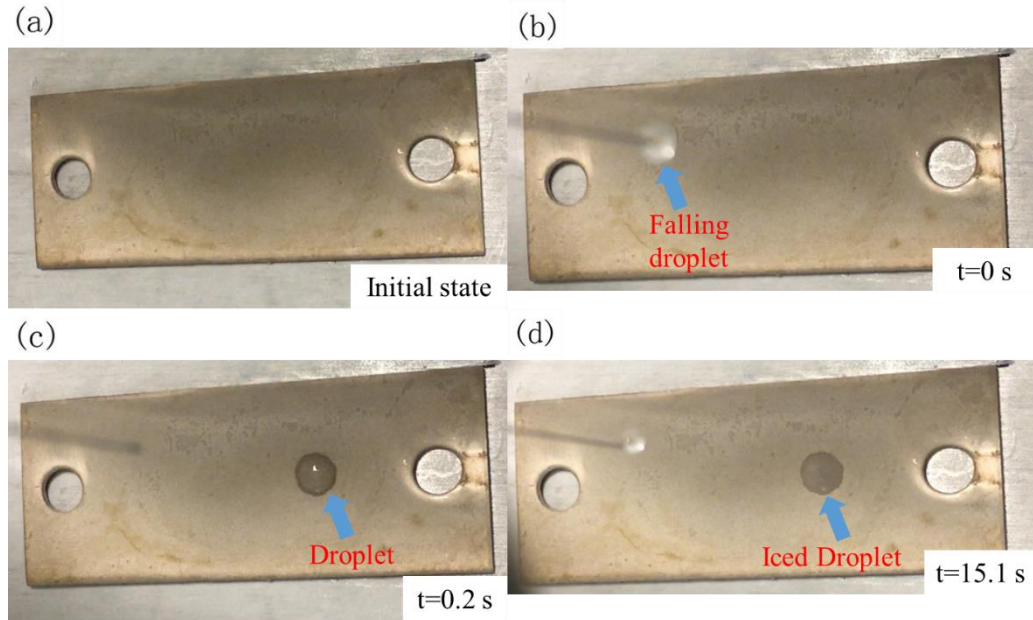


Figure 3.14 Optical images of the icing process of the water droplet on certain tested samples ((a) initial state; (b) $t=0$ s; (c) $t=0.2$ s; (d) $t=15.1$ s)

3.6.3.2 Icing test under frost environment

To better evaluate the anti-icing property of coatings, frost formation tests will be carried out. During the test, the backside of the samples was covered by tape, for the aim to ensure equal icing area. The cold plate will be set at -7°C , for the temperature which can obtain glaze. A sprayer with deionised water was utilized to produce moisture, the usage of deionised water could help to prevent the introduction of other variables. Due to the cold temperature inside the cold plate, the moisture would become glaze. There is glaze that keeps forming on the tested samples. The whole experiments last 60 min. The mass difference of the samples before and after the experiment has been monitored. The mass of formed glaze per unit area will be calculated. Samples with less glaze per unit area could verify the anti-icing performance. The existing errors during the tests include: the non-uniform distribution of moisture, the difference of surface structure between selected areas, the inherent error during the mass measurements. The electric fans were also applied to ensure the uniform distribution of the moisture, as indicated in Figure 3.15. Samples were also placed with the same distance to the sprayer output point for the aim to ensure icing conditions. Several experiments have been

carried out on one sample to ensure the data confidence.

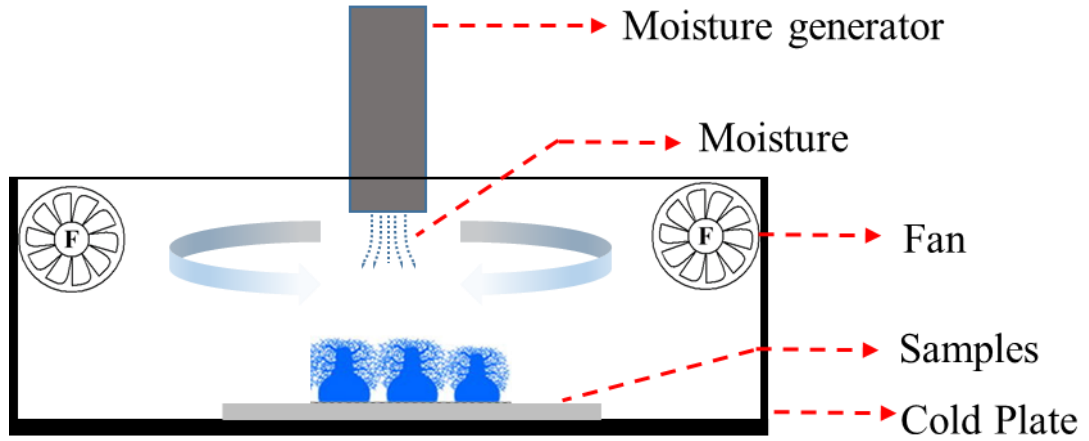


Figure 3.15 Schematic diagram of icing test under frost environment.

3.6.3.3 Ice adhesion strength

Ice adhesion tests will be performed using a centrifugal method with a glaze ice block in a low-temperature chamber with temperature of $-10\text{ }^{\circ}\text{C}$. In essence, a rotor with the ice block/substrate sample was spun at increasing rotation rates. With the induction of the rotor's rotation, the sample would stay with centripetal accelerating. The ice would then detach from the substrate once it is enough to overcome the adhesion strength of the ice to the substrate. Using the rotation speed at the detachment of the glaze ice block, the ice adhesion strength could be calculated using the ice block mass and beam length, shown in equations (3.3) and (3.4) [166]:

$$F = mrw^2 \quad (3.3)$$

where F is the centrifugal force (N), m is the mass of ice block (kg), r is the radius of the beam (m) and w is the speed of rotation (rad/s). From the centrifugal force, the shear stress is determined:

$$\tau = F/A \quad (3.4)$$

where A is the iced area (m^2), F is the shear stress (Pa). Several coating samples were measured for better accuracy.

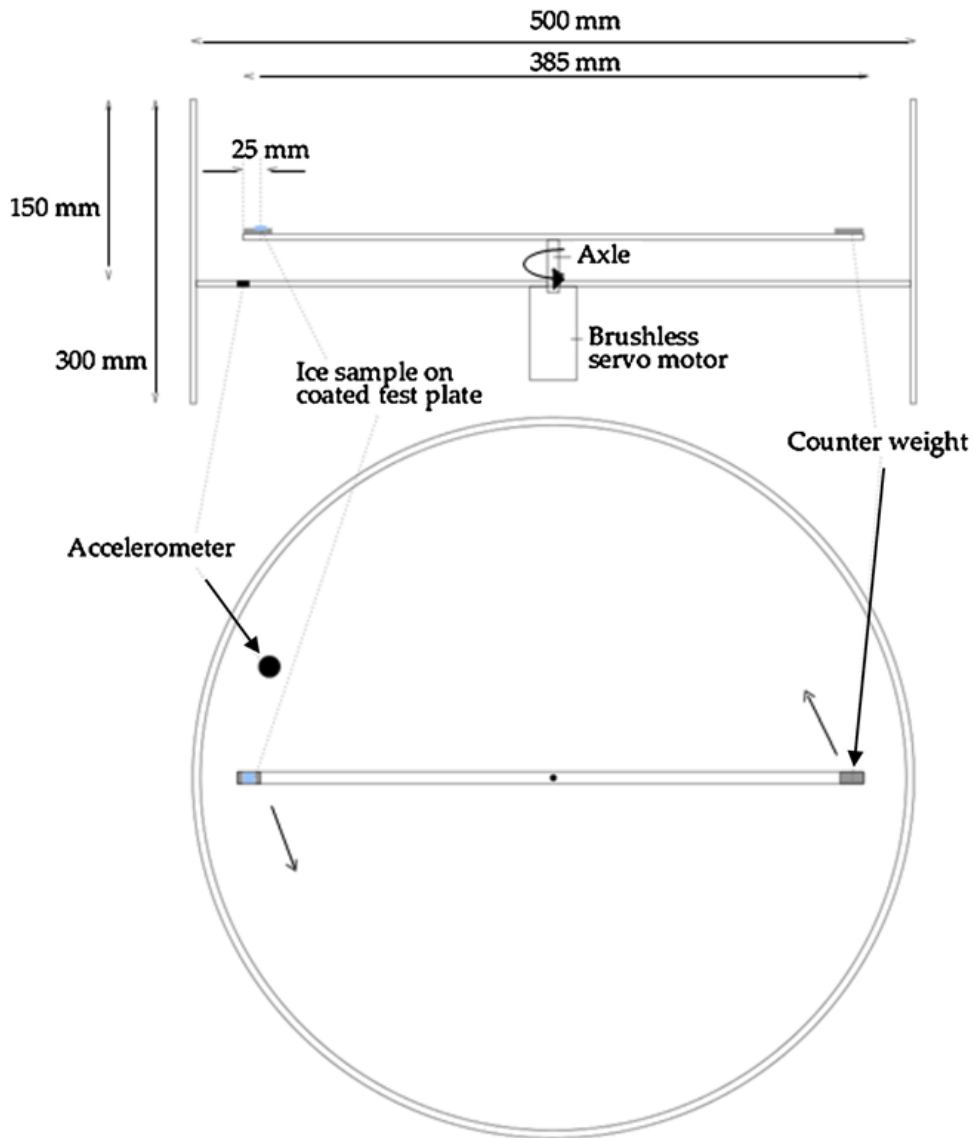


Figure 3.16 Schematic diagram of the centrifugal ice adhesion test setup [167].

The ice adhesion setup (as shown in Figure 3.16) consists of a stainless steel cylindrical drum with dimension of 300 mm depth and diameter of 500 mm. A motor is mounted beneath a steel floor within the drum, 150 mm below its top rim, with the shaft passing through the floor. The setup will be placed in an environment-controlled chamber (Design Environmental ALPHA 1550-40H) with an adjustable temperature. The errors during the ice adhesion tests often lie in these factors below: the existing error during ice sample preparation, the difference of ice attachment with the tested sample, the

inherent error when confirming the ice detachment duration. For the ice sample preparation, a silicone mould was fully filled with 1.31 ml deionised water using pipettor and carefully covered onto the sample surface. The iced area between the mould and the sample is always maintained at 1.38 cm², the whole mass of ice and mould is stabilised at 2 g. They were then kept inside the environment chamber at -10 °C for 24 h, to produce repeatable samples of pure glaze ice on each sample substrate. Because the consistent glaze samples can be grown artificially, the ice adhesion on samples could be measured more repeatedly. Also, five ice adhesion strength tests were carried out for each tested sample using parallel samples to ensure the data confidence.

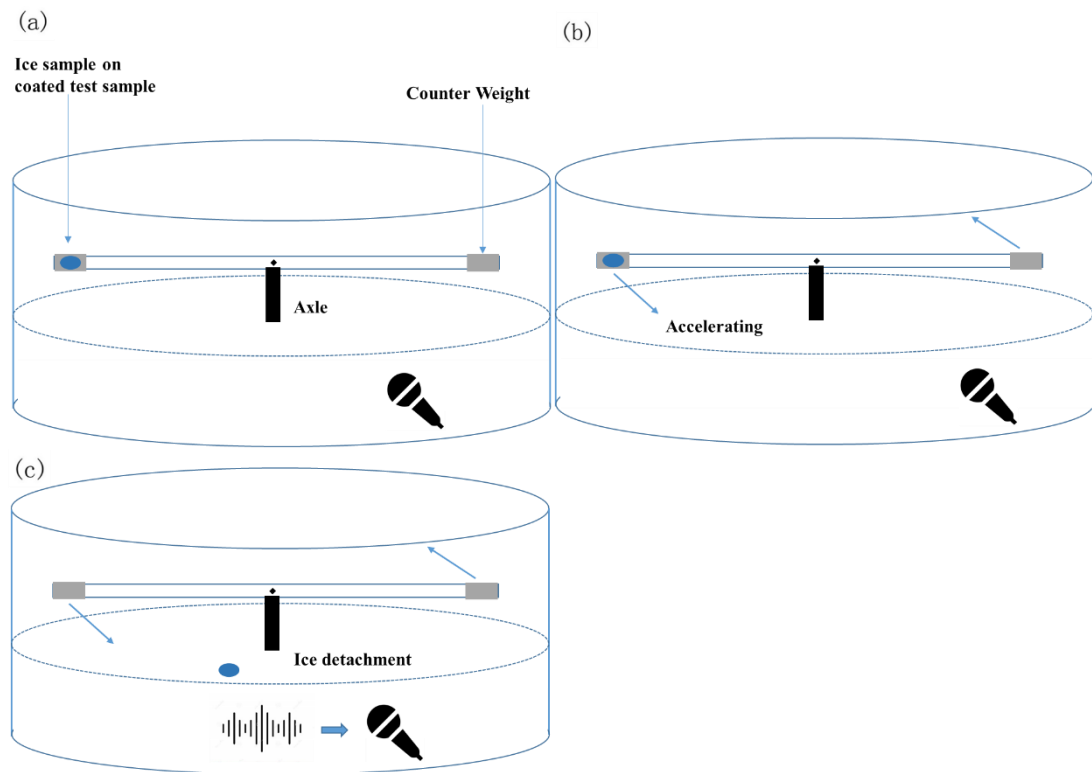


Figure 3.17 Schematic diagram of ice adhesion test and ice detachment duration calculation (a) before ice adhesion strength test (stationary state) (b) during test (accelerating state) (c) Ice detach from the sample (detached state)

A carbon fibre reinforced polymer rotor with an ice/substrate sample affixed ontop was

mounted on the motor shaft via a fixed coupling [167]. The rotor was driven by a servo motor (MOOG G403-2053A) at steady accelerations of 30 rpm/s from zero up to the motor's maximum speed of 4500 rpm. This motor was selected for performance at the sub-zero temperatures at which the ice adhesion tests were carried out. An accelerometer was mounted in the drum floor. As indicated in Figure 3.17, the microphone was placed underneath the drum during the test. The ice on coated test sample kept accelerating and the rotation speed kept increasing. Once the ice could overcome the adhesion strength, it then detached from the coated sample. The detached ice then hit onto the drum and the acoustical signal could be detected by the microphone and sent to the computer. Then the time from initiation could be corroborated. The final rotation speed could be calculated with the steady accelerations of 30 rpm/s. In this way, the ice adhesion strength could be confirmed.

3.6.3.4 Electro-thermal de-icing test

De-icing by electro-thermal heating method is normally an issue of heat conduction from a heating source beneath the concerned surface. To simplify the test, a one-dimensional multi-lamina heat conduction model was applied (as shown in Figure 3.18), and the schematic diagram of the electro-thermal heating test configuration is shown in Figure 3.19, which consist of a heating sheet, an insulation sheet, an aluminium plate and a testing specimen attached with a block of cubic glaze ice. The heating sheet was used to create electrical heating and the insulation (thermal protective) layer on top was to minimize the energy loss from the opposite side of the testing specimen. An aluminium plate was located below the heating sheet as a buffer, to provide constant heat transfer from the heating mat to the testing specimen. A thermocouple was inserted inside the aluminium plate to monitor the temperature change.

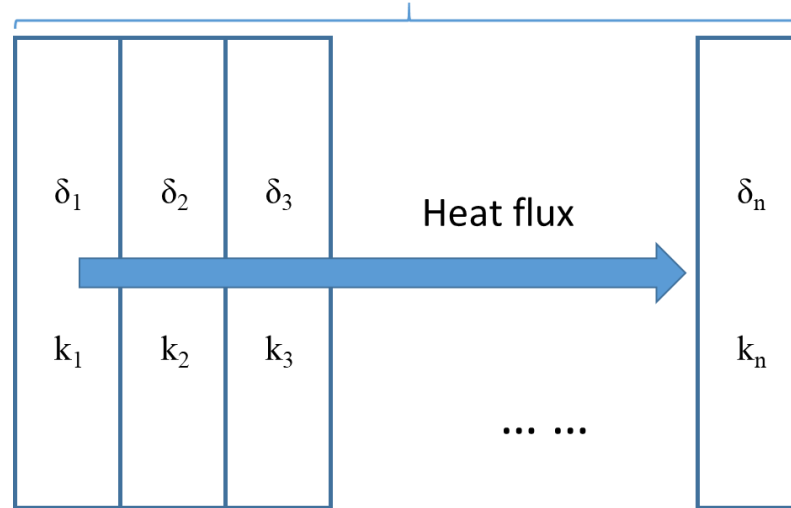


Figure 3.18 Model schematic of thermal conductivity of multilayer layers.

The test was conducted in a cold chamber with a temperature of -5 ± 0.2 °C. A precisely prepared glaze ice cube (20 mm × 20 mm × 20 mm) was attached to the specimen surface and faced down for the testing [168]. When the environmental temperature was stabilised, electro-thermal heating was applied with a power of 2.86 W (input voltage 22 V, input current 0.13 A). The heating duration and the temperature change of the thermal couple were recorded until the ice cube dropped from the specimen surface. The total energy consumption for each testing specimen will be calculated and used to evaluate the de-icing performance of the studied specimen surface. The errors during the electro-thermal heating tests also lie in the existing error during sample preparation, the difference of ice attachment with the tested sample, the inherent error during the heating process including the current and voltage input. To ensure the same testing condition, all of the parameters for attachments of ice cube onto samples are kept the same (same volume and shape of ice cube, same pre-cooling duration, same input power rate and same starting points). For each tested sample, three parallel tests were carried out to ensure the data confidence.

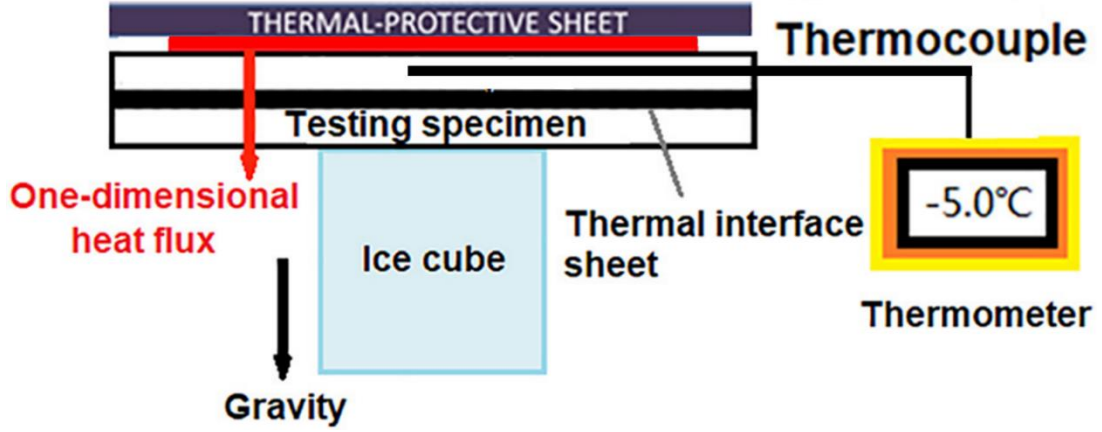


Figure 3.19 Schematic diagram of the electro-thermal de-icing test under the ice gravity (adapted from Ref [168]).

In the electro-thermal heating test, heat conduction is the major way of thermal transfer to melt the ice at the interface. The system can be analysed as a one-dimensional multi-lamina model. In this model, δ_n is the layer thickness and k_n is the thermal conductivity of each layer. The thermal energy which has been transferred to the coating-ice interface that used to melt the ice is proportional to the heat flow as well as the thermal conductivity. In a one-dimensional multi-lamina model, the heat transfer process could be seen as a cascade process. It also applies the principle of superposition of thermal resistance in series [169]. So the overall effective thermal conductivity normal to the layers $k_{overall}$ could be calculated using equations (3.5) and (3.6) [170]:

$$k_{overall} = \frac{\sum \delta}{\sum_{i=1}^n \frac{\delta_i}{k_i}} \quad (3.5)$$

$$\delta = \sum_{i=1}^n \delta_i \quad (3.6)$$

where δ is the layer thickness, and k is the thermal conductivity. The effective thermal conductivity normal to the layers is denoted by $k_{overall}$. $\frac{\sum \delta}{k_{overall}}$ represents the thermal resistances connected in series and consists of a sum of reciprocal conductivities.

In a given heating time, the energy available to melt the ice at the interface is proportional to the heat flow and the resistance to the heat conduction. The layer with

lower thermal conductivity and higher thickness would contribute more to the overall heat resistance, and thus more influence on the heat conduction in the system.

Thermal resistance (R) as one possible explanation can be carried out to explain the results as material having high thermal resistance requires more energy to transfer certain heat and the slower transfer speed. Thermal resistance can be calculated through the equation (3.7) below [171]:

$$R = \frac{\delta}{kA} \quad (3.7)$$

where δ is the thickness of the layer, A is the conduction area and k is the thermal conductivity. All specimens have the same conduction area as the dimensions and mass of the attached ice cube were strictly controlled. The thermal resistance of specimens could be calculated and compared. If the layers possess poor thermal conductivity, it contributes more to the total thermal resistance and further affects the thermal conduction of the whole system. For every tested sample, several electro-thermal heating tests will be conducted to minimize the existing errors and ensure the data accuracy.

3.6.4 Water condensation and icing study via environmental scanning electron microscopy (ESEM)

In-situ water condensation and ice formation process was studied by an ESEM equipped with a Peltier cooling stage (FEI Quanta 650, ThermoFisher). By means of a differential pumping system and a gaseous secondary electron detector (GSED), hydrated samples could be imaged. The ESEM column is equipped with a multi-stage differential pressure pumping unit. The pressure in the upper part is about 10^{-6} to 10^{-7} Torrs, but pressure of about 1-6.5 Torrs can be maintained in the observation chamber. When the electron beam (primary electrons) knocks out secondary electrons from the surface of the sample, the secondary electrons collide with gas molecules in the ESEM

chamber, which in turn functions as a cascade amplifier, delivering the secondary electron signal to the positively biased GSED. The positively charged ions are attracted toward the specimen to neutralize the negative charge produced by the electron beam [172].

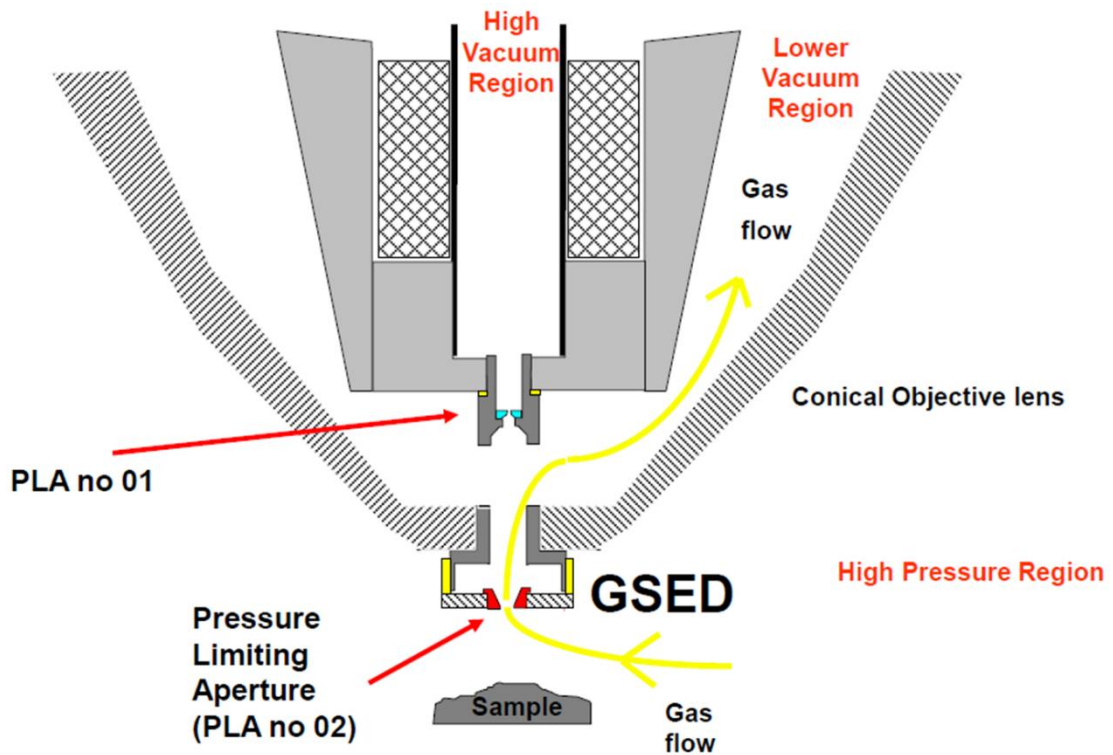


Figure 3.20 Schematic diagram of three zones of ESEM vacuum system (adapted from Ref [173]).

If the water condensation observation were conducted at room temperature, it could be seen from Figure 3.20 that the required pressure to maintain saturated vapour in the chamber is extremely high. So it is still not practical to imaging under these conditions. To achieve saturation, it is more appropriate to decrease the temperature of the cooling stage to a bit higher or just above freezing, which could be reflected from the phase diagram shown in Figure 3.21, and then only a modest gas pressure is needed to stabilise water [174]. To ensure a better thermal stability, it would be beneficial to place sample in a well or covering with a washer. The tighter the contact, the better the heat conduction.

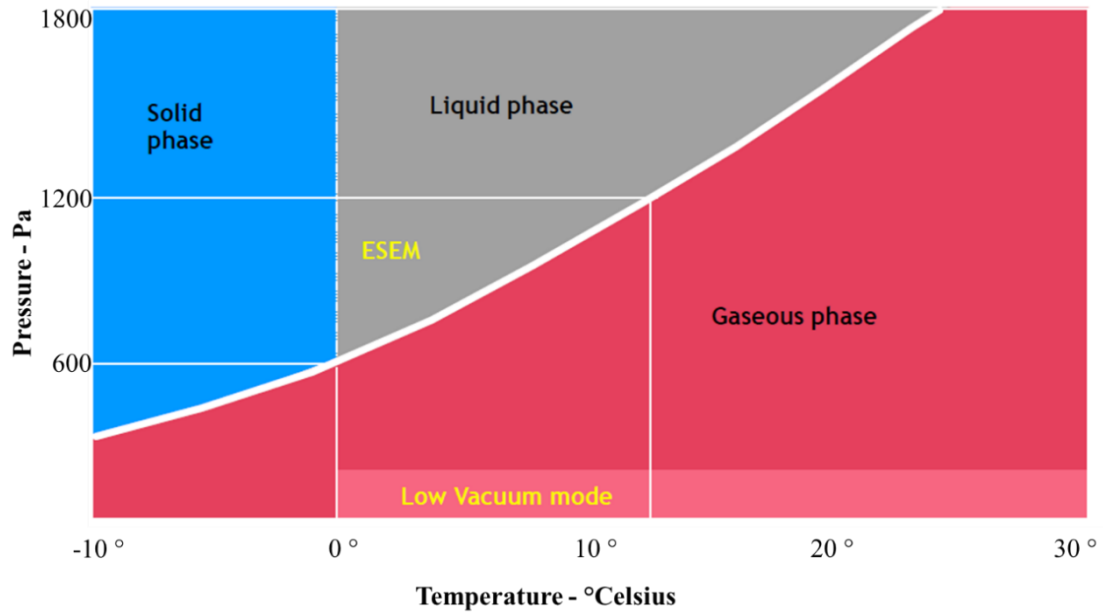


Figure 3.21 Pressure/Temperature phase diagram for H₂O (adapted from Ref [175]).

By controlling the pressure and temperature simultaneously, the in-situ wetting and icing could be monitored. Samples which are not thermally conductive could have a larger temperature gradient than thermally conductive samples, and mounting can play an important part in minimizing the difference and making an experiment successful. The voltage of the electron beam was 15 kV and the distance of the specimen from the final aperture was about 6-8 mm. During the ESEM observation, the water vapour pressure and humidity of the chamber, the temperature of the cooling stage could be adjusted according to the phase diagram in Figure 3.21, which could help the water condensation and ice formation and diminishment on sample surfaces. The water condensation and in-situ icing process on different sample surfaces have been analysed in a controlled environment with a certain temperature and humidity.

3.6.5 Measurement of surface free energy

The surface energy of the coating is an important parameter for the icephobic surface. Owens-Wendt approach is one of the most commonly used methods for calculating the surface free energy of the materials. In this work, Owens-Wendt method was applied to measure the surface energy of the coatings [176]. In this method, it is assumed that the

total surface free energy is the sum of the two components: dispersion components γ_S^D and polar components γ_S^P , as indicated in equations (3.8) and (3.9) below:

$$\frac{1}{2}(1 + \cos \theta)\gamma_L = (\gamma_S^D \cdot \gamma_L^D)^{1/2} + (\gamma_S^P \cdot \gamma_L^P)^{1/2} \quad (3.8)$$

$$\gamma_S = \gamma_S^D + \gamma_S^P \quad (3.9)$$

where θ is the contact angle between the liquid droplet and coating surface, γ_L is the liquid total surface tension, γ_L^D is the dispersion component of liquid surface tension, and γ_L^P is the polar component of liquid surface tension. γ_S^D is the dispersion component of the solid surface free energy. γ_S^P is the polar component of the solid surface free energy. γ_S is total surface free energy of the solid surface. All of the value of surface tension of liquids and their two components are referred to standard conditions of ambient temperature and pressure at sea level. (T= 20 °C, P= 1 bar) [177].

Table 3.4 Detailed parameters of liquid surface tension of three different liquids.

Liquids	γ_L (mN/m)	γ_L^D (mN/m)	γ_L^P (mN/m)
Distilled Water	72.8	21.8	51.0
Formamide	58.0	39.0	19.0
Methylene Iodide	50.8	50.8	0

The liquids employed are given in Table 3.4. Three liquids including distilled water, formamide and methylene iodide were employed to determine the surface energy. Six droplets of each liquid were deposited on each sample to measure the contact angle between these liquids and samples. The volume of each droplet is 5 μ L. All of the measurement processes were conducted under atmospheric conditions at temperature of 20 °C and pressure of 1 bar. The errors during the surface energy measurements mainly lie in the contact angle measurements on tested samples with different liquids and the inherent error during the whole experiments. Several repeating measurements were also conducted on the same sample to increase the data confidence

Chapter 4 Fabrication and Wettability of Electrodeposited Ni-Cu-P Ternary Coatings

In recent years, metallic-based surface and coatings have been attracting significant interests due to their outstanding mechanical durability and possible multifunctionalities. Among these metallic coatings, Ni-Cu-P ternary coating system is a promising candidate for practical hydrophobic/icephobic applications because of its high mechanical properties and anti-corrosion performance [31, 178]. The anti-corrosion performance of Ni-Cu-P coatings are superior to common Ni-based coatings. Ni-Cu-P coatings also possess improved anti-friction and anti-wear performance, as compared with ordinary Ni-based coatings [33, 158]. Ni-Cu-P ternary coatings are selected as the main research object in this chapter using electrodeposition method.

Electrodeposition is a convenient method to create micro/nanostructures metallic coatings, which could be readily controlled by adjusting deposition parameters. There are two key factors influencing the surface hydrophobicity: surface topography, e.g. hierarchical micro/nanostructures, and surface energy determined by the material composition. The two factors are both affected by the deposition parameters. In this chapter, the processing parameters of the Ni-Cu-P coatings by electrodeposition will be investigated. In order to find the appropriate preparation parameters, several sets of Ni-Cu-P samples prepared with different parameters were prepared and characterised. After the parameters have been determined, the properties of as-deposited Ni-Cu-P coating including wettability, durability will be studied.

4.1 Processing Parameters of Ni-Cu-P Coating via Electrodeposition

Method

For electro-deposition, there are many different contributing parameters which would affect the coating properties, such as deposition current density, deposition time, pH, and temperature of the electrolyte. In this work, most of the parameters have already been predetermined, the pH value was set at 5.5, the temperature of the water bath was kept at 25 °C, and the deposition time was set at 30 min [30, 40]. The further optimised deposition parameter should ensure that the as-prepared samples possess the highest WCA with proper hierarchical surface morphology. Hence, several sets of Ni-Cu-P samples prepared with different parameters were prepared and characterised to carry out the optimization process.

4.1.1 Effect of current density

As shown in Table 4.1, two sets of parallel experiments were carried out to determine the applicable current densities: (1) the preliminary deposition group, including 30 mA/cm², 100 mA/cm², 150 mA/cm², 200 mA/cm² (to estimate the range of current density); (2) the precise control group, including 30 mA/cm², 40 mA/cm², 50 mA/cm², 60 mA/cm² (to determine the optimised current density). Here, all of the data of sample prepared with 30 mA/cm² current density including XRD pattern, SEM images, WCA, Ra value in both preliminary deposition group and precise control group will be shared.

Table 4.1 Sets of experiments with different current density.

	Preliminary deposition	Precise control
Current density (mA/cm²)	30	30
	100	40
	150	50
	200	60

4.1.1.1 Preliminary deposition group

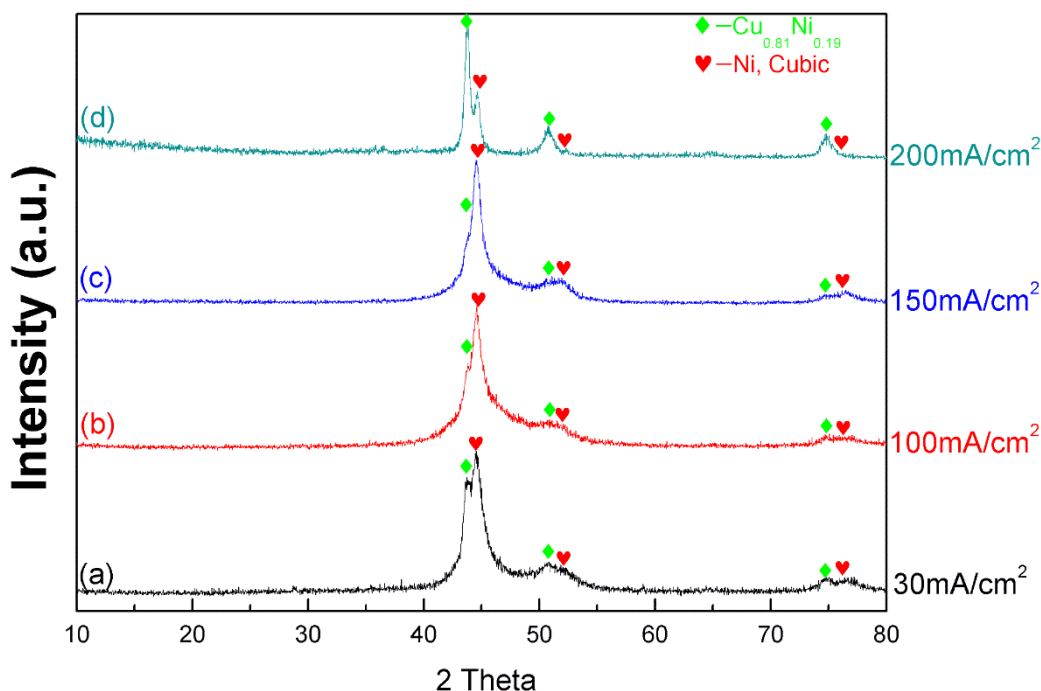


Figure 4.1 XRD patterns of as-deposited electrodeposited Ni-Cu-P coating with different current density (a) 30 mA/cm² (b) 100 mA/cm² (c) 150 mA/cm² (d) 200 mA/cm².

Figure 4.1 is the XRD patterns of the as-deposited Ni-Cu-P samples prepared with different current densities. There are four lines corresponding to different samples. There are several diffraction peaks in the image, Cu_{0.81}Ni_{0.19} and Ni, cubic phase and Ni, hexagonal phase emerged at the same position of the four lines. With the increasing current density, the intensity of Ni, cubic phase increases at first from 30 mA/cm² to 150 mA/cm², but the trend then stop when the intensity reached 200 mA/cm². There is a huge decrease in the peak intensity of Ni, cubic phase. It should correspond to the increase of Cu_{0.81}Ni_{0.19} phase simultaneously, which indicates that there is a generation of the copper nickel solid solution. Nevertheless, the relative amount of Cu_{0.81}Ni_{0.19} phase first decreases from 30 mA/cm² to 150 mA/cm² and then increases from 150 mA/cm² to 200 mA/cm².

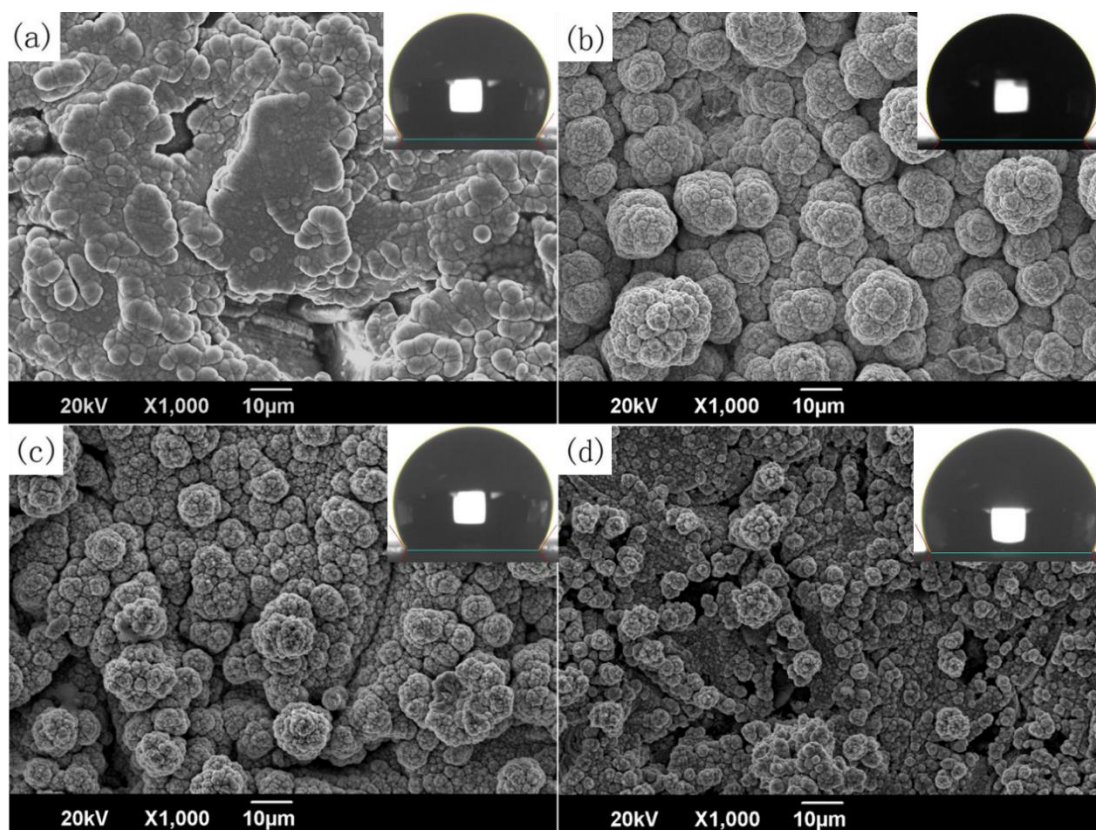


Figure 4.2 SEM images of surface morphologies with insets of WCA results of as-deposited electrodeposited Ni-Cu-P coating with different current density (a) 30 mA/cm² (b) 100 mA/cm² (c) 150 mA/cm² (d) 200 mA/cm².

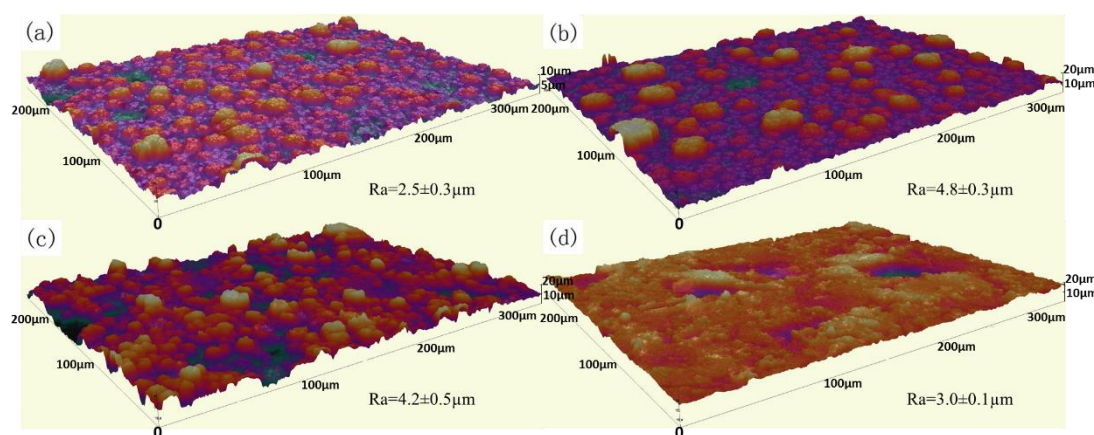


Figure 4.3 3D topography images of as-deposited samples with different current density (a) 30 mA/cm² (b) 100 mA/cm² (c) 150 mA/cm² (d) 200 mA/cm².

Figure 4.2 and Figure 4.3 show the surface morphologies and 3D topography of different samples. The WCA results of the samples have also been added as insets. In

Figure 4.2 (a), the clustered spheres form quite flat structures and cover the substrate. Some defects like surface pores still can be observed. Although the coating surface consists of spherical deposits, it does not form a very hierarchical structure, displaying a quite flat surface with surface roughness (Ra) of $2.5 \pm 0.3 \mu\text{m}$. The reason for this may be the low current density. These structures may grow into spheres if higher current density has been applied [158]. The 3D images in Figure 4.3 (a) also show a quite flat surface with some small bump structures. The water contact angle of the sample is $124.1 \pm 2.5^\circ$. For Figure 4.2 (b), the surface is made up of many spheres and forms a so-called cauli-flower structure. There are many continuous papillate dots and it creates a highly rough structure [179]. The 3D topography images clearly show the peaks and valleys, the measured Ra is $4.8 \pm 0.3 \mu\text{m}$. The WCA has also been measured, $126.6 \pm 2.4^\circ$. When moving to Figure 4.2 (c), it shows a similar cauli-flower structure surface morphology. The observed difference is that the size of the deposits is smaller than before, the fluctuations and coating coverage are also lower than before. The quality of the deposits begins to deteriorate as distortion is observed, which is believed to come from the high internal stress. This phenomenon is consistent with the results reported by Kim and Weil [180]. The Ra value also confirms this, $4.2 \pm 0.5 \mu\text{m}$, the WCA also decreases to $124.1 \pm 2.8^\circ$. The lower WCA may come from the incomplete surface structure. For Figure 4.2 (d), it shows the same trend as before, the size of deposits are smaller than before, the percentage of coating coverage is also lower. It looks like that the Ra decreases quite a lot than before with value of $3.0 \pm 0.1 \mu\text{m}$. The reason could be ascribed to the very high current density - 200 mA/cm^2 . The electro-deposition reaction here would be very intense. Huge quantities of bubbles will generate at the electrodes and remain there [181]. Then it could be difficult for the supposed newly formed spheres to stay there, which leads to the disappearance of spherical structures. Based on the worsen surface morphology, the WCA has a further decrease, only $118.3 \pm 3.1^\circ$.

Combined with the displayed SEM, WCA, Ra, and XRD results, it shows that coatings prepared by current densities between $30\text{-}100 \text{ mA/cm}^2$ show better surface morphology (more hierarchical) and hydrophobicity (higher WCA). To determine a more accurate

current density, the precise determination group containing samples with four different current densities (30, 40, 50, and 60 mA/cm²) will be fabricated and characterised.

4.1.1.2 Precise control group

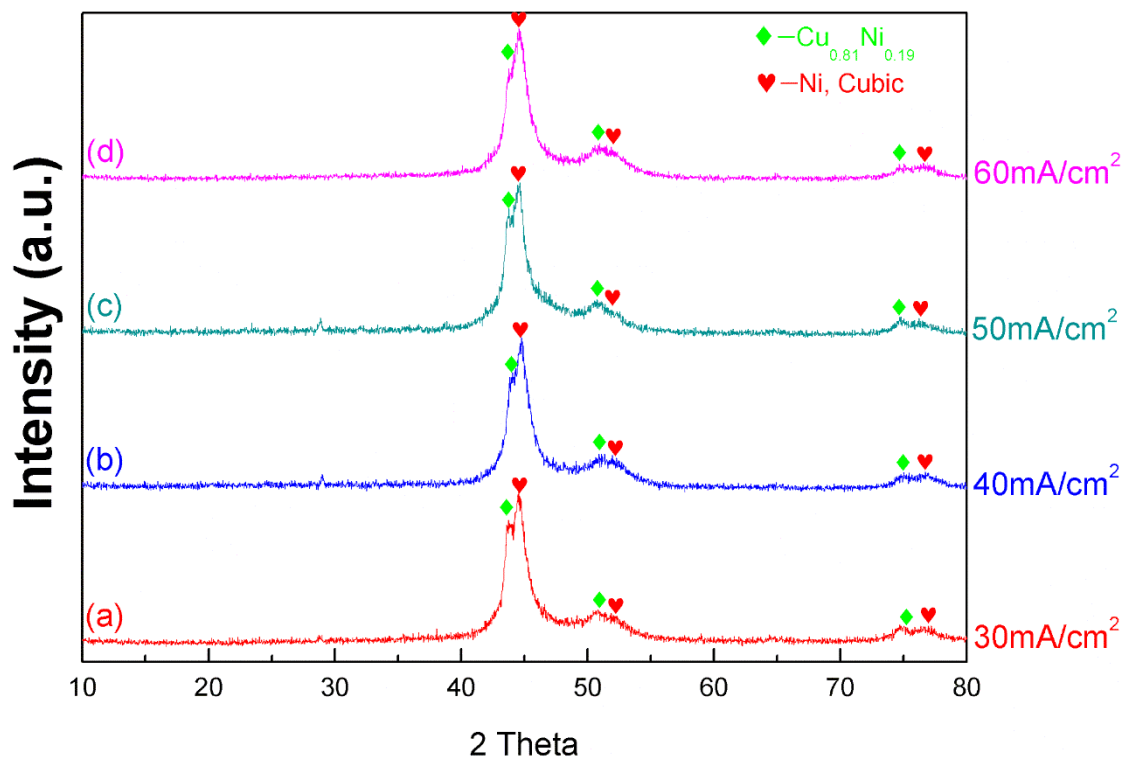


Figure 4.4 XRD patterns of as-deposited electrodeposited Ni-Cu-P coating with different current density (a) 30 mA/cm² (b) 40 mA/cm² (c) 50 mA/cm² (d) 60 mA/cm².

The XRD patterns of samples prepared with 30 to 60 mA/cm² current densities are shown in Figure 4.4. The four lines correspond to the XRD diffraction patterns of electrodeposited Ni-Cu-P coating with current densities from 30 to 60 mA/cm². The results show the similar diffraction peaks as before in Figure 4.1. The main phases are also Cu_{0.81}Ni_{0.19} and Ni, cubic phases, but no Ni, hexagonal phase appears. From Figure 4.4 line (a) to (d), with the increasing current densities, there is little change in the intensity of Ni, cubic phase and Cu_{0.81}Ni_{0.19} phase. No peak shift and phase transformation take place.

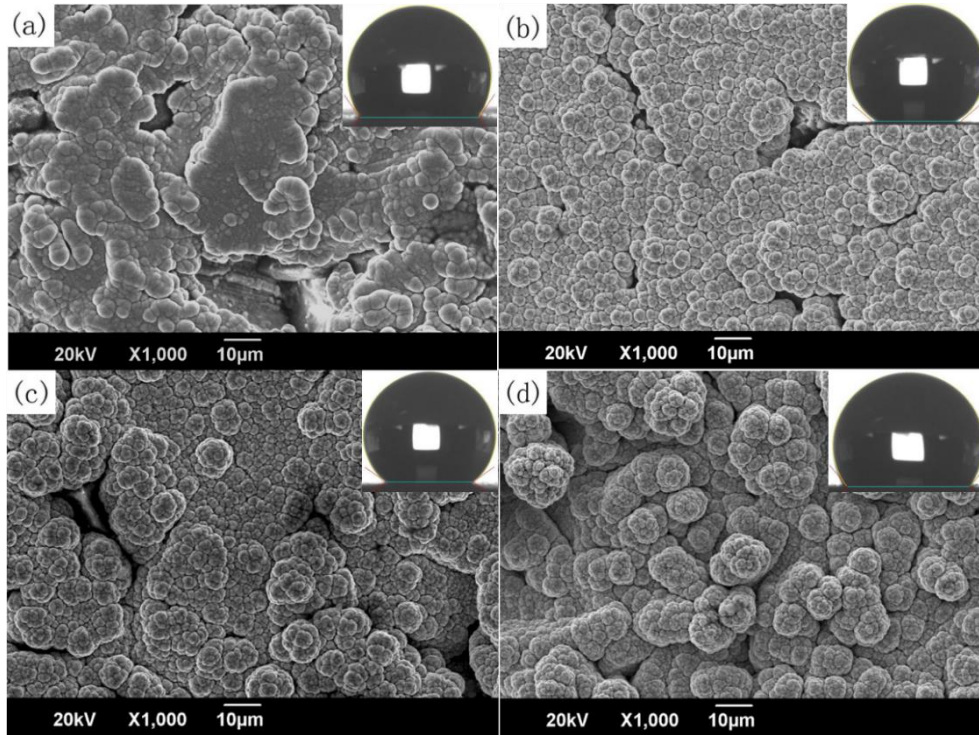


Figure 4.5 SEM images of surface morphologies with insets of WCA results of as-deposited electrodeposited Ni-Cu-P coating with different current density (a) 30 mA/cm² (b) 40 mA/cm² (c) 50 mA/cm² (d) 60 mA/cm².

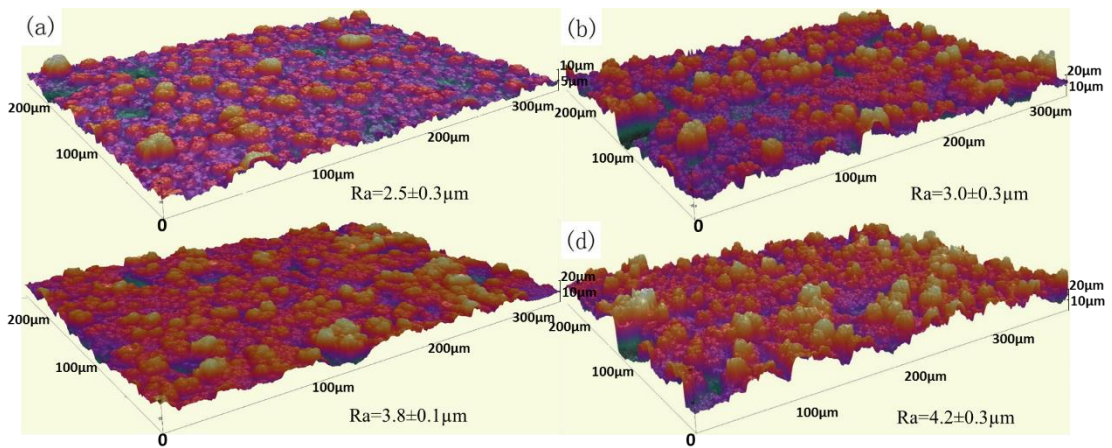


Figure 4.6 3D topography images of as-deposited samples with different current density (a) 30 mA/cm² (b) 40 mA/cm² (c) 50 mA/cm² (d) 60 mA/cm².

As observed in Figure 4.5 and Figure 4.6, the SEM images with insets of WCA results and 3D topography images of the samples prepared with 30, 40, 50, and 60 mA/cm² current densities are shown. The four images show quite similar trends and mainly

consist of cauliflower-like hierarchical structures which consist of many tiny spherical deposits that are tightly attached. They all display hierarchical structures. The main difference comes from the size of the spheres and the formed cauli-flower structures. From Figure 4.5 (a), the size of the spheres is quite large, but it is smoother and has fewer edges. From Figure 4.5 (b) to (d), the surface morphologies are very similar and the percentage of coating coverage is also very close. But the size of the cauli-flower structures keeps diminishing while the density of the cauli-flower structures becomes higher. The Ra value keeps increasing from $2.5 \pm 0.3 \mu\text{m}$ (Figure 4.6 (a)) to $4.2 \pm 0.3 \mu\text{m}$ (Figure 4.6 (d)). There is an obvious difference in the displayed WCA, sample prepared with 50 mA/cm^2 possess the highest static WCA, which is very essential for hydrophobic application.

Besides SEM, surface roughness, and WCA results, some other characterisations have also been carried out. The CAH and EDX results are listed in Table 4.2. The Ra of the four samples keeps increasing, from $2.5 \pm 0.3 \mu\text{m}$ to $4.2 \pm 0.3 \mu\text{m}$. Normally, higher surface roughness leads to better WCA and CAH. But it is different when referring to the sample prepared with 60 mA/cm^2 , the WCA is lower with higher Ra. The reason may be ascribed to: (1) the spheres become smaller and will not help to improve hydrophobicity; (2) the hydrophobicity is also affected by the surface chemical composition, the change in Ni, Cu, P contents would also affect the wetting behaviour [30]. For 50 mA/cm^2 , it has the highest WCA $143.8 \pm 3.9^\circ$ and lowest CAH 5.5° . Since the main purpose is focused on hydrophobic/icephobic application, it could be inferred that samples with the best hydrophobicity could be the appropriate one. From the above listed results, 50 mA/cm^2 could be the most suitable current density and will be chosen to prepare electrodeposited Ni-Cu-P coatings in this work.

Table 4.2 Different characterisation results of samples prepared with different current density.

	Ra (μm)	WCA (°)	CAH (°)	EDX		
				Ni (at%)	Cu (at%)	P (at%)
Sample prepared with 30 mA/cm ²	2.5±0.3	126.4±3.2	10.4±0.1	52.4	4.5	6.6
Sample prepared with 40 mA/cm ²	3.0±0.3	139.0±1.9	9.5±0.1	55.9	2.6	10.4
Sample prepared with 50 mA/cm ²	3.8±0.1	143.8±3.9	5.5±0.1	60.6	3.8	4.4
Sample prepared with 60 mA/cm ²	4.2±0.3	129.7±1.6	11.9±0.1	63.7	4.3	7.5

4.1.2 Effect of annealing treatment

Another influencing factor that could affect the surface hydrophobicity is the surface composition. Different current density could lead to both different sample element distribution and surface morphology. However, the two could remain unchanged if the current density has been settled. The annealing treatment was then applied to the as-deposited coatings because it could improve the crystallization performance and further lead to composition change to the samples. It could also help to release the stress concentration between the crystal lattice which generate during the deposition process [182]. So two sets of samples with different annealing treatments (atmospheric annealing and vacuum annealing) have been carried out to find whether there is a suitable annealing treatment.

4.1.2.1 Atmospheric annealing treatment

A chamber furnace (Blue-M, Thermo Scientific) was used to carry out the atmospheric annealing treatment. 200 °C, 400 °C, 500 °C, 600 °C, and 700 °C were selected as the annealing temperature. The annealing duration lasts 1 hour, followed by furnace cooling. All the samples were prepared by electrodeposition methods using 50 mA/cm² current density.

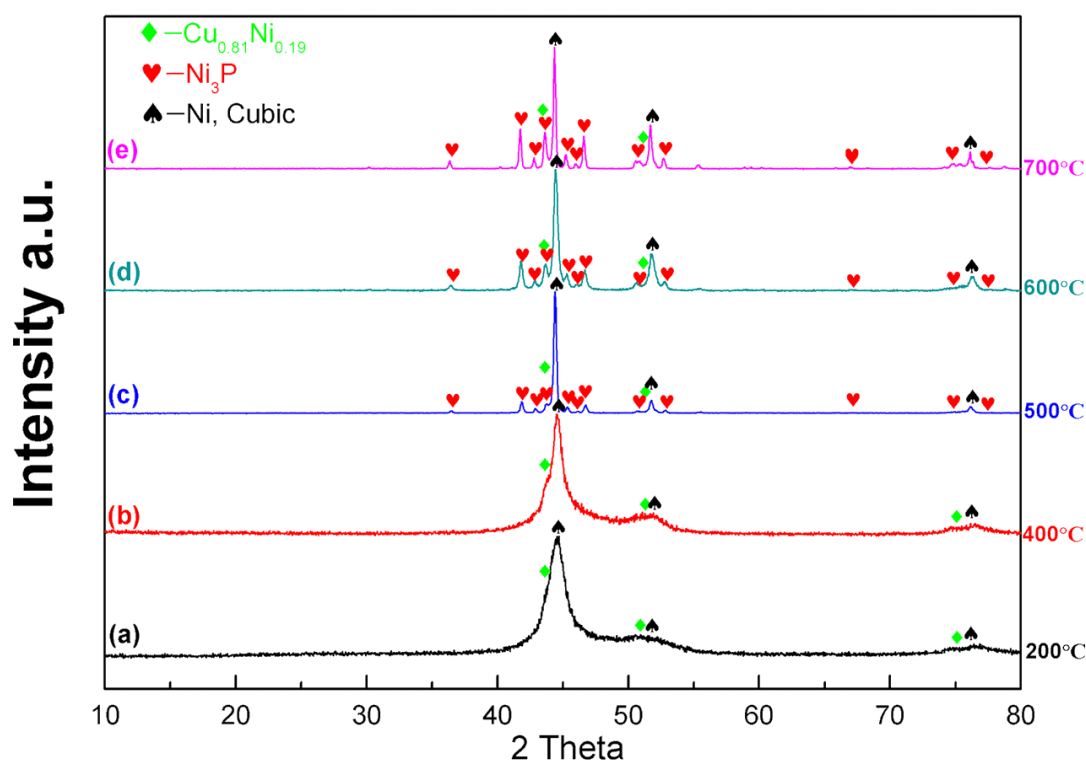


Figure 4.7 XRD patterns of different samples (a) 200 °C annealing (b) 400 °C annealing (c) 500 °C annealing (d) 600 °C annealing (e) 700 °C annealing (all in ambient air).

Figure 4.7 is the XRD diffraction patterns of samples with different annealing treatments. For line (a), the annealing temperature is 200 °C, the annealing treatment could help to release the internal stress and would not change the coating composition and do no damage to the coating surface [183]. Therefore, no obvious change could be detected from the diffraction patterns. The diffraction peaks also remain unchanged after 400 °C annealing due to the low temperature annealing. When the annealing temperature increase to 500 °C, 600 °C, and 700 °C, the annealing treatment will lead to

the phase transformation. The former amorphous phosphorus phase disappears while the $\text{Cu}_{0.81}\text{Ni}_{0.19}$ and Ni, cubic, phases remain during the whole annealing process. The coating exhibits excellent crystallization, Ni_3P phase (JCPDS # 74-1384, tetragonal crystal structure with $a = 8.954 \text{ \AA}$ and $c = 4.386 \text{ \AA}$) appeared, which can be indexed to the phases of tetragonal structured Ni_3P of $I4$ space group [184]. Moreover, they show preferred orientations. It is caused by a nucleation mechanism of synthesis: with the annealing temperature increasing, the peak intensity of the Ni_3P phase becomes higher. The Ni_3P phase would finally decompose into different metastable phosphides under high temperature annealing treatment [185] and could also be oxidized and converted into NiO if the annealing temperature is $800 \text{ }^\circ\text{C}$ [186]. This is also the reason why the annealing temperature up to $700 \text{ }^\circ\text{C}$ has been chosen.

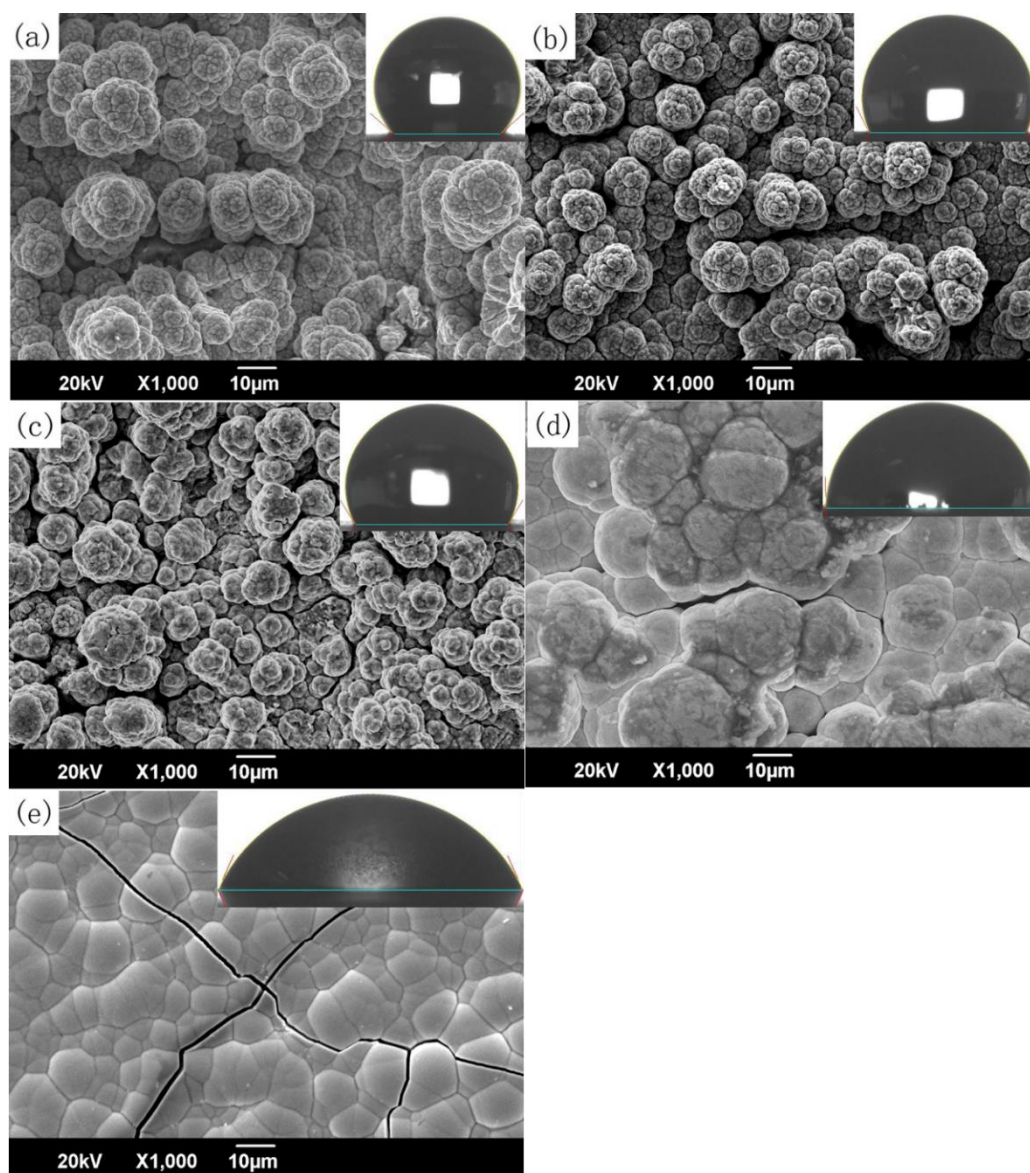


Figure 4.8 SEM images of surface morphologies and WCA results insets of different samples (a) 200 °C (b) 400 °C (c) 500 °C (d) 600 °C (e) 700 °C (all in ambient air).

Figure 4.8 shows the surface morphologies and WCA results of samples with different annealing treatments. Figure 4.8 (a), (b) clearly shows that there are still dense cauliflower-like structures remaining on the surfaces, showing quite hierarchical structures. The size of surface structures varies. With higher annealing temperature, the spherical structure becomes smaller. From the WCA insets, sample with 200 °C annealing treatment possesses WCA of $136.5 \pm 0.9^\circ$ while the WCA of sample with 400 °C annealing treatment is $129.0 \pm 0.5^\circ$. For Figure 4.8 (b), the trend is more obvious, the density of cauliflower-like structures becomes higher while the size becomes smaller.

For Figure 4.8 (c), it shows a different surface morphology. Some of the spherical structures seem to shrink and connect more tightly. The change affects the surface roughness and further leads to the decrease of the static WCA of the annealed sample, only $121.1 \pm 0.6^\circ$. For Figure 4.8 (d), the annealing temperature is higher than before. It could be observed that the high temperature seems to destroy the coating surface. The spheres seem to be pressed together and the surface becomes rather flat. With the damage of the cauli-flower structures, combined with the phase change which has been mentioned previously in Figure 4.7, the WCA decreases sharply and the surface becomes less hydrophobic with a WCA of $90.9 \pm 0.3^\circ$. For Figure 4.8 (e), the changing trend is more obvious, the surface becomes flatter, the deposits adhere to each other more crowded than before and the former cauli-flower structure disappears. Cracks also form on the coating surface. The reason could be the very high annealing temperature. The hydrophobicity keeps deteriorating and becomes hydrophilic with a WCA of only $66.2 \pm 0.2^\circ$. The series of results indicate that high temperature annealing treatment in ambient air does no good to the coating hydrophobicity and may be not suitable for improving coating hydrophobicity.

4.1.2.2 Vacuum annealing treatment

Considering that all the annealing treatments described in section 4.1.2.1 were carried out in ambient air, the coating might be oxidized if higher annealing temperature is applied. So vacuum annealing treatment was then carried out to avoid the oxidation effect. The temperature was set at 900°C , for the reason that 910°C is the austenite phase transition temperature [187], it is easier to investigate the effect of C element if temperature is 900°C . The vacuum degree of the vacuum oven could reach as high as 1.4×10^{-6} bar. Since C element may play an important role in affecting the coating wetting behaviour, another set of parallel experiments need to be carried out to see the impact of the C element. The reference sample was buried in pure C powder during the annealing treatment.

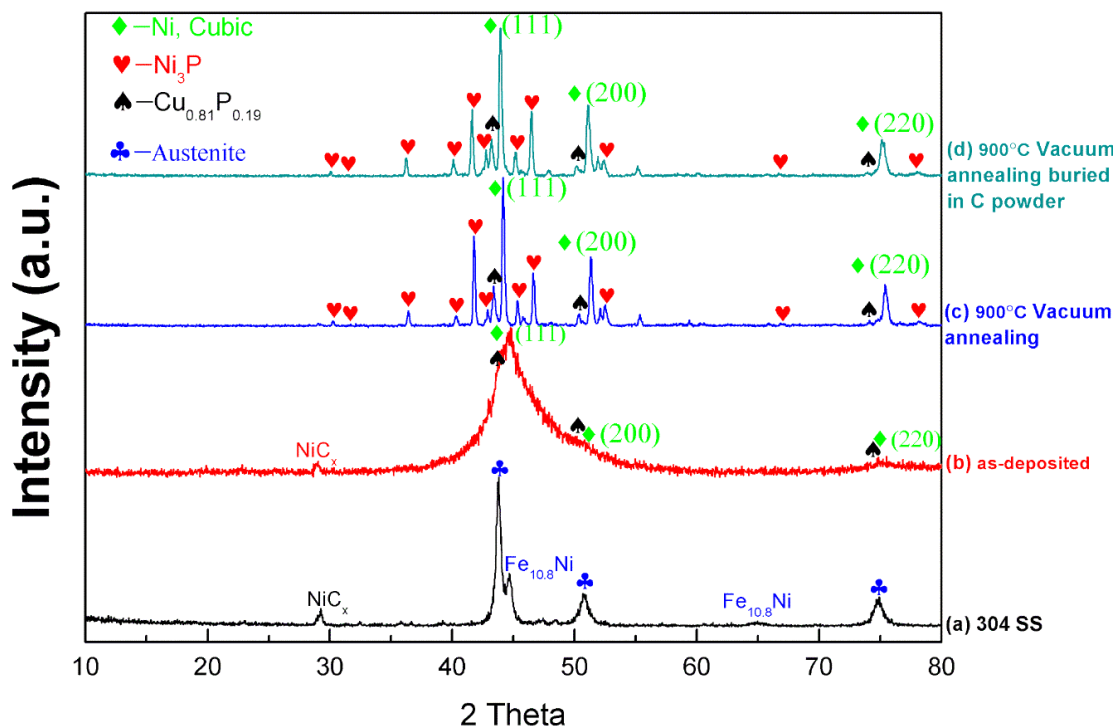


Figure 4.9 XRD patterns of samples (a) 304 SS (b) as-deposited (c) with 900 °C vacuum annealing (d) with 900 °C vacuum annealing buried in carbon powder.

As indicated in Figure 4.9, the XRD patterns of samples with different treatments have been shown. There are mainly four diffraction peaks in Figure 4.9. Line (a) is the XRD patterns of 304 SS substrate, as reference. Line (b) indicates the XRD patterns of the coated samples without vacuum annealing. There are mainly two kinds of diffraction peaks $\text{Cu}_{0.81}\text{Ni}_{0.19}$ and Ni Cubic, phases after the electrodeposition process. It implies that Ni-Cu-P coatings with high purity were obtained. The XRD patterns between 40° to 50° show like this due to the amorphous state phosphorus [188]. It could also be found that the $\text{Cu}_{0.81}\text{Ni}_{0.19}$ and Ni, cubic, phases maintain stable during the whole vacuum annealing. The intensity of these two phases both increases significantly. For the increasing intensity, the annealing process may help to improve the crystallization performance. Another significant phenomenon is that new phase Ni_3P occurs after the vacuum annealing treatment. According to the former result, the Ni_3P phase transformation would occur at over 400°C temperature by a nucleation mechanism of synthesis. It should have decomposed into the phases Ni_{12}P_5 and Ni_2P and finally result

in the oxidation of nickel phosphides through a complex mechanism. But the experiment was in vacuum, the reactions did not take place [186], so the main phase is still Ni_3P . Comparing line (c) and (d), there is little difference between the two phase compositions, and it seems that the C powder has little effect on the phase transformation.

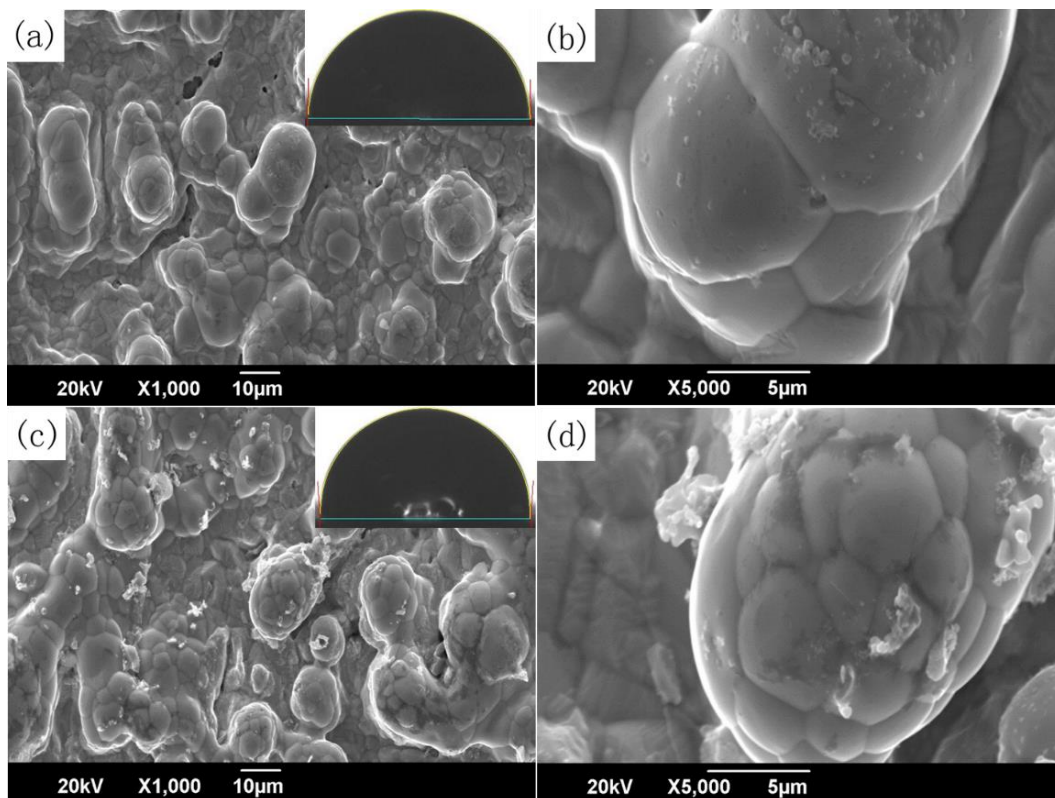


Figure 4.10 SEM images of surface morphologies (a) and (b) of samples with 900 °C vacuum annealing; (c) and (d) of samples with 900 °C vacuum annealing buried in carbon powder with insets of WCA results in (a) and (c) of the two samples.

In Figure 4.10, the SEM images and WCA results of the treated samples have been shown. The images show that the surface morphologies are a bit similar to the former coating surfaces. However, some differences still could be detected. The spheres seem to become bigger and connect with each other more crowded than before. The edges also become smoother than before. No crack could be observed on the surface due to the vacuum annealing. The two samples show the same trend. The reason could be that

the oxidation of nickel phosphides under vacuum does not take place [186]. There is some C powder remaining on the surface of second sample. The surface also becomes a bit flatter. From the measured Ra, the as-deposited coating without any treatment is about $3.8 \pm 0.1 \text{ }\mu\text{m}$, while the Ra after vacuum annealing decreases to $2.3 \pm 0.1 \text{ }\mu\text{m}$, the sample buried in C powder is $2.2 \pm 0.1 \text{ }\mu\text{m}$. It reveals that the surface roughness decreases after the vacuum annealing treatment. The insets in Figure 4.10 shows the WCA of the samples after the treatments. They are both lower than 90° , suffering obvious decreases. The corresponding results show that the vacuum annealing treatment is also not beneficial to the hydrophobicity. There could be several reasons for the decreasing hydrophobicity: (1) the surface roughness decreases after the annealing process; (2) the crystallization performance becomes better than before and the surface free energy, therefore, increases; (3) the occurrence of Ni_3P phase may also influence the hydrophobicity.

From the above listed results, the annealing treatment in both ambient air and vacuum alter the surface composition, and they also lead to the deterioration of coating hydrophobicity. Therefore, it might not be good to carry out annealing treatment on the as-deposited Ni-Cu-P coatings. In general, the most appropriate preparation parameters in this study has been determined based on the hydrophobic performance and surface morphology, current density of 50 mA/cm^2 , pH of 5.5, temperature of the water bath at 25°C , deposition time of 30 min without any annealing treatment. The as-deposited Ni-Cu-P coatings in later parts will be prepared using the above parameters.

4.2 As-deposited Ni-Cu-P coating with Optimised Deposition Parameters

4.2.1 Microstructure of Ni-Cu-P coating

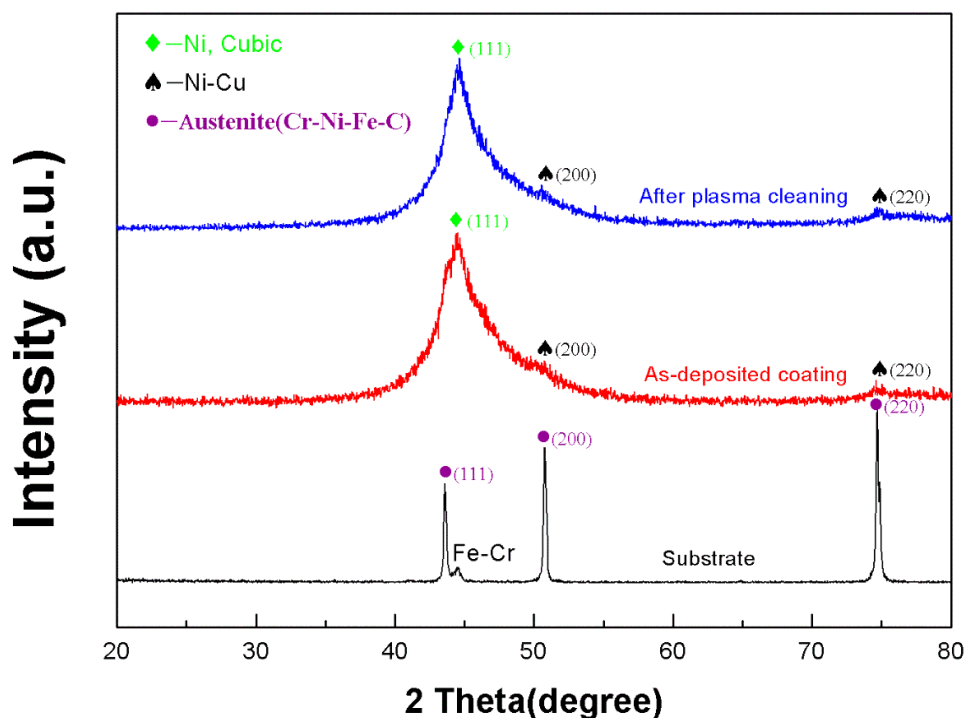


Figure 4.11 XRD patterns of 304 SS substrate and the Ni-Cu-P ternary coatings.

Figure 4.11 shows the XRD patterns of as-deposited Ni-Cu-P ternary coatings before and after plasma cleaning and the stainless steel substrate for comparison. The diffraction patterns for the as-deposited coatings before and after plasma cleaning both have a broad peak at around 2θ of 44° , which can be attributed to the amorphous phosphorus in as-deposited form [189]. There is also a relatively large peak at 2θ of 44.6° , which matches the (111) peak for face-centred cubic Ni at 44.5° (JCPDS # 65-2865). The diffraction patterns also contain relatively small peaks at 2θ of 50.7° and 74.8° . Although these are close to the (200) and (220) peaks of the austenite phase in the substrate, they are broader, indicating the presence of another phase with smaller crystallite size. They could be the (200) and (220) peaks for another face-centred cubic phase, with a lattice parameter of about $3.59 \text{ \AA}$. This is likely to be a solid solution of

Cu in Ni, since Ni and Cu can completely dissolve within each other, and the observed lattice parameter is intermediate between those of pure Ni, 3.52 Å, and pure Cu, 3.62 Å (JCPDS # 65-9743). Both Ni and Ni-Cu phases remain stable after the plasma cleaning treatment and no new phase appears.

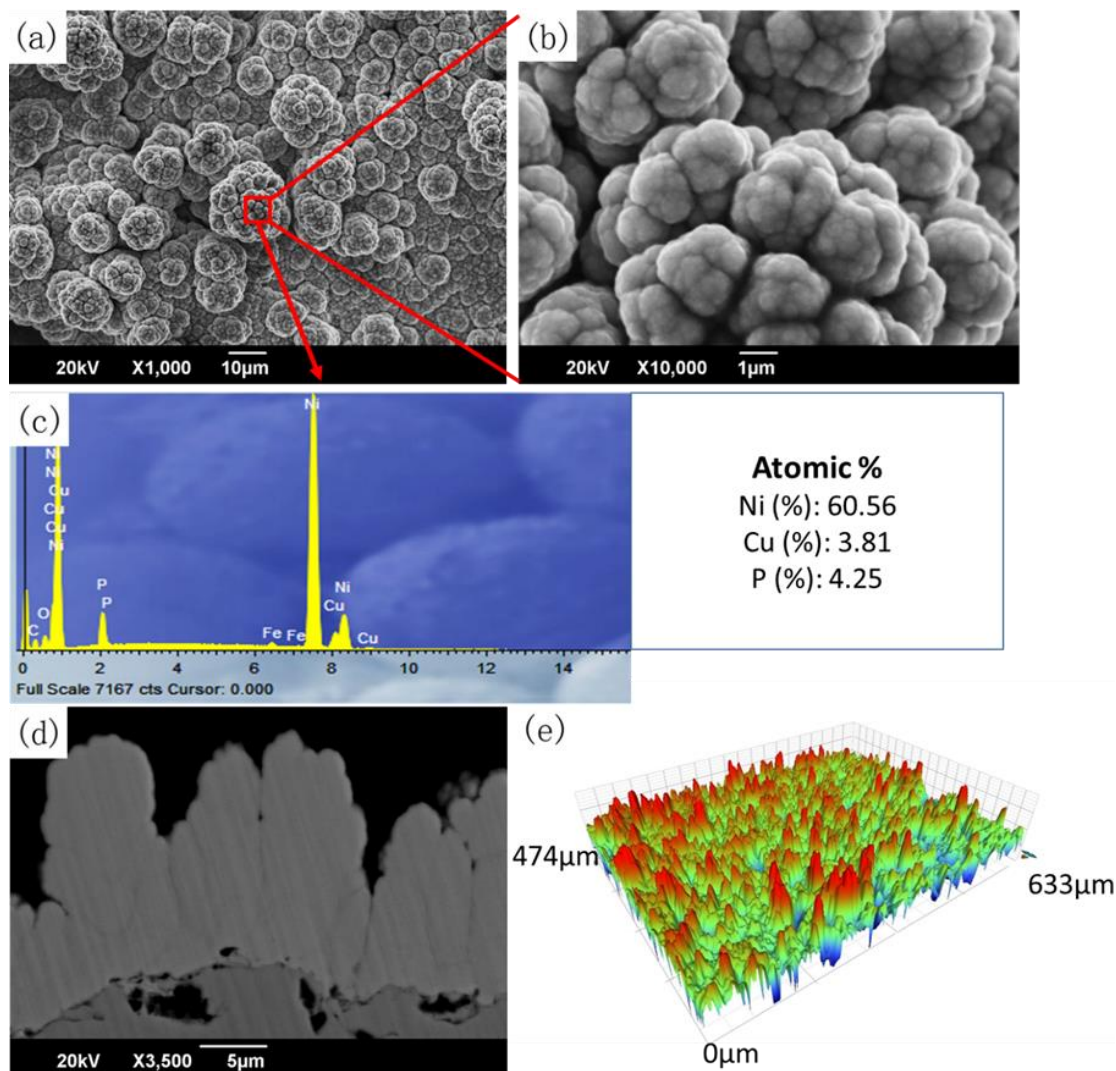


Figure 4.12 (a) and (b) SEM images of surface morphologies (c) EDX results (d) Cross-sectional morphology and (e) 3D image of the as-deposited Ni-Cu-P ternary coating.

Figure 4.12 (a) and (b) show the secondary electron SEM surface morphology of the as-deposited coating. The surface exhibits regular cauliflower-like hierarchical structure that consists of many tiny spherical deposits and are tightly attached to each other. From the image with high magnification, the spherical deposits range from about

300 nm to 500 nm and the cauliflower-like structure is around a few microns. Figure 4.12 (c) shows the EDX spectrum result of the selected area as indicated in Figure 4.12 (a). There is roughly 60.6 at% nickel, 3.8 at% copper, and 4.3 at% phosphorus, which confirms the presence of phosphorus. Figure 4.12 (d) shows the cross-sectional image of the as-deposited coating surface using backscattered electron. The hierarchical structure can be clearly observed on the coatings. The coating thickness varies from 10 μm to 20 μm due to the high roughness of the surface profile. Figure 4.12 (e) is the 3D surface topography of the coatings with a selected area of $633 \times 474 \mu\text{m}$. The measured average surface roughness R_a is about $3.9 \pm 0.1 \mu\text{m}$, with many peaks and valleys. The red peaks in the 3D topography image show the cauliflower structure that is consistent with the SEM observation. The hierarchical structure could provide the desirable specific surface area that will contribute to the improved hydrophobicity.

4.2.2 Wettability study of Ni-Cu-P coating

For as-deposited Ni-Cu-P coating, the stabilised WCA, advancing WCA, receding WCA, and CAH have been measured and listed in Table 4.3. The stabilised WCA of the Ni-Cu-P coating is $143.8 \pm 3.9^\circ$ with a CAH of $5.5 \pm 0.1^\circ$; the high WCA and low CAH value indicate that the coating could be a good candidate for the hydrophobic/icephobic application. The micro- and nano-structures provide sufficient roughness for hydrophobicity. The cauli-flower like structure is quite similar to the hierarchical micropapillae and nanofolds which are known to exist on rose petal's surface [190].

Table 4.3 Wettability results of as-deposited Ni-Cu-P coating.

	Stabilised WCAs ($^\circ$)	Advancing WCAs ($^\circ$)	Receding WCAs ($^\circ$)	CAH ($^\circ$)
Electrodeposited coating	143.8 ± 3.9	144.3 ± 3.8	138.8 ± 3.3	5.5 ± 0.1

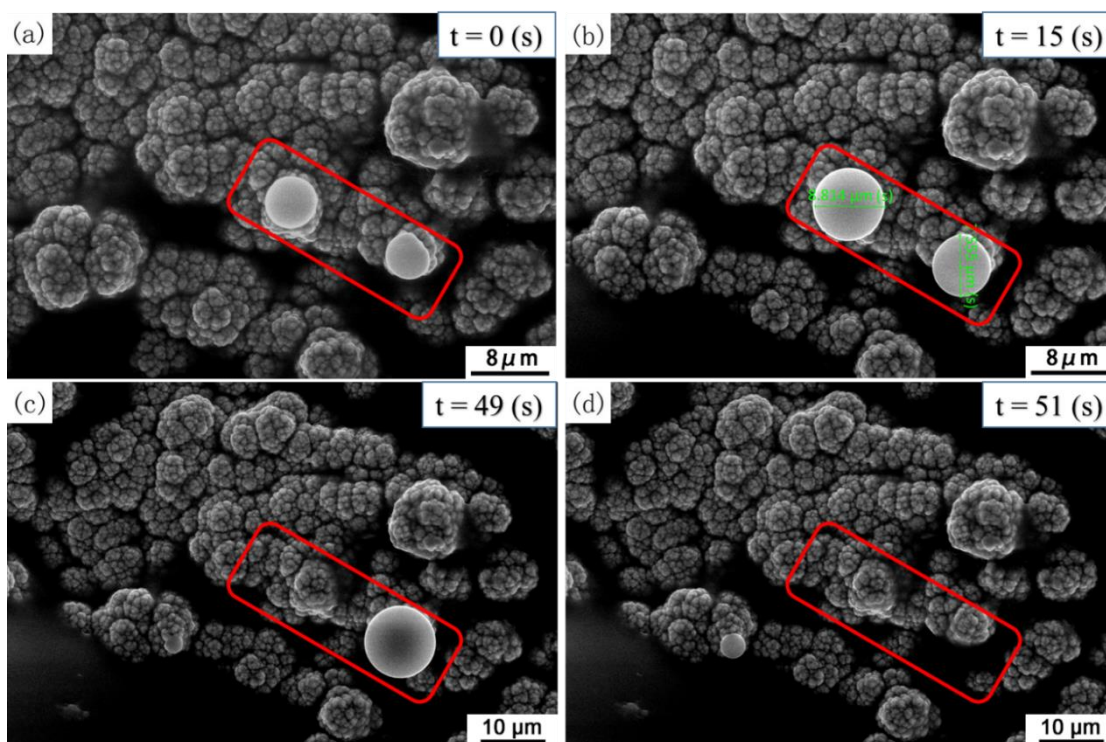


Figure 4.13 Water condensation and gathering process on electro-deposited Ni-Cu-P coating in aged state (a) $t=0$ s (b) $t=15$ s (c) $t=49$ s (d) $t=51$ s (Pressure: 4.7 torrs; Temp: $1.0\text{ }^{\circ}\text{C}$; Humidity: 95.0%).

Figure 4.13 displays the water droplet condensation on Ni-Cu-P coating with hierarchical structure in aged state via ESEM observation. By controlling the chamber humidity, temperature, and pressure, the micro water droplets will condense on the cauli-flower structure and keep growing in size. The coating surface hydrophobicity could be reflected from the geometry of the micro-droplet, with the high WCA observed by ESEM. When the droplet grows to a certain size, it could be too large to stand and would fall off and merges into the big water area (the black area). Because of the hierarchical structure, there are a lot of peaks and valleys, the gathered water normally stays at the lower area, while the higher position is less affected. The water droplet could nucleate and grow both within and on top of the cauli-flower structures. It could be speculated that the droplet growth rate is related to the generated positions because the heat transfer ontop would be different due to the vapour trapped inside any microcavities within the texture. So it is hypothesized that the difference in droplet

growth rate is related to the wettability of the microdroplets overlaying the microstructure [191].

4.2.3 Durability test of Ni-Cu-P coating (via water impinging test)

The coating durability is an important parameter for hydrophobic/icephobic applications. To evaluate the coating durability, water impinging test has been carried out. During the test, pressurized water droplets are sprayed onto the coated samples for certain durations. The other properties of the coatings including surface morphologies and wettability have also been monitored before and after the water impinging test.

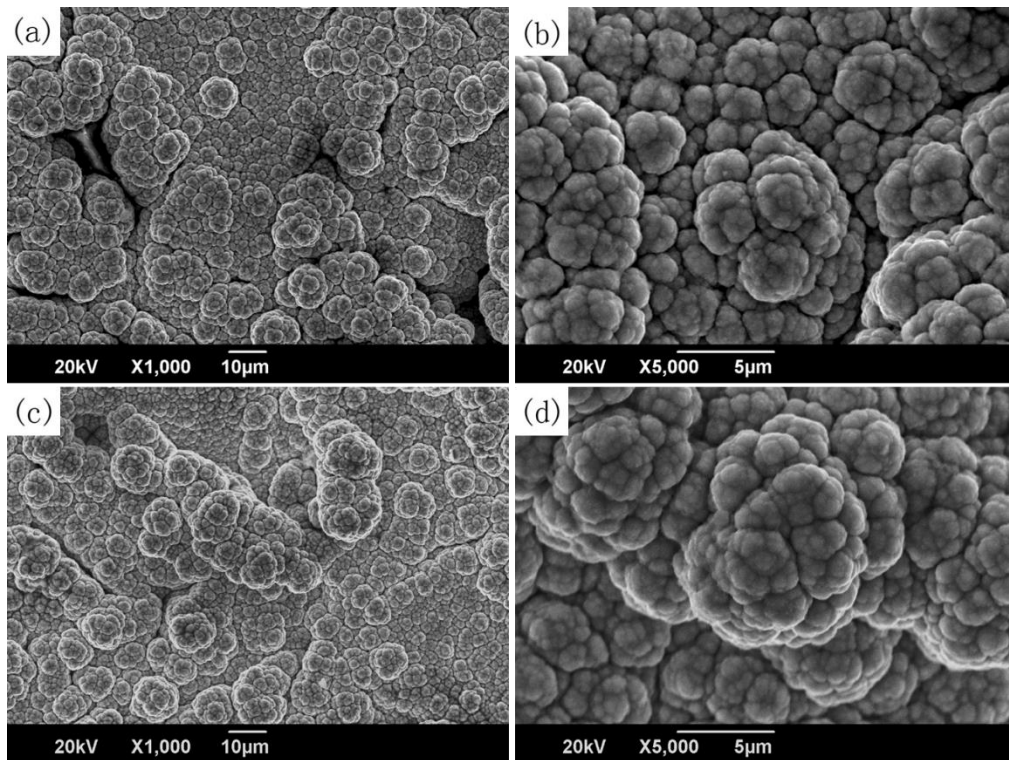


Figure 4.14 SEM images of surface morphologies of Ni-Cu-P coatings before (a) $\times$ 1K (b) $\times$ 5K; after (c) $\times$ 1K (d) $\times$ 5K; the water impinging tests.

Figure 4.14 shows the change of surface morphology of samples before and after water impinging tests. It is clear that there is no obvious change after the water impinging test. Before the test, it shows a highly rough structure. Afterwards, the hierarchical structure

remains there. No obvious damage could be detected. From the roughness measurement, it could be found that R_a is $3.9 \pm 0.1 \mu\text{m}$ before the impinging test. It then decreases a little bit to $3.8 \pm 0.1 \mu\text{m}$. The results indicate the good mechanical durability of the as-deposited Ni-Cu-P coating.

The WCA has also been measured after the water impinging test. Surprisingly, the WCA suffers a sharp decrease. It decreases to lower than 40° . Then the samples have been stored in ambient air without further treatment. It is found that the WCA of the sample keeps increasing during the ageing process. The WCA value increases from less than 40° to around 130° with time going. As observed in Figure 4.15, the gathering of optical images of the WCA changing process is shown and a more visualized evolution curve has been shown in Figure 4.16.

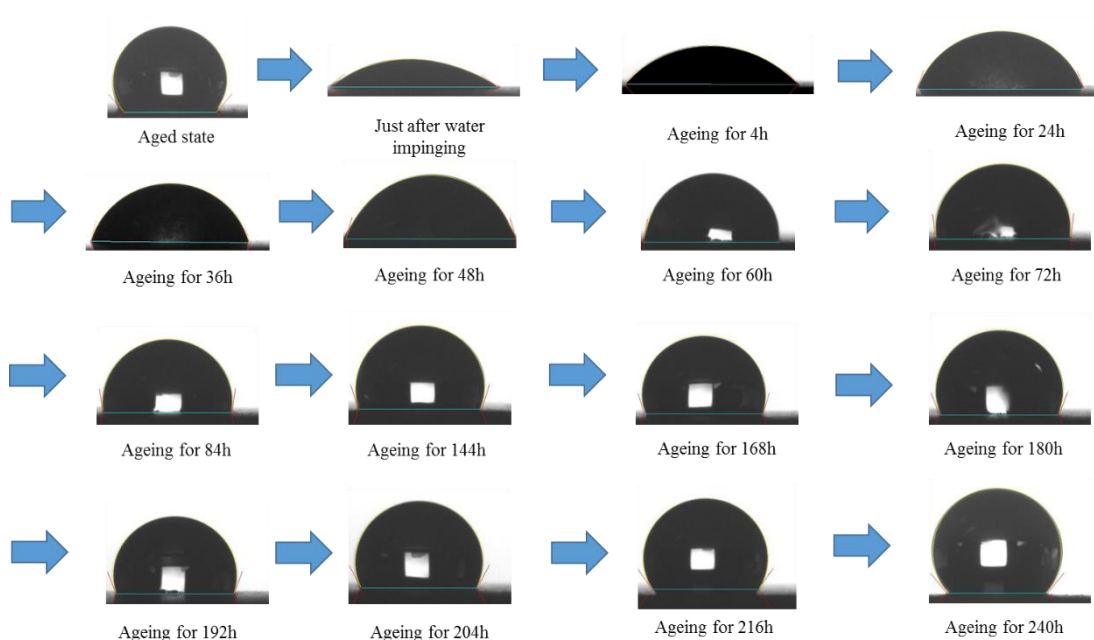


Figure 4.15 Optical images of WCA evolutions of as-deposited Ni-Cu-P coatings via exposure after water impinging tests.

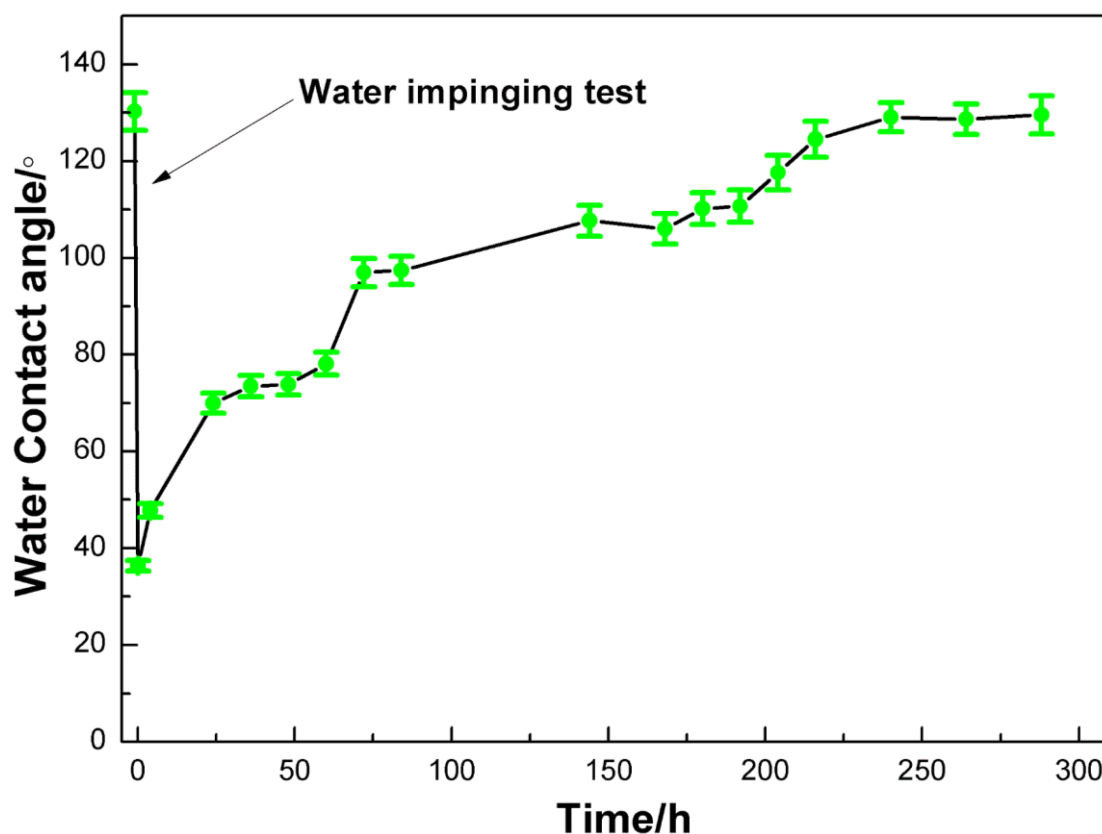


Figure 4.16 WCA evolutions of as-deposited electrodeposited coatings before and after water impinging test.

Before the water impinging test, the WCA is over 130° and it becomes hydrophilic (less than 40°) after the test. It is then stored in ambient air. The WCA increases slowly, the sample takes around 75 h to become hydrophobic again. The WCA finally recovers to its former value after around 10 days. Without altering the surface, the WCA evolution takes place spontaneously. It is also estimated that the WCA changing process could be reversible. It would be a great help to disclose this phenomenon and the possible underlying wetting mechanism, which is also likely to be applicable to other metallic coatings.

4.3 Evolution of Wettability of Ni-Cu-P Coating

The WCA of the Ni-Cu-P coatings could increase spontaneously in ambient air. Considering the unchanged surface morphology, the improved hydrophobicity could be ascribed to the change of surface free energy. To better study the phenomenon, plasma cleaning treatment has been applied. Because plasma cleaning could drive away the surface substance and would not destroy the surface morphology, it has similar treatment effect comparing to water impinging. In order to build a full understanding of the whole changing process, the WCA evolution of the Ni-Cu-P coatings will be monitored once the sample has been prepared during the whole storage in ambient air.

4.3.1 Wetting behaviour change of Ni-Cu-P coating

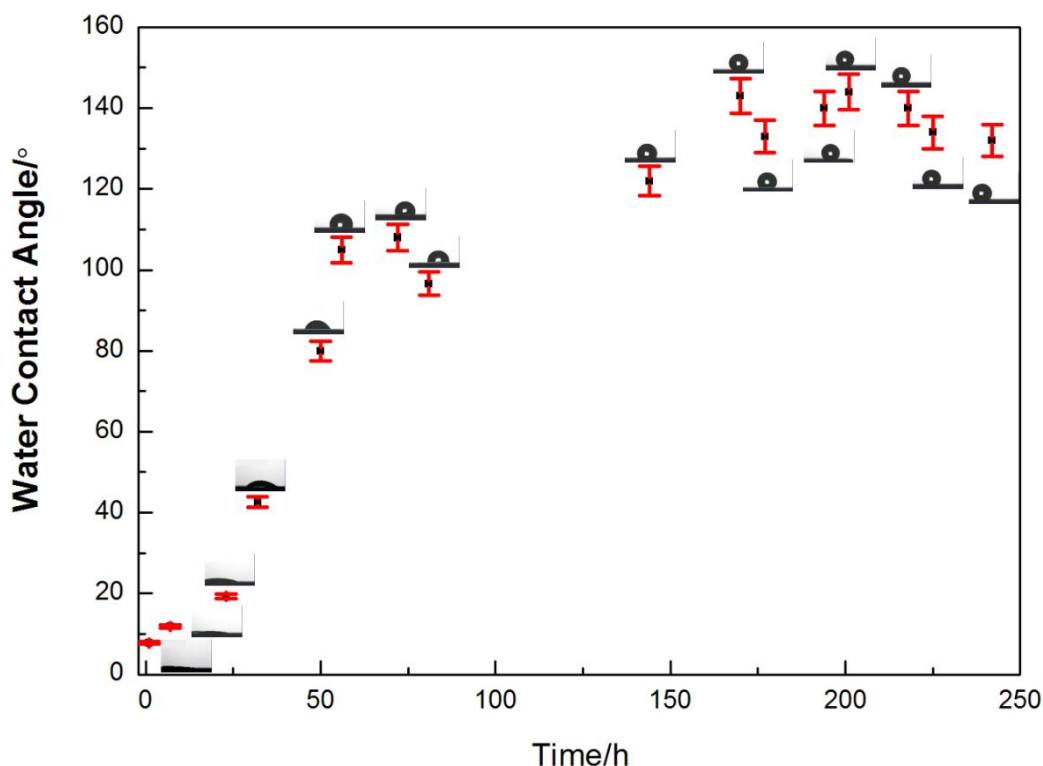


Figure 4.17 WCA change within exposure time in ambient air of the as-deposited electrodeposited coating.

Figure 4.17 shows the WCA value of the as-deposited coating with different ageing durations in ambient air. The insets show the optical images of the water droplets on

the coating surface. It can be seen that the WCA increases gradually from less than 10° (as-deposited state) to nearly 140° (aged state) after being aged in ambient air. The change from hydrophilic state to hydrophobic state takes about 60 h. After that, the WCA still increases at a slower rate and stabilises at around 140° .

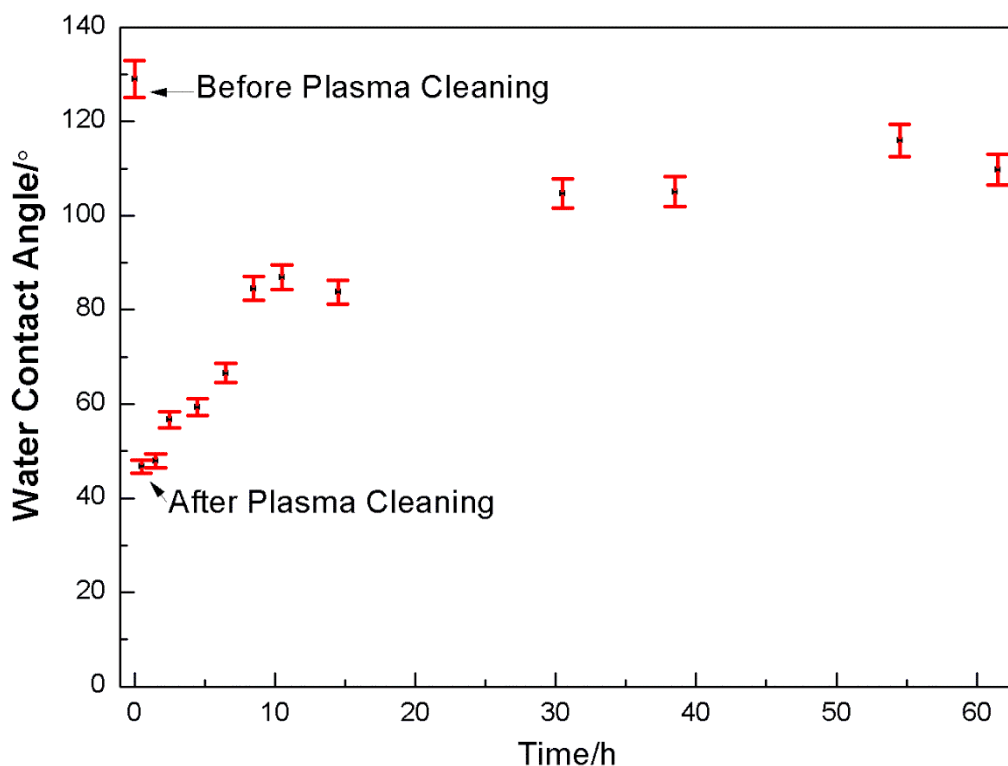


Figure 4.18 WCA change of electrodeposited coating before and after plasma cleaning treatment.

Figure 4.18 shows the WCA change of as-deposited coating before and after plasma cleaning treatment. Plasma cleaning was used to remove the adsorbed substances on the coating surfaces. It is a low energy process without changing the elemental composition and structural characteristics of the coating, and there is no etching or sputtering involved [192]. The as-deposited coating was taken out after plasma cleaning treatment and restored in ambient air. The wettability recovery appeared again. It is clearly evidenced that the WCA decreases sharply from over 130° to around 50° after the plasma cleaning. Then the WCA increases slowly again and nearly recovered to its previous level after a duration of 60 h. The transition from hydrophobic state to

hydrophilic state and recovery to hydrophobic state is consistent with the wettability transition of an Ag-coated surface [193]. The initial WCA decrease can be ascribed to the decreasing content of airborne hydrocarbon and increased oxygen groups. The pristine Ni-Cu-P ternary coatings might have high surface energy [194] and present as hydrophilic character. The reason for the later WCA recovery of the coatings can be explained that the hydrocarbon could be re-adsorbed onto the coating surface after being re-exposed to ambient air and the oxygen groups remaining on the coating also decrease. The surface energy then reduces and the surface hydrophobicity recovers accordingly.

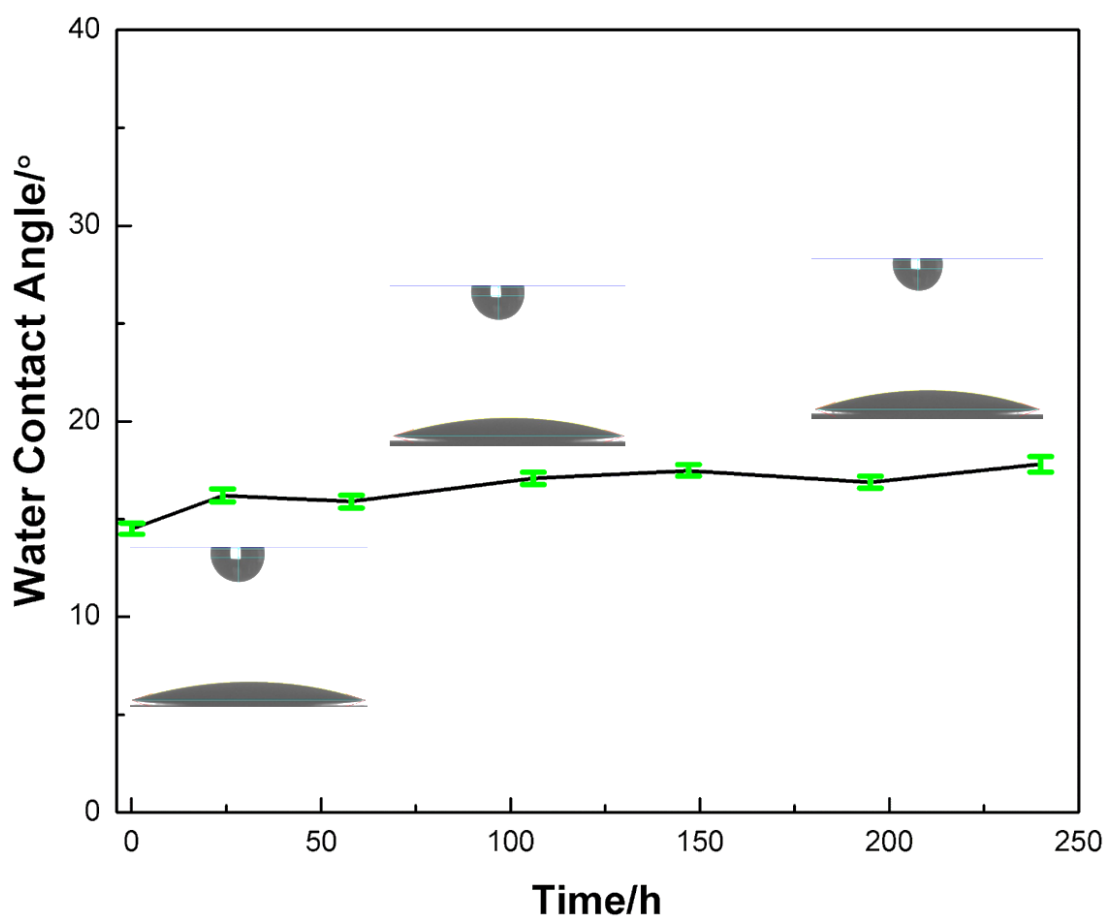


Figure 4.19 WCA change of electrodeposited coating stored in vacuum for different durations.

To better study the WCA evolution of as-deposited samples, another comparative experiment has also been conducted. Figure 4.19 shows the WCA change of as-deposited Ni-Cu-P coatings with different storage durations in vacuum environment.

Several parallel samples prepared with sample parameters would be put into vacuum bags once they have been prepared. They will be taken out after certain durations and the real-time WCA will be measured. It is obvious to see that the WCA value always remains at less than 20 ° even after over 10 days of storage in vacuum. It means that the coating did not show any WCA increase but just maintain its as-prepared WCA value. Compared to the WCA variation showing in Figure 4.17 and Figure 4.18 before, it indicates that the storage in ambient atmosphere could play a very important role with the WCA change in the as-deposited Ni-Cu-P samples. It also verifies the function of plasma cleaning which focuses on cleaning but not introducing the hydrophilicity.

4.3.2 Surface species variations of Ni-Cu-P coating using XPS spectrum analysis

Table 4.4 Atomic percent change of hydrocarbon groups and lattice oxygen groups versus different treatments.

Samples with different states	Hydrocarbon in all (At%)	Lattice Oxygen (At%)
As-deposited	78.7	27.9
After 10days	86.5	14.1
Before Plasma Cleaning (After 30 days)	82.3	10.3
After Plasma Cleaning	65.9	47.8

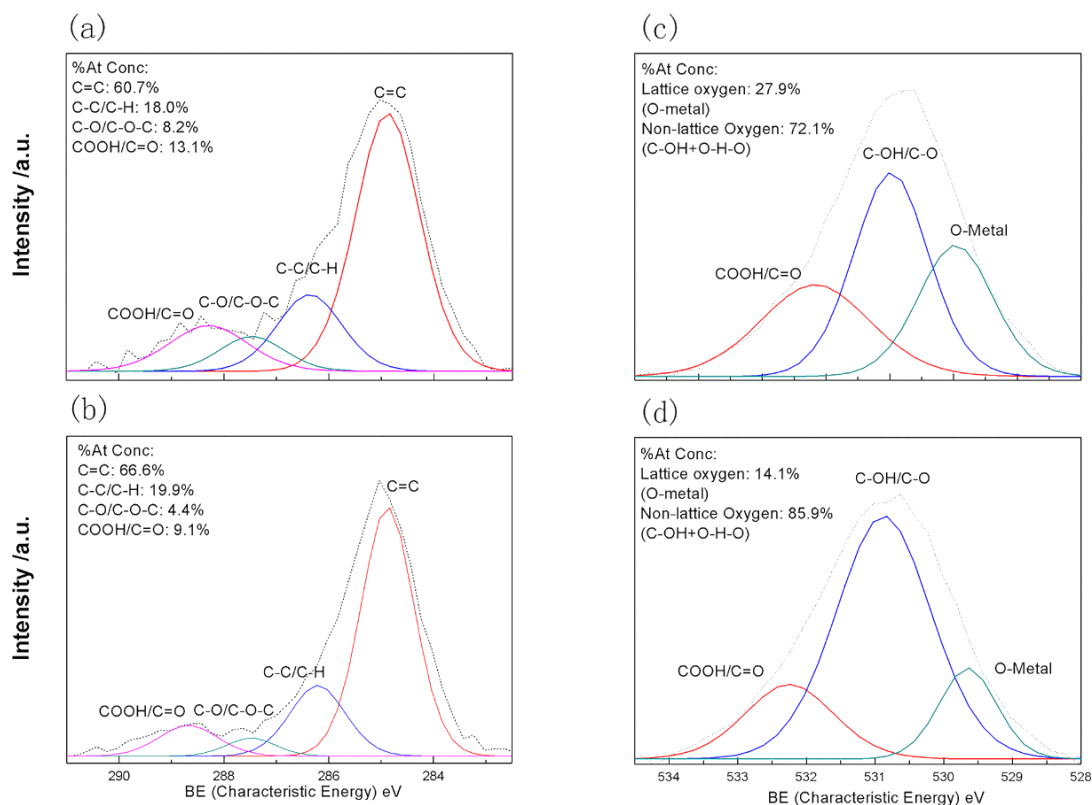


Figure 4.20 (a) and (b) C 1s XPS spectrum of the electrodeposited Ni-Cu-P coating (a) As-deposited (b) After 10 days (store in ambient air); (c) and (d) O 1s XPS spectrum of the electrodeposited Ni-Cu-P coating (c) As-deposited (d) After 10 days (store in ambient air).

Figure 4.20 compares the high resolution XPS spectra of C 1s (a) and (b) and O 1s (c) and (d) of the as-deposited coating and the coatings stored in air for 10 days, respectively. It can be seen that both C 1s and O 1s spectra changed significantly. To study the details, the C 1s spectra were resolved into several Gaussian-Lorentzian peaks using Shirley backgrounds and the nomenclature proposed by Modabberasl and Skaltsas et al. [195, 196]. Specifically, the C 1s satellite peaks were resolved with four different components C=C, C-C/C-H, C-O/C-O-C, and COOH/C=O, respectively, in which the hydrocarbon groups (C=C, C-C/C-H) predominate. The peaks were fitted according to the constraint of the intensity ratio between each peak. According to the fitting results, the atomic percentage of hydrocarbon was calculated and shown in Table 4.4. The atomic percentage of hydrocarbon increased from 78.7% (C=C plus C-C/C-H) to 86.5%, while the atomic percentage of the other two C 1s groups decreased from

21.3% to 13.5%. The O 1s spectra were also resolved into several constituent satellite peaks, O-metal which could be designated as lattice oxygen and C-OH and O-H-O groups as non-lattice oxygen identified using the nomenclature proposed by Wei and Khan [197, 198]. The atomic percentage of lattice oxygen decreased from 27.9% to 14.1% while the non-lattice oxygen increased from 72.1% to 85.9%. The non-lattice oxygen peaks are also attributed to surface adsorbed oxygen species such as hydroxyls or carbonates [199].

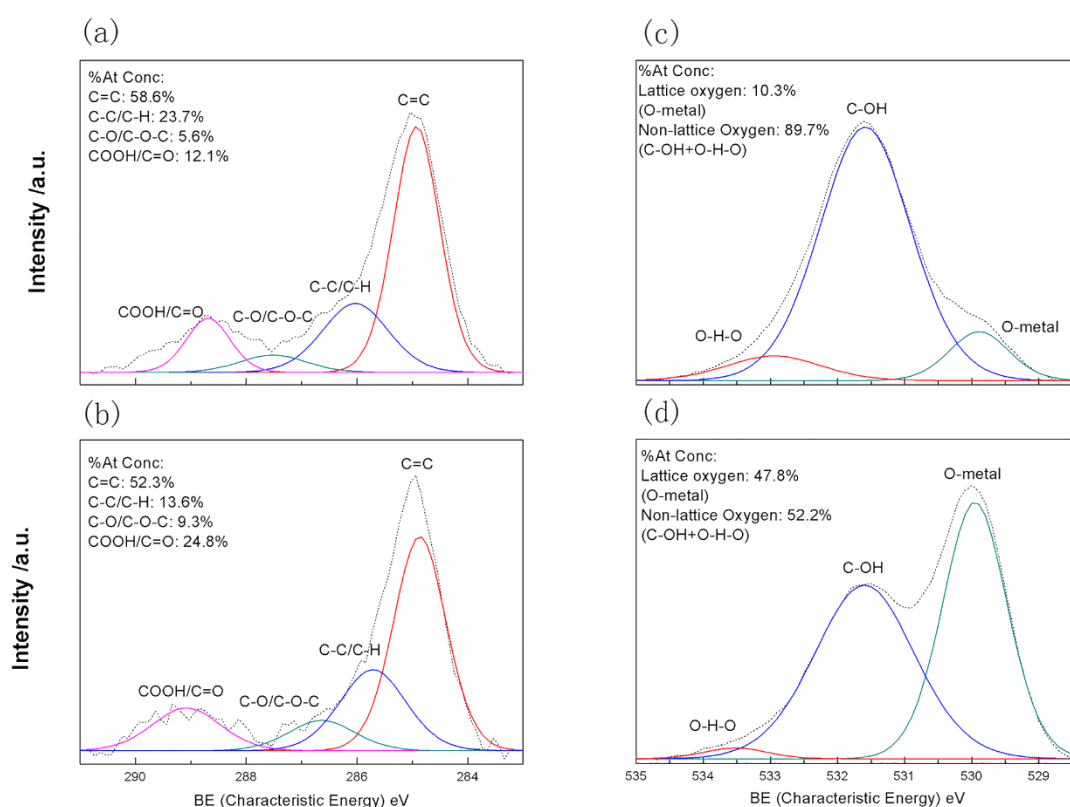


Figure 4.21 (a) and (b) C 1s XPS spectrum of electrodeposited Ni-Cu-P coating (a) before (b) after plasma cleaning treatment; (c) and (d) O 1s XPS spectrum of electrodeposited Ni-Cu-P coating (c) before (d) after plasma cleaning treatment.

Figure 4.21 shows the high resolution XPS spectra of C 1s (a) and (b) and O 1s (c) and (d) of the as-deposited Ni-based coating before and after plasma cleaning treatment. It clearly indicates that the C 1s contents suffer an obvious decrease. From the resolved peaks, after the plasma cleaning treatment, the atomic percentage of hydrocarbon

decrease from 82.3% (C=C plus C-C/C-H) to 65.9%, while both the C-O/C-O-C and COOH/C=O groups increase. COOH/C=O works as hydrophilic groups and increases the wettability. It is assumed that the slight shift of the groups before and after the plasma could be associated with the removal of adsorption from the surface and formation of new functional groups. The carbon atoms are bonded to the oxygen atoms and the incorporation of new species from the plasma treatment can cause degradation and lead change to the groups [200, 201]. This also indicates that the main components of adsorbed airborne hydrocarbon are C-C/C-H groups and C=C groups. For O 1s spectra, there is also a considerable change after plasma cleaning. The lattice-oxygen increases from 10.3% to 47.8% while the non-lattice oxygen groups decrease from 89.7% to 52.2%. The lattice-oxygen included O-Ni and O-Cu groups. The increased oxygen level on the surface may increase the possibility to form hydrogen bonds with interfacial water and lead to lower wettability [198].

4.4 Discussion

4.4.1 Impact of current density on coating microstructure and wettability

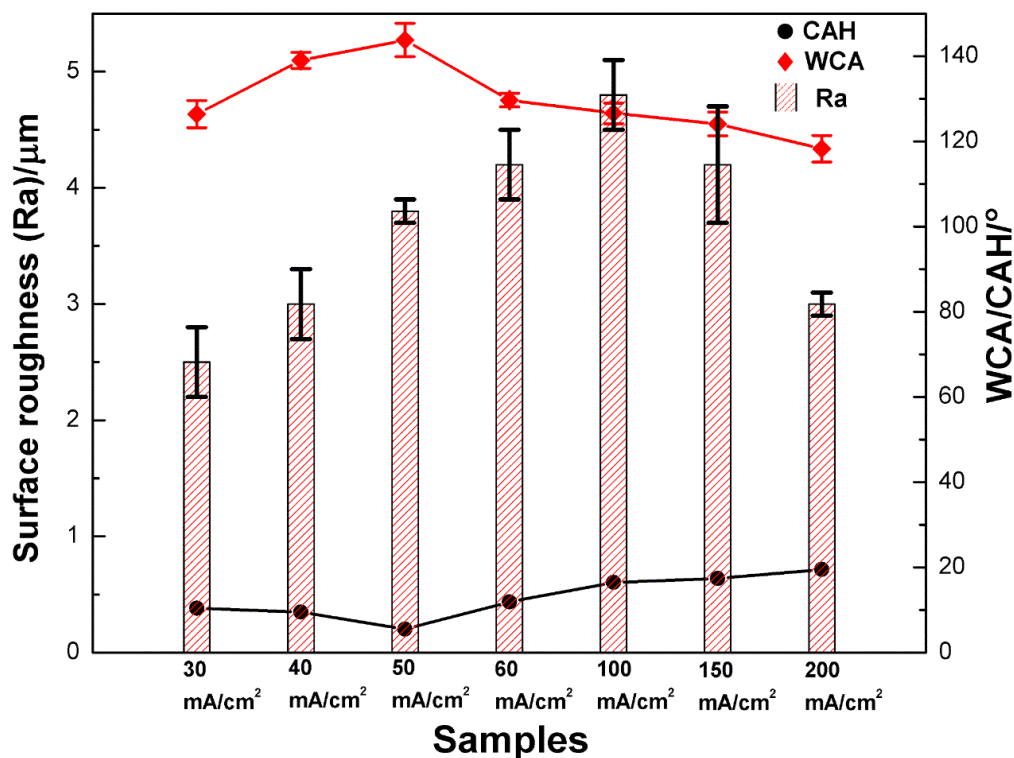


Figure 4.22 Correlation between wetting parameters (WCA and CAH) with surface roughness of different Ni-Cu-P samples prepared with different current densities.

Figure 4.22 shows the relationships between the wetting parameters including WCA and CAH and surface roughness on different Ni-Cu-P samples prepared with different current densities. It clearly indicates the impact of current density on coating microstructure and wettability. With current densities keep increasing, the surface roughness first increases from 30 mA/cm^2 to 100 mA/cm^2 and then decreases. The microstructure and properties of the as-deposited Ni-Cu-P coatings could vary with different current densities. It can be clearly seen that the surface morphology is strongly influenced by the current density. As indicated in Figure 4.2, samples prepared with 150 mA/cm^2 and 200 mA/cm^2 have more deposits in quantity, but the sizes of the deposits are smaller than the former two samples. The cauliflower-like structure also changes to the dendritic structure when higher current density is applied. The reason

could be ascribed to the higher deposition rate derived from higher current density. The high current density can accelerate the formation of crystal nucleus and also inhibit the growth of deposits. The electro-deposition reaction can be very intense. Huge quantities of bubbles then generate at the electrodes and remain there. Then it can be difficult for the supposed newly formed spheres to grow there. In this way, smaller cauli-flower structures are then obtained. With higher current density, the degree of crystallization also becomes higher, as indicated from the sharper diffraction peaks in Figure 4.1. The amorphous phosphorus in as-deposited form becomes less.

According to Faraday's law, the quantity of electrochemical reaction occurs on electrode is proportional to the quantity of electric charge. With constant current efficiency, the relationship between deposition rate and current density could also be linear [202]. The lower the current density, the more positive the potential at the cathode. While at low current densities scale, the potentials on the cathode are positive enough (with less negative potentials) to deposit more copper than nickel [203]. Lower current densities help with the growth of normal cauliflower-like hierarchical structures.

From the XRD results, there is still slight difference between samples with different current densities. Figure 4.4 shows that all samples show a tendency toward (111) texture, the nickel deposits grow preferentially along with the (111) directions [204]. The increase of the current density from 30 to 60 mA/cm² results in the coarsening of the crystallite size. This is consistent with the results reported by Cziraki et al. [205], who used a sulfate-based electrolyte with preparation current densities in the range of 100 to 500 mA/cm². The slight rightward peak-shift shown in Figure 4.4 corresponds to the increasing lattice constants, the Ni-Cu solid solution enriches in nickel with the decreasing copper ion concentration [206]. It is clear that the increase of the current density and nickel content in the alloy results in the decrease of crystallite size. The increase in the crystallite size is associated with the increasing current density (30 to 60 mA/cm²), which causes rougher surfaces, as viewed in Figure 4.5. It should be noted

that the apparent roughness observed on the surface is related to the crystallite but is usually much larger than the actual crystallite size.

The sample prepared with 50 mA/cm² current density reaches the highest WCA value with the lowest CAH. This also shows that the wettability does not have a proportional correlation with the surface roughness. The surface chemistry and the phase composition also affect, they could affect the surface energy and further the hydrophobicity [177]. The results confirm that the current density could place huge impact on the microstructure and wettability of the Ni-Cu-P ternary coatings. Increasing the current density would lead to the increase of the number of deposits and deposition rate and change to the surface chemistry. The overall results suggest a complex current-electrode potential relationship, appropriate current density needs to be confirmed when preparing samples.

4.4.2 Influencing factors of wettability recovery speed

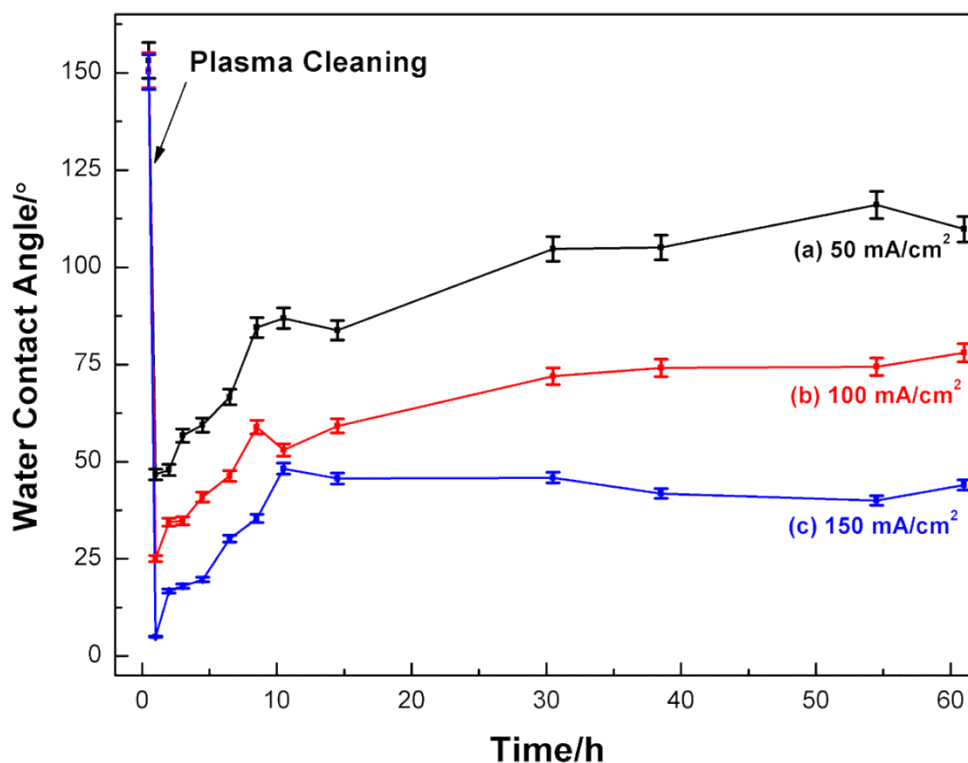


Figure 4.23 WCA changes of Ni-Cu-P coatings before and after plasma cleaning treatment with different deposition current density (a) 50 mA/cm² (b) 100 mA/cm² (c) 150 mA/cm².

As indicated in section 4.1.1, different current densities affect the surface microstructure and surface composition. This would further affect the WCA recovery speed of different samples. Similar WCA recovery phenomenon has been observed on other electrodeposited Ni-Cu-P samples with different current densities, as shown in Figure 4.23. The WCA changing curves of the samples show the same variation trends. The three samples differ in surface morphology and phase compositions. It is believed that the intrinsic WCA is determined by the surface chemical composition, while the apparent WCA largely comes from the combined results of intrinsic WCA and the contribution from other factors [207]. The value of WCA just after the plasma cleaning treatment also varies a lot. Moreover, the recovery speed of the three samples varies a lot. The main reason for the different recovery speeds lies in the surface morphology difference. For the same type of coating surfaces, samples with more hierarchical structures have higher WCA recovery speed. More hierarchical structures could supply larger specific surface areas and increase the adsorption of related groups during the recovery period. This contributes to higher absorption speed. The airborne hydrocarbons would take less time to finish the process of replacing, inserting into, and/or covering the formerly adsorbed hydrophilic groups at the surface.

4.4.3 Wetting state of as-deposited Ni-Cu-P ternary coatings

Normally, there are two wetting states schemes: Wenzel's state and Cassie's state. The former state represents a wetting contact mode of water and rough surface, where water droplet on the surface forms a high CAH. The latter scheme represents a dewet-contact mode and water droplets could roll off easily owing to the low CAH.

It is obvious to confirm the existing Cassie's wetting state on as-deposited Ni-Cu-P ternary coatings. The ESEM observation results in Figure 4.13 clearly show the slide-off of the formed water droplet, showing a dewet-contact mode. The measured CAH is also very low, only $5.5 \pm 0.1^\circ$. According to Cassie's law [81], the micro/nano structures could be regarded as heterogeneous surfaces composed of solid and air. The apparent

contact angle θ' of the coating is described by equation (4.1):

$$\cos \theta' = f_1 \cos \theta - f_2 \quad (4.1)$$

where f_1 is the normalized interfacial area of the micro/nano structures; f_2 is the normalized interfacial area of air among the micro/nano structures; θ' is the contact angle of micro/nano structure surface; and θ is the contact angle of the smooth surface.

Air cushion could form at the coating-water interface due to the trapped air between the hierarchical microstructures. This could prevent the coating from being wet. The formed air pocket is the reason why Ni-Cu-P coatings have better hydrophobic characteristics. When the formed water droplet is too large to be held by the existing air cushion, it would slide off and form into the big water area, as indicated in Figure 4.13.

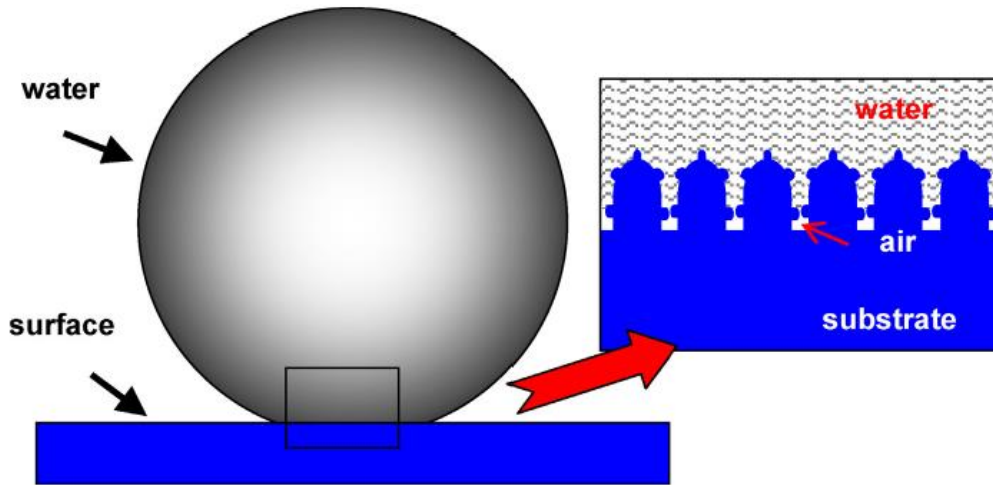


Figure 4.24 Schematic illustration of the Cassie impregnating wetting state [30].

Herein, the water droplet aforementioned in Figure 4.13 could be explained by Cassie's impregnating model, as shown in Figure 4.24. According to the theory of combination of Cassie's and Wenzel's modes, air pockets are assumed to be trapped underneath the liquid which helps to form a composite surface. These highly rough cauliflower-like structures would allow the water droplet to partially sit on the air pockets, showing their

hydrophobic characteristic.

4.4.4 Effect of surface adsorption (airborne hydrocarbon and lattice oxygen) on surface wettability

The changing wetting behaviour of the Ni-Cu-P coating appears with the undertaking treatment while the structures and micro-morphologies all remain the same. The possible mechanisms were investigated to interpret this phenomenon.

The wettability of a solid surface is mainly affected by two factors: surface roughness and surface chemistry. Surface roughness plays a crucial role in the wetting behaviour. In the electrodeposition process, cauliflower-like hierarchical coating structure is constructed. The hierarchical structure not only significantly increases the coating surface roughness, but also provides a large specific surface area which is desirable for the airborne hydrocarbon adsorption, leading to the driving away of the hydrophilic groups and lowered surface energy [208]. Therefore, a hydrophobic state can be formed gradually.

The changing wettability of Ni-Cu-P ternary coatings could be attributed to the adsorption and re-adsorption process of airborne hydrocarbon and the changing ratio of lattice oxygen on the coating surface, as indicated by the relationship between the WCA and surface carbon and oxygen content over time. The changing wettability may be ascribed to two factors: (i) adsorption of airborne hydrocarbon and (ii) influence of lattice oxygen.

Firstly, the XPS analysis shows that the amount of hydrocarbon groups present on the surface is indeed increasing with exposure time, indicating that hydrocarbons are adsorbed onto the coating surface in ambient air. As shown in Table 4.4, the surface carbon content changes obviously. The highly rough cauliflower surface structure could provide greater specific surface area than a smooth surface, which is easier for airborne

hydrocarbon to be adsorbed. The surface carbon increases from less than 20 at% to around 35 at%. The increased carbon content is attributed to the physisorption of airborne hydrocarbons, which include C=C and C-C/C-H groups. They could then form a thin layer on the coatings, leading to lower surface energy [209]. The atomic ratio of the airborne hydrocarbon increases with time, as shown in Table 4.4, which indicates that partial adsorption [210] of these groups was undergone on the Ni-Cu-P ternary coating surface. This may also have led to the continuous decrease of surface energy over time. Similar phenomena have been reported for a variety of metal oxide materials including zirconium dioxide (ZrO_2) and titanium dioxide (TiO_2) [194, 211]. In the present work, van-der-Waals and hydrogen bonding are the two typical bonding, besides possible electrovalent bonding of Ni-O and Cu-O [212]. The mechanism for this phenomenon can be explained by considering the adsorbed hydrocarbons as hydrophobic defects on hydrophilic surface [213]. A hydrocarbon molecule would diffuse along the surface, and the van der Waals bonding between the surface and the adsorbed hydrocarbon could help to increase the stability of the studied coating systems. Hence, the diffusion of hydrocarbon molecules is likely to occur. After the plasma cleaning, the WCA decreases with the removal of adsorbed hydrocarbon, which is also consistent with the decreased surface carbon content.

The second factor, the changing oxygen groups may also contribute to the change of surface wettability. Excess lattice oxygen and hydroxyl groups may exist on the surface after the electrodeposition. The surface lattice oxygen could be released during the following long-time exposure to ambient air. The lattice oxygen could be desorbed from the surface and the surface hydrocarbons also work in conjunction with the incident photon energy to release oxygen from the coating lattice [214]. With the extensive surface relaxation, less lattice oxygen remains. Such process may also contribute to the coatings surface transition from hydrophilic to hydrophobic, while the main reason could be the notable change in surface carbon content. After the plasma cleaning, with the removal of the adsorbed hydrocarbon, the increased lattice oxygen (O-metal) makes it easier to form hydrogen bonds with interfacial water on the surface [198, 215].

Hydrophilic groups such as hydroxyls could also be introduced onto the surface during the process, which also benefits the increase of the surface energy.

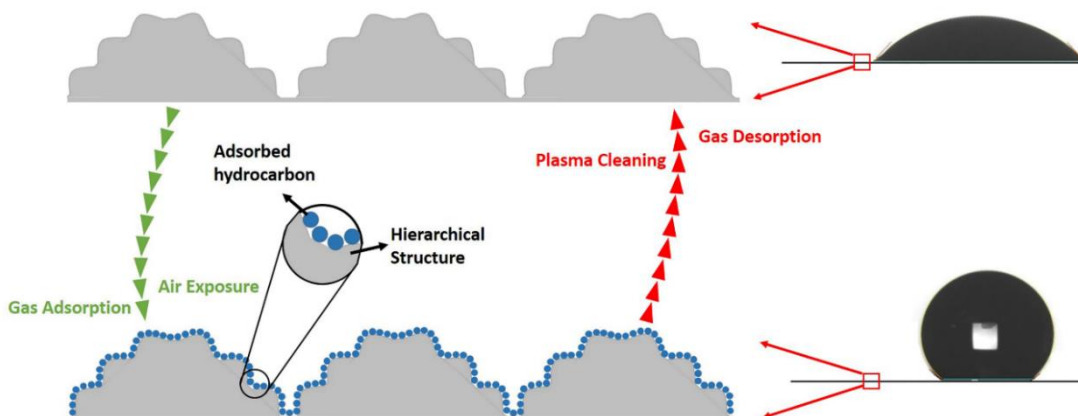


Figure 4.25 Schematic of the changing wetting behaviour of the Ni-Cu-P coating.

Herein, the changing wetting behaviour could be clearly explained by the schematic diagram in Figure 4.25. There are very limited hydrocarbons adsorbed on the as-deposited coating surface or coating after plasma cleaning treatment. The hydrophilic functional groups (mainly non-lattice O-metal groups including O-Cu and O-Ni) account for a large part, which presents a hydrophilic state. After stored in ambient air, a great amount of hydrocarbons are adsorbed onto the coating surface, the content of free functional groups is significantly increased. With these hydrophobic functional groups attached onto the hierarchical surface, it reduces the surface energy significantly and turns the surface into a hydrophobic wetting state. Water could not flow into the space between the hierarchical structures and some air pockets then form. As a result, the Cassie state takes place.

4.5 Summary

To sum up, the Ni-Cu-P ternary coatings have been prepared using electrodeposition method on 304 SS substrates. The appropriate processing parameters of the electrodeposition have been investigated. 50 mA/cm² was chosen as the optimised current

density. No further annealing treatment should be used during the preparation because it can introduce the deterioration effect to the wettability. The as-deposited Ni-Cu-P coatings showed highly rough structure. There were cauli-flower like structures formed which built hierarchical surface morphologies with WCA up to $143.8 \pm 3.9^\circ$. The coating thickness could reach 20 μm . The XRD patterns showed the main phases are $\text{Cu}_{0.81}\text{Ni}_{0.19}$ and Ni Cubic phase.

The coatings show good mechanical durability and hydrophobic character, but the hydrophobicity is not stable. The underlying mechanisms between the changing wetting behaviour and the coating surface morphologies and surface chemical composition have also been studied. The hydrophobicity could be reversible with the help of plasma cleaning treatment and ambient air storage. The phenomenon could be called the time-dependent wettability. The changing wettability of Ni-Cu-P ternary coating is a combined result of airborne hydrocarbon adsorption and lattice oxygen variation. The adsorption of airborne hydrocarbon takes the major effect, while the lattice oxygen on the coating surface also influences the surface wettability. The two factors alter the surface energy and introduce more hydrophobic groups onto the coating surface, resulting in the changes of wetting behaviour. This part of study provides insight into the wetting mechanism of the metallic materials and highlights the importance of controlling hydrocarbon adsorption for material wetting behaviour. To better investigate the phenomenon, more specified studies related to time-dependent wettability will be carried out in the next chapter.

Chapter 5 Time-dependent Wettability Phenomenon and Investigation on Coating Icephobicity

Icephobicity of materials has received intensive attention recently due to the increasing requirement of ice protection in different areas. However, the influencing factors of material icephobicity still have not been well identified. For example, in certain circumstances, the hierarchical surface that is necessary for hydrophobicity could increase the ice adhesion strength which is contradictory for icephobic applications. There is still extensive controversy on whether icephobicity is related to the hydrophobicity among scholars [90]. With no doubt, the concept of hydrophobicity could be used to guide the design and fabrication of icephobic surfaces.

The changing wettability phenomenon has been confirmed in the electrodeposited Ni-Cu-P coating system in the last chapter, which could be named as “time-dependent wettability”. To better unfold the time-dependent wettability, Ni-Cu-P coating via electroless deposition has been selected as the research object to give an overall comparison because the electroless deposited coating could show both sensitivities to the surface adsorption and significant difference in surface morphology and wettability. Other different solid surfaces including SS and ceramic systems (CeO_2) have also been chosen and studied in detail. Here, the SS has been chosen due to its typical and wide usage in daily application. While CeO_2 rare earth oxide is one of the representatives for ceramic system and has been reported for its hydrophobicity before [216]. The unique electronic structure of the rare-earth metal atom inhibits hydrogen bonding with interfacial water molecules resulting in a hydrophobic hydration structure where the surface oxygen atoms are the only hydrogen bonding sites [216]. So it could be of significance to carry out these studies. The effect of time-dependent wettability on icing behaviour of materials and the relationship between surface gaseous adsorption and coating icephobicity will also be investigated systematically. The samples prepared by electroless deposition and electrodeposition methods are designated as ELD and ED,

respectively. The samples prepared with 0.5 g/L, 1.0 g/L, and 1.5 g/L CuSO_4 addition were designated as ELD-0.5, ELD-1, and ELD-1.5, respectively. The samples prepared with 0.5 g/L, 1.0 g/L, and 1.5 g/L CuSO_4 addition were designated as ELD-0.5, ELD-1, and ELD-1.5, respectively. SS-smooth, SS-polish, and SS-rough represent as-received 304 SS substrate, 304 SS with polishing, and 304 SS with sandblasting, respectively.

5.1 Time-dependent Wettability Phenomenon in Electroless-deposited Ni-Cu-P Coatings

The role of surface adsorption on surface wettability has already been confirmed on electro-deposited Ni-Cu-P ternary coating before. Therefore, Ni-Cu-P coatings could be a good research object to unfold the mechanism. In this part, Ni-Cu-P coating prepared by electroless-deposition was utilized due to its sensitivity on surface gaseous adsorption with ageing duration.

5.1.1 Investigation of processing parameters of electroless-deposited Ni-Cu-P coatings

For electroless deposition, there are also many different contributing parameters which affect the coating properties, such as electrolyte composition, deposition time, pH and temperature of the electrolyte. In this work, most of the parameters have already been predetermined, the pH value was maintained at the range of 5.0-5.3, the temperature of the water bath was kept at 90 °C, and the deposition time was set at 60 min. The copper content in electroless deposited Ni-Cu-P coatings could have a significant effect on the surface microstructure and property of the coatings, which could improve the thermal stability and corrosion resistance of the coatings [158]. To obtain the optimised deposition parameter, a series of parallel experiments with different addition of Cu contents of Ni-Cu-P samples were prepared and characterised, the concentration of

CuSO_4 in electrolyte were controlled, as shown in Table 5.1. The samples prepared with different CuSO_4 additions were designated as ELD-0.5, ELD-1, and ELD-1.5, respectively.

Table 5.1 Set of electroless deposition experiments with different CuSO_4 additions.

Samples	CuSO_4 addition (g/L)
ELD-0.5	0.5
ELD-1.0	1.0
ELD-1.5	1.5

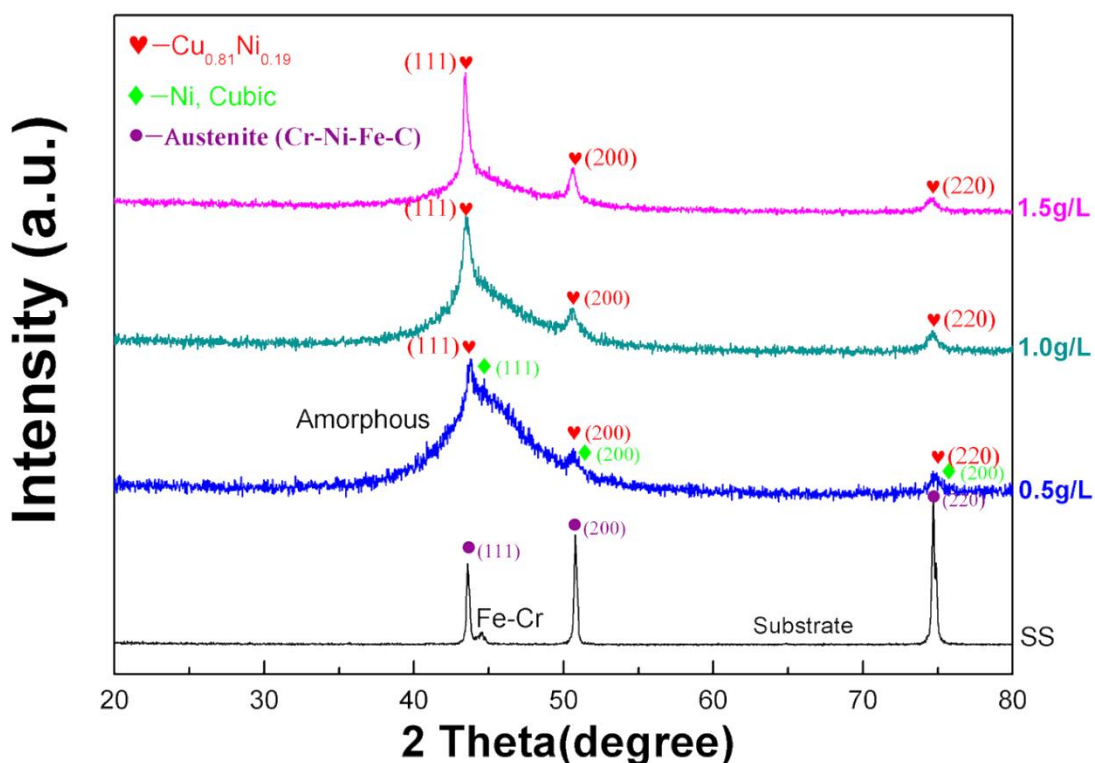


Figure 5.1 XRD patterns of ELD coatings with different CuSO_4 additions and SS substrate.

Figure 5.1 shows the diffraction patterns and corresponding peak position of all three ELD coatings and SS substrate for comparison. The lines have relatively large, narrow peak at 2θ of 43.7° , which corresponds to the (111) plane of $\text{Cu}_{0.81}\text{Ni}_{0.19}$ at 43.6° (JCPDS # 47-1406), indicating the presence of dominant phase of copper nickel phase. For ELD-1 and ELD-1.5, it is evident that the peak has become narrower and sharper compared to the former peaks. The reason could be ascribed to the increased grain size

of the deposit due to the presence of more copper atoms in face centred cubic (fcc) nickel matrix, which would have influenced the formation of crystalline structure [217]. It is obvious that the phase crystallinity is increased. There are also two relatively small peaks at around 50.6° and 74.7° , which could be the (200) and (220) peaks of $\text{Cu}_{0.81}\text{Ni}_{0.19}$ phase. The broad peak at around 44° could be attributed to the as-deposited amorphous phosphorus [189]. For ELD-0.5, there are some other small peaks, the peaks at around 44.6° , 51.8° and 76.4° all match the peaks (111), (200) and (220) of fcc Ni (JCPDS # 04-0850). For ELD-1 and ELD-1.5, the diffraction patterns of the coatings clearly show a changing trend, all of these diffraction peaks no longer appear. The intensity of $\text{Cu}_{0.81}\text{Ni}_{0.19}$ (111) peaks keep becoming stronger, the reason could be the increasing Cu ion concentration. The interplanar spacing of $\text{Cu}_{0.81}\text{Ni}_{0.19}$ phase increases as the Cu content increases, which could be explained by the formation of $\text{Cu}_{0.81}\text{Ni}_{0.19}$ solid solution [218]. While for Ni (111) peaks, it becomes weaker and weaker and then it could not be detected in ELD-1 and ELD-1.5. The reason could be that with the increasing addition of Cu ions, more Cu ions could react with Ni ions and form the solid solution of Cu in Ni. No remaining fcc Ni phase could be detected then.

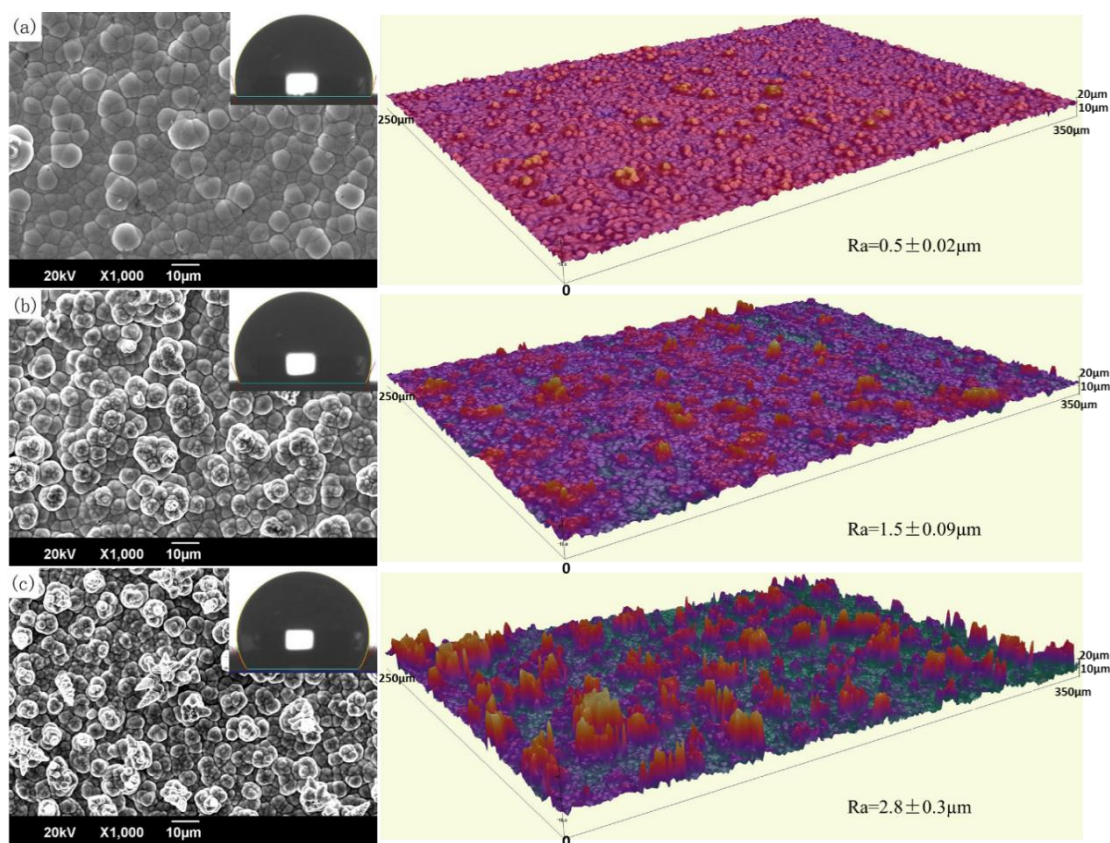


Figure 5.2 SEM images of surface morphologies with insets of WCA results and 3D topography images of (a) ELD-0.5 (b) ELD-1 (c) ELD-1.5.

Figure 5.2 shows the SEM images of surface morphology and 3D topography as well as the WCA insets of the three ELD samples. For ELD-0.5, as shown in Figure 5.2 (a), the surface morphology exhibits quite flat and smooth structure, the spherical nodular deposits are tightly connected to each other. There is no obvious crack and void on the surface, it clearly shows the size of the nodular structures which ranges from about 1 μm to 5 μm . The coating covers the substrate quite well. The co-deposited copper ions play an important role in activating the natural nucleation sites and retarding the nodule growth by reducing the activation of additional nodule sites [31]. Some coarse nodular deposits seem to distribute sparsely on the surface. The reason for the formation of such structures could be the predominant deposition of Cu. With the addition of Cu ions, it is bound in a strong complex, and will not shift negatively its potential to the region that nears Ni ions [219]. These places are nobler than Ni, preferential deposition of copper ions would take place and form Cu-rich zone [220]. It is evident that the

extruded nodules are presented in the image. The surface roughness R_a of ELD-0.5 is about $0.5 \pm 0.02 \mu\text{m}$, the red peaks in the 3D image represent the spherical nodular structures that are consistent with the former SEM observation. The WCA of ELD-0.5 is $105.1 \pm 3.5^\circ$ with CAH of $19.3 \pm 0.3^\circ$, which could be ascribed to the low surface roughness and surface composition. Figure 5.2 (b) shows the surface morphology of ELD-1, compared to the former images, the obvious difference could be found. More nodular structures are deposited on the surface, showing a more hierarchical structure. The density of nodular structures distribution is higher than before. The surface roughness R_a is $1.5 \pm 0.09 \mu\text{m}$. It could be found that smaller nodular structure seems to grow on the formerly formed structures, showing the preferential deposition of copper ions. A large number of nucleates with a similar growth rate of each nucleus are observed [221]. However, there are also some non-uniformity in the growth of these structures. The WCA of ELD-1.0 is a bit higher, $112.7 \pm 3.9^\circ$ with CAH of $23.9 \pm 1.1^\circ$. Figure 5.2 (c) is the SEM image of ELD-1.5. It also confirms the changing trend. The surface becomes more hierarchical with more preferential depositions formation. Some micro-flowerlike structures are distributed on the coating surface. The image also shows that these micro-flowers are featured with nano-cones of diameters ranging around several microns. Enlarging the Cu ion addition results in the hierarchical cone structures in some local areas of the ELD coating. The surface roughness R_a is $2.8 \pm 0.3 \mu\text{m}$. There are many peaks and valleys showing the hierarchical structure. The WCA of ELD-1.5 also keeps increasing, $124.8 \pm 4.4^\circ$ with CAH of $24.9 \pm 1.3^\circ$.

By considering the results, it is easy to find the surface morphology of the ELD samples is becoming rougher with higher Cu ions addition, there are more and more hierarchical structures, and the surface roughness also increases from $0.5 \pm 0.02 \mu\text{m}$ to $2.8 \pm 0.3 \mu\text{m}$. This also leads to higher WCA. For ELD-1.5, it possesses WCA of $124.8 \pm 4.4^\circ$. But high WCA may not be essential here, since the main purpose of this part of study is focused on the investigation of time-dependent wettability, so it would be proper to prepare samples with a smooth surface morphology compared to hierarchical electrodeposited Ni-Cu-P coating. Besides, the electroless deposition method is also

good for preparing coating samples with larger areas which is essential for later icephobicity study. So 0.5 g/L CuSO_4 was chosen to prepare electroless deposited Ni-Cu-P coatings in this work. The later displayed ELD sample will be prepared with 0.5 g/L CuSO_4 addition.

5.1.2 Microstructure of the as-prepared electroless-deposited Ni-Cu-P coatings

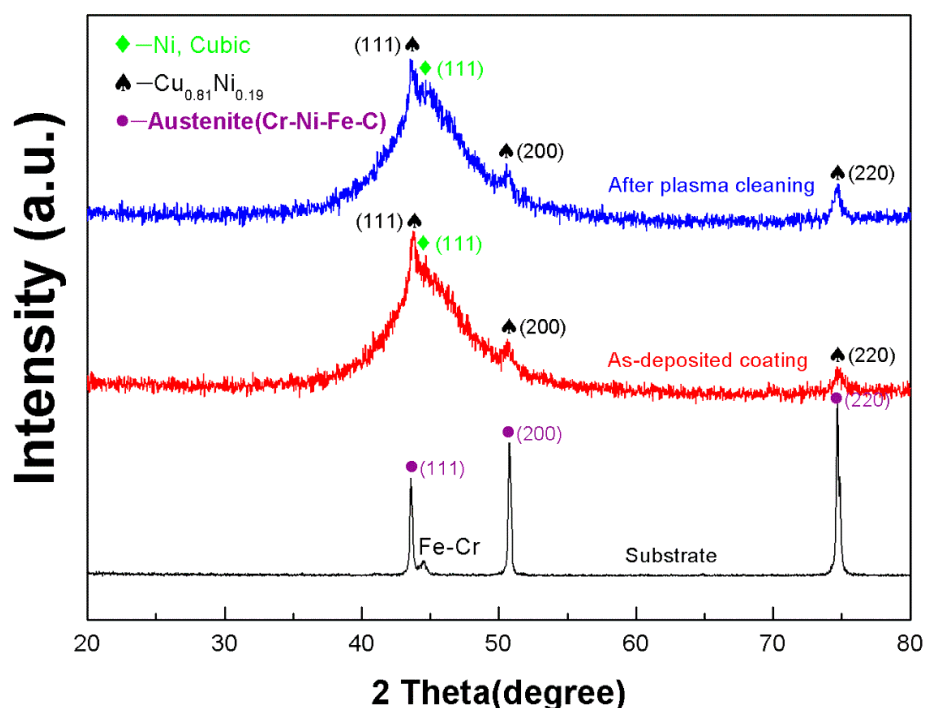


Figure 5.3 XRD patterns of 304 SS, ELD coatings before and after plasma cleaning.

Figure 5.3 shows the XRD patterns of ELD coatings before and after plasma cleaning as well as 304 SS as reference. The phosphorus in amorphous state could contribute to the broad peak positioned at 2θ of 44° of the diffraction pattern, which remains stable before and after the plasma cleaning [189]. The strong sharp peak at 2θ of 43.7° could be assigned as the (111) peak of $\text{Cu}_{0.81}\text{Ni}_{0.19}$ (JCPDS # 47-1406) [222], which indicates the predominance of copper-nickel phase. Here, $\text{Cu}_{0.81}\text{Ni}_{0.19}$ (around 3.59 Å) is the solid solution of copper in nickel, as nickel and copper are fully soluble. For the lattice parameters of pure Ni and pure Cu (JCPDS # 65-9743), they are 3.524 Å and 3.615 Å, respectively. While for $\text{Cu}_{0.81}\text{Ni}_{0.19}$, the calculated lattice parameter is between these two values. All of the diffraction patterns consist of two relatively low peaks at 2θ of

50.6 ° and 74.7 °. These peak positions are close to the (200) and (220) diffraction peaks of the austenite phase in the substrate [223]. The broader peaks indicate the existence of an additional phase with finer grain size. Regarding the ELD coatings, the peaks match with the (200) and (220) peaks of $\text{Cu}_{0.81}\text{Ni}_{0.19}$ phase. The diffraction peaks of ELD coatings at around 2θ of 44.7° matches the (111) peaks for Ni fcc at 2θ of 44.5 °. Both Ni and $\text{Cu}_{0.81}\text{Ni}_{0.19}$ phases remain unchanged with plasma treatment and no new phase forms.

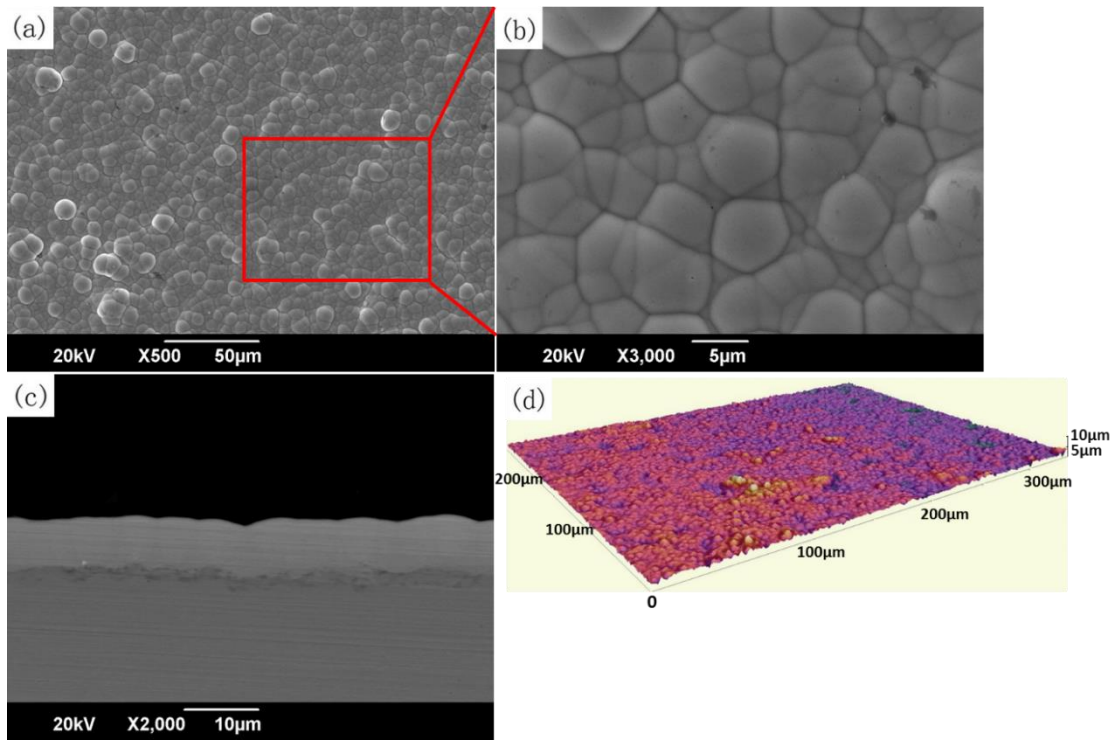


Figure 5.4 SEM images of (a) and (b) surface morphologies (c) cross-sectional (d) 3D topography images of the as-deposited ELD coating (ELD-0.5).

Figures 5.4 (a) and (b) show the SEM images of surface morphology of the as-deposited ELD coating (ELD-0.5, all of the ELD coating shown later are ELD-0.5). The surface exhibits quite a flat and smooth structure which is made up of spherical nodular deposits that are tightly connected to each other. There is also some coarse nodular structure uniformly distributed on the surface. The co-deposited copper ions play an important role in activating natural nucleation sites and retard the nodule growth by reducing the activation of additional nodule sites. In addition, the copper ion concentration is not so

high that it exhibits a uniform microstructure and component distribution [31]. At the high magnification image, the size of the nodular structures ranges from about 1 μm to 5 μm . The coating covers the substrate quite well. Figure 5.4 (c) shows the cross-sectional image of the ELD coating surface. The displayed structure is quite consistent with the surface morphology. The coating is uniform and the coating thickness is around 8 μm . The ELD coating adheres to the substrate quite well. Figure 5.4 (d) is the three-dimensional surface topography of the coatings with a selected area of $350 \times 250 \mu\text{m}$. The measured average surface roughness R_a is about $0.5 \pm 0.02 \mu\text{m}$. It is evident that extruded nodules are presented in the image. The red peaks in the 3D image represent the spherical nodules, which is indicated in the former SEM observation.

5.1.3 Reversible wettability transition

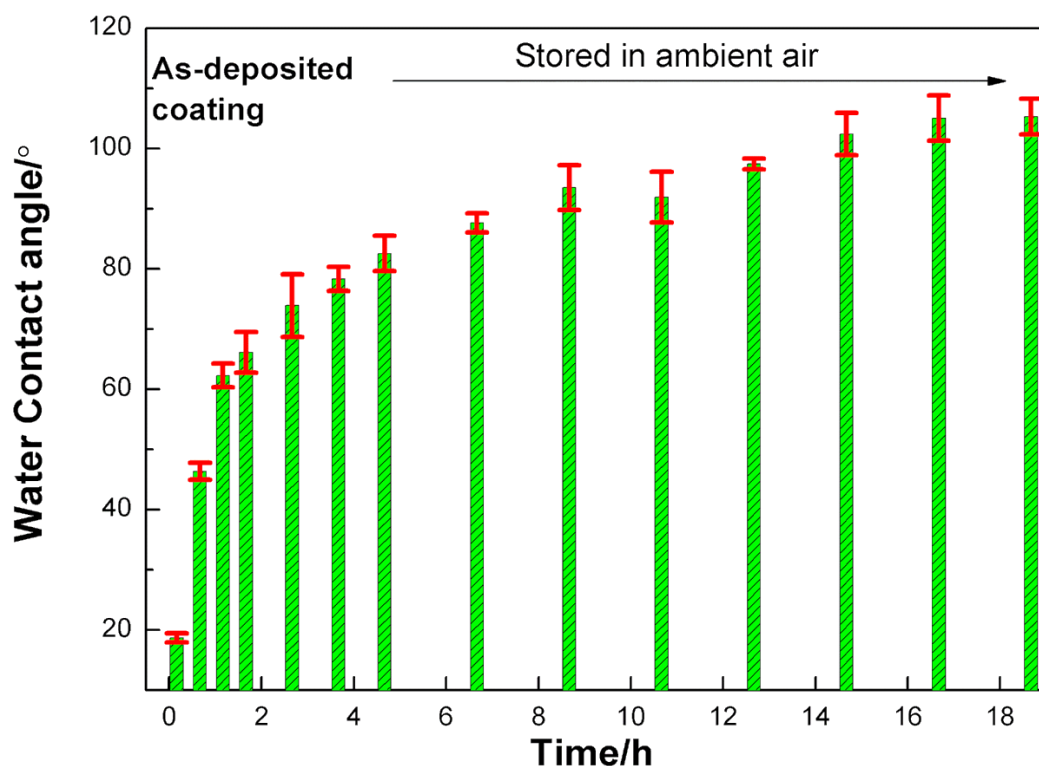


Figure 5.5 WCA change within exposure time in ambient air of the as-deposited ELD coating.

Figure 5.5 shows the WCA of the as-deposited coating with different ageing durations in ambient air. The phenomenon could also be defined as time-dependent wettability. It can be seen that the WCA increases gradually from less than 20° to around 100° after

being aged in ambient air. The change from hydrophilic state to hydrophobic state takes about 9 h. After that, the WCA continues increasing and stabilises at about 100° after 18 h. Compared to the increasing speed of ED coating (60 h for the WCA to rise to nearly 140°), the WCA increasing rate of ELD coating is much faster than that of the ED coating. The ELD coating may take less time to finish the process of replacing, inserting into and/or covering the formerly adsorbed hydrophilic groups on a smoother surface [224].

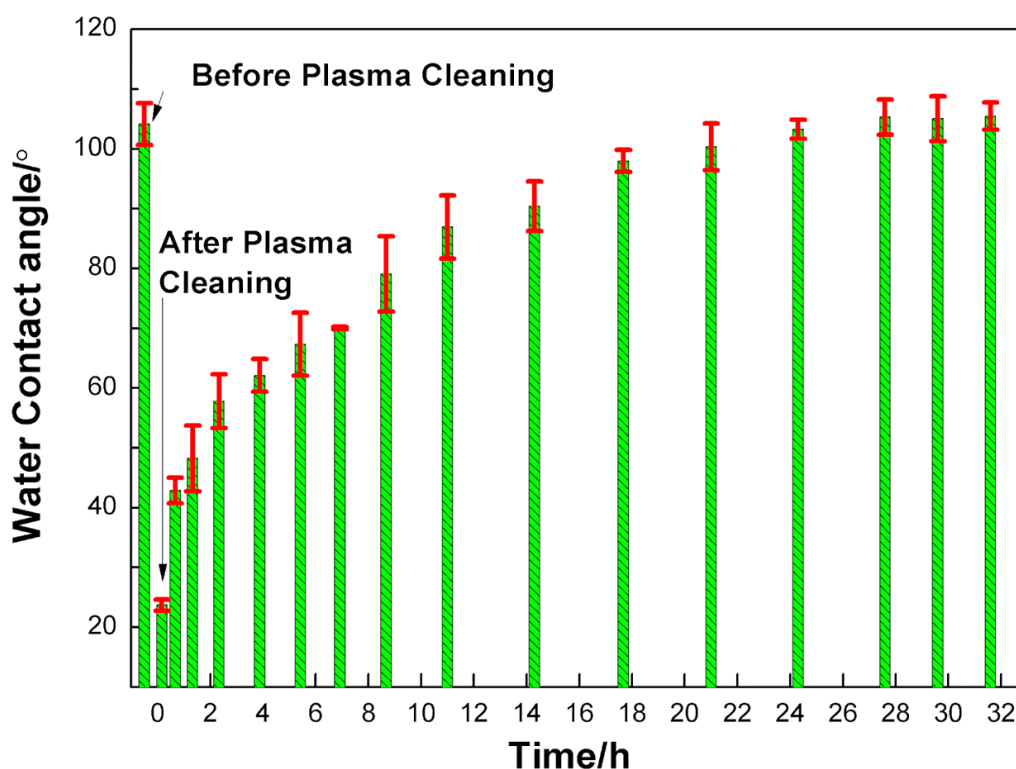


Figure 5.6 WCA change of as-deposited ELD coating before and after plasma cleaning.

Figure 5.6 elucidates the WCA evolution of as-deposited ELD coating versus plasma cleaning. The coating surfaces could be cleaned by removing the adsorbed substances via the plasma treatment, without altering the surface structural characteristics and elemental compositions. Due to the very low energy, no sputtering or etching is involved [210], the surface morphologies of ELD and ED remain unchanged. After the plasma cleaning treatment, the ELD sample is re-stored in ambient air, and the time-dependent wettability has been observed again. Just after the plasma cleaning, the WCA

suffers a sharp decrease from over 100 ° to about 20 °. After that, the measured WCA rises again and nearly recovers after around 32 h. The wettability change in ELD coating is similar to the wettability transition of the ED coating which has been previously mentioned. The removal of adsorbed airborne hydrocarbon groups could well explain the WCA decrease after plasma cleaning. The ELD coating may initially present high surface energy and demonstrate hydrophilic characteristics [194]. After being restored in ambient air, the adsorption process occurs again, so that the coatings eventually demonstrate recovery of WCA.

5.1.4 Surface analysis via XPS spectra

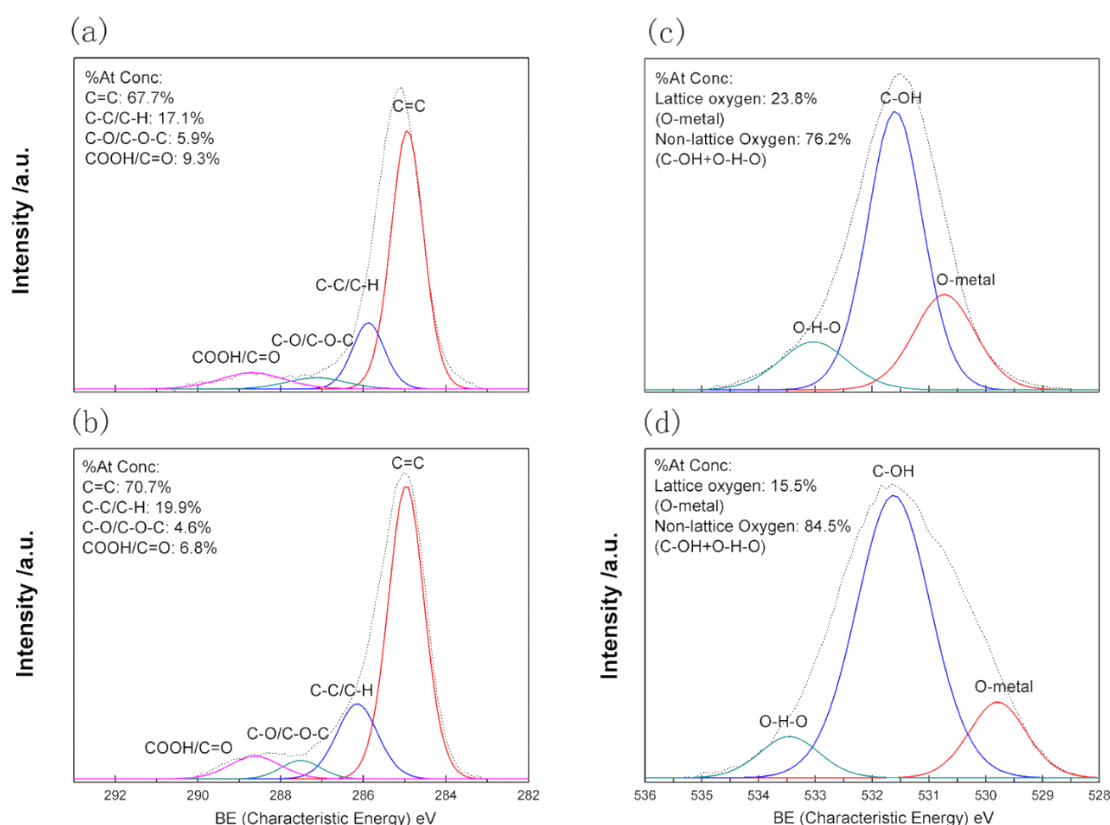


Figure 5.7 (a) and (b) C 1s XPS spectrum of the ELD coating (a) as-deposited (b) aged in ambient air; (c) and (d) O 1s XPS spectrum of the ELD coating (c) as-deposited (d) aged in ambient air.

As indicated in Figure 5.7, the high-resolution XPS analysis of C 1s and O 1s of the ELD coating, as-deposited state, and after being aged for 18 h have been shown. Both

C and O spectra have appreciable changes during the ageing process. For further analysis, the C 1s spectrum has been split into a few constituent components and investigated using the methodology proposed by Skaltsas and Modabberasl et al. [195, 196]. The C 1s main peak has been resolved into four components, including C=C, C-O/C-O-C, C-C/C-H, and COOH/C=O. C=C and C-C/C-H are the major components which are non-polar. The fitting is processed based on the constraint of the intensity ratio of all the involved components. The atomic percentages of the components are shown in Table 5.2. C=C and C-C/C-H group increase from 84.8 at% to 90.6 at%, while C-O/C-O-C and COOH/C=O reduce from 15.2 at% to 9.4 at%. The O 1s spectrum has also been split into three different components. Here, referring to the nomenclature from Wei and Khan [197, 198], C-OH and O-H-O are designated as a combination of non-lattice oxygen and O-metal groups as lattice oxygen. The lattice oxygen reduces from 23.8 at% to 15.5 at%, while the ratio of non-lattice oxygen increases from 76.2 at% to 84.5 at%. The non-lattice oxygen on the surface could also be contributed from the surface adsorption of oxygen gaseous species, e.g. hydroxyls and carbonates [199, 225]. These oxygen groups might react with the moisture on the metallic coatings, leading to the occurrence of water dissociation, affecting the bonding between water molecules, and inhibiting the formation of water clusters [226]. It is estimated that one oxygen atom may influence about 5~8 water molecules in its vicinity [227]. This could explain why the increased oxygen groups lead to the hydrophilicity.

Table 5.2 Atomic percent change of hydrocarbon groups and lattice oxygen groups versus different treatments of ELD and ED coatings.

	Detailed Condition	Hydrocarbon in all (at%)	Lattice Oxygen (at%)
ELD coating	As-deposited	84.8	23.8
	After 18 hours	90.6	13.3
	Just after Plasma cleaning	73.7	34.5
	32 hours after Plasma cleaning	89.8	25.1
ED Coating	As-deposited	78.7	27.9
	After 10 days	86.5	14.1
	Before Plasma cleaning (after 30 days)	82.3	10.3
	Just after Plasma cleaning	65.9	47.8

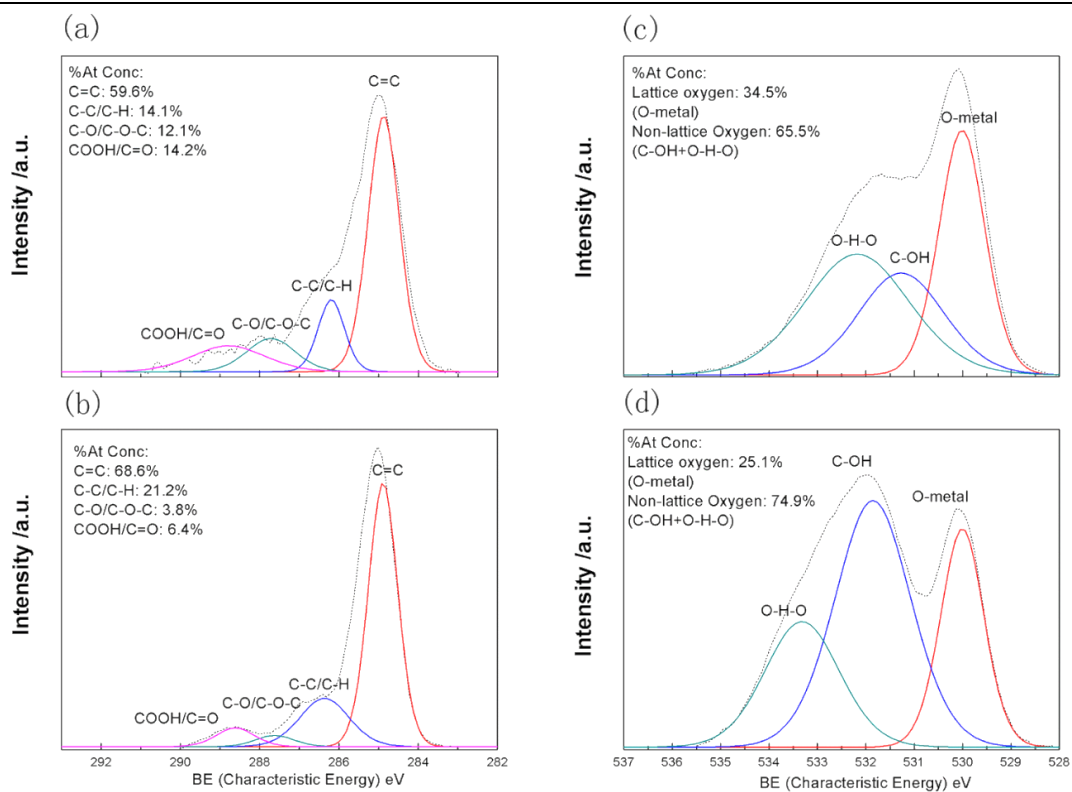


Figure 5.8 (a) and (b) C 1s XPS spectrum of the ELD coating (a) just after plasma cleaning treatment (b) aged in ambient air again; (c) and (d) O 1s XPS spectrum of the ELD coating (c) just after plasma cleaning treatment (d) aged in ambient air again.

After the plasma cleaning, the overall ratios of C=C and C-C/C-H decrease from 90.6 at% to 73.7 at%, which implies that these groups are the main parts of adsorbed airborne hydrocarbon species, as shown in Figure 5.8. The increase of COOH/C=O and C-O/C-O-C indicates that the extent of hydroxylation of the surface increases. COOH/C=O groups may work as hydrophilic groups and result in the hydrophilicity. Once an OH-rich surface forms, wettability transition of the surface could be induced via the H-bonds with OH groups and other hydrophilic groups [228, 229]. For O 1s spectrum, an obvious change also takes place after the plasma cleaning process. The lattice-oxygen rises from 13.3 at% to 34.5 at%. As a contrast, the non-lattice oxygen reduces from 86.7 at% to 65.5 at%. The increased surface oxygen may prompt the formation of hydrogen bonds with interfacial water and induce lowered wettability [198]. After being stored in air, with enough surface adsorption, the atomic percentage of hydrocarbon recovers to 89.8 at%, while the non-polar groups, C-O/C-O-C and COOH/C=O decrease from 26.3 at% to 10.2 at%, showing the re-adsorption of the hydrocarbon groups. Possible adsorption on the surface may include different types of hydrocarbons, such as methyl, alkenes, acyclic C=C, aldehyde, and so on, which come from the atmosphere [230]. The coverage of hydrocarbons would reach a certain value to turn into the hydrophobic state on micro-structured metal surfaces, it would take some time to build up the adsorption ratio of hydrocarbons (C=C and C-C/C-H) [40]. When the adsorbed hydrocarbon molecules contact water, a repulsive hydrophobic force would take into effect [94]. In addition, the ratio of lattice oxygen decreases to 25.1 at% and non-lattice oxygen increase to 74.9 at%. These polar groups are desorbed from the ELD coating surface, which reduces the surface energy again to a critical value when being stored in ambient air. The C-OH and O-H-O groups re-predominate the surface, and the hydrophobic surface is recovered. The reversible wettability transition clearly indicates the effects of hydrocarbons and lattice oxygen on the coating surface.

5.1.5 Observation of water condensation via ESEM

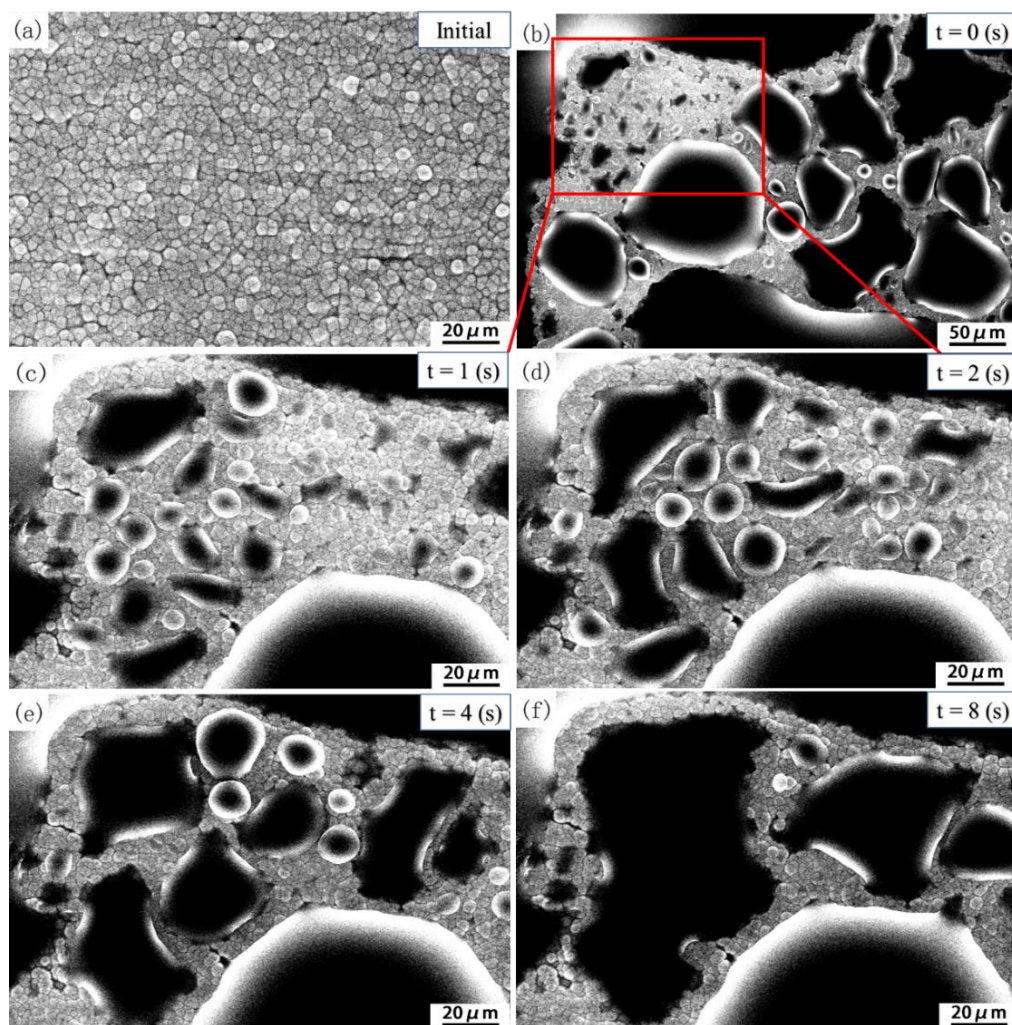


Figure 5.9 Water condensation and gathering process on ELD coating aged in ambient air (a) initial state (as-deposited) (b)-(d) timeline of water distribution (Pressure: 5.4 torrs; Temp: 3.0 °C; Humidity: 95.0%).

Figure 5.9 shows the water droplet condensation on ELD coating that has been stored in ambient air for 18 h using ESEM. Figure 5.9 (a) is the initial state of the ELD coating, while in Figure 5.9 (b), with the humidity and pressure control, the water droplet condenses and distributes randomly on the surface, and the droplet size varies across the observed surface. The water condensation starts along with the rough asperities of the coatings, which may act as the nucleation seeds for the water condensation [16]. From the area circled in red, which is enlarged in Figure 5.9 (c) - (f), water droplets form and keep growing. In the beginning, only small water droplets appear. With

increasing condensation by controlling humidity, pressure, and temperature, water droplets gradually increase and then merge together to form a big area of water. These ESEM images clearly indicate the growth and gathering of the water droplets. As the temperature decreases, micro-droplets ($\leq 1 \text{ mm}$) are randomly scattered on the coating surface, and the hydrophobic characteristics of the ELD coating could be clearly reflected. Once a dynamic equilibrium has been obtained between the micro-droplet condensation and evaporation, the static WCA could be determined, which is consistent with the measured static WCA [172].

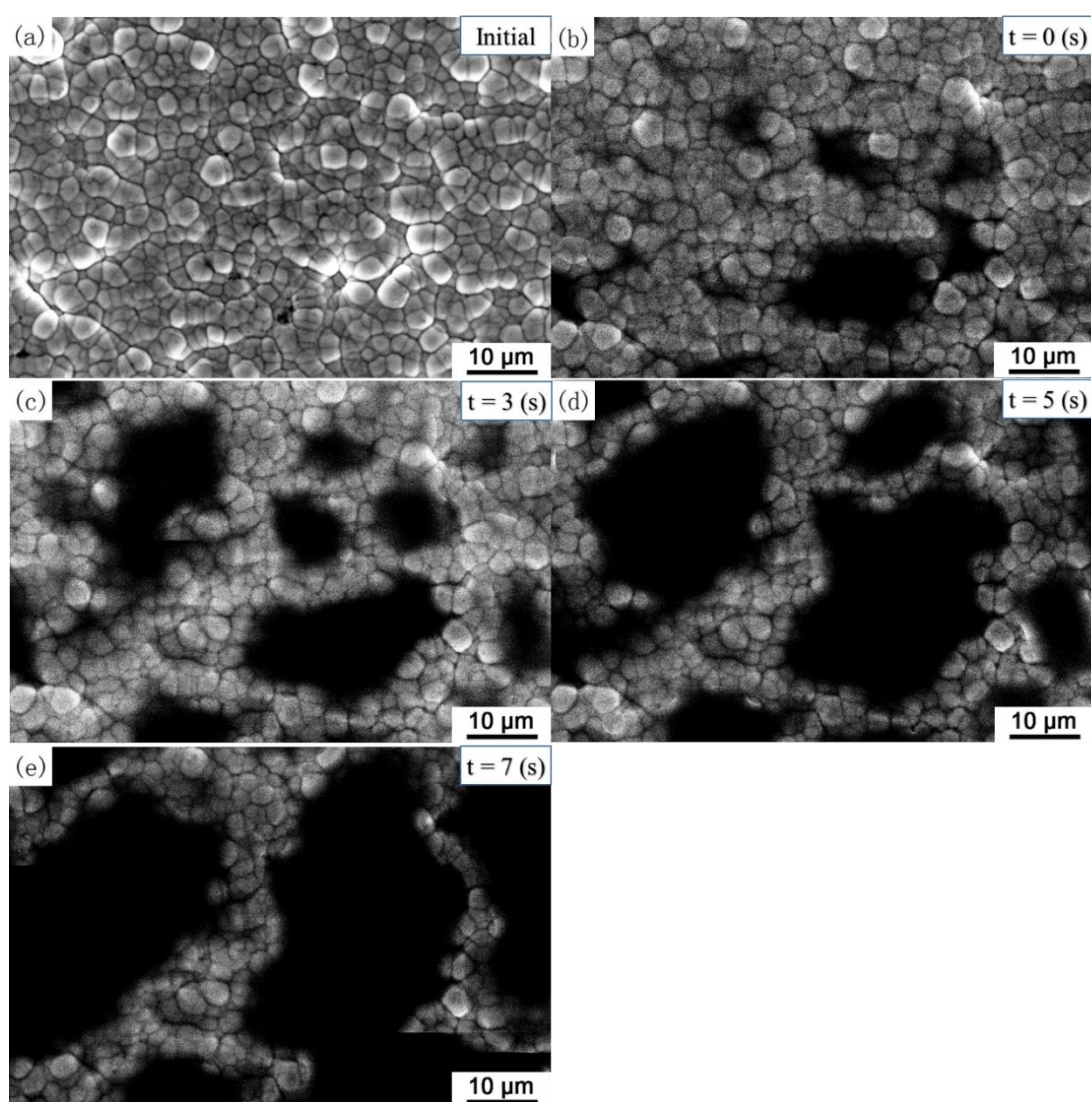


Figure 5.10 Water condensation and gathering process on ELD coating after plasma cleaning (a) Initial state (as-deposited) (b)-(e) timeline of water distribution (Pressure: 5.3 torrs; Temp: 2.0 °C; Humidity: 100%).

Figure 5.10 shows the water condensation of ELD coating immediately after plasma cleaning, which means the surface is hydrophilic with WCA lower than 20° . The major difference lies that the condensed water does not appear in the form of hydrophobic micro-droplets. The water droplets condense and merge into a big area of water, showing hydrophilic characteristics. With the continuous condensation, water would finally spread to the whole observation area.

The time-dependent wettability phenomenon was also found in the Ni-Cu-P coating system which is prepared on 304 SS substrates using electroless deposition method. The surface of the as-deposited coatings changed from hydrophilic state to hydrophobic state after ageing in ambient air. The main reason for the changing wetting behaviour could be ascribed to the adsorption of airborne hydrocarbon and the change of lattice oxygen on the coating surfaces. The two factors alter the surface energy and introduce more hydrophobic groups onto the coating surface, resulting in the changes in wetting behaviour.

5.2 Comparative Study of Time-dependent Wettability Phenomenon on Other Solid Surfaces

Airborne hydrocarbons exist almost everywhere, even inside a high-end nano-fabrication clean room. The adsorption of airborne hydrocarbons at certain surfaces could hardly be prevented in practice of wetting investigations. So the time-dependent wettability could be widely found in other material systems [40, 44]. To verify the widespread existence, related studies have also been carried out in ceramic, metallic and polymeric systems, such as 304 SS, bulk CeO_2 , PDMS layer systems.

5.2.1 Metallic surface (304 stainless steel)

Stainless steel (SS) could be a good candidate to investigate the time-dependent wettability. Several SS samples with different surface roughness (without further modification) have been chosen, including SS-smooth (as-received), SS-polish (after polishing), and SS-rough (after sandblasting). Comparison between surface morphologies, wettability changing speeds, and icephobicity evolution will be introduced later.

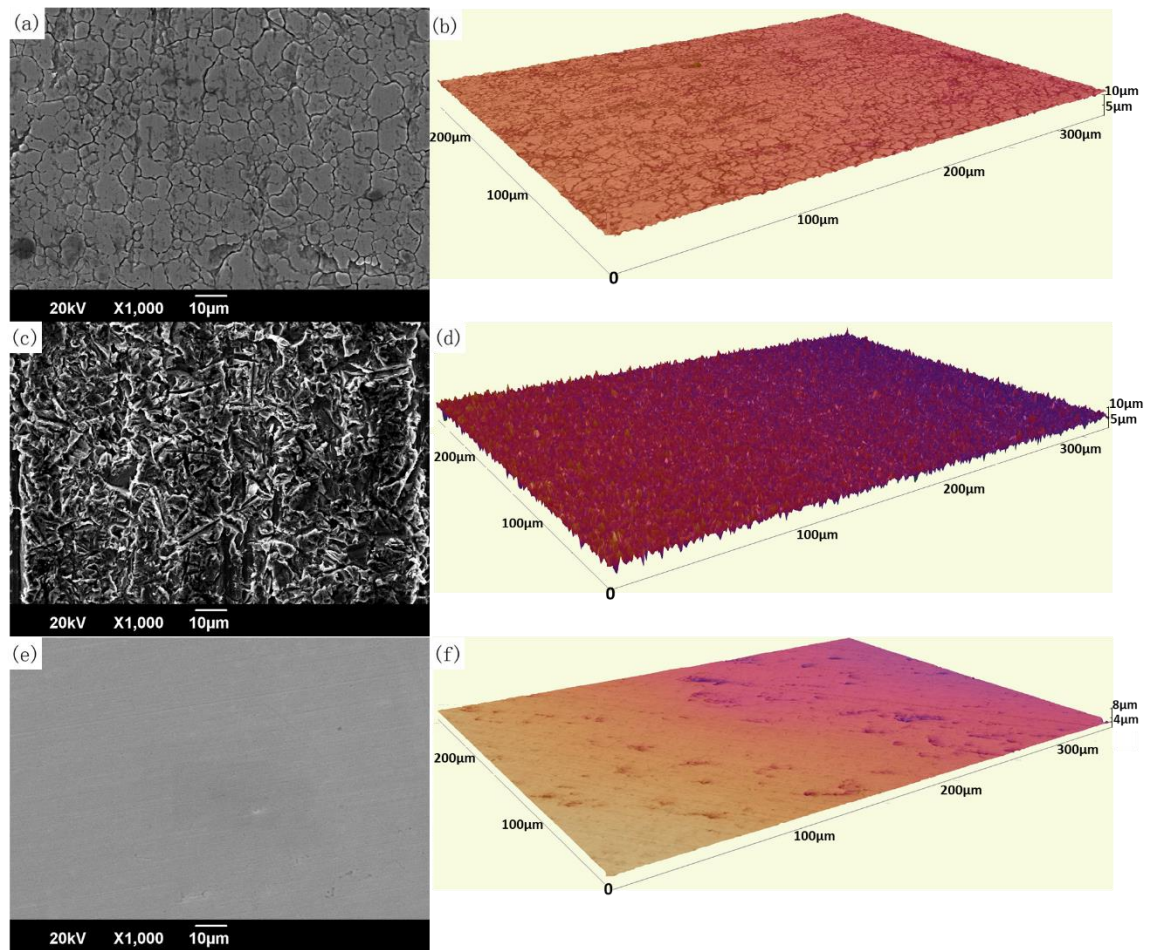


Figure 5.11 SEM images of surface morphologies (a) SS-smooth (c) SS-rough (e) SS-polish; 3D topography images of (b) SS-smooth (d) SS-rough (f) SS-polish.

Figure 5.11 shows the SEM images and 3D topography images of surface morphology for SS samples. For SS-smooth, it is in as-received state, no further operation has been carried out except cleaning. The surface is quite smooth and flat with clear grain

boundaries. No void and crack could be found from the surface. The 3D images show that the measured R_a is $0.2 \pm 0.01 \mu\text{m}$. For SS-rough, sandblasting treatment has been conducted on the samples substrate. The surface becomes much rougher than before, displaying regular hierarchical structures. The measured R_a is $1.0 \pm 0.03 \mu\text{m}$. For SS-polish, the as-received SS substrate has been polished and the surface is very smooth, with none hump or any structures. The surface roughness is only $0.06 \pm 0.01 \mu\text{m}$ after the polishing. The displayed surface is very smooth and flat. For the three samples, the chemical composition is the same, while there is a big difference in the surface specific area.

5.2.1.1 Wettability change

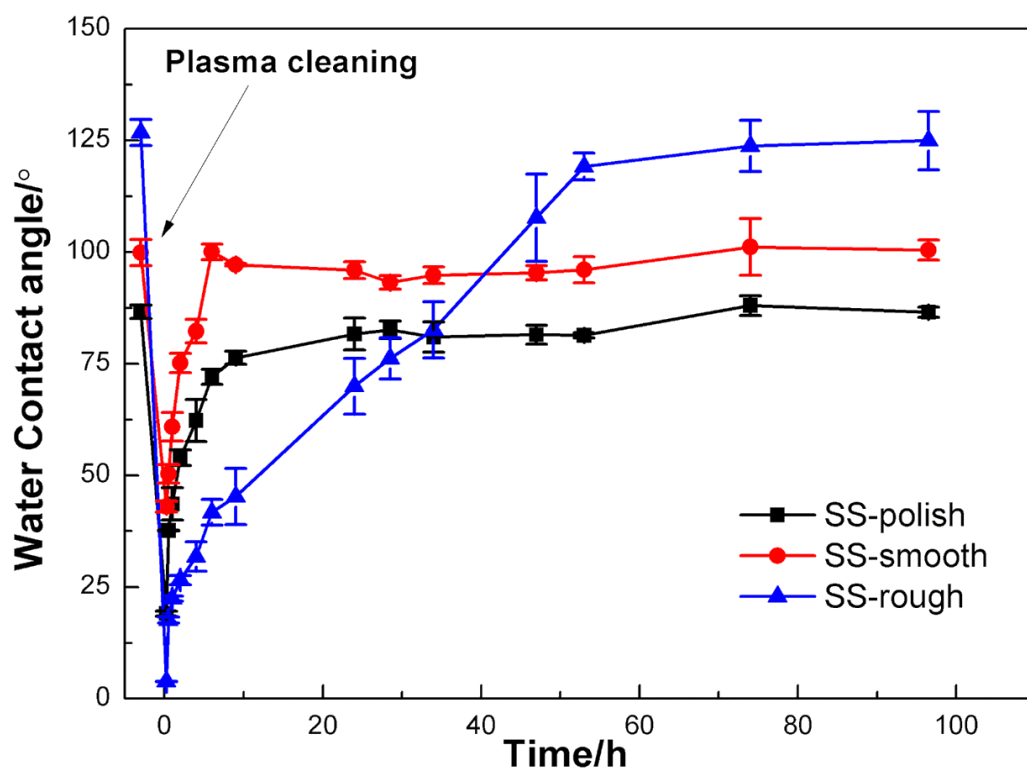


Figure 5.12 WCA evolution of SS-polish, SS-smooth, and SS-rough versus plasma cleaning treatment.

Figure 5.12 shows the WCA changing curves of the three samples before and after plasma cleaning treatment. It is obvious that all the three samples clearly show the same WCA changing trend. Their initial stabilised WCAs are different which mainly come

from the surface roughness difference. SS-rough possess the highest WCA ($126.8 \pm 2.9^\circ$), SS-smooth is a bit lower ($99.9 \pm 2.8^\circ$) and SS-polish has the lowest value (only $86.6 \pm 1.5^\circ$). The three samples show the same WCA changing trend. First, a sharp decrease takes place after the plasma cleaning, and then the WCA increases while being stored in ambient air. Another difference that could be detected is that the WCA decrease versus the plasma cleaning is also different. Sample with a smoother surface would have a smaller decrease. Because both surface morphology and surface composition contribute to WCA, the surface composition is the same while the surface roughness is different, higher surface roughness could supply larger specific area and help to form more air pockets and lead to higher WCA. When the air pockets are removed, the WCA would suffer a decrease. Another main difference lies in the WCA recovery speed. With higher surface roughness, the replacement of hydrophilic groups might be slow down during the recovery period. With the smoother surface structure and lower surface roughness, the adsorbed groups could be replaced more easily, and the surface could change back to the hydrophobic state accordingly. This is also consistent with the previous content in ED and ELD coating systems.

5.2.2 Ceramic system (Bulk CeO_2)

Apart from the metallic system, several papers have already reported that some ceramic (rare-earth oxides) surfaces also have altered wettability [231, 232]. In this part, bulk CeO_2 sample has been chosen as research object to give examples of time-dependent wettability. The freshly sputtered ceria is hydrophilic due to excess surface oxygen, and it finally becomes hydrophobic with airborne hydrocarbon adsorptions.

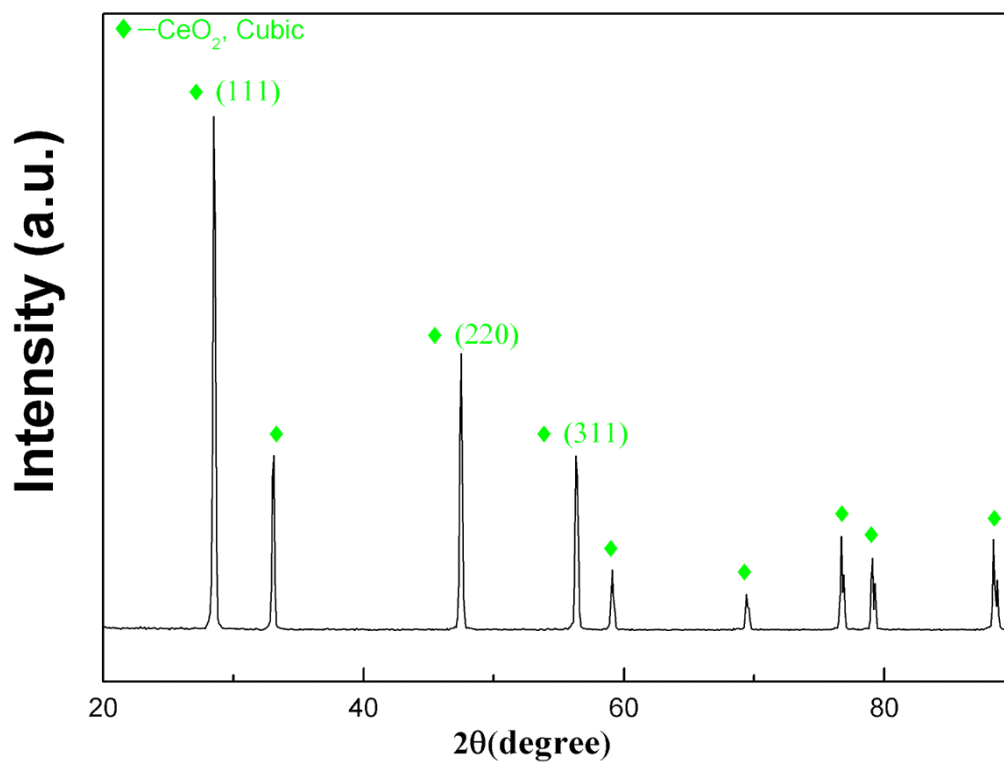


Figure 5.13 XRD pattern of as-deposited bulk CeO₂ system.

Figure 5.13 shows the XRD pattern of bulk CeO₂ sample, only a cubic CeO₂ phase (JCPDS # 34-0394) with good crystallization is identified, with three relatively high peaks (111), (220), and (311). The XRD patterns fully retain the original CeO₂ cubic phase from the feedstock powder with no phase transformation.

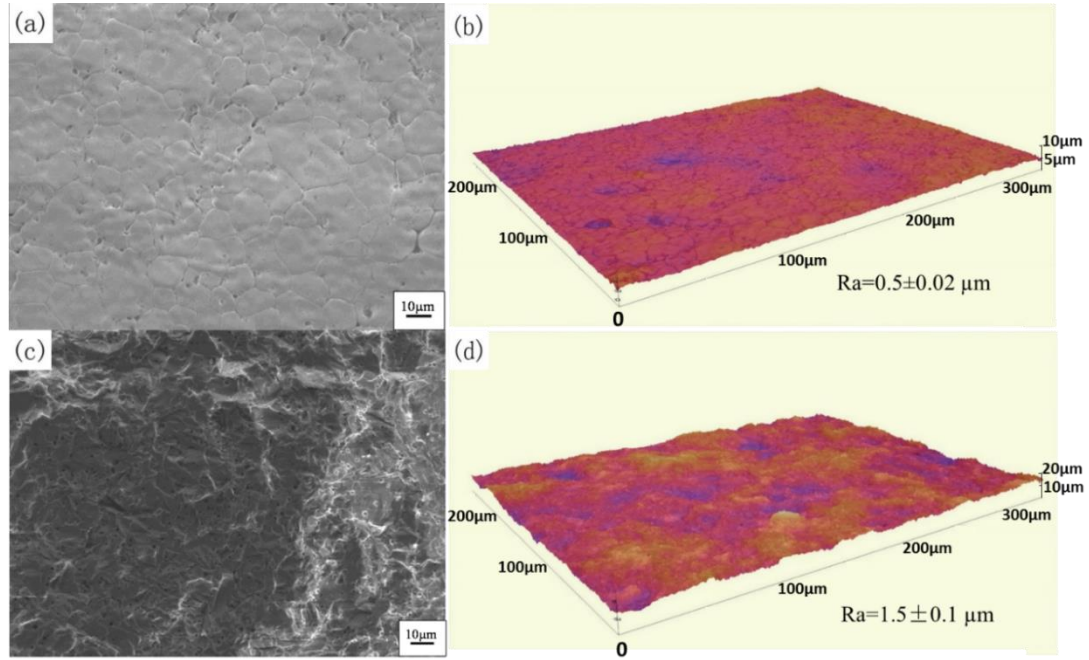


Figure 5.14 SEM images of CeO₂ bulk samples (a) surface morphologies (b) 3D topography image of the smooth surface (c) surface morphologies (d) 3D topography image of the rough surface.

Figure 5.14 shows the SEM images and 3D topography images of the surface of bulk CeO₂ samples before and after sandblasting treatment. From Figure 5.14 (a), the as-prepared surface appears rather smooth, some voids and micro cracks could be detected around the grain boundary. The reason could probably be associated with the shrinkage of the sample which is caused by dehydration process during sintering process. It can be observed that the as-prepared surface of CeO₂ bulk sample is quite smooth with an average surface roughness of about $0.5 \pm 0.02 \mu\text{m}$. Figure 5.14 (c) is the image of rough surface after sandblasting treatment. The surface becomes rough and hierarchical, voids and grain boundary can still be detected from the image. The abraded surface is ragged and cratered are formed under the impact abrasive wear effect [233]. The measured average Ra is $1.5 \pm 0.1 \mu\text{m}$ with an increase of about 200%.

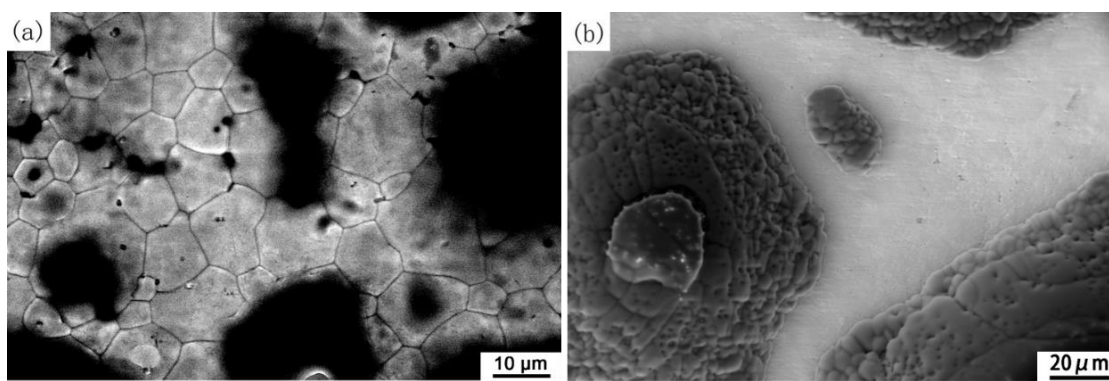


Figure 5.15 (a) Water droplet distribution (Pressure: 5.0 torrs; Temp: 2.0 °C; Humidity: 95.7%) (b) Ice distribution (Pressure: 2.6 torrs; Temp: -6.5 °C; Humidity: 91.6%) on smooth CeO₂ bulk sample.

Figure 5.15 shows the water condensation and ice formation results on the smooth bulk CeO₂ sample. Figure 5.15 (a) shows the water droplet distribution, and it appears that water is more likely to condense around the grain boundaries. The existing voids could also be easier for water droplets to condense because these places might act as wetting defects [135]. The condensed water droplet does not show any rounded shape and hydrophobic characteristics. Figure 5.15 (b) is the formed ice on the CeO₂ sample surface. Since there are few hierarchical structures on the surface, it is inferred that there could be little ice anchoring or retardation, there is also no preference for ice formation on the surface.

5.2.2.1 Wettability change

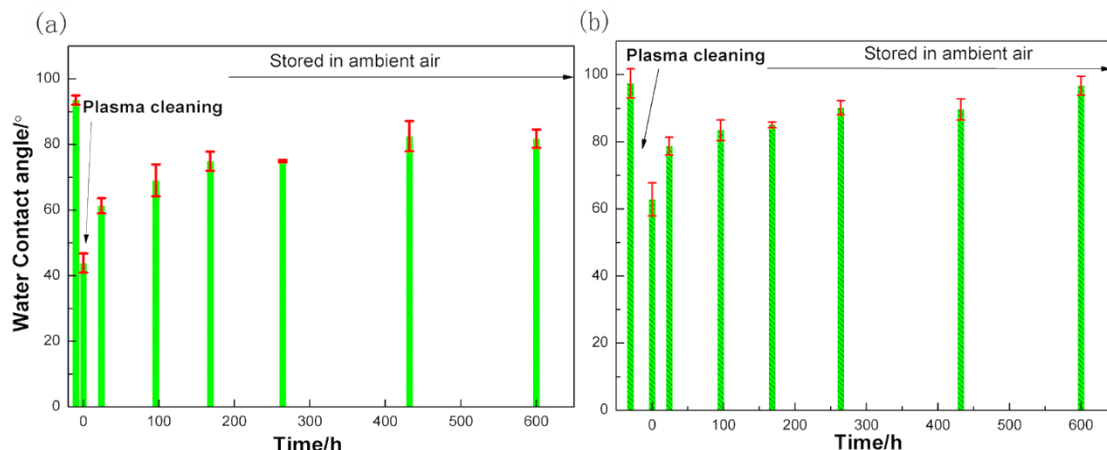


Figure 5.16 WCA change of (a) smooth bulk CeO_2 sample (b) rough bulk CeO_2 sample versus plasma cleaning treatment

Figure 5.16 shows the WCA change of smooth and rough bulk CeO_2 samples versus plasma cleaning treatment. The WCA of smooth CeO_2 decreases sharply from around 90° to only 40° after the plasma cleaning treatment. After that, it was stored in ambient air. Then the WCA increases slowly and finally reaches the previous level after around 400 h duration. This process is similar to the time-dependent wettability showing before. While for rough CeO_2 , it shows the same changing trend. The surface becomes hydrophilic and then the WCA increases to its previous level with quicker duration. The reason for the WCA decrease could be the same as the Ni-Cu-P coatings, the decreasing content of airborne hydrocarbon, and increased oxygen groups. The later storage in ambient air helps the surface to re-adsorb the airborne hydrocarbon groups and contribute to the recovered wettability. It seems that rough surface possesses faster WCA increasing speed than that on smooth surface. The reason mainly lies in the difference of surface roughness and specific surface area.

5.2.2.2 Surface analysis via XPS spectrum

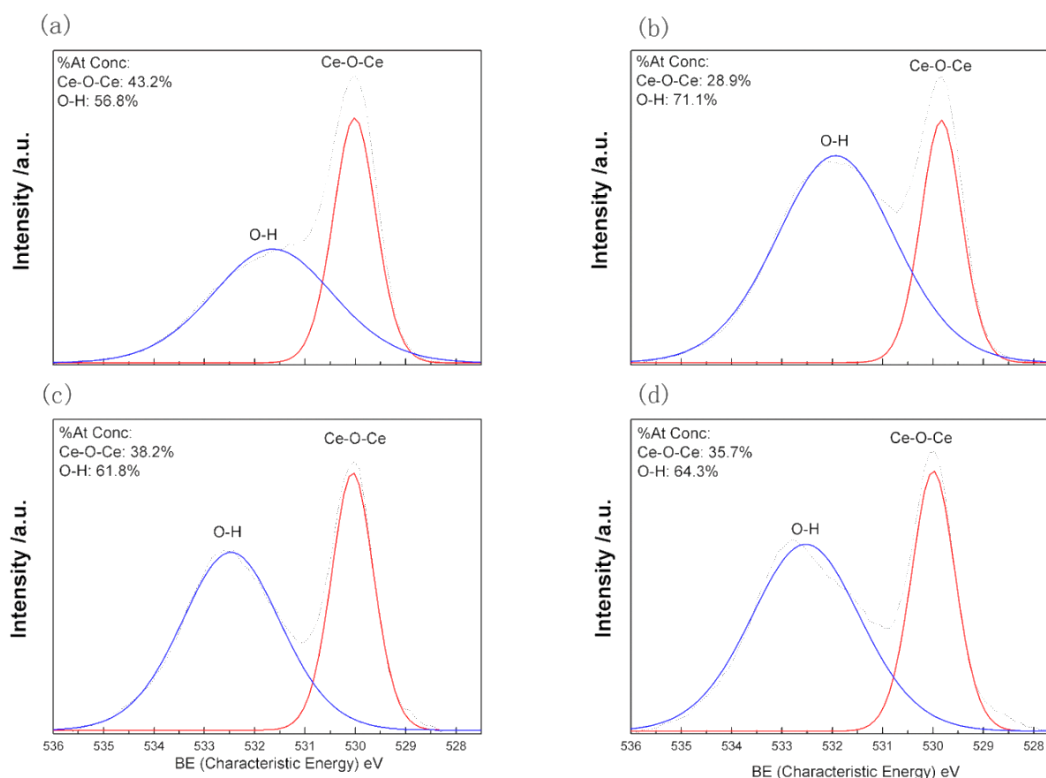


Figure 5.17 O 1s XPS spectrum change (a) just after plasma treatment and (c) stored in ambient air for enough time on rough bulk CeO_2 ; (b) just after plasma treatment and (d) stored in ambient air for enough time on smooth bulk CeO_2 .

Figure 5.17 shows the change of high resolution XPS spectra of O 1s in plasma cleaned state and aged state on both smooth and rough CeO_2 samples, respectively. The O 1s peaks in Figure 5.17 are resolved into two different components, Ce-O-Ce and O-H, which are mainly defective oxide or carbonate oxygen [198]. During the air exposure, the atomic percentage of Ce-O-Ce on smooth bulk CeO_2 increases from 28.9 at% to 35.7 at% while the O-H groups decrease from 71.1 at% to 64.3 at%, as indicated in Table 5.3. The decreased oxygen level on the surface may reduce the possibility to form hydrogen bonds with interfacial water and lead to increasing hydrophobicity.

Table 5.3 Atomic percentage change of hydrocarbon and oxygen groups versus different treatments of CeO₂ samples.

	Detailed Condition	Hydrocarbon in all (at%)	Lattice Oxygen (at%)
Smooth CeO₂ sample	As-deposited/plasma cleaned	90.4	71.1
	aged	94.1	64.3
Rough CeO₂ sample	As-deposited/plasma cleaned	89.4	56.8
	aged	93.9	61.8

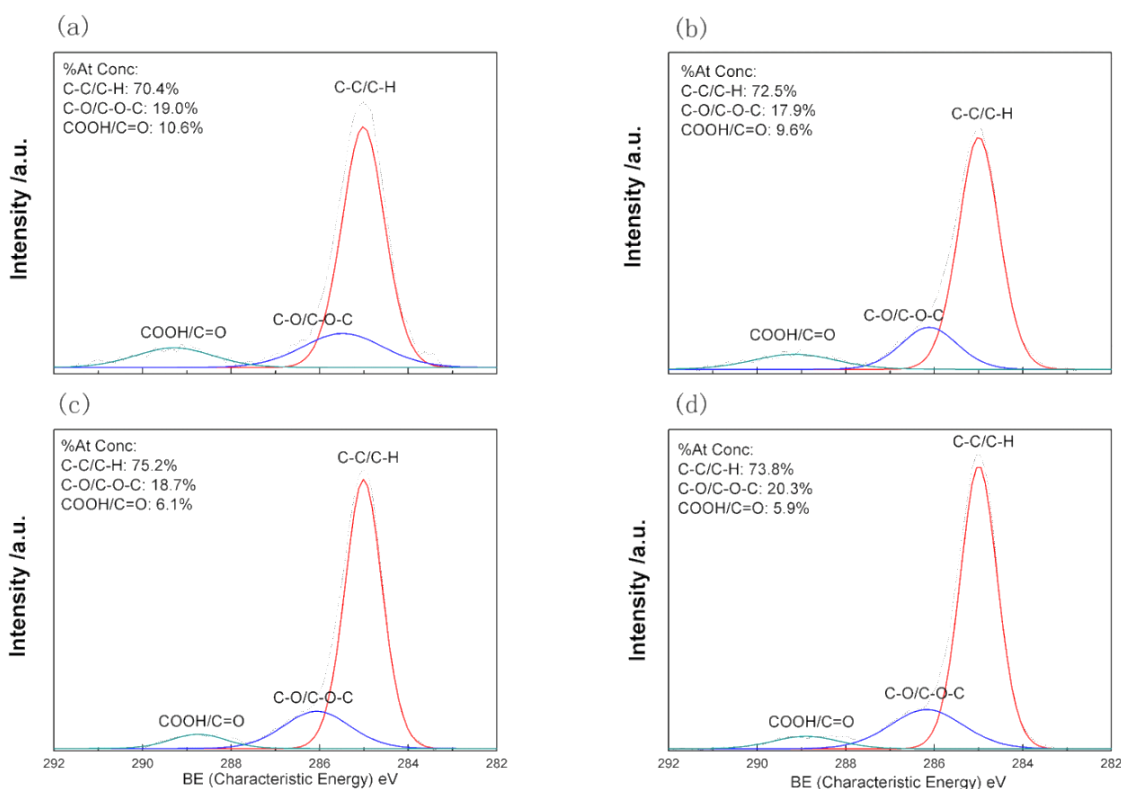


Figure 5.18 C 1s XPS spectrum change: (a) just after plasma treatment and (c) stored in ambient air for enough time on rough bulk CeO₂; (b) just after plasma treatment and (d) stored in ambient air for enough time on smooth bulk CeO₂.

The C 1s spectra as shown in Figure 5.18 are resolved into three constituent satellite peaks, C-C/C-H, C-O/C-O-C, and COOH/C=O, respectively, where hydrocarbon

groups C-C/C-H is the main part. According to the fitting results, the atomic percentage of hydrocarbon increases from 70.4 at% to 75.2 at%, indicating the accumulation of hydrocarbon layer on the CeO₂ surface. The reason for the slight shift of the carbon groups here could be similar to that in Section 4.3.2. The atomic percentage of the other two C 1s groups decrease from 29.6 at% to 24.8 at%. Compared to the former ED and ELD coatings, the reason for the smaller change in CeO₂ system may be ascribed to the unique surface chemistry of CeO₂ and lower surface specific area. The intensity of C-O/C-O-C peaks remains unchanged during the process. The small peak at around 289.0 eV is assigned to carboxyl or carbonate species [226], whose intensity decreases a little bit during air exposure. The intensity of the peaks increases sharply with air exposure, which could be ascribed to the adsorption of hydrocarbon.

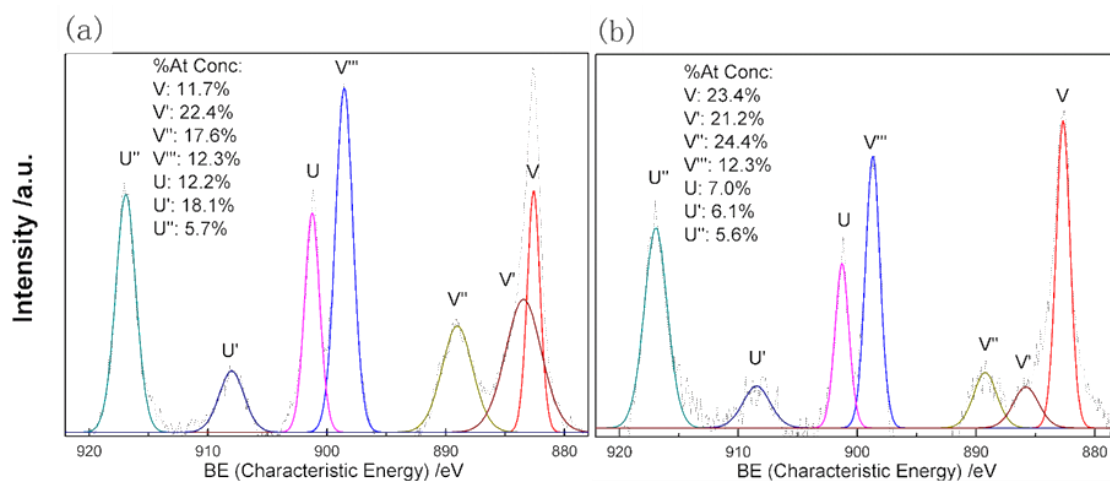


Figure 5.19 Ce 3d spectrum with constituent satellite peaks and detailed atomic percentage (a) just after plasma treatment and (b) stored in ambient air for enough time on rough bulk CeO₂.

Besides the O 1s and C 1s spectrum, the high-resolution XPS spectra for cerium (Ce 3d) obtained before and after plasma cleaning treatment is shown below in Figure 5.19. It can be seen that the peak intensity of the cerium spectrum changes considerably after the plasma cleaning treatment. The Ce 3d spectra could be designated as two multiplets for the two **3d** components (i.e., v and u) according to the nomenclature proposed by Burrough et al. [234], which correspond to the spin orbit split **3d_{5/2}** and **3d_{3/2}**, respectively. The peaks are fitted according to the constraint of the intensity ratio

between each v peak and its corresponding u peak [198]. Here, v is for $3d_{5/2}$ and u represents $3d_{3/2}$ peaks. (With exception of u_0 and v_0 which could not be resolved at their characteristic peak positions due to lack of intensity). Such surfaces release lattice oxygen to maintain a net zero dipole moment which is perpendicular to the surface, which potentially explains the reason for decreasing lattice oxygen sites after long time ageing in air. Peaks v , v'' , v''' , u , and u'' are associated with the Ce^{4+} state, while v_0 , v' , u_0 and u' are associated with the Ce^{3+} state, as demonstrated in equations (5.1) and (5.2) [235].

$$A(Ce^{3+}) = A(v_0) + A(v') + A(u_0) + A(u') \quad (5.1)$$

$$A(Ce^{4+}) = A(v) + A(v'') + A(v''') + A(u) + A(u'') \quad (5.2)$$

Here, $A(x)$ above refers to the peak area (and corresponding peak intensity) as determined from the XPS spectra.

Table 5.4 Changes of Ce^{3+} and Ce^{4+} in aged and after plasma cleaning states.

State	Ce^{3+} (at%)	Ce^{4+} (at%)
After Plasma	40.5	59.5
Aged	27.3	72.7

The atomic percent change of hydrocarbon groups and oxygen groups vary with different treatments on different bulk CeO_2 samples. The changing trend remains the same, but there is still some difference. For lattice oxygen, although the relative amount of rough CeO_2 did not always decrease, the absolute amount of the oxygen groups on the surface does decrease. The oxygen groups of the samples stored in air do have an obvious decrease, indicating the desorption of lattice oxygen groups and adsorption of hydrocarbon groups. For hydrocarbon group, there is an increasing trend on both smooth and rough samples shown from the images.

5.2.3 Polymeric system (PDMS layer)

The time-dependent wettability study has also been carried out in polymeric system. Considering that the plasma cleaning treatment has surface activation effect on polymeric system [236], another simple and easy way to remove the adsorbed airborne gaseous groups has been applied - hot water boiling treatment. The PDMS layer samples will be put into the boiling deionised water for 2 hours, and then dry them with compressed air, store in ambient air and take record of the WCA change during the whole process. The other four samples (ED, ELD, SS-smooth, and SS-rough) that have been investigated before via plasma cleaning treatment have also been tested as reference.

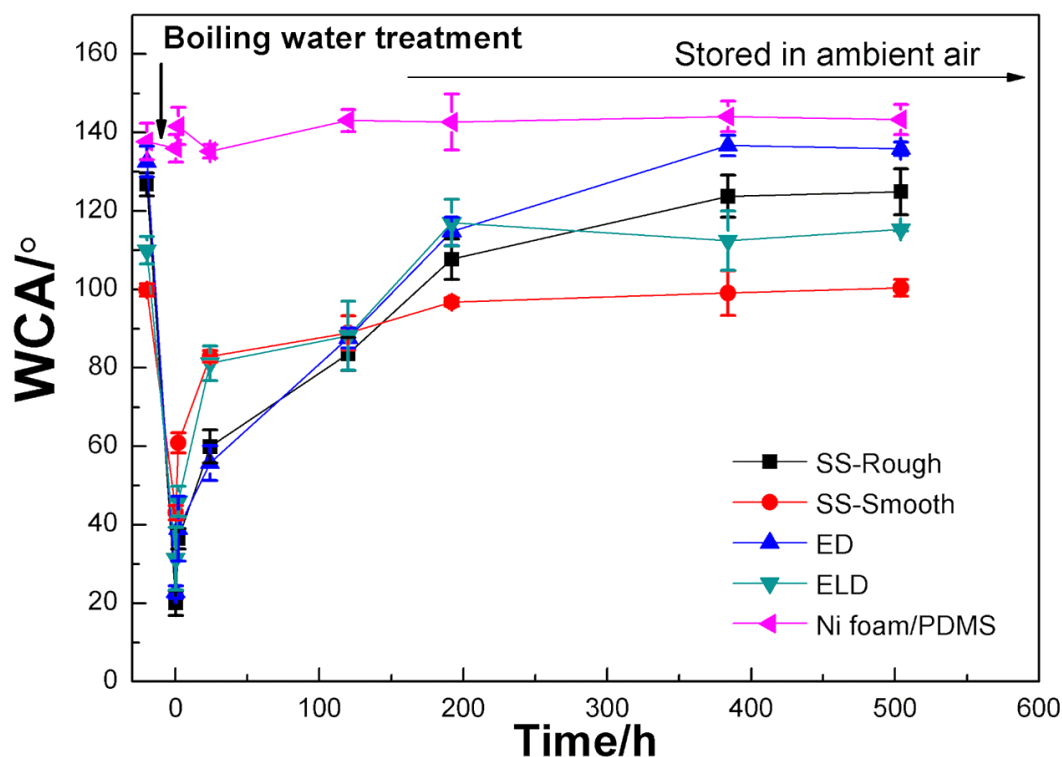


Figure 5.20 WCA evolution of different samples before and after 2 h hot water boiling treatment.

Figure 5.20 clearly shows the obvious difference of WCA change on different samples before and after boiling treatments, including SS-rough, SS-smooth, ELD, ED, and Ni foam/PDMS samples. First, the purple curve corresponds to Ni foam/PDMS samples, the WCA always remains at around 140°, and the WCA value does not change versus

the boiling treatment. By taking the existing error into consideration, it is thought that there is no change in WCA. The wettability remains at that level, indicating that there is little surface adsorption on the Ni foam/PDMS coating surface. No time-dependent wettability shows. The polymeric surface may not adsorb hydrocarbon groups. The reason may be ascribed to that the PDMS layer is chemically inert and cannot bond easily to other materials. There is no absence of polar and reactive functional groups in their structure [237]. The results also indicate the important roles of polymeric layer system in hydrophobic/icephobic applications. For other samples, the overall tendency is similar to the former results via plasma cleaning treatment, all of the WCAs decrease at first after the treatment, which means that the adsorbed substance has been removed. Then the WCA would increase gradually after being stored in ambient air. The recovered WCA values are quite close to the stabilised value of as-deposited states.

5.3 Coating Icephobicity versus Time-dependent Wettability

5.3.1 Anti-icing performance evaluation

5.3.1.1 Icing delay performance of water droplet

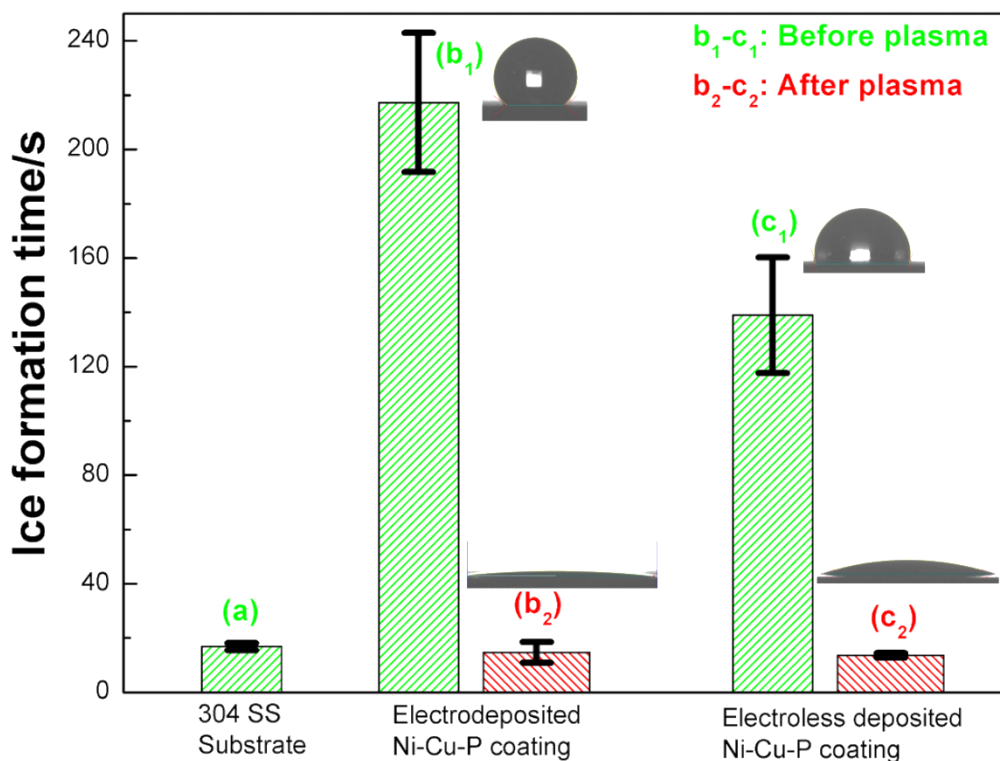


Figure 5.21 Ice formation time of 304 SS, electro-deposited, electroless-deposited Ni-Cu-P coating aged in ambient air and after plasma cleaning.

Figure 5.21 displays the icing behaviour of water droplets on ED and ELD coatings and 304 SS substrate as a reference. The pillars represent the ice formation time before and after plasma cleaning. The ice formation time is an important parameter for icephobicity evaluation because it reflects the nucleation and growth of ice on certain surfaces [165]. Longer icing time means longer ice formation delay and a better anti-icing performance. The water droplet on 304 SS cools down rapidly and ice nucleation has been triggered quickly with a duration of 16.8 ± 1.3 s. For ED and ELD samples, the ice formation is significantly delayed with respect to 304 SS, and it takes a prolonged period of time (217.3 ± 25.6 s for ED coating and 139.0 ± 21.3 s for ELD coating, respectively) to form

ice. The difference reveals that the hydrophobic state of the coatings plays an important role in the delay of ice formation compared to the bare substrates. There would be air pockets remaining on the coating surface, helping to form a solid-liquid interface with reduced contact areas which could decrease the thermal exchange [238]. Smaller water-solid contact area also leads to lower liquid-solid nucleation rate under the icing condition. The air pockets could impede thermal conduction and result in icing delay [128]. The adsorbed hydrocarbon groups may also form a thin low surface energy layer at the interface, providing an additional barrier for the water droplets, and making them difficult to penetrate into the surface pores and cavities. A composite solid-air-liquid interface would be formed, in contrast with the homogeneous solid-liquid interface [239].

Table 5.5 Wettability and surface roughness results of ED and ELD coatings.

Sample	Stabilised WCAs (°)	Advancing WCAs (°)	Receding WCAs (°)	CAH (°)	Roughness, (μm)
ED coating	143.8±3.9	144.3±3.8	138.8±3.3	5.5±0.1	3.8±0.1
ELD coating	105.1±3.5	104.9±3.4	85.6±2.3	19.3±0.3	0.5±0.1

The icing delay effect of ED coating is better than that of ELD coating. The difference in icing duration may come from the difference in surface morphology and wettability. The hierarchical structures of ED coatings could supply a larger specific area and the cavities of the hierarchical structure could create more opportunity to form air pockets at the interface and further lead to a smaller solid-liquid interface fraction. From Table 5.5, the WCA of ED is 143.8±3.9°, and CAH is 5.5±0.1°, while the WCA of ELD is 105.1±3.5°, and CAH is 19.3±0.3°. The high WCA and low CAH reduce the ice-solid contact area and the energy of the adhesive bond at the interface [167]. These factors help ED coatings with better icing delay effect than ELD coatings.

Table 5.6 The WCAs and water droplet base width versus different treatments of electroless-deposited and electro-deposited Ni-Cu-P coating.

	Detailed Condition	WCAs (°)	Water droplet base width (mm)
ED coating	Aged in air	143.8±3.9	1.9±0.1
	Just after plasma cleaning	7.8±0.1	7.6±0.3
ELD coating	Aged in air	105.1±3.8	3.2±0.1
	Just after plasma cleaning	18.6±0.2	6.7±0.2

After the plasma cleaning, the icing times of ED and ELD coatings greatly decrease to only 14.7 ± 3.8 s and 13.6 ± 0.8 s, respectively. There are several possible reasons. Firstly, with the removal of surface adsorption, the trapped air pockets will no longer form immediately after the plasma cleaning, and the solid-liquid interface fraction increases. Secondly, the WCA decreases sharply. The WCA of ED becomes $7.8 \pm 0.1^\circ$ while the value for ELD becomes $18.6 \pm 0.2^\circ$. The WCA insets in Fig 5.21 give the profiles of the water droplets on the coating surface. With the same water droplet volume, the difference in WCA and CAH could lead to the change of water droplet base width difference and the actual solid-liquid contact area. In Table 5.6, the WCA and base width of the water droplet on ED and ELD before and after plasma cleaning have been presented. The base width of ED before plasma cleaning is only 1.9 ± 0.1 mm and then it increases sharply to 7.6 ± 0.3 mm after plasma cleaning. In addition, for ELD sample, the base width increases from 3.2 ± 0.1 mm to 6.7 ± 0.2 mm. The corresponding increase of solid-liquid contact area means more thermal exchange between the solid-liquid interfaces, as well as more solid-liquid nucleation sites. Thirdly, the plasma cleaning treatment removes the adsorbed hydrocarbons on the coating surface, which previously forms a thin low surface energy layer at the interface. Then the droplet would have more direct interaction with the solid surface. The introduction of hydrophilic groups on the coating surface after the plasma cleaning might also accelerate the icing formation.

5.3.1.2 Frost growth test

The frost formation tests were carried out to evaluate the anti-icing property of different samples. Table 5.7 and Figure 5.22 display the mass of formed glaze per unit area on different samples before and after plasma cleaning treatment.

Table 5.7 Increased mass of formed glaze on different samples versus plasma cleaning treatment.

Samples	Treatment	Increased Mass (g/cm ³)
SS-rough	Before plasma cleaning	0.09 ±0.01
	After plasma cleaning	0.21 ±0.03
Electroless deposited Ni-Cu-P coating	Before plasma cleaning	0.09 ±0.01
	After plasma cleaning	0.17 ±0.02
Electrodeposited Ni-Cu-P coating	Before plasma cleaning	0.11 ±0.02
	After plasma cleaning	0.18 ±0.02

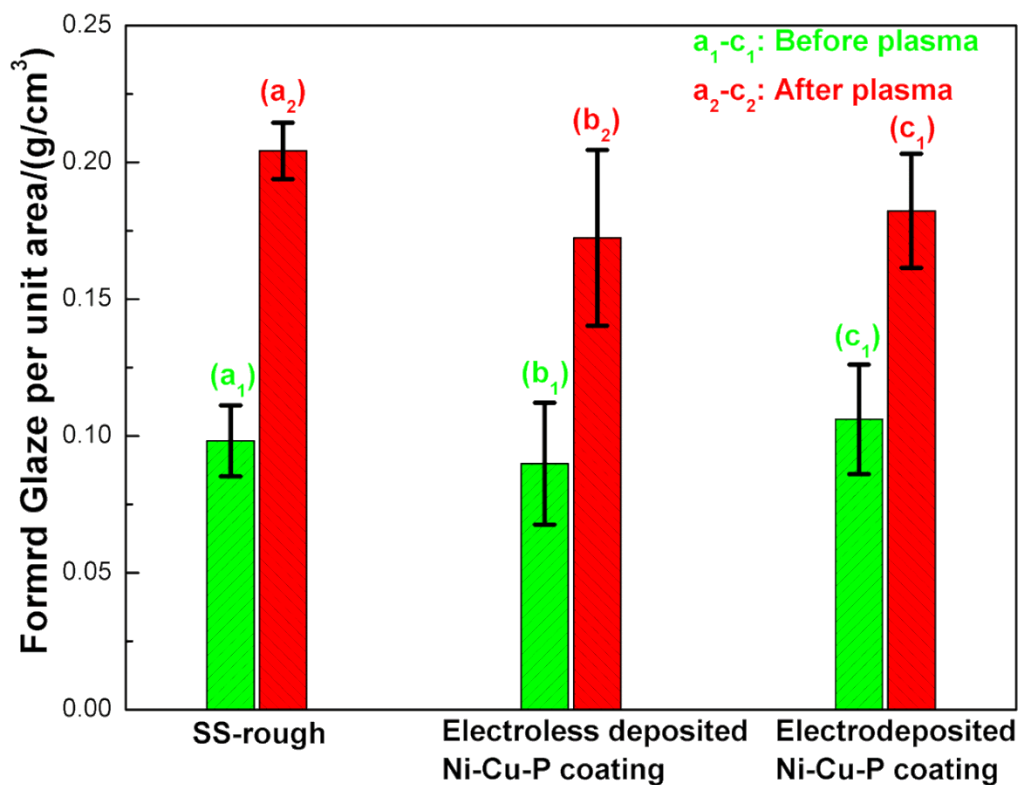


Figure 5.22 Increased mass of formed glaze on different samples before and after plasma cleaning treatment.

Figure 5.22 clearly shows that the formed glaze per unit area on different samples all have huge increase after the plasma cleaning treatment. All of the three samples obtain much more glaze after plasma cleaning. The mass of formed glaze on certain surfaces also indicates the anti-icing performance. The glaze formed per unit area on SS-rough is $0.09 \pm 0.01 \text{ g/cm}^3$. After the plasma cleaning, it increases to $0.21 \pm 0.03 \text{ g/cm}^3$ with an increase of 108%. This could be ascribed to the deteriorated hydrophobicity. The frost formation process consists of three steps: crystal growth period, frost layer growth period, and frost layer full growth period. During the crystal growth period, ice crystals formed on the cold surface. With deteriorated wettability, there would be more rod type crystal on the surface and more frost branch would form later and lead to the increased formed glaze [240]. For ELD coatings, with a quite flat surface and a relatively low surface roughness, the value is also the lowest, only $0.09 \pm 0.01 \text{ g/cm}^3$ and it is $0.17 \pm 0.02 \text{ g/cm}^3$ with an increase of 93.3% after the plasma cleaning. The lower surface specific area help with it. Then for ED coatings, the formed glaze per unit area is $0.11 \pm 0.02 \text{ g/cm}^3$, the reason could be the hierarchical structure and porosity of the structure, which supplies more specific surface area. After the plasma cleaning, it increases a lot to $0.18 \pm 0.02 \text{ g/cm}^3$, this could be ascribed to the sharply decreased WCA. The hierarchical micro-structures also lead to more glaze formation under a high humidity environment [20]. The results are consistent with the conclusion obtained before, the coating anti-icing performance also deteriorates. The reason could be the same as before, the removed air pockets and hydrocarbon groups. The increased hydrophilic groups would increase the possibilities of moisture condensation on the coating surfaces [241].

5.3.2 De-icing performance evaluation

5.3.2.1 Ice adhesion strength evaluation

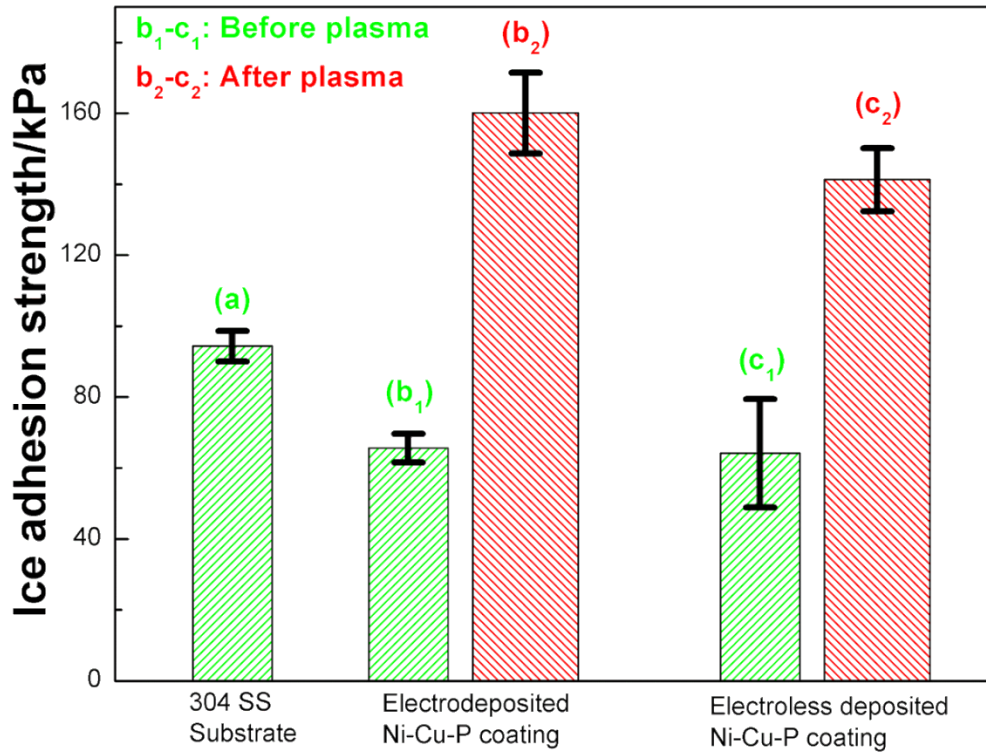


Figure 5.23 Ice adhesion results of 304 SS, electro-deposited, electroless-deposited Ni-Cu-P coating aged in ambient air and after plasma cleaning.

The determination of ice adhesion on a surface is a common approach for icephobicity assessment. Lower ice adhesion strength means easier detachment of the ice from the surface that is desirable for de-icing. Figure 5.23 shows the ice adhesion results of ED coatings, ELD coatings, and 304 SS substrate, respectively. The pillars represent the shear strengths before and after plasma cleaning. The shear strength of 304 SS substrate is 94.3 ± 4.3 kPa, while the shear strength of ED is 65.6 ± 4.0 kPa, and the shear strength of ELD is 64.1 ± 15.2 kPa. This means that the coatings could reduce the ice adhesion strength, with a decrease of around 35%. From Table 5.6, the ED coating possesses higher WCA and lower CAH than ELD coating. Lower CAH could reduce the surface contact area and the energy of the adhesive bond, which may also attribute to the formation of air pockets and help to reduce the bonding of the ice-solid interface [167]. But the surface morphology of ED coating is more hierarchical than that of ELD coating

with higher surface roughness. The maintained air pockets on the rougher structure tend to have a higher possibility of interface defects, crack nucleation, and propagation [94]. After the plasma cleaning, the shear strengths of ED and ELD coatings increase to 160.1 ± 11.3 kPa and 141.2 ± 8.9 kPa, respectively. The two coatings present a similar rising trend, displaying the deterioration of de-icing performance.

5.3.2.2 Ice removal test with heat input (Electro-thermal icing test)

The electro-thermal tests were conducted on both ED and ELD coatings. In order to study the change of de-icing performance with different wettability. There are two key experimental outputs from the electro-thermal heating test: melting time of ice cube prior to dropping and the temperature of the heating source versus heating time. The temperatures at the end of the curves indicate the difference of thermal conduction on samples during the electro-thermal heating [168]. The electro-thermal heating was conducted with input voltage of 22 V and current of 0.13 A, the starting tested temperature is -5°C .

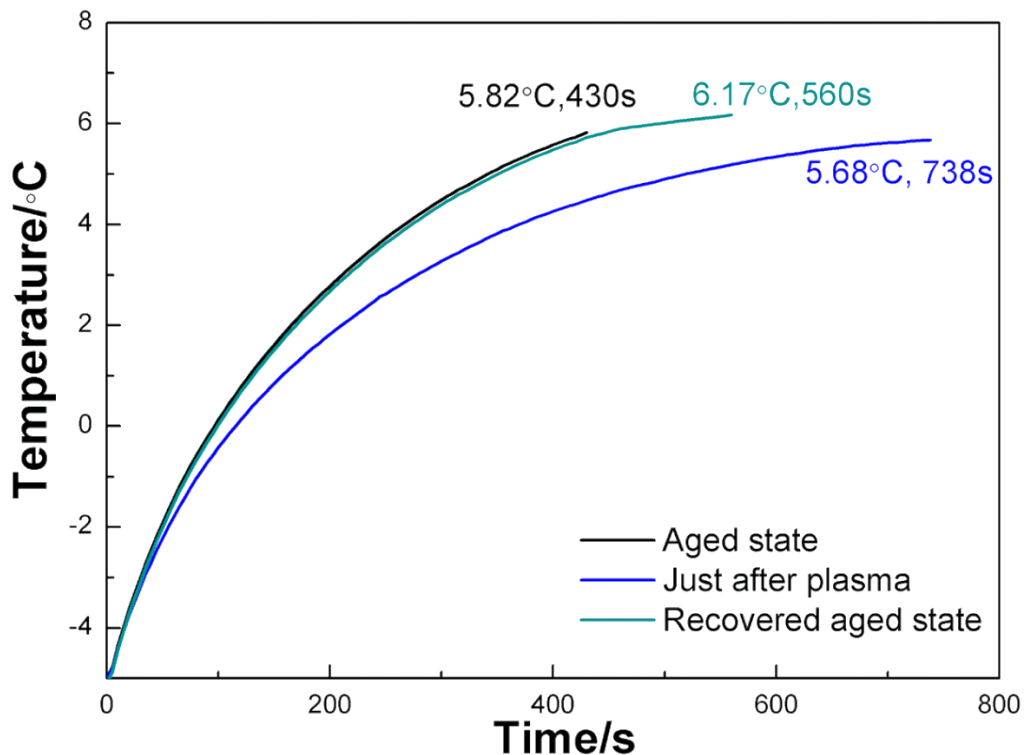


Figure 5.24 Time temperature curve of electro-thermal heating tests on electrodeposited Ni-Cu-P coating versus plasma cleaning treatment.

Figure 5.24 shows the temperature changes of the electrodeposited Ni-Cu-P coatings versus the plasma cleaning treatment. There are three plottings that correspond to the sample in different states: aged state, just after plasma cleaning and recovered aged state. The three curves are determined by the repeated electro-thermal heating tests conducted on ED sample in different states, as demonstrated in Figure 5.25. For the other time temperature curves displayed in this thesis, they are also selected based on the same methods (more data could be supplied if requested). The figure clearly shows the temperature change of samples with different WCA. For aged state samples with WCA over 140° , the detachment time is only 430 s and the detachment temperature is 5.82°C . After the plasma cleaning, the WCA decreases sharply to less than 20° . The curve also has a big change, the real-time temperature in the same duration is lower than that of the aged state, which means that the thermal transfer efficiency has been improved. With the same duration, the temperature increase becomes lower, which means less thermal energy remains and is detected by the thermocouple. It takes 738 s (with an increase of 71.6%) to make the ice detach and the final detachment temperature is 5.68°C , nearly the same as before. The low WCA leads to a broader ice contact area and further serious mechanical interlock and this results in the prolonged detachment duration. For curves of sample in recovered aged state, the WCA recovers nearly back to the former level, around 130° . Then it takes 560 s (a bit higher than before) to detach and the detachment temperature is 6.17°C . The curve nearly overlaps with the one in aged state, indicating similar thermal transfer efficiency. The reason for the increased time could still be the increased contacting ice which come from the WCA difference. Higher WCA helps the ice easier to detach from the surface.

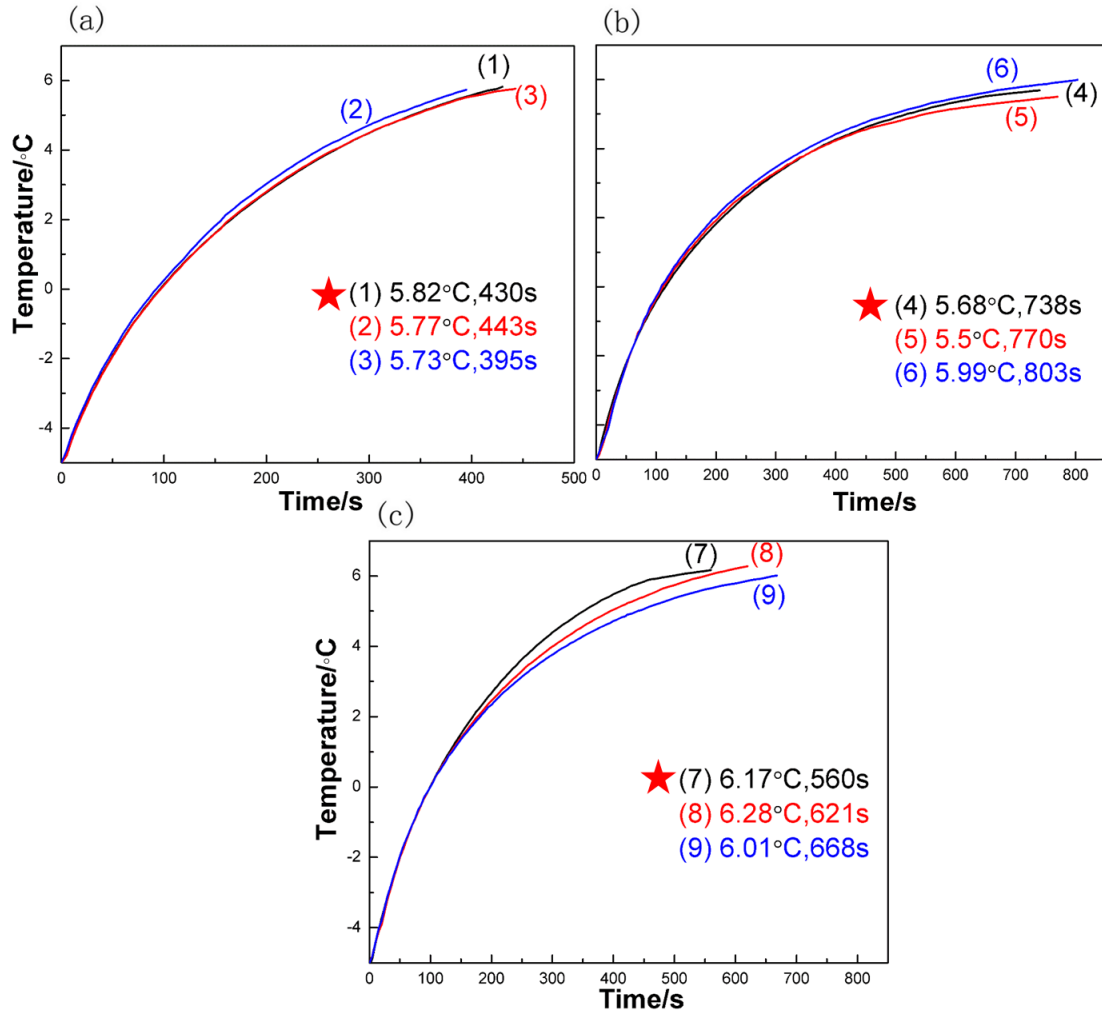


Figure 5.25 Time temperature curves of repeated electro-thermal heating tests on ED coating (a) aged state (b) just after plasma cleaning (c) recovered aged state (Here, (1)-(3) are the investigation on ED coating in aged state, the detachment duration and temperature of each separate experiments are also attached in the figure, the final chosen one have also been marked with pentastar. For sample in just after plasma cleaning, it corresponds to (4)-(6); and sample in recovered aged state it corresponds to (7)-(9)).

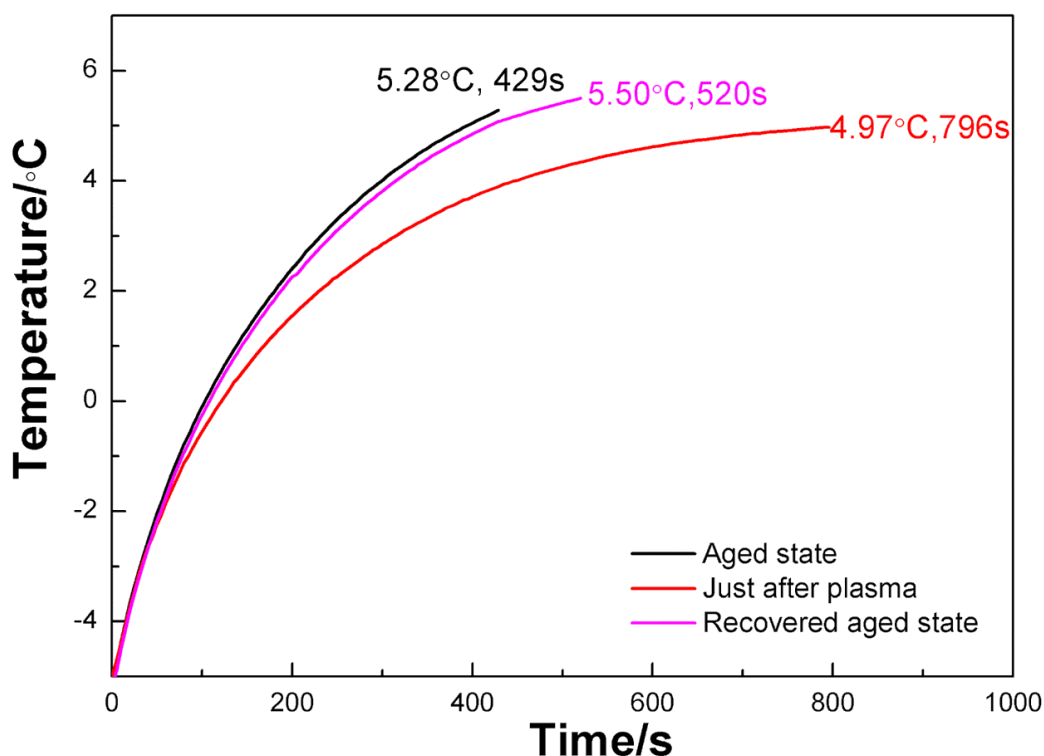


Figure 5.26 Time temperature curve of electro-thermal heating tests on ELD coating versus plasma cleaning treatment.

Similar test has also been carried out on ELD samples. Figure 5.26 shows the temperature changes of the ELD coatings versus plasma cleaning. The three curves correspond to the sample in different states: aged state (around 100 °); just after plasma (about 20 °) and recovered aged state (around 95 °). For aged state ELD sample, the detachment time is 429 s and the detachment temperature is 5.28 °C. After the plasma cleaning, the WCA decrease to less than 20 °, the thermal transfer efficiency also changes, showing the same trend as ED. It takes 796 s (with an increase of 85.5%) to make the ice detach and the final detachment temperature is 4.97 °C. The reason here could be consistent with the one in ED coatings. For recovered aged state, it takes 520 s (a bit higher than before) to detach and the detachment temperature is 5.50 °C. The curve is very close to the one of aged state, indicating a similar thermal transfer efficiency. The two similar figures confirm that the time-dependent wettability could affect the de-icing performance of samples.

The electro-thermal tests had also been carried out on SS-smooth, SS-polish, and SS-

rough samples. The temperature changing curves are shown in Figure 5.27, Figure 5.28, and Figure 5.29, respectively.

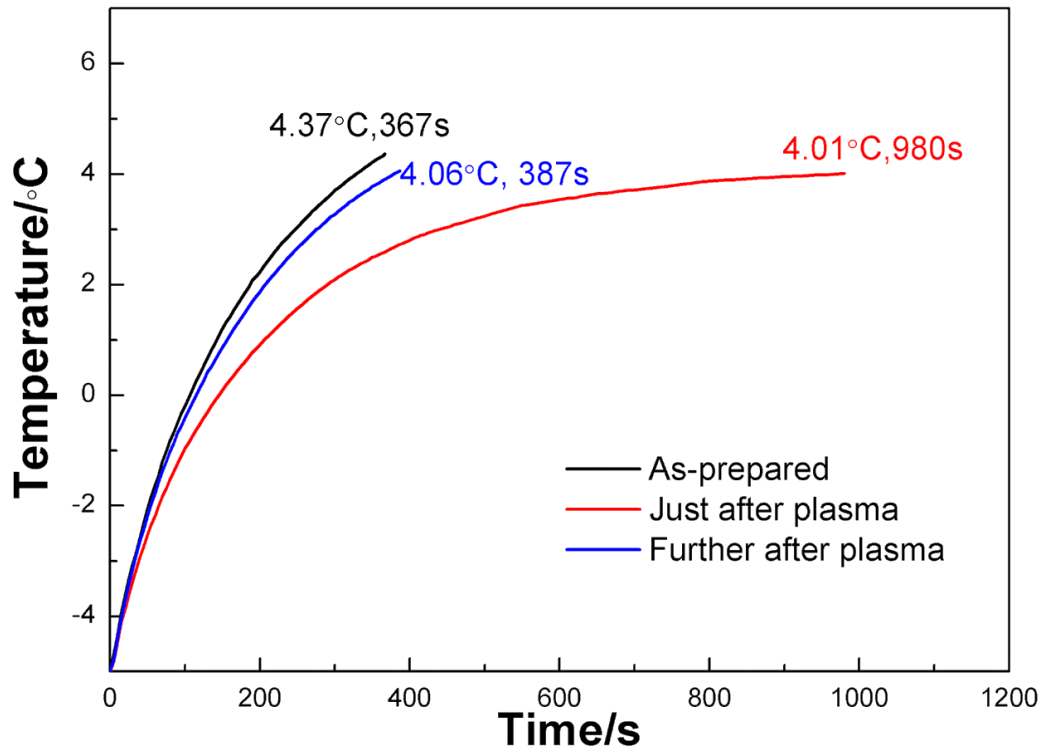


Figure 5.27 Time temperature curve of electro-thermal tests on SS-smooth versus plasma cleaning treatment.

Figure 5.27 shows the temperature changes of SS-smooth versus plasma cleaning treatment. The three curves correspond to aged state, just after plasma cleaning and further after plasma (10h recovery in ambient air). The figure clearly shows the temperature change of samples with different WCAs. For samples in aged state (with WCA over 100 °), the detachment time is only 367 s and the detachment temperature is 4.37 °C. For samples just after the plasma cleaning, the WCA decreases to less than 40 °. The real-time temperature of the curve is much lower than that of the aged state, which means that the thermal transfer efficiency has been improved. With the same duration, the temperature increase becomes lower. It indicates that more energy input has been transferred to the sample-ice interface in unit time, showing a lower thermal resistance. The overall thermal resistance of the samples would be reduced because the former existing surface structures which are filled by air (the thermal conductivity of air is only

0.024 W•m/K at 0°C) would be replaced by water (the thermal conductivity of water is 0.55 W•m/K at 0 °C). But another change is that it takes as long as 980 s (with an increase of 167%) to make the ice detach. The reason here could be ascribed to that there is more adequate contact between the ice and sample surface, more contacting ice can form due to the larger base width of the water droplet which comes from the low WCA, leading to more ice-coating contacting points. More serious mechanical interlock ice would form and the ice adhesion strength becomes larger [242], so it would take much more time to make the ice detach, more energy needs to be inputted and adsorbed to melt the contacting ice. For curves of recovered aged state, the WCA recovers back to the former level, around 100°. Then it takes 387 s (a bit higher than before) to detach and the detachment temperature is 4.06 °C. The curve is quite close to the former one, indicating similar thermal transfer efficiency and volume of contacting ice. The reason for the increased time could still be the not-fully recovered WCA and more contacting ice.

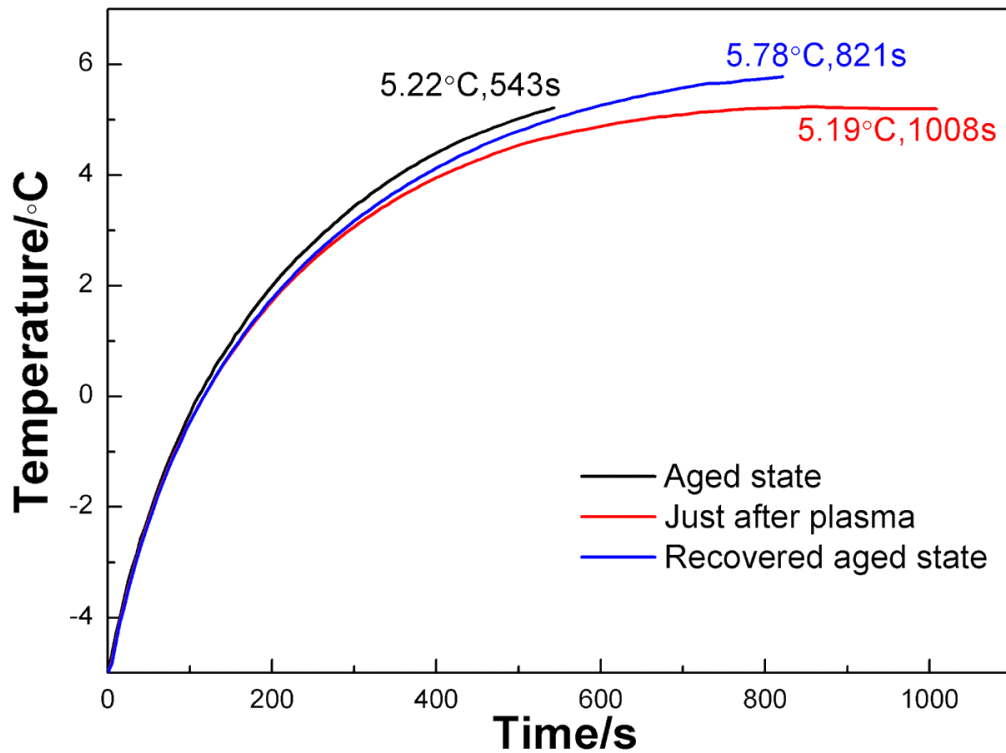


Figure 5.28 Time temperature curve of electro-thermal tests on SS-rough substrate versus plasma cleaning treatment.

Figure 5.28 shows the temperature changes of SS-rough versus plasma cleaning treatment. There are three plottings that correspond to aged state (with WCA over 130 °), just after plasma (less than 10 °) and recovered aged state (around 110 °). The detachment duration and the temperature of sample in just after plasma state are 5.22 °C and 543 s, respectively. The detachment duration is the shortest, the real-time temperature is also the highest. It indicates less mechanical interlock ice at the interface due to the better hydrophobicity, and also relatively poor thermal transfer efficiency which mainly comes from the hierarchical surface structure filled by air. For sample just after plasma cleaning, they change to 5.19 °C and 1008 s, respectively. The real-time temperature of the line is the lowest comparing to the other two, showing more thermal energy can be transferred in the same duration. It indicates the highest thermal transfer efficiency. The reason is quite similar to the one in SS-smooth, the filling of water droplet replace the air inside the existing hierarchical surface structure. But low WCA leads to broader ice contact area and further serious mechanical interlock and this results in the prolonged detach duration. It would cost much more time for the ice to melt and detach. The WCA of the samples keeps recovering. The detachment time of the sample in recovered aged state is 821 s and the detachment temperature is 5.78 °C. Recovered WCA would help with the generation of air pockets and minimize the amount of contacting ice and mechanical interlock and also the decrease of thermal transfer. With the WCA keep recovering, the temperature changing curve would finally overlap with the one in aged state.

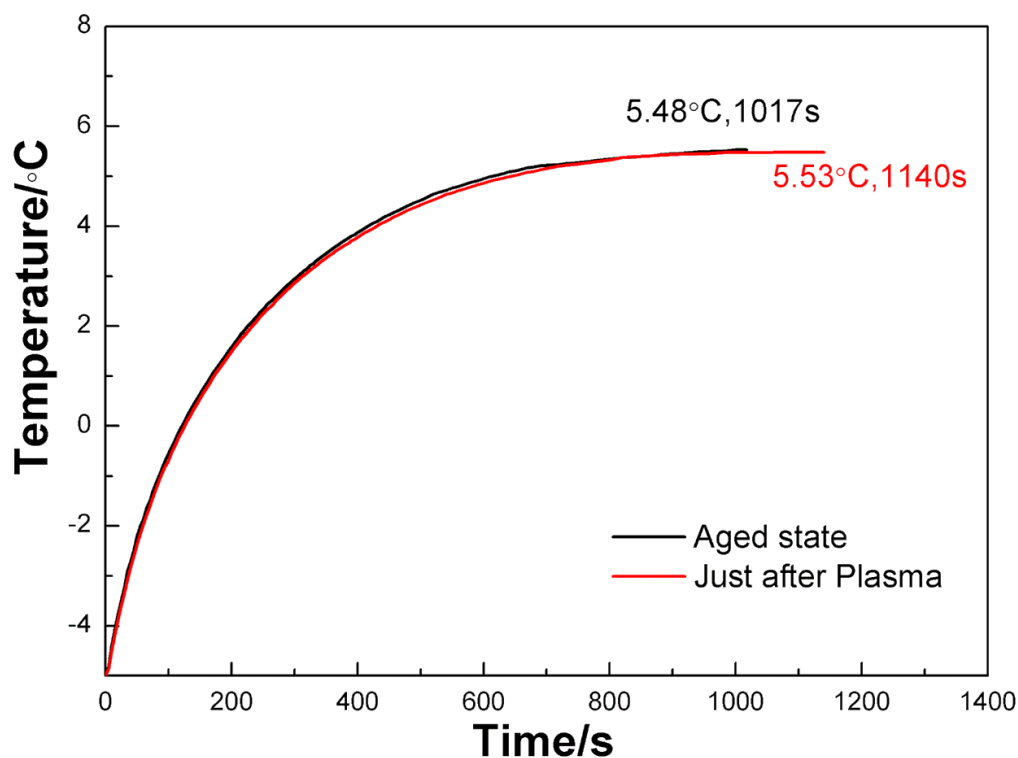


Figure 5.29 Time temperature curve of electro-thermal tests on SS-polish versus plasma cleaning treatment.

Figure 5.29 shows the temperature changes of SS-polish versus plasma cleaning. There are two plottings that correspond to aged state (a bit lower than 90 °) and after plasma cleaning states (about 40 °). The detachment duration and temperature in aged state are 5.48 °C and 1017 s, respectively. Just after the plasma cleaning treatment, it becomes 5.53 °C and 1140 s. There is no big difference between the two curves, they nearly overlap. The results indicate that even the WCA of SS-polish decreases a lot after the plasma cleaning, the samples have similar thermal transfer efficiency and the ice detachment process does not prolong a lot, while the volume of contacting ice may increase a little bit due to the adsorbed hydrophilic groups [224].

From the displayed results, it could be obtained that the ice detachment on certain surfaces using electro-thermal heating is quite complex, it depends on the amount of existing contacting ice and the thermal transfer efficiency. If the surface roughness on a certain surface is low enough, the ice detachment and the sample thermal transfer efficiency would not be affected obviously even the surface wettability changes a lot.

5.3.3 Icing formation process observation with different wettability via ESEM

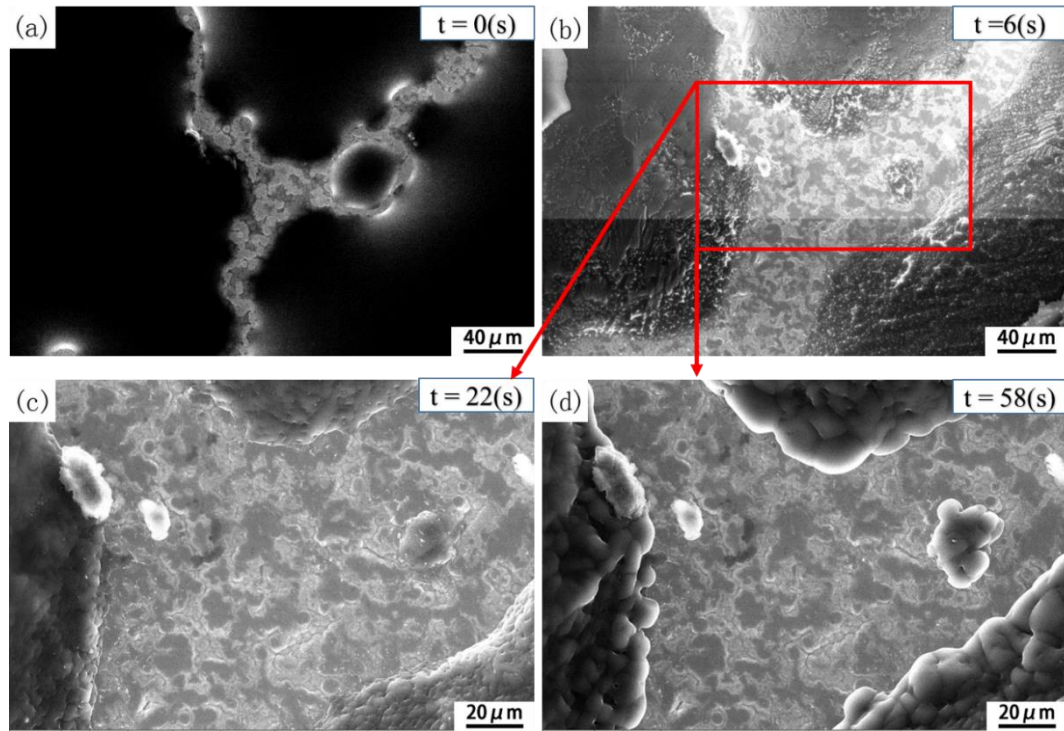


Figure 5.30 (a) Water droplet distribution (supercooled state) (Pressure: 2.3 torrs; Temp: -8.2°C ; Humidity: 92.4%) (b)-(d) Ice formation and growth process on electroless deposited Ni-Cu-P coating in aged state (Pressure: 2.2-2.4 torrs; Temp: -7.0 to -5.7°C ; Humidity: 85.7 to 89.8%).

Figure 5.30 demonstrates the water droplet distribution and icing process on ELD coating before plasma cleaning. By controlling the conditions in the chamber, water will condense on the surface, as indicated in Figure 5.30 (a). There is a large area of water on the surface. Most of the surface parts have been covered by water, the formed spherical water droplet also demonstrate the coating hydrophobicity. The temperature is already lower than 0°C . Ice could easily be obtained when reaching an ice trigger point. From Figure 5.30 (b), ice formation could be detected. There is a sharp change in both temperature and humidity at the moment when ice form. The chamber temperature (the observation chamber of ESEM) suffers a sudden increase due to the great deal of latent heat generated in the phase transformation from water to ice. The boundary of ice block is not very clear. There is a small ice nucleus in the circled area, the ice keeps growing with proper humidity and pressure. The enlarged images in Figure 5.30 (c)-(d) clearly show the ice growth process on ELD coatings in aged state.

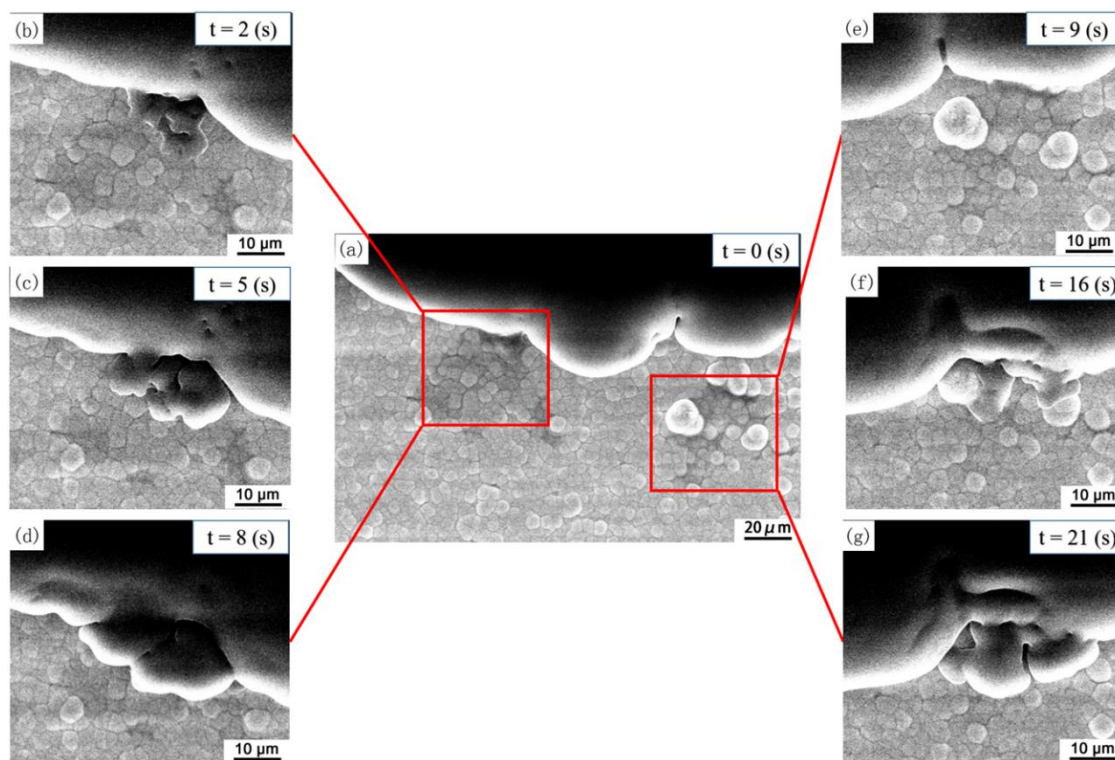


Figure 5.31 Ice formation process on electroless-deposited Ni-Cu-P coating after plasma cleaning (a) initial state (b)-(d) ice growth from the left part (e)-(g) ice growth from the right part (Pressure: 3.1 torrs; Temp: $-4.5\text{ }^{\circ}\text{C}$; Humidity: 92.3%).

Figure 5.31 demonstrates the in-situ icing process of ELD coating after plasma cleaning. Further to the water condensation, the temperature has been adjusted to below $0\text{ }^{\circ}\text{C}$, the surface rough structures of the coating provide the ice nucleation sites, where ice nucleation and growth occur [243]. In Figure 5.31 (a), there is a large piece of ice block formed on the coating. There are two dark areas (marked in red) in the images. The dark area is water that remains in these lower parts surrounded by some nodular structures. Indicated by the enlarged Figure 5.31 (b)-(d) and (e)-(g), these areas will induce the formation of ice earlier than other places. The water remaining areas seem to have preferences in icing, and the formed ice would also have strong links with the substrate, in which ice interlock could be found. This could explain the high ice adhesion strength in Figure 5.23. With proper humidity and pressure, the ice would keep growing.

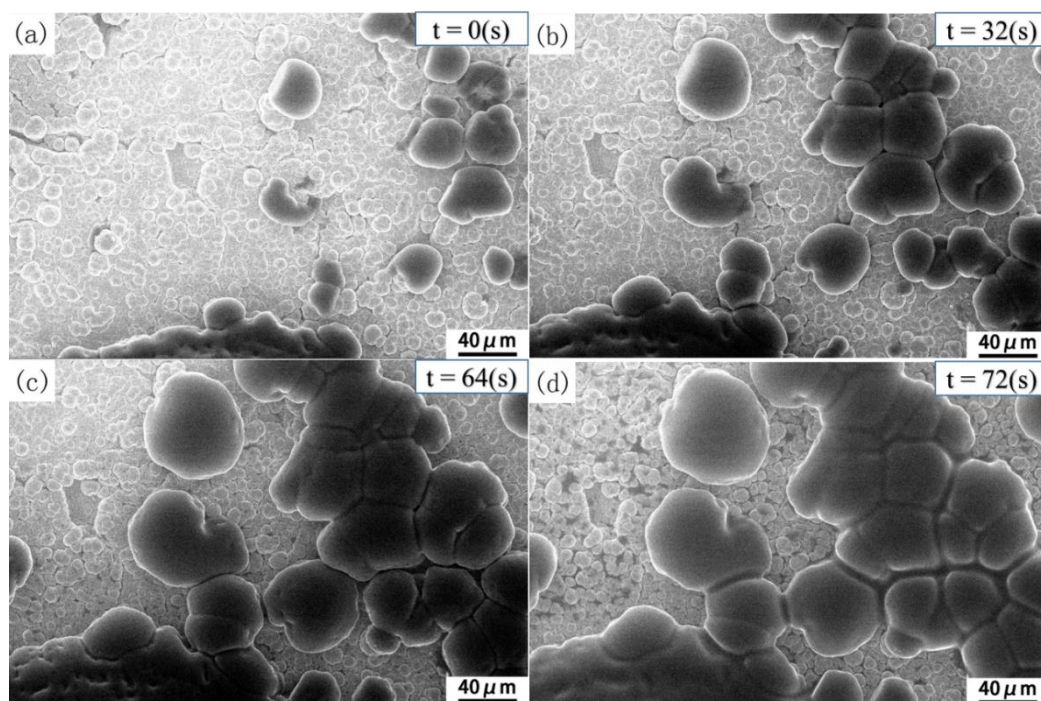


Figure 5.32 (a)-(c) Ice growth process on electrodeposited Ni-Cu-P coating in aged state (Pressure: 4.2-4.6 torrs; Temp: -1-0 °C; Humidity: 91.5-92.8%) (d) Co-existence of water and ice on electrodeposited Ni-Cu-P coating (Pressure: 4.2 torrs; Temp: 0.2 °C; Humidity: 92.0%).

Figure 5.32 shows the icing process on ED coating in aged state. The formation of ice blocks on the surface is clearly observed. From Figure 5.32 (a), it seems that ice forms in the microscopic pores and show some preferences in icing areas (around the hierarchical structures), not indiscriminate over the coating surface. For Figure 5.32 (b) and (c), the ice growth mainly takes place between some of the hierarchical structures. With ice keep growing, they would finally contact with each other. Figure 5.32 (d) shows a special state, the temperature is over 0 °C, the remaining ice seems to melt and water can also be observed, indicating an ice-water co-existence state. Because of the hydrophobic state and existing air pockets, the formed ice would have less contact and mechanical interlock with the coating surface, it is also consistent with the low value of ice adhesion strength.

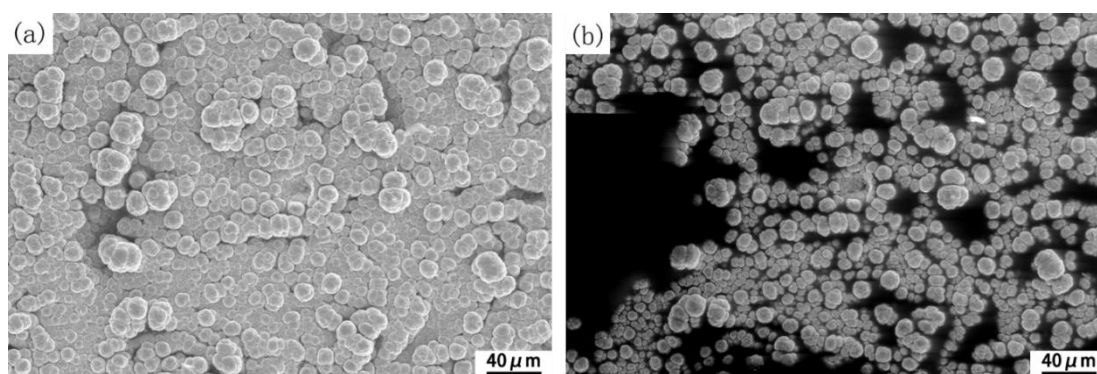


Figure 5.33 (a) Initial state (b) Water condensation and gathering process on electro-deposited Ni-Cu-P coating after plasma cleaning (Pressure: 5.3 torrs; Temp: 2.5 °C; Humidity: 96.7%).

Figure 5.33 (a) and (b) show the water droplet condensation on ED coating after plasma cleaning with WCA around 10°. Due to the hydrophilic surface, the formed water droplet could not stand on the cauli-flower like structures and would rather gather at the lower area. Since the WCA is low and the adsorbed hydrocarbon has been removed, air pockets no longer form. The wetting state also changes into the Wenzel's mode. There is no hydrophobic characteristic of micro droplets. The hierarchical structure with peaks and valleys are inundated with the condensed droplets.

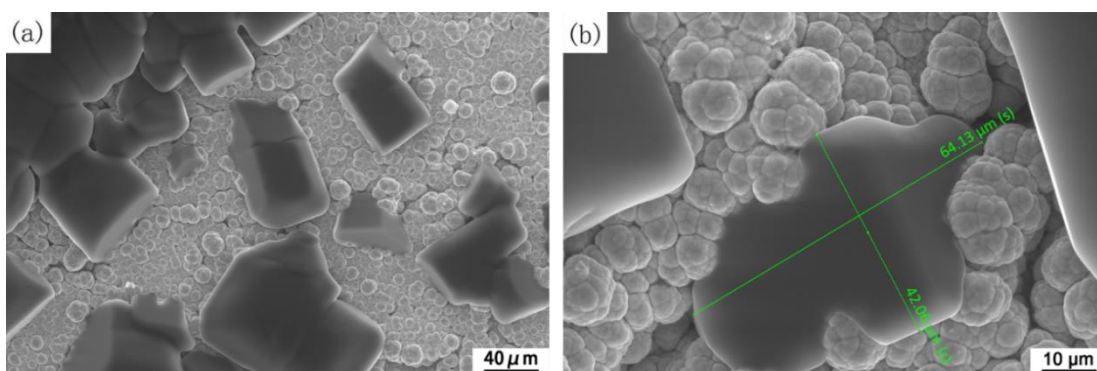


Figure 5.34 (a) Ice formation (b) formed interlocked ice cube between hierarchical structure on electro-deposited Ni-Cu-P coating after plasma cleaning (Pressure: 2.6 torrs; Temp: -6.6 °C; Humidity: 94.0%).

Figure 5.34 (a) shows the ice distribution on ED coating after plasma cleaning. The formation of ice blocks on the surface is clearly observed. From Figure 5.34 (b), it seems that some ice forms in the microscopic pores and the preferred icing area is

around the hierarchical structures [244]. The ice build-up between the hierarchical structures could generate mechanical interlock. It is expected that the value of ice adhesion strength would be much higher for coating with the interlocked ice block, as indicated in Figure 5.23.

Through the detailed study of ED and ELD samples versus plasma cleaning treatment, the wettability will decrease after the plasma cleaning, the surface free energy become lower. The anti-icing and de-icing performance will also deteriorate significantly after the surface gaseous absorption has been removed. The results confirm the significant effect of time-dependent wettability on coating icephobicity.

5.4 Discussion

5.4.1 Effect of gaseous adsorption on surface free energy

The surface free energy of certain coatings is a very important parameter. Coating with low surface energy would minimize the molecular interaction between water and coating surface [245]. As is known, the surface free energy may be defined as the increase in Gibbs free energy of the whole system per unit increase in the interfacial area [246]. It is conceived that the adsorption of airborne hydrocarbon and de-adsorption of lattice oxygen groups onto the Ni-Cu-P coating surfaces would affect the surface energy. The surface free energy on both ED and ELD coatings in the aged state and plasma cleaned state has been measured and calculated using Owens-Wendt method.

Using Owens-Wendt method, it is assumed that the total surface free energy γ_S is the sum of the two components: dispersion components γ_S^D and polar components γ_S^P . The Owens-Wendt model is representing as equations (5.3) and (5.4) below [176, 177]:

$$\frac{1}{2}(1 + \cos \theta)\gamma_L = (\gamma_S^D \cdot \gamma_L^D)^{1/2} + (\gamma_S^P \cdot \gamma_L^P)^{1/2} \quad (5.3)$$

$$\gamma_S = \gamma_S^D + \gamma_S^P \quad (5.4)$$

where θ is the contact angle between the liquid droplets and coating surface, γ_L is the liquid total surface tension, γ_L^D is the dispersion component of liquid surface tension, γ_L^P is the polar component of liquid surface tension. γ_S^D is the dispersion component of the solid surface free energy. γ_S^P is the polar component of the solid surface free energy. γ_S is the total surface free energy of the solid surface.

All of the value of surface tension of liquids and their two components are referred to standard conditions of ambient temperature and pressure at sea level. (T= 20 °C, P= 1

bar) [247]. For this study, all of the surface free energy measurements were conducted at conditions with $T = 20\text{ }^{\circ}\text{C}$, $P = 1\text{ bar}$. For other testing conditions, the Karbanda's equation could be applied to rescale the values of surface tension from the temperature point of view [177].

Table 5.8 Surface free energy results of ED and ELD coatings.

Samples	Treatments	Surface Free Energy (mJ/m^2)
ED coating	Aged in ambient air	4.6
	After plasma cleaning	72.7
ELD coating	Aged in ambient air	33.4
	After plasma cleaning	69.2

As indicated in Table 5.8, the surface free energy of ED coating aged in ambient air is only 4.6 mJ/m^2 . The low surface energy should come from the adsorbed airborne hydrocarbon. It helps with the low ice adhesion strength. The ice adhesion strength is largely related to hydrogen bonding, van der Waals forces, and electrostatic interaction. Among them, the electrostatic interaction could be the dominant factor. Icephobic coating with low surface energy would minimize the molecular interaction between water and coating surface. After plasma cleaning, the surface energy increases to 72.7 mJ/m^2 , which is much higher than before. The reason could be the removed hydrocarbon and adsorption of oxygen gaseous species, with more polar groups on the surface, the surface free energy would have an undoubted increase. As for ELD coating, the surface energy is 33.4 mJ/m^2 for the sample that aged in ambient air and the value increases to 69.2 mJ/m^2 after plasma cleaning. The reason here is similar to ED coating.

5.4.2 WCA recovery in different material systems

It is obvious that the WCA recovery speeds vary a lot in the displayed results from Ni-Cu-P coatings and 304 SS. The main reason lies in the difference of surface composition and surface morphology. Considering the difference of WCA recovery on samples with

different surface roughness, it is assumed that the rate of the WCA change should depend on how much surface area is still available to be covered by the airborne hydrocarbon. There should be a proportionality between the rate of hydrocarbon adsorption and the available surface area. The rate of change of sample surface S covered by the airborne hydrocarbon depends on the amount of available surface area. Hence equations (5.5) can be obtained:

$$\frac{dS}{dt} = S_0 - S \quad (5.5)$$

where S_0 is the total surface available. It is speculated that the measured water contact angle is proportional to the amount of surface coated by the airborne hydrocarbon.

$$\frac{dW}{dt} = WCA_{inf} - WCA \quad (5.6)$$

where WCA_{inf} is the value of WCA after infinite recovery time. To solve this differential equation (Eq 5.6), a boundary condition ($t=0$, $WCA=WCA_0$) could be applied. WCA_0 is the value of WCA immediately after plasma cleaning. Then a solution of the sort of the exponential WCA recovery with a time constant (τ) will be obtained. Here, τ represents the characteristic timescale of the process, and should depend on how convoluted or rough the sample surface is.

To make more obvious illustration to the influencing factors of WCA recovery process, an exponential model are applied to fit the WCA recovery processes on different samples based on the former hypothesis. An analysis of the time constants with respect to a measure of surface roughness is also attached. A model for exponential WCA recovery based on the empirical evidences has been proposed shown as equations (5.7):

$$WCA(t) = WCA_0 + (WCA_{inf} - WCA_0)(1 - \exp(-t/\tau)) \quad (5.7)$$

Where WCA_0 , WCA_{inf} , τ are fitting parameters, WCA_0 is the value of WCA immediately after plasma cleaning; WCA_{inf} is the value of WCA after infinite recovery time, and τ is a time constant associated with the speed of recovery which is specified for certain samples.

The researched samples including SS-polish, SS-smooth, SS-rough, ELD coating and ED coating have been fitted into this model with the three parameter with the data sets using excel solver. The detailed results are shown in Figure 5.35. The values of the constants and the quality of fit together with the surface roughness of the different samples are also shown in Table 5.9.

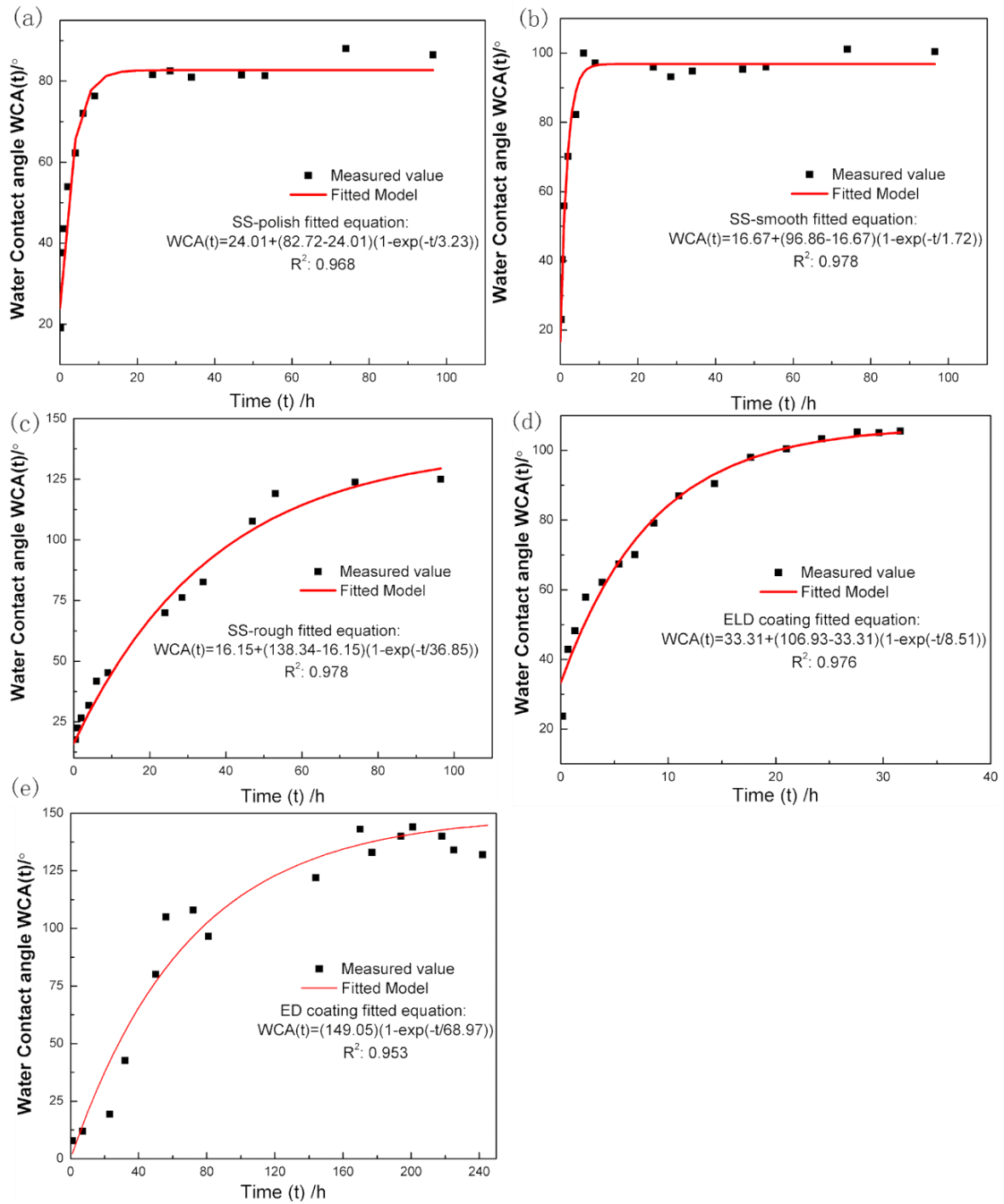


Figure 5.35 Exponential fitted models between the WCA change and time on different samples including SS-polish, SS-smooth, SS-rough, ELD coating and ED coating. The fitted equations and quality of fit are also attached (the former WCA of the samples before plasma cleaning have been deleted for the aim to ensure the accuracy of the fittings).

Table 5.9 Various parameters of different samples

Samples	Quality of fit (R^2)	Time constant (τ)	Surface roughness/ μm
SS-polish	0.968	3.23	0.06 ± 0.01
SS-smooth	0.968	1.72	0.2 ± 0.01
SS-rough	0.978	36.85	1 ± 0.03
ELD	0.976	8.51	0.5 ± 0.02
ED	0.953	68.97	3.9 ± 0.1

Figure 5.35 shows the fitting results of WCA change on different samples, the scattered points are the experiment data while the curve are the fitting results. The fitted equations and quality of fit of the WCA changing curves have also been attached. Here, R^2 is the quality of fit, if R^2 is close to 1, it indicates a higher fitting match degree [248]. It is obvious to see the model we applied (Eq 5.5) work fairly fine with the sample data sets. The corresponding equations and the three fitting parameters of each fitted curved are also shown in Figure 5.35. Table 5.9 give the detailed value of the parameters. For Figure 5.35 (a) to Figure 5.35 (c), the three samples have the same chemical composition, the only difference lie in the surface roughness. The SS-rough possesses the highest WCA and suffers the biggest descend range, while for the SS-smooth and SS-polish, the WCA decrease is smaller. SS-rough takes much more time than the other two samples to recover to their previous WCA level. The phenomenon is also consistent with the one in ED and ELD coatings showing in Figure 5. 35 (d) and (e).

After the time constant (τ) has been confirmed, the relationship between the time constant and the sample surface roughness also need to be established. As shown in Figure 5.35, an attempt has been made to plot the surface roughness as X axis versus τ as Y axis together. We have also made a linear fit to the data set. The line fits quite well.

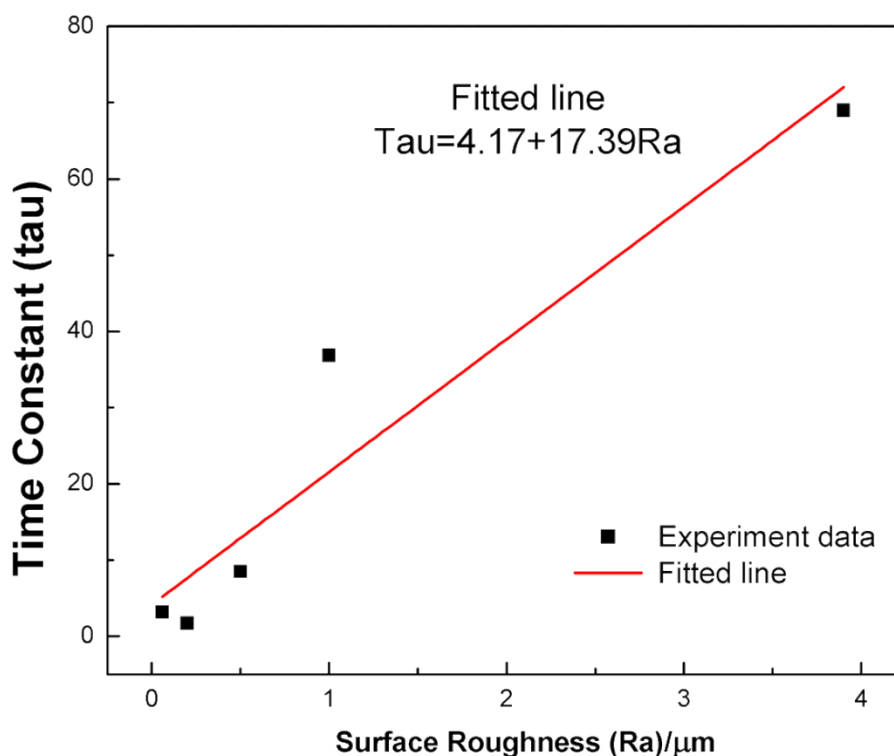


Figure 5.36 Relationship and fitted line between surface roughness and time constant (τ) during WCA recovery process on different samples

From Figure 5.36, it is obvious to see that higher surface roughness contributes to larger time constant (τ). As known before, higher surface roughness contribute to quicker WCA recovery speed. So it could be proposed that τ represents the characteristic timescale of the whole WCA recovery process, and it should depend on how convoluted or rough the surface is. With more surface specific area, there will be more available coating areas and more airborne hydrocarbon adsorbed onto the surface. The rougher the surface, the larger the surface specific area. This could accelerate the diffusion of airborne hydrocarbon species in the ambient atmosphere. With the use of this particular model on WCA recovery process, it also supplies good theoretical justification to relevant time-dependent wettability study.

But on the other hand, the rougher surface also increases the difficulty to finish the WCA recovery since the WCA drop during the plasma cleaning treatment is also much larger, the whole duration could be longer. The surface would take less time to finish

the process of replacing, inserting into, and/or covering the formerly adsorbed hydrophilic groups, such as OH, COOH/C=O, lattice oxygen (O-metal) groups. [224].

5.4.3 Influencing factors of time-dependent wettability

The displayed results show that the changing wettability could occur on different types of surfaces. The microstructure and chemical composition of the tested samples all remain unchanged during the ageing process. Nevertheless, the wettability changes with time going. According to the former study in both ED and ELD coatings as well as the SS and CeO₂ material systems, the evolution of hydrocarbon groups and oxygen groups versus plasma cleaning on samples may explain it.

Compared with the studies of time-dependent wettability on different surfaces, it could be inferred that the surface chemistry of the materials plays a significant role in determining the wettability. The results of CeO₂ system also indicate this. As shown in Table 5.4, the Ce³⁺ contribution to the overall surface cerium decrease from 40.5 at% to 27.3 at% after being exposed in ambient air, which means that the sample underwent a partial reduction in the state from Ce³⁺ to Ce⁴⁺. The ceria could release surface lattice oxygen as part of a wider surface reconstruction process [249]. While for the change in the oxidation state from Ce⁴⁺ to Ce³⁺ after the plasma cleaning treatment, it could be correlated with a net decrease in the Ce/O ratio. The change in cerium chemistry is consistent with the hypothesis that plasma cleaning could lead to an overall decrease in the surface Ce/O ratio. The decreasing Ce/O ratio could affect the wettability. Because the greater the oxygen sites on the surface, the higher the possibility to form hydrogen bonds with interfacial water and lead to more hydrophilicity.

For ED and ELD coating systems, the results also support this. If the surface is to be modified in that the surface lattice oxygen sites increased relatively to the metal sites, its hydrophobicity would be affected. In other words, a net increase in the surface oxygen-to-metal ratio beyond the typical stoichiometric value is detrimental because an

increase in surface lattice oxygen provides more avenues for hydrogen-bonding with interfacial water which further breaks down the hydrophobic hydration structure [198]. It indicates that the chemical composition of the upmost layer of the surfaces is altered gradually. This is mainly ascribed to the surface gaseous adsorption. The surface gaseous adsorption occur on both metallic surfaces and ceramic systems. Airborne hydrocarbons exist almost everywhere, even inside a high-end nanofabrication clean room, the adsorption of airborne hydrocarbons at certain surfaces can hardly be prevented in the practice of wetting investigations.

The possible scenario for the time-dependent wettability is that the adsorption of airborne hydrocarbon onto the upmost layer of the surfaces. The as-deposited/as-prepared surfaces would have a large number of polar sites composed of unsaturated metal or rare earth and oxygen atoms that act as Lewis acid and base sites, respectively, which lead to an overall hydrophilic surface [250]. With more hydrocarbon adsorbed, the polar component of the surface would be reduced, the surface polarity would also decrease. The sites on their surface could be quickly hydroxylated and effectively passivated. This would further lead to the reduction of the total surface free energy and increased WCA. For most of the hydrocarbon (such as alkyl groups - principal component for most organic molecules), it could increase the relative content of C-C (H) bond. Higher C-C (H) bond leads to a more nonpolar surface. For samples stored in ambient conditions, the high carbon content and medium C-C (H) value are caused by the complex surface organic adsorbates that present in ambient air. Various organic species adsorb onto the surface and reduce the surface polarization in this way, resulting in the transition of surface wettability [194, 251].

But the time-dependent wettability does not exist in the polymeric system, as indicated in Figure 5.20. It is obvious that no time-dependent wettability shows on the polymeric surface. The PDMS layers would not adsorb any hydrocarbon group. There is no absence of polar and reactive functional groups in their structure. They are chemically inert and cannot bond easily to the organic groups, which could also be verified from

the unchanged WCA of polymeric layer versus boiling treatment. The results clearly indicate the important roles of surface adsorption in causing time-dependent wettability.

Based on the former discussion, the universality of time-dependent wettability has been confirmed in different material systems except for the polymeric system. The main reason could be the adsorption of airborne hydrocarbon groups and the change of surface oxygen groups. The surface chemistry of these surfaces plays a significant role in determining the wettability. The main adsorption mode on these surfaces is physisorption (gas molecules are bound by the sum of attractive or repulsive forces between molecules and electrostatic forces). The interaction force between gaseous groups and the coating surface could be more related to Van der Waals force. The phenomenon could be considered in practical operation, the importance of controlling hydrocarbon adsorption for material wetting behaviour should also be highlighted. The consideration on how to accelerate or control the time-dependent wettability or adsorption speed could also be a good direction which can be further investigated later. Apart from the surface specific area, the corresponding temperature and pressure could also affect. An increase in the pressure of the adsorbate gas will increase the extent of adsorption, the speed of adsorption could even boost rapidly with increasing pressure at low temperature scale [252]. While for temperature, the adsorption speed should decrease with constant rising temperature because the adsorption (in the form of physisorption) is accompanied by evolution of heat according to the Le-Chatelier's principle [253]. With the work, more in-depth understanding about the surface composition and surface chemistry changes in metallic or ceramic samples exposed to the ambience and its effect on surface wettability transition could be obtained.

5.4.4 Effect of time-dependent wettability on coating icephobicity

It is believed that icephobicity of a certain material surface is affected by many factors: surface condition, relative humidity of atmosphere [37], liquid water content [38], and mechanical adhesion [39], etc. Among them, the surface condition could be one of the

dominating factors. Based on the previous contents, the significant role of surface adsorption on surface wettability has been confirmed. The effect of time-dependent wettability on coating icephobicity has also been investigated systematically.

The different icing durations in Figure 5.21 indicate that the hydrophobic state of the coatings plays an important role in the delay of ice formation. The existence and removal of surface adsorption would result in the change of trapped air pockets and solid-liquid interface fraction on coating surfaces. This would further lead to the thermal exchange difference between the solid-liquid interfaces.

The icing process on a certain surface could be considered as a phase transition. The whole process would certainly be affected by the WCA. The phase transition causes the decrease of Gibbs free energy. The water droplet needs to overcome the potential barrier to fulfill the phase transition (from liquid phase to solid state), it could be inferred as equations (5.5) and (5.6) [88]:

$$\Delta G_c = \frac{4}{3} \pi r_c^2 \sigma_{1v} f(\theta) \quad (5.5)$$

$$f(\theta) = \frac{(2 - 3 \cos \theta + \cos^3 \theta)}{4} \leq 1 \quad (5.6)$$

where ΔG_c is the critical potential barrier (J); r_c is the critical radius (m); σ_{1v} is the surface tension between air and the liquid phase (N/m); and θ is contact angle between the water droplet and solid surface (°).

The critical radius r_c for a certain surface is a constant. While the surface tension σ_{1v} has some influencing factors, including the molecular forces, temperature, pressure, and so on. In this system, the molecular forces, temperature, pressure remains unchanged.

The WCAs are different on the ED and ELD coating, and different θ could lead to variation in ΔG_c . High WCA produces high ΔG_c , which makes the water droplet phase

transition more difficult. After the plasma cleaning, the hydrophilic groups are introduced onto the surface, these polar groups would act as the surfactant, which helps to decrease the surface tension. More hydrophilic groups mean higher surfactivity and lower surface tension value. So after the plasma cleaning, the potential barrier needed for icing process is also significantly reduced, and the ice formation becomes much quicker than before [254].

The ice adhesion strength results in Figure 5.23 also show the effect of time-dependent wettability on coating icephobicity. Herein, the ice adhesion strength is largely related to hydrogen bonding, van der Waals forces, and electrostatic interaction [47]. Among them, the electrostatic interaction could be the dominant factor [48]. The surfaces change into the hydrophilic state after plasma cleaning, and the water and substrate could have more direct contact. The low WCA makes the water droplet easily penetrate into the cavities at the interface and form the ice inside which can be called interlocked ice. Therefore, the ice adhesion becomes much stronger than that in the hydrophobic state. The formation of interlocked ice on the coating surface would increase the ice adhesion inevitably, which is further evidenced later. The changes in surface energy could also confirm the effect of gaseous adsorption on the surface icephobicity of the coatings.

The de-icing performance tests of ED and ELD using the electro-thermal heating test in Figure 5.24 and Figure 5.26 also indicate the changing wettability could affect the coating icephobicity (mainly on de-icing performance). The two samples both show prolonged ice detachment duration and lower real-time detected temperature after the plasma cleaning treatment. This means the deterioration of de-icing efficiency and thermal transfer efficiency has been seriously affected. The decrease of real-time temperature means that more energy could be transferred in unit time and indicate good thermal transfer. The reason could be the decreased thermal resistance. After the wetting state has been changed into hydrophilic, the incoming water droplet could fill in the space between the coating hierarchical structures. There would also be more contacting

areas between the coating and the formed ice, and the thermal resistance would be much lower than before since the former existing air (the thermal conductivity of air is only 0.024 W m/K at 0°C) has been replaced by ice (the thermal conductivity of ice is only 0.55 W m/K at 0°C). With the recovered hydrophobicity, there will be less water staying at the surface structures, the thermal resistance then increases. But from the other side, the prolonged ice detachment also comes from this. The low WCA leads to the larger base width of the water droplet, leading to more ice-coating contacting points. The adequate contact would result in serious mechanical ice interlock, forming around the hierarchical surface structures, leading to larger ice adhesion strength. So it would take much more time to make the ice detach although the thermal transfer efficiency has improved. More energy needs to be inputted and adsorbed to melt the contacting ice and fulfill the de-icing purpose. So from this point, the time-depend wettability affects the de-icing performance of Ni-Cu-P coatings.

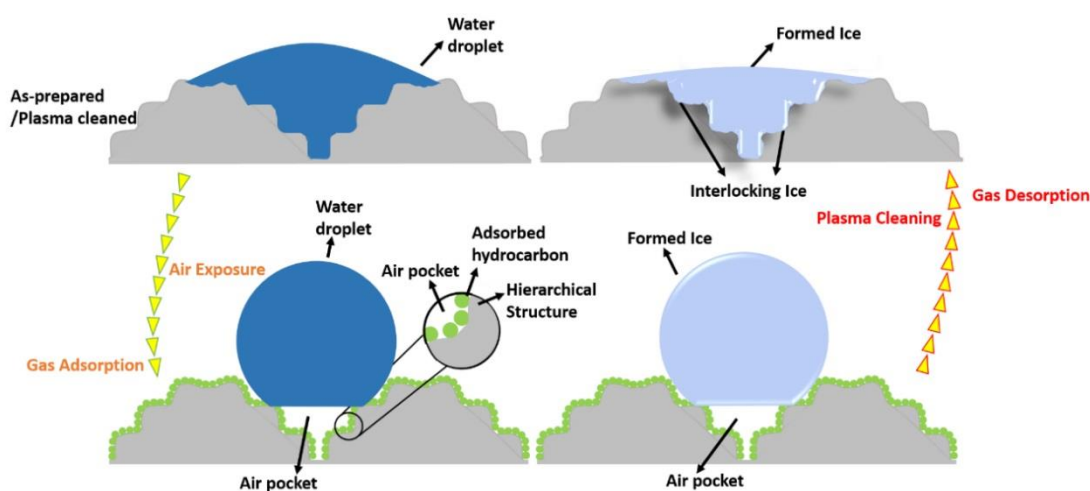


Figure 5.37 Schematic of the behaviour of water droplet and formed ice of the Ni-Cu-P coating (there are some hydrophilic groups on the as prepared/ plasma cleaned coating, it has not been shown for better comparison).

In order to better explain the effect of time-dependent wettability on coating icephobicity, the schematic diagram has been made in Figure 5.37 to indicate the effect and mechanism of surface adsorption on coating icephobicity. The upper images are the

coatings in as prepared/plasma cleaned states, with some hydrophilic groups on the surface. When limited hydrocarbon species are adsorbed on the coating surface, it shows a hydrophilic state with a quite high surface energy. The interaction of the water droplet on the coating surface is indicated in the upper-left image, showing typical hydrophilic character and the water droplet occupies the space between the rough asperities. There is no air trapped and few air pockets form. The upper-right image is the ice accretion on the coating surface, and the formed ice fills in the space between the hierarchical structures. The formed ice has close interaction with the rough asperities, which could lead to mechanical interlock and increase the ice adhesion strength. The images below are the water condensation and ice formation on the coating surface after being stored in ambient air for enough time. After being stored in air, a large amount of hydrocarbon species are adsorbed onto the coating surface, leading to a significant decrease in surface energy. The surface becomes hydrophobic then. Due to the contribution of the adsorbed hydrocarbon species and the hierarchical structures, the formation of air pockets is demonstrated. The generation of these air pocket has some common physical mechanism as the growth of the bubbles in microfoams: needs to be driven into a supercritical state, in which small bubbles nucleate spontaneously and then grow [255]. Also, a benefit from the lowered surface energy is that the formed ice would have much less interlocking effect and bonding on the coating surface, indicating a better surface icephobicity and much lower ice adhesion strength value.

5.5 Summary

The time-dependent wettability has been investigated via electroless deposited Ni-Cu-P ternary coating, 304 SS, and CeO₂ systems. The surface of the as-prepared surfaces changed from hydrophilic state to hydrophobic state after being aged in ambient air. The main reason for the changing wetting behaviour could be ascribed to the adsorption of airborne hydrocarbon and the change of lattice oxygen. The stable hydrophobicity in PDMS layer system has also confirmed the significant role of surface gaseous

adsorption. The two factors alter the surface energy and introduce more hydrophobic groups onto the coating surface, resulting in the changes in wetting behaviour.

The effect of time-dependent wettability on icing behaviour of Ni-Cu-P ternary coatings has also been studied systematically. When the Ni-Cu-P samples are changed from hydrophobic to hydrophilic, the icing time of water droplets on the Ni-Cu-P coatings increased significantly; the frost growth also become much quicker, the ice removal effect with electro-thermal input also deteriorated obviously with prolonged duration and increased energy input, and the ice adhesion strength also increased sharply with the removal of surface gaseous adsorption. XPS analysis indicated that the adsorbed hydrocarbons play an important role in the change of icing behaviour of the coatings. With the removal of surface adsorption by plasma cleaning, the surface icephobicity of the Ni-Cu-P coating deteriorated. ESEM observation confirmed the role of air pockets and the presence of the interlocked ice. The adsorbed hydrocarbons would help to form a good amount of air pockets at the water-solid interface, which could decrease the interfacial contact effectively between the water droplets and coatings and further hinder the formation of interlocked ice. The significant changes of surface free energy could also confirm the effect of gaseous adsorption on coating icephobicity. Due to the universal surface adsorption phenomenon in air, the mechanism disclosed in this study is likely to be applicable to other metallic coatings and surfaces.

Chapter 6 Metallic Skeleton Promoted Two-phase Durable Icephobic Layers

Currently, the polymeric layer systems are still the mainstream for practical icephobic applications. A myriad of reports has been published on polymeric icephobic coating systems or coating surfaces with polymer modification [5, 256]. These surfaces possess the virtue of having a very large water contact angle and exhibiting little adhesion to the formed ice block. Notwithstanding the significant theoretical and experimental progress in the polymeric icephobic coating systems, challenges remain there. First and foremost, there are concerns on issues of robustness and surface fragility. The practicality of these polymeric surfaces is hampered by the poor mechanical durability of microscopic surface topography that is essential for good icephobicity. This could be a major restriction for the practical applications as they cannot survive long-termly under harsh environmental conditions. Even moderate forces caused by touching or rubbing the surfaces are frequently strong enough to destroy the microscopic surface topography and lead to the deterioration or loss of the hydrophobic/icephobic properties.

In order to solve this problem, it is of great significance to develop icephobic layer system with good mechanical durability and also anti-corrosion performance. Among the current research direction, metallic-based coating systems with good mechanical properties and anti-corrosion performance could be good solutions. However, as mentioned in former chapters, the unusual feature of time-dependent wettability lies in most of the metallic coating systems that would lead to the evolution of coating icephobicity. The direct link between the changing wettability and icephobicity would limit and affect the practical application of metallic-based icephobic coatings.

To eliminate or minimize the effect of time-dependent wettability in metallic-based systems, new material systems need to be developed. In order to develop proper hydrophobic/icephobic layers, multi-phase structure layer structures combined with

good icephobicity and mechanical durability could be designed. By combining different phases with various functions into one layer structure, polymers (hydrophobic and icephobic substances) could provide the necessary hydrophobicity and icephobicity while the metallic structure can offer significantly improved mechanical properties (e.g. strength and elastic modulus) and durability, as well as good thermal conductivity, which is of significance for the active de-icing process. Using this assumption, the layer structures could take full advantage of both hydrophobic/icephobic characteristics of polymer filling and mechanical durability of the metallic skeleton. With the help of polymer filling, there would be no time-dependent wettability phenomenon existing in the layer structures. The new design could supply feasibility for practical icephobic applications.

In this chapter, nickel (Ni) foam was chosen as the porous skeleton (phase I), polydimethylsiloxane (PDMS) was selected as the filling material (phase II) to prepare multi-phase structure icephobic layer structures. Here, the Ni foam has been used instead of the previously studied Ni-Cu-P coatings in combination with the PDMS. The reason could be ascribed to: 1. the durability issue still exist if we use ED coating with PDMS deposited on top because the PDMS layer is still exposed to the severe working environment and the PDMS layer could easily be damaged, as indicated later in Section 6.3.3; 2. the usage of Ni foam could avoid these kinds of problem which could act as the armour of the PDMS layer; 3. the design thinking could be lack of novelty since there are many similar reported works [10, 138, 257]. This chapter will present a systematic study mainly on durable icephobic layers based on the impregnation of hydrophobic/icephobic substances (PDMS) into porous metallic skeletons (Ni foam). There are mainly four kinds of samples prepared and investigated in this part: the pristine as-received Ni foam substrate was designated as AR-Ni, Ni foam/PDMS samples with rough and smooth surface were designated as Ni/PDMS-A and Ni/PDMS-S, respectively. The 304 SS substrate with PDMS layer was abbreviated as SS-PDMS.

6.1 Detailed Investigation of As-received Pure Ni Foam

6.1.1 Micro-structures of AR-Ni

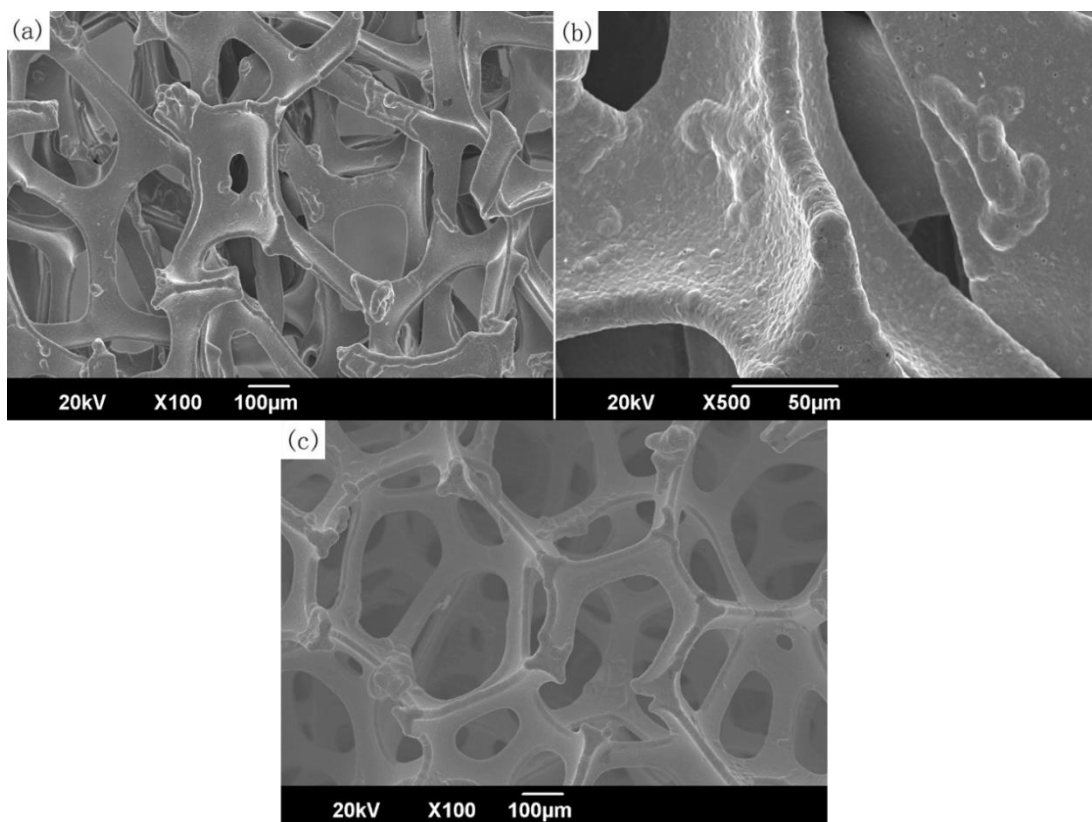


Figure 6.1 SEM images of (a) surface morphology (low magnification) (b) surface morphology (high magnification) and (c) cross-sectional image of AR-Ni.

Figure 6.1 shows the SEM images of surface morphology with different magnifications and cross-sectional images of AR-Ni. Figure 6.1 (a) clearly shows the highly porous structure of the Ni foam skeleton with calculated porosity of around 90% (80-110 pores per inch). The AR-Ni substrate has excellent extensibility with lengthwise $\geq 5\%$, widthwise $\geq 12\%$, the lengthwise tensile strength $\geq 1.25 \text{ N/mm}^2$, while in the widthwise direction $\geq 1.00 \text{ N/mm}^2$. The existing numerous pores and foam skeletons could help with the impregnation of hydrophobic/icephobic substances. Figure 6.1 (b) is the amplified view field of Figure 6.1 (a), it clearly shows the detailed structure of Ni foam skeleton. It is expected that the Ni foam skeleton could play important roles in increasing the durability to prolong the attended time and accelerate the thermal

conduction when doing de-icing applications. Figure 6.1 (c) is the cross-sectional image of the AR-Ni. It displays a similar morphology as the surface morphology, showing the porous structure of the Ni foam skeleton. The material exhibits 3D uniformity of the Ni foam in the entire density range [258].

6.1.2 Water condensation and ice formation on AR-Ni

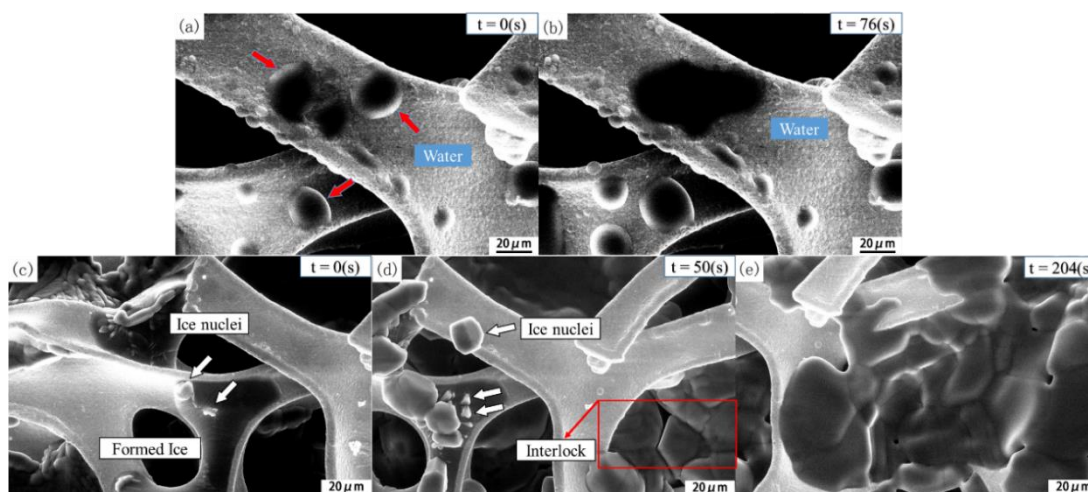


Figure 6.2 (a) (b) Water condensation (Pressure: 3.2-3.7 torrs; Temp: -4 to -2 °C; Humidity: 93-95%); (c)-(e) Ice formation process on AR-Ni (Pressure: 2.3-2.4 torrs; Temp: -7.8 to -7 °C; Humidity: 89-91%).

Figure 6.2 (a) and (b) show the water droplet condensation process on AR-Ni. The detailed conditions of pressure, humidity, and temperature for each image have also been listed. The WCA could be reflected from the displayed formed water droplet, which is quite low. It is difficult to confirm whether it is hydrophobic characteristic or hydrophilic. There is no obvious preference for the condensed droplets to gather on Ni foam. Figure 6.2 (c) shows the formed ice on Ni foam. Some ice nuclei could be observed and some of the condensed water areas disappear. Some ice nuclei have been observed to grow out from it. From Figure 6.2 (c) to (d), the view field of the observation has been moved a bit rightward. The formed ice did not show the regular angular structure. There are also more ice nucleation points that emerged from the former water covered area, other than the remaining substrate area. It could also be

observed that some other ice forms around the microscopic pores and skeleton structures. The ice block fills in the pores and the large block of ice leads to serious mechanical interlock, as shown in Figure 6.2 (e). The ice build-up between the hierarchical structures could generate mechanical interlock

6.2 Preparation and Microstructural Characterisation of Ni foam/PDMS Samples

6.2.1 Preparation process of Ni foam/PDMS layer samples

For the preparation of Ni/PDMS-A, a two-part elastomer silicone PDMS was used as the icephobic substance. Part A and Part B (1:1) were mixed separately in xylene using magnetic stirring for 3 h. The two solutions were then mixed using magnetic stirring for one more hour. The Ni foam substrate was put into the mixture and make it fully immersed. Then it was transferred into the vacuum oven for 30 min to degas the existing air bubbles among the porous structure, followed by post-baking treatment at 75 °C for 45 min (to remove solvent) and 150 °C for 135 min (elevated temperature curing). The degassing process could minimize the amount of air bubbles generated during the curing process effectively.

For Ni/PDMS-S, it was prepared based on the previously prepared Ni/PDMS-A. Additional PDMS was applied onto the sample surface using the same mixture solution and spin-coated at a speed of 1500 RPM for 1 min. The hierarchical extent and thickness of the samples could be easily controlled by the spinning coating process. The samples were then heated in the vacuum oven for similar post-baking treatments. For further comparison purposes, a PDMS layer was coated onto sandblasted 304 SS substrates using spin coating with same PDMS layer and post-baking treatment conditions.

6.2.2 Microstructure of the Ni foam/PDMS samples

6.2.2.1 Surface morphology of as-prepared samples

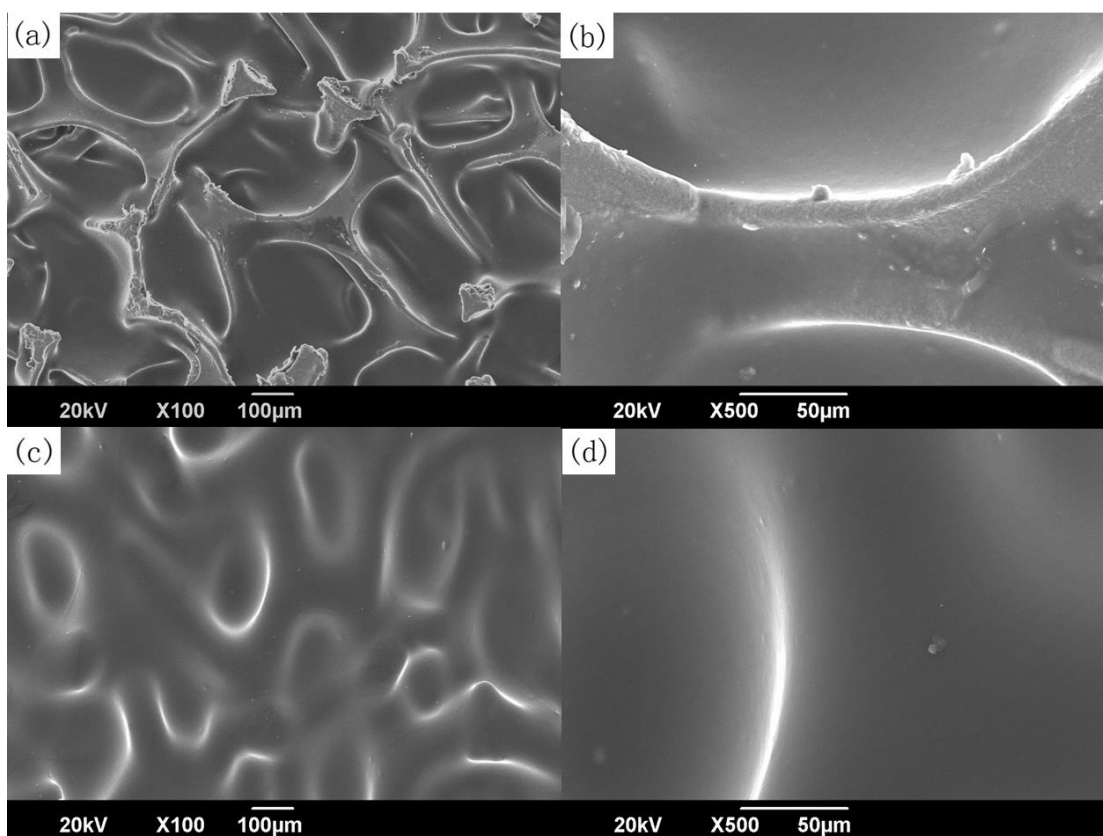


Figure 6.3 SEM images of surface morphology of (a) (b) Ni/PDMS-A; (c) (d) Ni/PDMS-S.

Figure 6.3 (a) and (b) are the SEM images of Ni/PDMS-A. It clearly shows the highly porous structure of the Ni foam skeleton. It is clear that some of the internal porosity has been filled, while some sharp and deep surface pores remain on the surface. The porosity of Ni/PDMS-A has also been calculated with a value of 21.4%. Here, the porosity of AR-Ni could be easily obtained by calculating the ratio between the actual weight of AR-Ni and the theoretical weight of pure Ni plate with the same dimension. From the amplified image in Figure 6.3 (b), the detail also shows that there should be a single layer of PDMS fully covered on the observed Ni foam skeleton, which could be confirmed by the later EDX and XPS spectra results. The unfilled sharp and deep surface pores could be an issue for the de-icing process [224]. Then Figure 6.3 (c) and (d) are the SEM images of Ni/PDMS-S. By controlling the volume of deposited PDMS,

the former existing hierarchical parts and the big pores on the surface will be filled. The remaining surface cavities all have been significantly reduced by the additional PDMS layer on top, leaving some fine and shallow surface cavities. The porosity of the sample has reduced to only 11.6%. The whole cavity size of the Ni foam skeleton has been reduced and no sharp metallic feature is observed, while the profile of the Ni foam could still be detected from the image. There is also no void and crack on the surface, showing good surface integrity and uniformity.

6.2.2.2 3D topography of Ni foam/PDMS samples

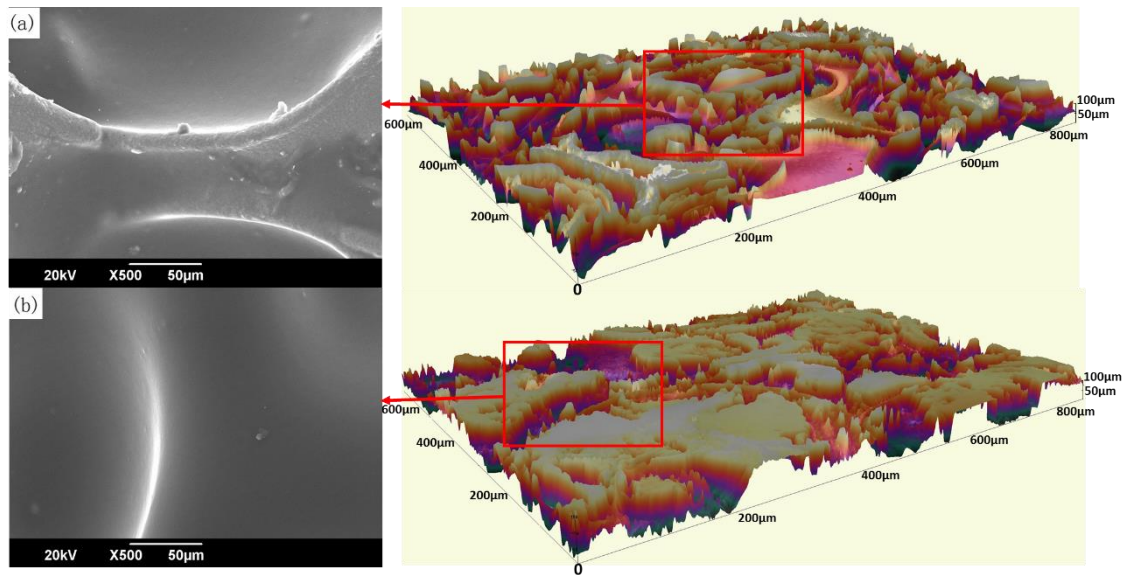


Figure 6.4 SEM images and 3D topography images of (a) Ni/PDMS-A and (b) Ni/PDMS-S.

Figure 6.4 shows the 3D topography images of the samples. Figure 6.4 (a) shows Ni/PDMS-A. The detected area is $850 \times 650 \mu\text{m}$. The 3D images are very consistent with the SEM images. The yellow parts are the Ni foam skeleton. Other dark parts are the remaining deep and sharp surface cavities. The measured R_a is $36.8 \pm 2.8 \mu\text{m}$. Then moving to Figure 6.4 (b), the surface of Ni/PDMS-S is rather flat and smooth, and there are also some smooth and flat surface cavities. The surface roughness is also a bit lower than the former one, with a value of $24.1 \pm 0.9 \mu\text{m}$. It is evident that the yellow smooth parts are PDMS fillings and the lower dark red parts are Ni foam skeleton area. The size of the surface cavities is around 100 to 300 μm and the depth ranges from 50 to

150 μm , which could be obtained from the surface profilometer.

6.2.2.3 Element composition with EDX spectrum of Ni/PDMS-S

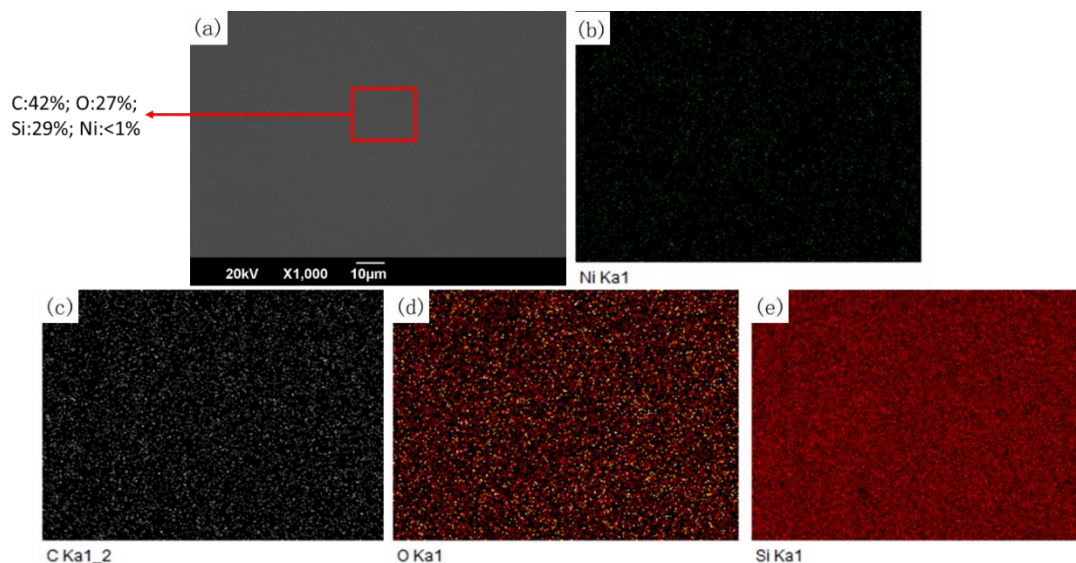


Figure 6.5 SEM images (a) and element mapping results of smooth parts of Ni/PDMS-S (b) Ni (c) C (d) O (e) Si.

Figure 6.5 is the EDX spectrum results of smooth part of Ni/PDMS-S. Figure 6.5 (b)-(e) indicates the distribution of Ni, C, O, and Si elements. For smooth part, the C, O, Si elements confirm the PDMS fillings and all these elements distribute uniformly on the viewfield. Very few Ni could be detected on the surface. This confirms that all of Ni foam skeleton have been fully covered by the PDMS layer. The Ni foam skeleton underneath is difficult to observe even though considering the penetrability of EDX spectrum. For other three elements, all of the mapping results show uniform distribution.

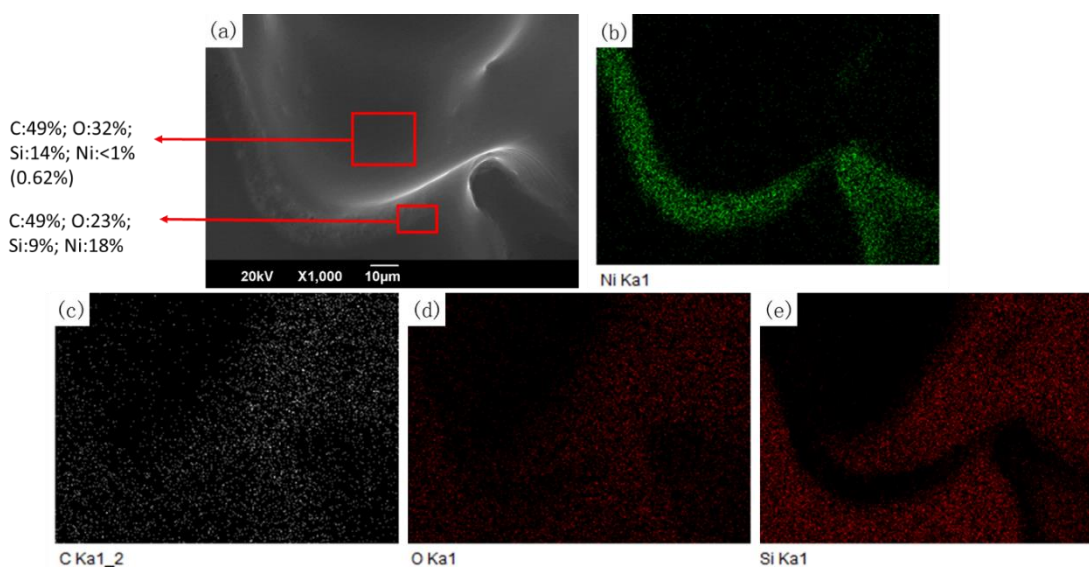


Figure 6.6 SEM images (a) and element mapping results of surface cavity parts of Ni/PDMS-S (b) Ni (c) C (d) O (e) Si.

Figure 6.6 shows the EDX spectrum results of remaining surface cavity parts of Ni/PDMS-S, which also mainly consist of elements of C, O, Si, and Ni. Among them, C, O, Si still correspond to the PDMS layer. From Figure 6.6 (b)-(e), it could be observed that the obvious strip area with green colour indicates the Ni foam skeleton. Considering the strong penetrability of EDX spectrum, it does not mean there is no PDMS layer on the strip parts, but it indicates that the PDMS layer here is quite thin, otherwise, the Ni percentage would be relatively high. For the upper area circled in red, the chemical composition is quite close to the result in Figure 6.5. For the element mapping results of C and O, they distribute quite uniformly on the surface. The characteristic of the distribution of Si is just the opposite of that of Ni.

6.2.2.4 Surface substance via XPS spectrum

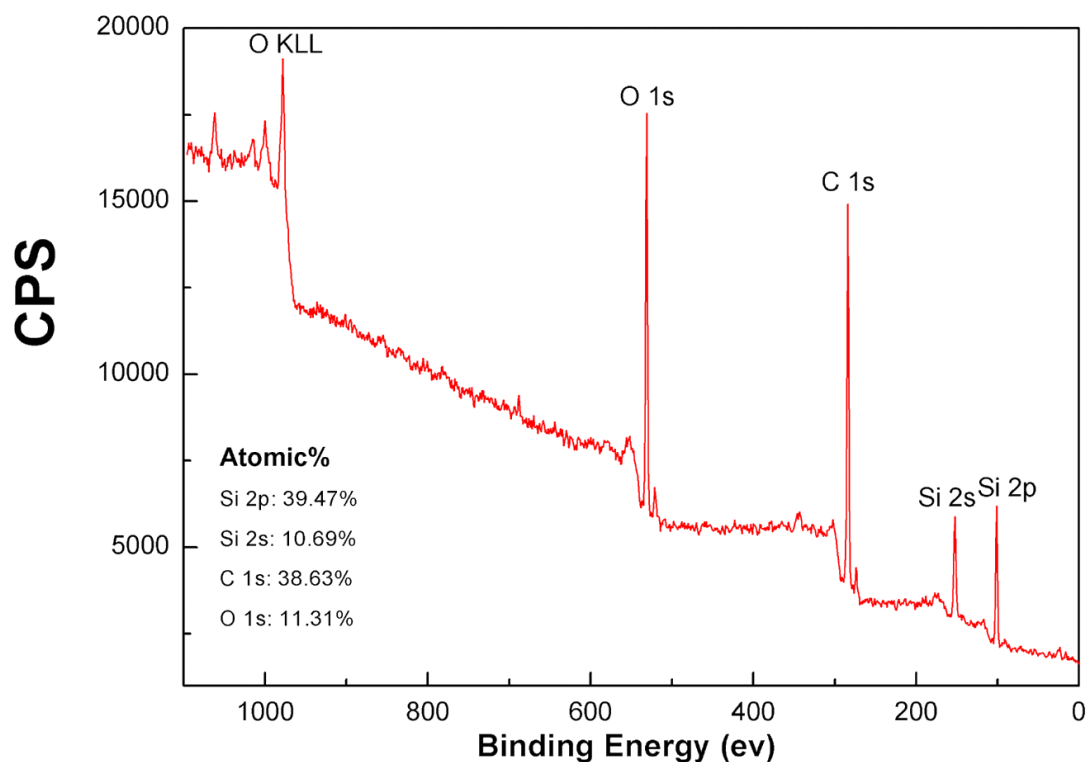


Figure 6.7 Survey spectrum of Ni/PDMS-A and atomic percentage of relevant surface elements.

Figure 6.7 shows the survey spectrum of Ni/PDMS-A. There are several main peaks showing in the spectra including Si 2s, Si 2p, C 1s, and O 1s, and none Ni peak could be detected, including Ni 2p $3/2$ and Ni 2p $1/2$. The atomic percentage of these elements has also been listed in the figure. Considering the full coverage of PDMS layer, the main part is Si, C, and O, with none Ni. This is also consistent with the EDX results in Figure 6.5 and Figure 6.6. The XPS spectrum results obviously verify that a thin layer of PDMS layer is fully covered on the observed Ni foam skeleton because no Ni element and Ni-related group could be detected. It gives a clear illustration of the surface composition of the sample.

6.2.3 Wettability evaluation of the as-prepared samples

Table 6.1 Detailed wettability of different samples.

Samples	WCA (°)	Advancing WCA (°)	Receding WCA (°)	CAH (°)
AR-Ni	130.8±4.8	130.8±4.7	125.1±3.8	5.7±0.1
Ni/PDMS-A	121.1±2.3	123.1±2.6	117.3±2.1	5.8±0.1
Ni/PDMS-S	112.8±0.4	109.3±0.9	101.8±1.2	7.5±0.1
Flat PDMS	109.9±1.7	112.9±1.1	101.2±1.0	11.7±0.2

Table 6.1 shows the detailed surface wettability including WCA, advancing WCA, receding WCA, and CAH of the different samples. The WCA of AR-Ni could reach $130.8 \pm 4.8^\circ$ and CAH is only $5.7 \pm 0.1^\circ$. This leads to the discrepancy with the low WCA of AR-Ni indicated by the geometry of condensed water droplet in Figure 6.2, the reason here could be that the AR-Ni could be in a metastable state. The highly rough surface could introduce the huge specific surface area and lead to time-dependent wettability to the Ni foam substrate, the WCA would easily decrease after the adsorbed species and air pockets have been removed [188]. Under the high humidity environment, the Cassie-Baxter wetting state could easily transform into the Wenzel state and lead to the low WCA [259]. For Ni/PDMS-A, the WCA is a bit lower, $121.1 \pm 2.3^\circ$ and CAH is $5.8 \pm 0.1^\circ$. Because of the full coverage of PDMS layer on top, there should be non-existence of time-dependent wettability (which has been demonstrated in Chapter 5.2.3). The WCA could come from the combined reason for roughness effect of Ni foam skeleton and PDMS filling. For Ni/PDMS-S, with additional PDMS layer on top and reduced surface cavities, the static WCA is $112.8 \pm 0.4^\circ$ with a CAH of $7.5 \pm 0.1^\circ$, which is very close to the inherent WCA value of pure smooth PDMS. The smoother and reduced surface cavities on Ni/PDMS-S result in the surface wettability. For SS-PDMS, it is prepared as reference sample, the WCA is $109.9 \pm 1.7^\circ$, with CAH of $11.7 \pm 0.2^\circ$, which should come from the rough structure and PDMS layer [260].

6.3 Icephobicity and Mechanical Durability Evaluation for Ni foam/PDMS Samples

6.3.1 Anti-icing performance

6.3.1.1 Icing of water droplets on the samples

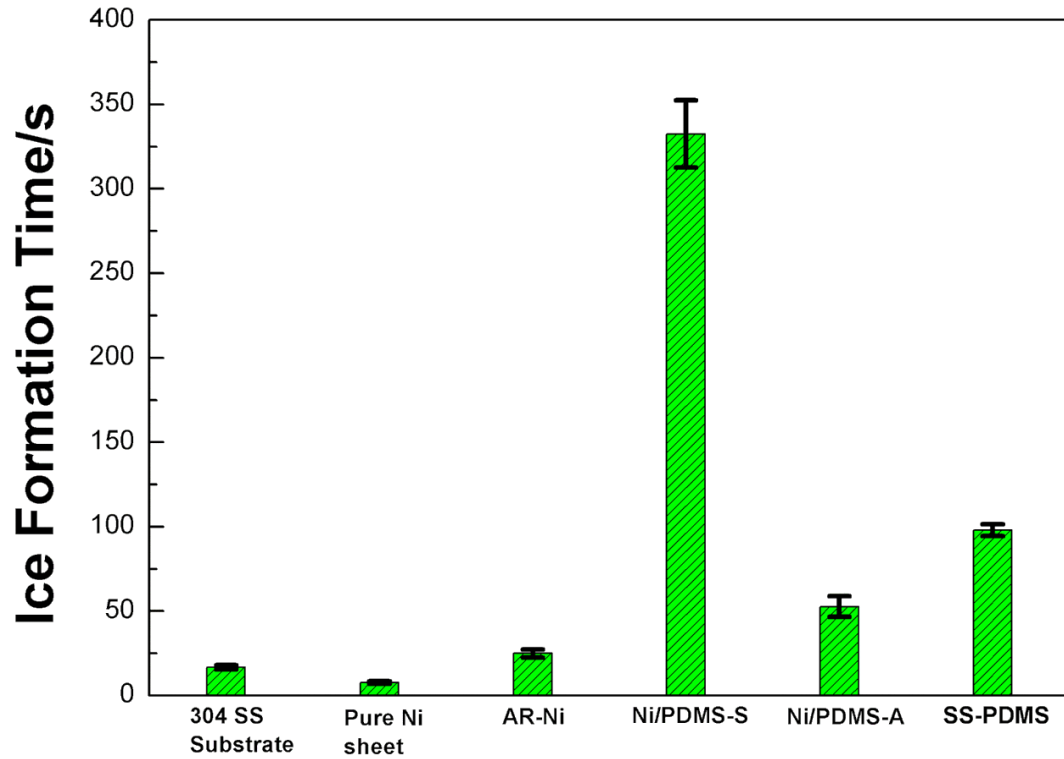


Figure 6.8 Ice formation time of 304 SS, pure Ni sheet, AR-Ni, Ni/PDMS-S, Ni/PDMS-A, and SS-PDMS.

Figure 6.8 displays the ice delay time of water droplets on 304 SS substrate, pure Ni sheet, AR-Ni, Ni/PDMS-S, Ni/PDMS-A, and SS-PDMS, respectively. The columns indicate the ice delay time. It is an important parameter for icephobicity evaluation and reflects the duration required for a water droplet to become ice on certain surfaces with constant temperature [165]. It is also closely related to the ability of thermal transmission at the apparent solid-liquid contact interface [261]. The droplet remaining on a cold surface would lose heat to the cold substrate through thermal conduction. The icing of the water droplet on 304 SS is only 16.8 ± 1.3 s. The thermal conductivity of

304 SS is 16.2 W m/K . For pure Ni sheet, the icing trigger is even quicker than that of 304 SS, only $7.6 \pm 0.7 \text{ s}$. This could be ascribed to the good thermal conductivity of Ni sheet (the thermal conductivity of Ni is 82.9 W m/K), and the thickness of Ni sheet is also very thin (only 0.05 mm), which makes the thermal transfer more effectively. The ice formation time of SS-PDMS could reach $98.0 \pm 3.5 \text{ s}$. Compared to the 304 SS substrate, it is a large improvement, and the increase may be ascribed to that the thin PDMS layer brings some hydrophobic characteristic. While for AR-Ni, the icing time is a bit longer, $24.8 \pm 2.4 \text{ s}$. Compared to the Ni sheet and 304 SS, the existence of pores and holes on Ni foam skeletons affects the contacting areas and affect the thermal conduction between the interfaces. Then the icing process on Ni/PDMS-S has been significantly delayed with respect to the substrates and it takes a prolonged period of $332.4 \pm 19.9 \text{ s}$ to form ice. The difference reveals that the PDMS layer plays an important role in the delay of ice formation compared to the bare substrates. The existing shallow and smooth surface cavities would also help to prolong the icing delay effect. The Ni/PDMS-A becomes quicker with a duration of $52.6 \pm 6.2 \text{ s}$ compared to the smooth surface. The reason could be ascribed to the remaining surface pores because it will affect the overall contacting area and the thermal conduction (the standing water droplet would have large contact with the pore structure, which also increase the thermal transfer), the ice nucleation sites (the surface rough structure could supply more nucleation points) [262].

6.3.1.2 Frost growth test

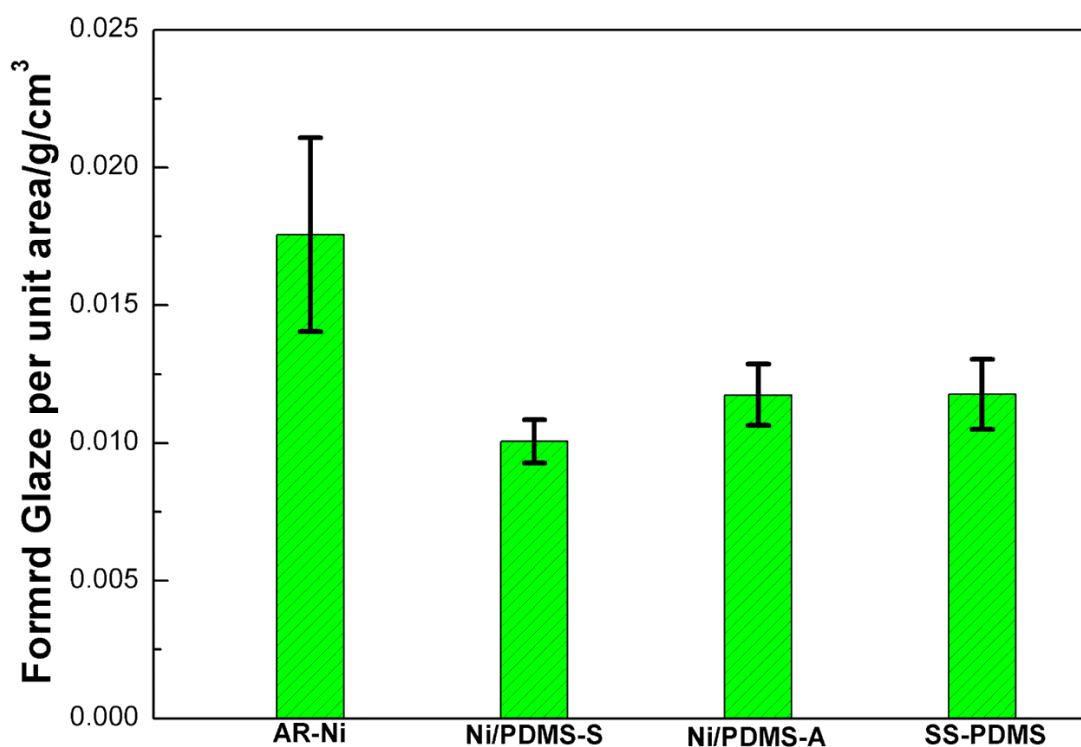


Figure 6.9 Formed glaze per unit area on AR-Ni, Ni/PDMS-S, Ni/PDMS-A, and SS-PDMS.

Figure 6.9 displays the mass of formed glaze per unit area on Ni foam/PDMS samples, AR-Ni, and SS-PDMS as references. The mass of formed glaze on certain surfaces also indicates the anti-icing performance. The glaze formed per unit area on AR-Ni is $0.018 \pm 0.003 \text{ g/cm}^3$. The reason could be the hierarchical structure and numerous pores of the Ni foam skeleton, which could supply more specific surface area. For Ni/PDMS-S, all of the existing surface pores have been covered, only some smooth and shallow surface cavities could be observed. The sites and position for frost formation have been decreased significantly. Frost would not be easy to form on the low surface energy PDMS layer. The value of Ni/PDMS-S is also the lowest, only $0.010 \pm 0.001 \text{ g/cm}^3$, with a reduction of 42.7%. The anti-frosting effect has been greatly improved. Then for Ni/PDMS-A, the formed glaze per unit area is $0.012 \pm 0.001 \text{ g/cm}^3$, which is a bit higher than Ni/PDMS-S. Although there is already a full layer of PDMS covered on the surface, the remaining deep and sharp surface pores could still supply quite large specific surface area for the frost formation. For SS-PDMS, the smooth and flat surface morphology

decrease the specific surface area and the covered PDMS layer leads to the improved icephobicity of the surface, which increases the anti-icing performance and helps with the low mass value of the formed frost.

6.3.2 De-icing performance

6.3.2.1 Ice adhesion strength of the samples

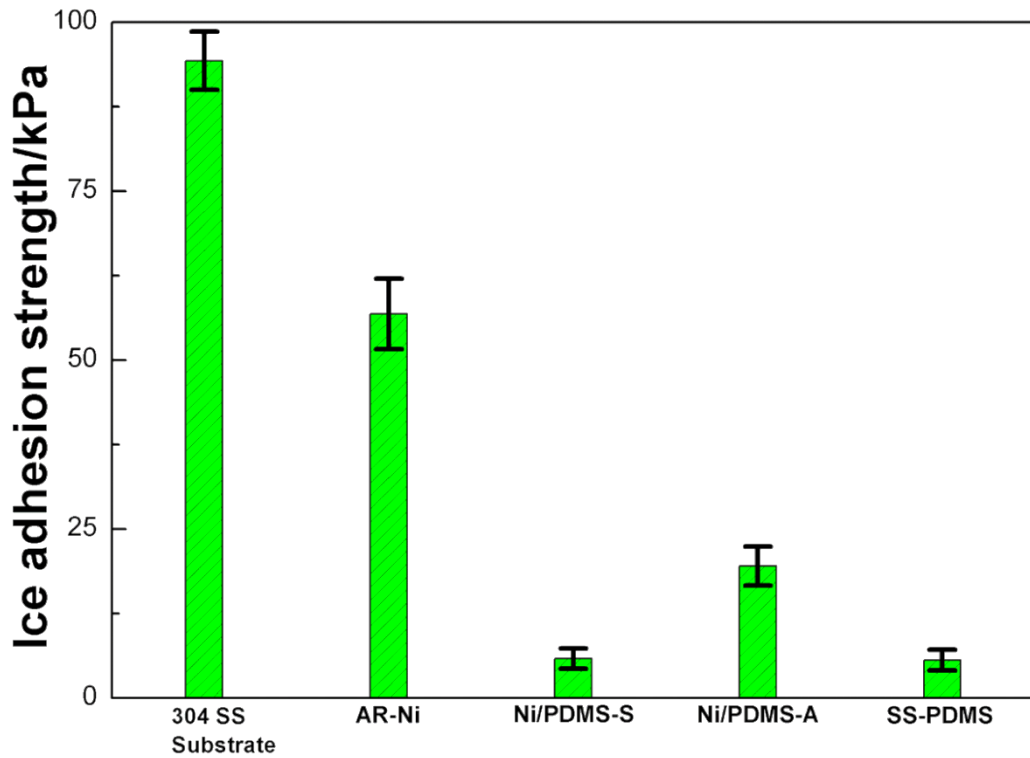


Figure 6.10 Ice adhesion results of 304 SS, AR-Ni, Ni/PDMS-S, Ni/PDMS-A and SS-PDMS.

Figure 6.10 shows the ice adhesion results of AR-Ni, Ni/PDMS-S, and Ni/PDMS-A. The results of 304 SS substrate and SS-PDMS are also shown as references. The columns represent the shear strengths. It provides an indication of how easy the formed ice could be removed from the substrate. As well known, icing is an inevitable process under the condition of sufficient supercooling [263]. Lower ice adhesion strength could help to reduce the energy consumption during the de-icing operation effectively coupled with some de-icing approach such as electro-thermal heating approaches. The results of 304 SS substrate are 94.3 ± 4.3 kPa, while for AR-Ni, the value of shear strength is

56.9 $\pm$ 5.2 kPa. This indicates that the ice is formed on the Ni foam skeleton conforming to the Cassie-Baxter state. The trapped air pockets in the Cassie-Baxter interface could act as the stress concentrators and cause a reduction in the ice adhesion strength. But the Ni foam skeleton might not reduce the ice adhesion strength effectively because the initial Cassie-Baxter mode could be damaged under supercooled airflow condition, which produces a strong action of mechanical interlock between ice and solid [90]. For the other three samples, the obvious difference could be found. Ice adhesion strength is largely related to hydrogen bonding, van der Waals forces, and electrostatic interaction. Among them, the electrostatic interaction could be the dominant factor [24]. Icephobic coating with high surface energy would increase the electrostatic interaction between ice and the coating surface. The ice adhesion strength of SS-PDMS is only 5.6 $\pm$ 1.6 kPa. This could indicate the good de-icing performance of PDMS layer, the low surface free energy of PDMS helps with the low ice adhesion strength. For Ni/PDMS-A, the ice adhesion strength increases to 19.6 $\pm$ 2.9 kPa. The reason may come from a combined factor of PDMS layer coverage and mechanical interlock. The full coverage of PDMS layer reduced the surface free energy significantly. Some of the formed ice blocks could completely penetrate into the sharp and deep surface cavities and introduce some mechanical interlock. Then the ice adhesion strength of Ni/PDMS-S is also very low, only 5.9 $\pm$ 1.5 kPa. The smoother and reduced surface cavities help to reduce the volume of existing mechanical interlocked ice. The difference in CAH reduces the surface contact area and the energy of the adhesive bond and helps to reduce the bonding of the ice-solid interface if compared Ni/PDMS-S and SS/PDMS [167].

6.3.2.2 De-icing performance via electro-thermal heating test

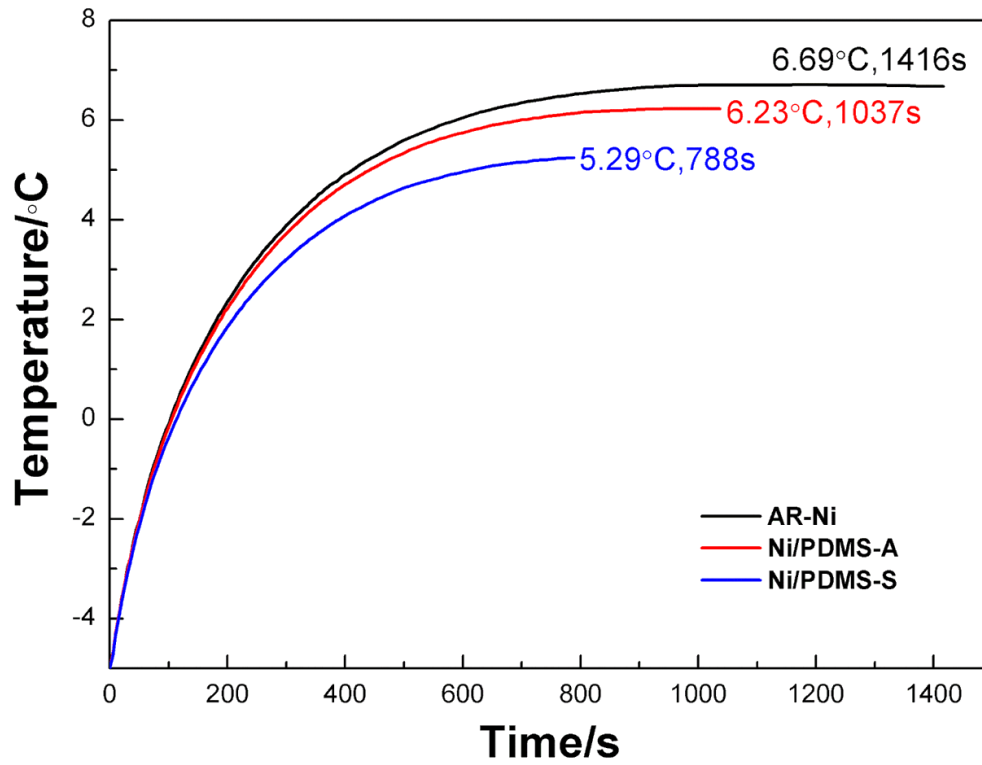


Figure 6.11 Time temperature curve during electro-thermal tests for different samples.

The electro-thermal de-icing test was carried out to evaluate the overall de-icing performance of the different samples. The experimental apparatus [168] and the detailed experimental conditions were mainly based on the demonstration showing before in Section 3.6.3.4. In the experiment, the only variant is the sample layer, all of the other parts are the same. The time temperature changing curve of the three samples during the test is shown in Figure 6.11, corresponding to AR-Ni, Ni/PDMS-A, and Ni/PDMS-S, respectively. The temperatures at the end of the curves indicate the difference of thermal conduction on samples during the electro-thermal heating. The three curves show similar changing trends. The real-time temperature of AR-Ni is the highest in equal times among the three samples. The final detachment temperature of AR-Ni is also the highest, 6.69 ± 0.22 °C. The time it uses for ice detachment is also the longest, 1416 ± 14 s. The highest real-time temperature should come from the high thermal resistance deriving from the remaining surface porosity, while the long detachment duration could come from the serious mechanical interlock induced by the

porous surface structure. For Ni/PDMS-A, the curve sits in the middle, the detachment temperature is $6.23 \pm 0.07^\circ\text{C}$ and the time becomes shorter, 1037 ± 10 s. The slight decrease should be ascribed to introduction of PDMS layer. The Ni/PDMS-S has the quickest ice detachment time of 788 ± 6 s and the lowest detachment temperature $5.29 \pm 0.18^\circ\text{C}$. With additional PDMS layer on top, there will be fewer surface pores existing, the degree of mechanical interlock will be much lowered and the thermal transfer could be improved, contributing a short detachment duration.

6.3.3 Mechanical durability evaluation of Ni foam/PDMS structures

To better evaluate the mechanical durability of the Ni foam/PDMS sample, the water-sand impinging erosion tests have been carried out. The changes in both sample surface morphology and icephobicity versus the erosion tests have also been displayed below.

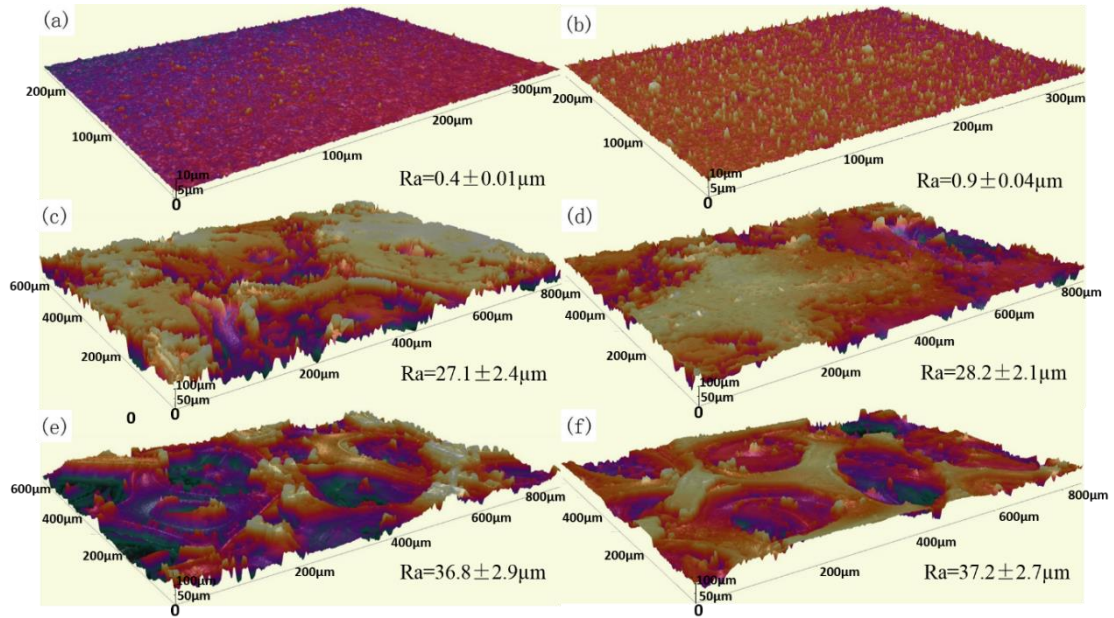


Figure 6.12 3D topography images of (a) before and (b) after water impinging tests of SS-PDMS, (c) before and (d) after water impinging tests of Ni/PDMS-S; (e) before and (f) after water impinging tests of Ni/PDMS-A.

Table 6.2 Surface roughness changes of different samples via water impinging tests.

Samples	Treatments	Surface Roughness (μm)
SS-PDMS	Before water impinging	0.4 ± 0.01
	After water impinging	0.9 ± 0.04
Ni/PDMS-S	Before water impinging	27.1 ± 2.4
	After water impinging	28.2 ± 2.1
Ni/PDMS-A	Before water impinging	36.8 ± 2.9
	After water impinging	37.2 ± 2.7

The 3D topography images and surface roughness results of the three samples before and after water-sand impinging tests are shown in Figure 6.12. The corresponding surface roughness is also listed in Table 6.2. For SS-PDMS, it is clearly observed that the water/sand abrasive impregnate into the coating surface and subsequently removes parts of the coatings, causing the rough hump structures. The value of Ra increases from $0.4 \pm 0.01 \mu\text{m}$ to $0.9 \pm 0.04 \mu\text{m}$. For Ni/PDMS-S, no significant change could be observed from the surface shown in Figure 6.12 (c) and (d). The surface roughness only has a little increase. Figure 6.12 (e) and (f) are the 3D topography before and after water impinging tests of Ni/PDMS-A. There is also no observed change in surface morphology. The surface roughness nearly remains unchanged, from $36.8 \pm 2.9 \mu\text{m}$ to $37.2 \pm 2.7 \mu\text{m}$.

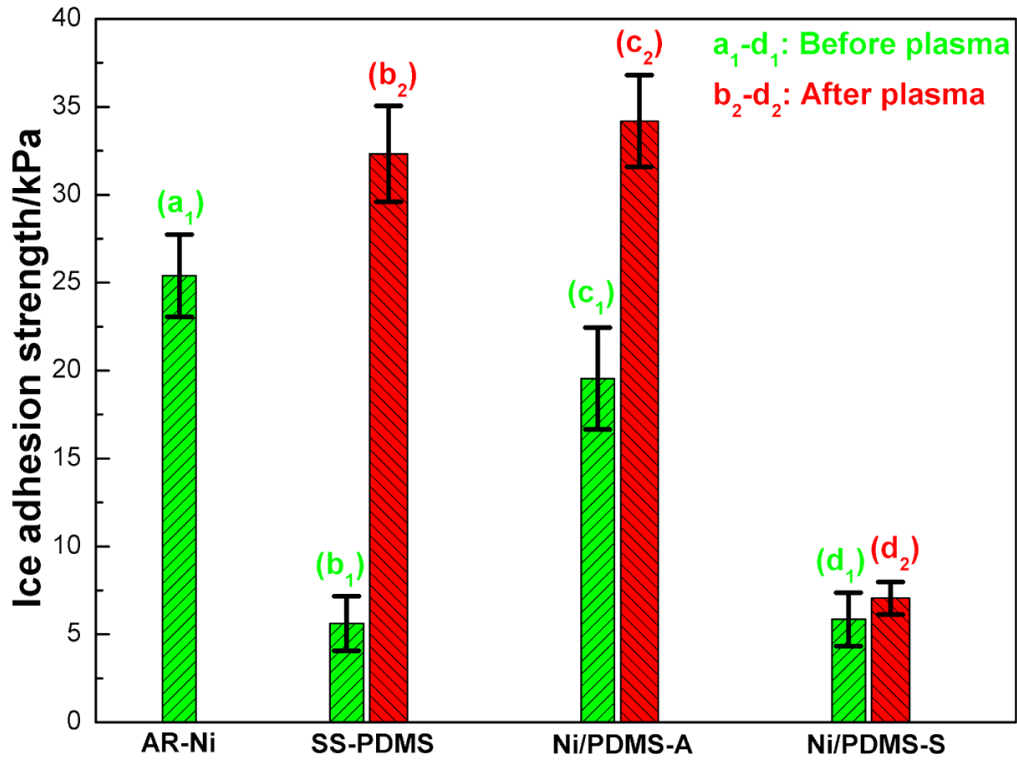


Figure 6.13 Ice adhesion strengths of different samples versus water-sand impinging tests.

Table 6.3 Ice adhesion strength results of different samples.

Samples	Treatments	Ice adhesion strength (kPa)
AR-Ni	Before water impinging	25.4±2.3
SS-PDMS	Before water impinging	5.6±1.6
	After water impinging	32.3±2.7
Ni/PDMS-A	Before water impinging	19.6±2.9
	After water impinging	34.2±2.6
Ni/PDMS-S	Before water impinging	5.8±1.5
	After water impinging	7.1±0.9

Figure 6.13 and Table 6.3 show the ice adhesion strength of different samples before and after water impinging tests. The value of AR-Ni, 56.9±5.2 kPa is listed as a reference. The ice adhesion strength of as-prepared SS-PDMS layer sample has a sharp increase from 5.6±1.6 kPa to over 32.3±2.7 kPa after the water impinging test. This is mainly ascribed to the mechanical interlock derived from the much roughened surface

structure. For Ni/PDMS-A, it changes from 19.6 ± 2.9 kPa to 34.2 ± 2.6 kPa. The Ni foam skeleton weakens the effect of water impinging and protects the surface from the water/sand erosion, this is also consistent with the small change in surface topography. For Ni/PDMS-S, the value of ice adhesion strength is 5.8 ± 1.5 kPa before and it increases to 7.1 ± 0.9 kPa after the water impinging test. The surface morphology of the sample remains unchanged. The impact energy could be effectively absorbed by the combined Ni foam/PDMS structure.

6.4 Water Condensation and Icing Study

6.4.1 Water condensation and ice formation on Ni/PDMS-A

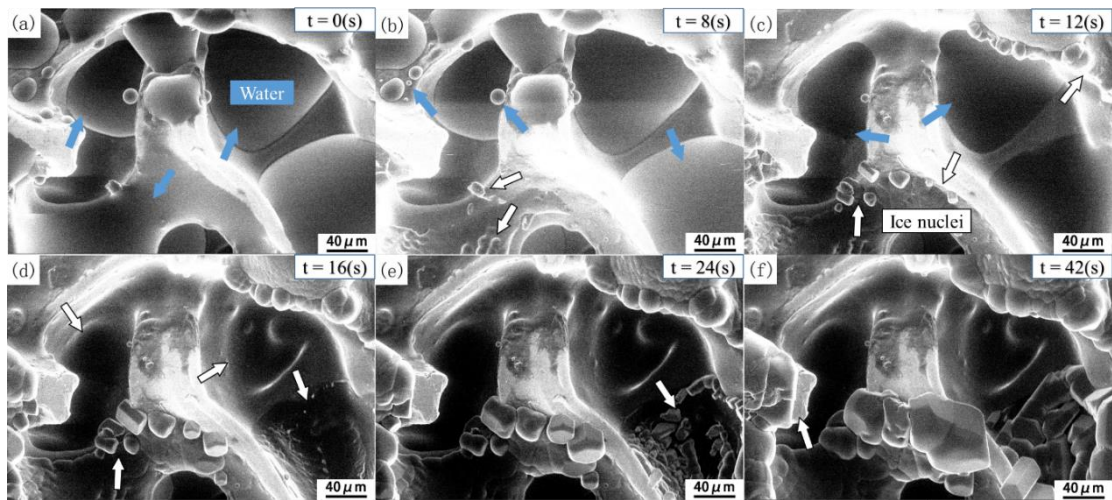


Figure 6.14 (a) water condensation (b) water-ice co-existence and (c)-(f) ice formation process on Ni/PDMS-A (Pressure: 2.4-2.6 torrs; Temp: -7.1 to -5.1 °C; Humidity: 83.9-90.5%).

The water condensation and ice formation from the vapours were carried out on Ni/PDMS-A using ESEM in Figure 6.14. From Figure 6.14 (a), the surface cavities are all full of water, both at the higher area of Ni foam skeleton covered by PDMS layer and the lower surface cavities. It is found that no ice crystal nucleates on the surface by desublimation under the condition of $T \approx -7.1$ °C and relative humidity (RH) $\approx 88.0\%$. This observation shows the delayed icing nucleation performance of the layer. These

water droplets are in a supercooled state. As temperature decreases, the trigger of ice nucleation could take place in certain circumstances. After 8 s, the ice formation has been observed in Figure 6.14 (b). At the moment of ice formation, a great deal of latent heat generated in the phase transformation from water to ice would be released and a sudden temperature increase occurs. The condensed supercooled droplet on the surface cavities at the area of Ni foam skeleton covered by PDMS layer (bottom left corner) becomes ice crystal, while the water at the lower smooth surface cavities remains liquid form, showing a state of water-ice co-existence. It could be assumed that the ice nuclei has a preference to form on the surface cavities near the Ni foam skeleton. Once the ice is formed, the nucleus grows rapidly. Several more ice nucleation points have been observed in the area of Ni foam skeleton covered by PDMS layer. It could be observed that most of the ice nuclei are near the area of Ni foam skeleton covered by PDMS layer and no ice nucleation point could be observed at the lower surface cavities, as indicated in Figure 6.14 (c). Then from Figure 6.14 (c) to (e), the condensed supercooled droplet at the lower surface cavities also turns into ice after 16 s. From Figure 6.14 (e) to (f), the ice crystals keep growing and could form indiscriminately around the area of Ni foam skeleton covered by PDMS layer which further leads to some interlocks.

6.4.2 Water condensation and ice formation on Ni/PDMS-S

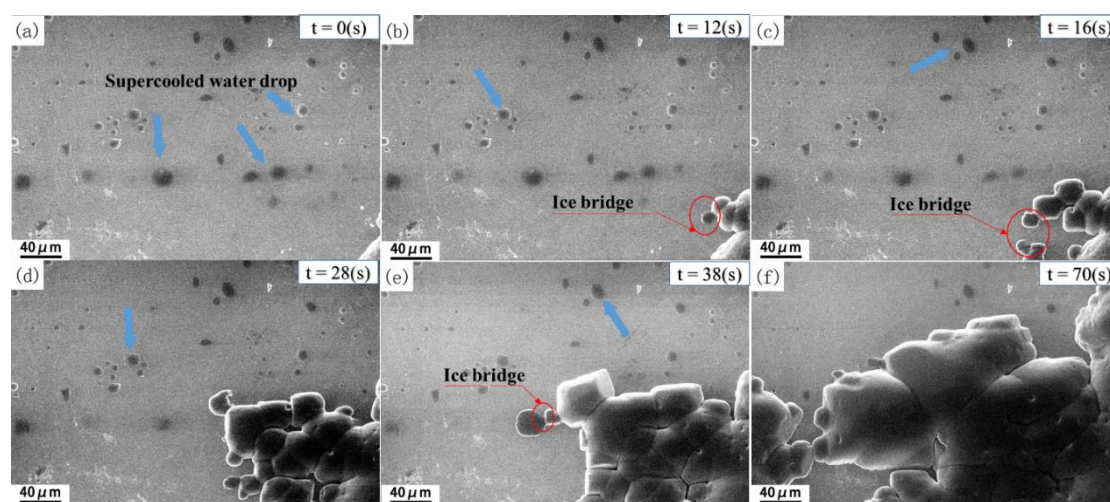


Figure 6.15 Ice formation process on Ni/PDMS-A (Pressure: 2.9 torrs; Temp: -5.3 °C; Humidity: 94.7%).

Snapshot images of the nucleation and growth of ice on Ni/PDMS-S are shown in Figure 6.15. The images demonstrate that ice forms discriminately over the surface on condensed supercooled droplets. There are several condensed supercooled droplets distributed on the surface. The initiated ice crystal will grow from the bottom right corner to the central area as indicated in Figure 6.15 (b) to (e). Comparing Figure 6.15 (c) and (d), the area with condensed supercooled droplets is more likely to form ice. These condensed supercooled droplets would act as the preferential ice nucleation sites to form ice and finally lead to the full coverage of ice on the surface. It is reported that the saturated water vapour pressure around the condensed supercooled droplets would always be higher than the ice-covered area at a constant temperature [135]. Because of this, some of these condensed supercooled droplets would evaporate and migrate into the ice crystal, which could form ice bridges toward the condensates [264]. If an ice bridge touches the nearby condensed droplet, the supercooled droplet would freeze much quickly. This could be explained by the Wegener-Bergeron-Findeisen process in meteorology: the propagation characteristic of ice crystal which comes from the saturated water vapour pressure difference between formed ice and supercooled droplets [265]. Due to the smoother and reduced surface cavities, the formed ice block will have much less contact area with the sample surface, this could also be favourable for reducing the ice adhesion strength, which has been further verified in Section 6.3.2.1.

6.5 Discussion

6.5.1 Effect of PDMS layer coverage in delaying ice formation

It is considered that the freezing process mainly consists of a precooling stage and ice growing stage, and most of the icing delay time (> 95%) is occupied by precooling. The thermodynamics of water droplet could be displayed as equation (6.1) [9]:

$$\Delta Q = \Delta Q_1 - \Delta Q_2 \quad (6.1)$$

where ΔQ is the heat change in unit time; ΔQ_1 is the transferred heat to the cold solid surface, and ΔQ_2 is the obtained heat from the air, which should be constantly zero in this experiment because the temperature of the whole chamber is kept at below 0 °C. The temperature change Δt of the droplet is expressed as equation (6.2) below [266]:

$$\Delta t = \frac{\rho_w C_p (T_0 - T_1)}{\Delta Q} \quad (6.2)$$

where Δt is the required time for water droplet freezing; ρ_w is the water density; C_p is the water specific heat capacity; T_0 corresponds to the initial droplet temperature; T_1 is the real-time surface temperature.

For Ni/PDMS-S, due to the deposited hydrophobic PDMS layer on top, the water droplet also keeps hydrophobic characteristic and keep small base width with the surface. The thermal transfer between the interfaces will be restricted. There will be less heat being transferred to the droplet layer interface, the transferred heat to the cold solid surface ΔQ_1 would become smaller while the obtained heat from the air ΔQ_2 would remain the same, in this way, the overall heat change ΔQ would be lower. Then the required time for water droplet freezing would also be prolonged, showing a longer ice formation time. While for Ni/PDMS-A, because of the remaining sharp and deep surface cavities, the water droplet would fill in the rough structure, the base width of the water droplet on the structure would inevitably increase, the contacting area will increase. Considering the covered thin PDMS layer and good thermal conductivity of Ni foam, the transferred heat to the coating surface could also be quite large. As indicated by Eq (6.2), the required time for water droplet freezing could be smaller, showing a quick ice formation time.

6.5.2 Impact of surface cavities on ice formation and diminishment

The condensation dynamics on Ni/PDMS-A and Ni/PDMS-S observed through in-situ ESEM observations clearly indicate the difference of ice formation and the effect of

remaining surface cavities. First, it is the ice formation. As indicated by Figure 6.16, it is assumed that the icing nucleation on Ni/PDMS-A has a preference to form on the surface cavities near the Ni foam skeleton. Once the ice forms, the nucleus grows in a quite quick rate, the ice would keep growing and ice can form indiscriminately. Due to the remaining sharp and deep surface cavities, some ice would grow around the Ni foam skeleton covered by PDMS layer which further leads to some interlocks.

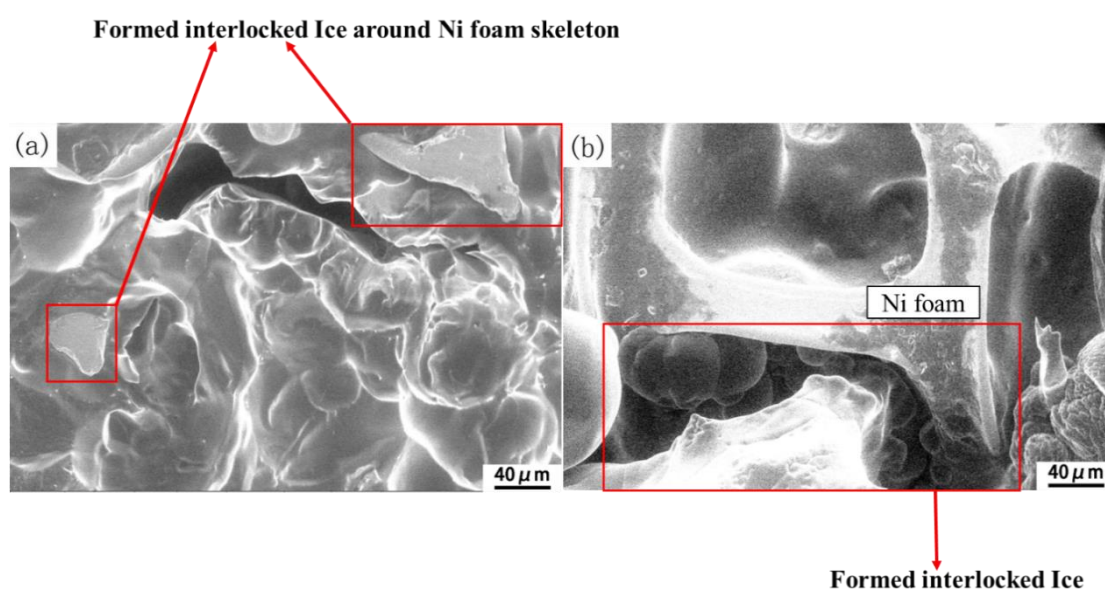


Figure 6.16 Interlocked ice between the sharp and deep surface cavities on Ni/PDMS-A (Pressure: 3.0 torrs; Temp: -4.8 °C; Humidity: 90.1%).

It is interesting to note that the ice adhesion of the ice crystals from the supersaturated vapours on the Ni foam/PDMS layers seems to be quite high which has been evidenced by the severe mechanical interlock around the Ni foam skeleton during its sublimation under reduced vapour pressure, as shown in Figure 6.16 (a) and (b). It is indicated that ice nearly exists in all of the available areas between the sharp and deep surface cavities. The red rectangles in Figure 6.16 clearly corroborate the interlocked ice. Especially in Figure 6.16 (b), the formed ice around the Ni foam skeleton could provide a lot of difficulties in the ice removal, causing high ice adhesion strength, which has been evidenced in Figure 6.10.

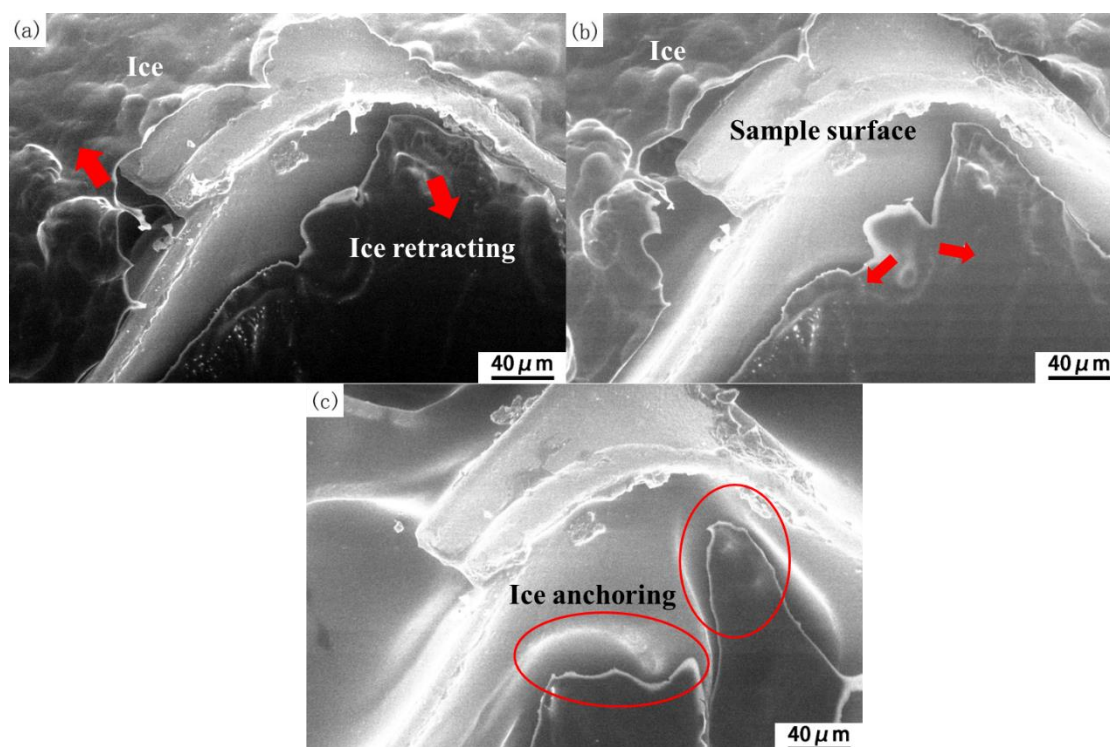


Figure 6.17 Anchoring of interlocked ice on Ni/PDMS-A when ice sublimates (Pressure: 1.9 torrs; Temp: $-4.0\text{ }^{\circ}\text{C}$; Humidity: 56.3%).

With reduced system humidity, the sublimation would occur and ice diminishment would take place. It could be observed that the surface morphology of Ni/PDMS-S maintain intact when the ice crystal recedes during the sublimation. Images representing this process is given in Figure 6.17. In Figure 6.17 (a), the ice around the sharp and deep surface cavities would diminish along with the directions indicated by the red arrows. From Figure 6.17 (b) to (c), the anchoring of ice into the sharp and deep surface cavities is clearly observed, as shown in the red circles of the embedded anchored ice.

While for Ni/PDMS-S, the surface morphology has been changed. Fewer surface cavities remain on the surface and they also become smoother and more flat. It can be obviously seen that there is less interlocked ice existing on Ni/PDMS-S. Due to the smoother and more flat surface morphology, the formed ice block has much less ice-surface contact area with the Ni foam skeleton and the sample surface. This could also verify the low value of ice adhesion strength, showing the good de-icing performance.

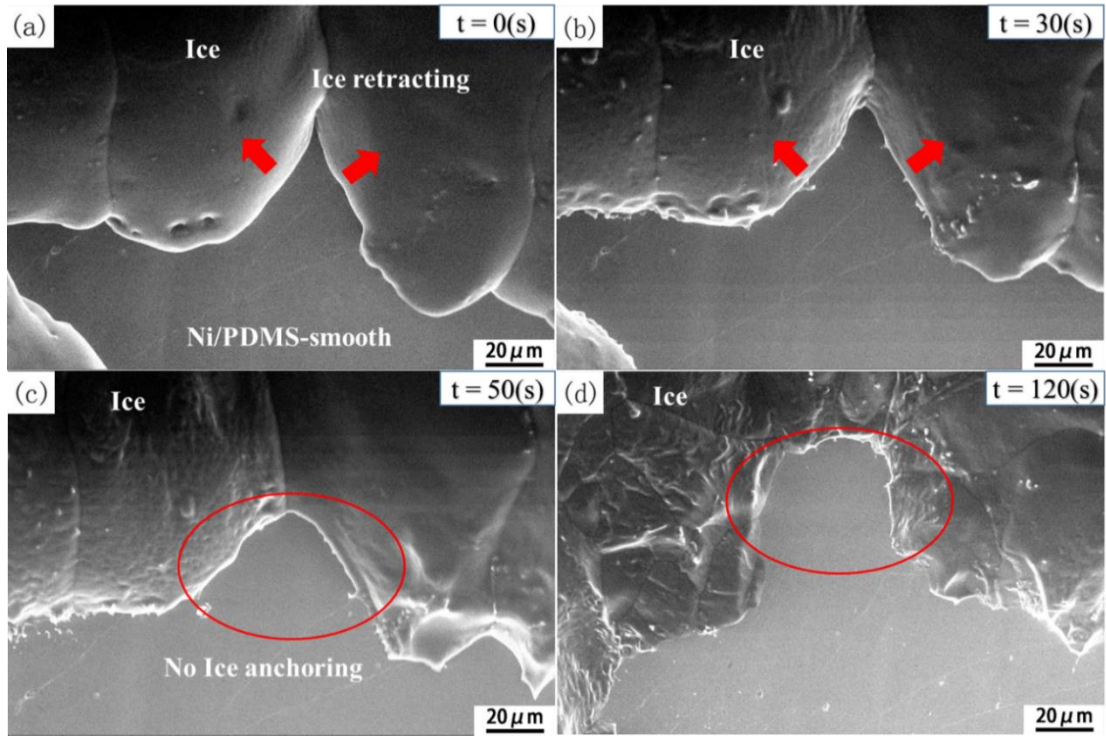


Figure 6.18 Ice diminishing process on Ni/PDMS-S (a) $t=0$ s (b) $t=30$ s (c) $t=50$ s (d) $t=120$ s (Pressure: 2.4 torrs; Temp: -6.3 °C; Humidity: 82.6%).

Figure 6.18 shows the diminishment process of ice on Ni/PDMS-S. From Figure 6.18 (a) to (b), the ice layer becomes thinner and the edge changes from rounded to angular. The icing field has moved a bit upper from Figure 6.18 (b) to (c). The direction of the disappearance of the formed ice crystal is just opposite to the propagation direction. Unlike Ni/PDMS-A, there is no ice anchoring or retardation of ice movement observed during the whole process, indicating good potential in de-icing.

From this point, it can be concluded that the surface cavities would affect the ice formation and ice disappearance. The sharp and deep surface cavities would lead to serious mechanical interlock and lower the icephobicity. While for Ni/PDMS-S, the flat and smooth surface cavities would reduce the interlocked ice and make the later de-icing easier.

6.5.3 Roles of Ni foam skeleton in lowering ice adhesion strength

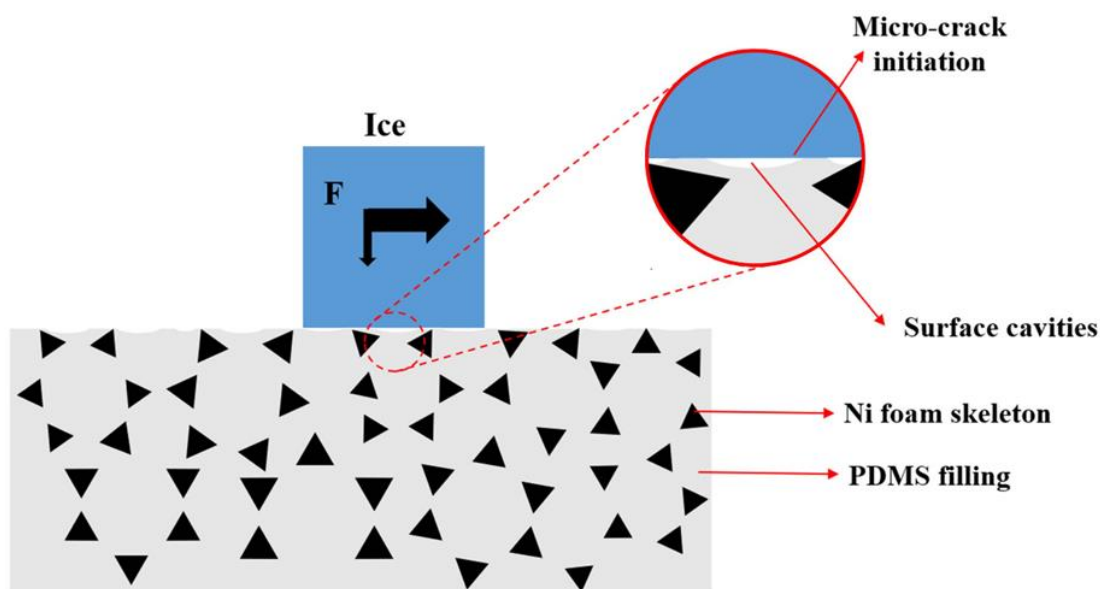


Figure 6.19 Schematic view of micro-crack initiation mechanism at the surface cavities between the ice-layer interface.

The schematic view of the micro-crack initiation mechanism at the surface cavities between the ice-layer interfaces is shown in Figure 6.19. In the figure, the triangles show the cross-sectional structures of the Ni foam skeleton, the surface cavities are also indicated, which could be evidenced in Figure 6.3. It is assumed that the Ni foam skeleton could help to introduce a micro-crack initiation mechanism. Because the difference in elastic modulus could result in different micro-distortions between the Ni foam skeleton and PDMS filling during ice detachment, which could generate microscopic cracks along with ice-layer interface and weaken the linkage between ice and layer surface, leading to a low ice adhesion strength [18, 153]. The microscopic crack initiation mechanism during the ice detachment may be contributed from the remaining smooth surface cavities and the difference in elastic modulus between Ni foam skeleton and PDMS filling. The interface deformation incompatibility and stiffness inhomogeneity between the layer materials help to establish the crack initiation mechanism [267]. In this way, the usage of the Ni foam skeleton also helps with the low ice adhesion strength.

6.5.4 Enhancement of energy saving by using Ni foam/PDMS layer structures

For coatings with low ice adhesion strength, if it is coupled with an active de-icing approach such as electro-thermal heating, the overall energy consumption for de-icing operation could be reduced effectively. So it is also important to evaluate the energy use efficiency of a certain icephobic surface structure. Here, the Ni foam/PDMS layer structures show good potential in energy saving. The Ni foam/PDMS layer structures could be analysed by a one-dimensional multi-lamina model as demonstrated in Section 3.6.3.4. In this model, the thermal transfer is perceived as a one-dimensional flux from the heating side to the sample interface. The thermal energy used to melt the interface ice is proportional to the heat flux and thermal conduction efficiency in a certain duration.

Table 6.4 Energy consumption of different samples.

Samples	Detachment temperature (°C)	Detachment time (s)	Energy consumption (J)
AR-Ni	6.69 ± 0.22	1416 ± 14	4050 ± 40
Ni/PDMS-A	6.23 ± 0.07	1037 ± 10	2966 ± 29
Ni/PDMS-S	5.29 ± 0.18	788 ± 6	2254 ± 17

As is shown in Figure 6.11, the three curves show similar changing trends. The slope of the curves at certain points could reflect the heating efficiency of the coatings. Samples with high thermal conductivity possess quicker heat flow speed and could transfer more thermal energy in unit time. The displayed temperature at the end of the curves is the detected temperature when the ice cube detaches. They all have reached platforms at the end of the curves, which indicate the detected temperature remains unchanged. This also means that a balance between the heat adsorption from ice melting and heat flow. The attached ice would keep melting. When the linked ice at the interface is melted to complete or the linked ice is no longer strong enough to against the gravity of the ice cube, the ice cube would then detach. The overall energy input of different samples could be calculated and shown in Table 6.4.

With the same power output, the temperature increase of the three samples is different. For AR-Ni, the real-time temperature is the highest in equal times among the three samples. The final detachment temperature and duration are both the highest, the total energy input could reach 4050 ± 40 J, seen from Table 6.4. The reason for the long detachment duration could be ascribed to the serious mechanical interlock induced by the porous surface structure, and the highest thermal resistance derived from the numerous existence of pores and holes which has around 90% porosity filled by air (the thermal conductivity of air is only 0.024 W m/K at 0°C). For Ni/PDMS-A, the curve sits in the middle with lower real-time temperature and shorter detachment duration. The overall energy consumption also decreases obviously, with a value of 2966 ± 29 J. Less energy is needed to make the ice cube detach. Because of the introduction of PDMS layer, some of the surface cavities have been covered. With a less porous structure, the serious mechanical interlock would have been reduced. Besides, the existing air which has been replaced by PDMS filling could help to reduce the overall thermal resistance of the samples (the thermal conductivity of pure PDMS is 0.15 W m/K). The thermal transfer efficiency would be improved to some extent. So the detachment duration is shortened and the final detachment temperature is also lower compared to AR-Ni. Ni/PDMS-S has the quickest ice detachment time and highest detachment temperature, while the energy consumption is the lowest, only 2254 ± 17 J, with a decrease of 79.6% compared to AR-Ni. The energy required to melt the interface ice mainly depends on the extent of mechanical interlock and the surface ice adhesion strength as well as the thermal transfer efficiency. Due to the smoother and reduced surface cavities, the mechanical interlock would be much reduced on the surface of Ni/PDMS-S, which is also shown from the low ice adhesion strength. With less sharp and deep surface cavities and also additional PDMS layer on top replacing former existing air, the overall thermal resistance of Ni/PDMS-S would also be lower. By considering the two factors, the total energy input would be much lower. The total energy input transferred for ice melting also decreases.

The Ni foam/PDMS layer structures play a significant role in enhancing the energy

efficiency and could help with the energy saving in practical icephobic applications. For the design of icephobic coatings, low thermal resistance could be an essential requirement for a hybrid ice protection involving heating [15], when the target is to minimise energy consumption. Ni/PDMS-S has demonstrated much improved performance to satisfy such requirements.

6.5.5 Mechanical durability enhancement with Ni foam skeleton

The stability of icephobicity against mechanical and environmental damages is an important consideration for practical applications of icephobic materials. The introduction of Ni foam skeleton also prove that it could help with the good mechanical durability and stable icephobic performance of Ni foam/PDMS systems. To better illustrate this, the schematic views of shock wave propagation process and impact energy re-distribution during the water-sand impingement on Ni foam/PDMS layer are shown in Figure 6.20.

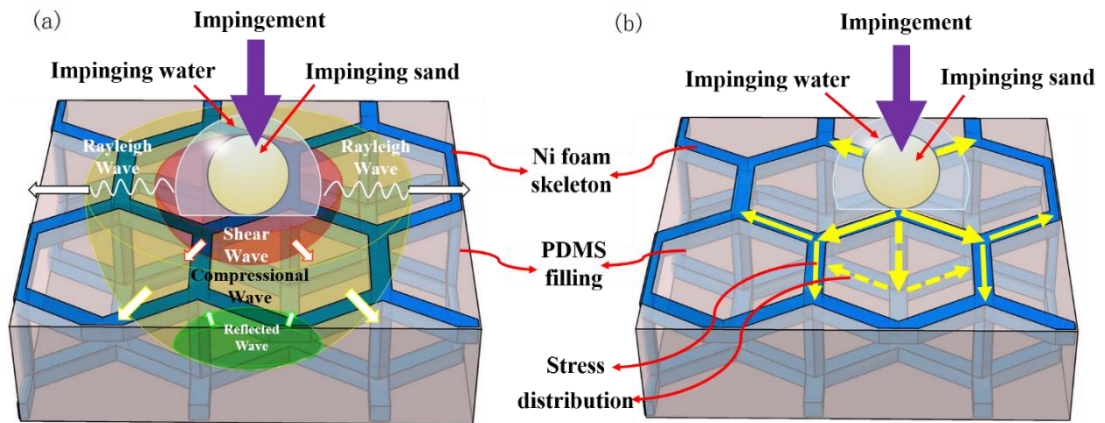


Figure 6.20 Schematic views of (a) shock wave propagation occurring upon impact of water-sand impingement on Ni/PDMS-S (b) re-distribution of impact energy of water-sand impingement on Ni foam/PDMS layer.

Figure 6.20 (a) shows the schematic view of the shock wave propagation process on Ni/PDMS-S. With the water-sand mixture impinges onto the layer surface at a certain angle, the impinging water droplet would deform and show a compressed shape while

the sand particle remains its original shape. It is assumed that the impact abrasion and direct shear abrasion brought by the impinging sand particles during the impingement would be reduced by the Ni foam/PDMS structure effectively. The impact of the droplet sphere onto a solid surface could be quite complex, the interaction of the waves generated during the impingement will depend upon the impact conditions and material properties [268]. We speculate that the two compressional wave fronts in the longitudinal direction would be initiated inside the layer structures and followed with the transverse shear wave. Combined with the deformation of impinging water droplets, the impact from the impingement may result in the appearance of the third wave, Rayleigh wave, which is confined to the surface of the target and contains approximately 2/3 of the impingement energy. The pressure generated on impact is referred to as the water-hammer pressure and the magnitude varies depending on the acoustic properties of the target material and the liquid [269]. Due to the local imbalance of tensile and shear stresses in regions that may be outside the direct impact area [270], the erosion failure of the surface layer could be initiated, as evidenced in Figure 6.19. But for the Ni foam/PDMS structure in Ni/PDMS-S, it is expected that the Ni skeleton could help to reduce the local damage and transfer the different wave propagations. This may contribute to build a balance between the tensile and shear stresses and increase the erosion resistance and avoid the erosion failure [271].

Figure 6.20 (b) shows the impact shock from water-sand suspension impingement on the Ni foam/PDMS structure. It is assumed that the impact abrasion could be significantly restrained and the impact energy could be transferred to a much larger area through the Ni skeleton. The PDMS filling, which is a highly-damped, visco-elastic polymer, may also help with such transfer and adsorb most of the energy. Therefore, the remarkable increase in the erosion resistance may be contributed from the Ni foam/PDMS structure, which is well maintained under the severe impact abrasion and direct shear abrasion, as evidenced by Section 6.3.3. The Ni foam skeleton could act as the armours for the filled PDMS, against possible mechanical scratch and removal from the high-velocity water droplets and sharp SiC particles [143].

6.6 Summary

In summary, a new type of highly durable icephobic layer structures using porous Ni foam skeletons and PDMS filling by two-step methods (vacuum impregnation and spinning coating) has been developed. The two-phase Ni foam/PDMS layer structures with fine surface cavities show very low ice adhesion strength of only 5.9 kPa with the help of the icephobic PDMS layer. The initiated micro-crack initiation mechanism may also contribute. Ice growth and diminishment on the Ni foam/PDMS layer was studied using ESEM, confirming good icephobicity of the two-phase structures. Furthermore, the Ni foam/PDMS layer remained stable under severe water-sand impinging erosion and good mechanical durability was confirmed. The usage of Ni foam skeleton could offer better protection and act as armours for the implementation of elastomers (filled PDMS). The energy efficiency of the Ni foam/PDMS layer in the electro-thermal de-icing test has also been improved, indicating that the new two-phase structural design could be a promising approach for hybrid ice protection with low energy consumption. The results indicate that the layer structures with a combination of Ni foam skeleton and PDMS layer could be a good choice for future icephobic applications. The design thinking of combining robust substrate skeleton and hydrophobic/icephobic filling could provide new insight into the design principles of icephobic surfaces. It also offers new feasibility and provides insight for designing durable icephobic surfaces.

Chapter 7 Conclusions and Future Work

7.1 Conclusion

In this project, new designs of hydrophobic/icephobic nickel-based coatings and structures with good mechanical durability have been developed, and the related mechanisms on wettability and icephobicity have also been studied.

- Initially, the Ni-Cu-P ternary coatings up to 20 μm with cauli-flower structures were prepared on 304 SS substrates using electrodeposition method. The processing parameters for the coating deposition were investigated and optimised. Samples prepared with 50 mA/cm^2 current density without further annealing showed regular hierarchical cauli-flower structures with surface roughness of 3.9 μm and good hydrophobic characteristic with WCA of 144.0° and CAH of 5.5° . The changing wettability was also observed and studied with the help of plasma cleaning and subsequent air exposure, which could be termed as time-dependent wettability. In addition, the underlying mechanisms of time-dependent wettability were also investigated with the help of XPS spectra and ESEM observation. The adsorption and desorption of airborne hydrocarbons and lattice oxygen groups could explain the determining factors of the time-dependent wettability on coating surfaces. The two factors would alter the surface energy and introduce more hydrophobic groups onto the coating surface, resulting in the changes of wetting behaviour.
- To better investigate the time-dependent wettability phenomenon, a comparison study using different surfaces and coatings including electroless deposited Ni-Cu-P coatings, 304 SS, CeO_2 and PDMS polymeric coatings have been carried out and led to a detailed mechanism of time-dependent wettability. The studies verified the

universality of time-dependent wettability in different surfaces and coatings (except for the polymeric coatings). The surface wetting state of the as-prepared samples all changed from hydrophilic to hydrophobic state after ageing in ambient air. The adsorption of airborne hydrocarbon and the ratio change of lattice oxygen on the coating surfaces could be the main factors. The stable hydrophobicity of PDMS polymeric coating also confirmed the significant role of surface gaseous adsorption.

- In addition, the relationship between time-dependent wettability and icing behaviour were also investigated using Ni-Cu-P coatings. The study indicated that the icephobicity of the coatings would be deteriorated when the coating hydrophobicity was lost. With the removal of surface gaseous adsorption, the hydrophobicity decreased. For anti-icing performance, the icing time of water droplets on Ni-Cu-P coatings also decreased sharply, and the frost growth became much quicker. For the de-icing performance, the ice removal effectiveness with electro-thermal heating deteriorated obviously with a significantly increased energy input and the ice adhesion strength also increased sharply. Moreover, the role of air pockets and the presence of the interlocked ice were emphasized by the ESEM observation. The adsorbed hydrocarbons would help to form a good amount of air pockets at the water-solid interface, which could decrease the interfacial contact effectively between the water droplets and coatings, further hindering the formation of interlocked ice. The changes of surface free energy could also confirm the effect of gaseous adsorption on coating icephobicity. Due to the universal surface adsorption phenomenon in air, the mechanism disclosed in this study is likely to be applicable to other metallic coatings and surfaces.
- A new design concept of combining robust porous metallic skeletons and icephobic filling to construct a two-phase structure has been proposed, which demonstrated good icephobicity with excellent mechanical durability. Ni foam was chosen as the

porous skeleton (phase I), PDMS was selected as the filling material (phase II). Ni foam/PDMS layers with fine surface cavities were prepared by a two-step method (vacuum impregnation and spinning coating). The results showed that the two-phase structure could maintain very low ice adhesion strength (only 5.9 kPa) which could be attributed to the icephobic PDMS layer. The initiated micro-crack initiation mechanism may also contribute. The energy efficiency of the Ni foam/PDMS layer in the electro-thermal de-icing test has also been improved. The introduction of Ni porous skeleton could significantly increase the surface durability under water-sand erosion impact. Both the icephobicity and the structural features of the Ni foam/PDMS layer remained stable under long-time water erosion. Furthermore, the in-situ ESEM observation exhibited the ice accretion and diminishment on the Ni/PDMS-smooth sample. The Ni foam/PDMS construction combines the mechanical advantages of Ni skeleton and the icephobicity of PDMS, and it offers new feasibility and provides insight for designing durable icephobic surfaces.

7.2 Future Work

For perspectives of future efforts in the development of icephobic materials, more attention will be focused on the fundamental science behind the wettability and icephobicity mechanisms, R&D of icephobic coatings with excellent mechanical durability, and the practical applications of the developed icephobic coatings. Some further suggestion and work plans are put forward based on the results obtained:

- The concept of time-dependent wettability is an indispensable supplement to current icephobicity study and could be implemented in a broad range of material systems. More in-depth and accurate studies between surface composition variation and properties on specific surfaces including the speed control on the adsorption and re-adsorption process could be carried out in the future and address the origins

of the fundamentals. The disclosed mechanism could, in turn, give guidance and supply new feasibility for designing hydrophobic/icephobic surfaces.

- For the effect of surface gaseous adsorption, it is a critical issue to consider the time-dependent wettability when evaluating the coating icephobicity under specific characteristic testing conditions. Due to the possible time-dependent surface wettability in common engineering applications, the standardization of icephobic performance tests is an urgent need. Reliable and repeatable testing standards are expected to be established with the mutual effort between international standard organizations, the funding agencies, research institutions, and interested end users.
- Multi-phase material layer structures offer excellent icephobicity with no compromise in mechanical durability, which also conform to the main expected figures of merit for future icephobic coatings in practical use. The proposed two-phase structural design opens a new avenue for durable icephobic coatings. New types of materials and coating designs could be constructed on the basis.
- Different definitions of icephobicity correspond to different related properties of anti-icing and de-icing surfaces. More prototype tests that correspond to different icephobic performance are needed under the simulated working environments, such as wind tunnel test for airfoil applications, etc.
- More simulation work could be conducted to give better guidance to the R&D of icephobic coatings, including stress analysis, thermal transfer analysis and material response under erosion impact. The scale for modelling could also be diverse, macroscale, microscale and even nanoscale. Finite element analysis, molecular dynamics or other appropriate simulation methods could be applied to unfold the underlying mechanisms.

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