MECHANICALLY ROBUST, (SUPER)HYDROPHOBIC SURFACES

by

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Abstract

In this doctoral study, applied and fundamental research on mechanically robust, (super)hydrophobic surfaces was performed. On the applied front, a simple electro-codeposition process was developed to fabricate non-wetting metal matrix composite coatings with exceptional hardness and resistance to degradation of non-wetting characteristics from abrasive wear compared with a commercial superhydrophobic surface coating. The composites were made of ultra-fine grain / nanocrystalline nickel matrix with embedded hydrophobic particles: polytetrafluoroethylene (PTFE) or rare earth oxide (i.e. cerium oxide) distributed throughout the thickness of the composite coating. Various characterization techniques, including wetting property measurements, electron microscopy, microhardness measurements, and abrasive wear testing were performed to develop the structure – property - performance relationships for this new class of non-wetting material.

On the fundamental side, the inherent wettability of rare earth oxides was investigated, as there is currently an active debate in the literature as to whether these ceramics are hydrophobic or hydrophilic. To develop a better understanding on the wettability of rare earth oxides, a study of single crystals with near perfect surfaces was carried out. Epitaxial films of CeO₂ and Er₂O₃ were grown on low Miller index oriented yttria stabilized zirconia single crystal substrates by a pulsed
laser deposition technique. Through this study, the crystal orientation – surface energy - wetting property relationships for rare earth oxides were established. Fresh REO epitaxial films were hydrophilic, the water contact angle (WCA) strongly depending on the crystallographic orientation; $WCA_{(111)} > WCA_{(110)} > WCA_{(001)}$, which reflects the differences in surface energy (SN); $SN_{(111)} < SN_{(110)} < SN_{(001)}$. Moreover, upon exposure to air, WCA on CeO$_2$ and Er$_2$O$_3$ increased rapidly and converged to about 80°, regardless of the crystallographic orientation, due to surface adsorption of airborne hydrocarbon species. The importance of airborne hydrocarbon adsorption in other areas of science and technology is discussed.
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<th>Full Form</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BF</td>
<td>Bright field</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electron</td>
</tr>
<tr>
<td>CSHST</td>
<td>Commercial superhydrophobic spray treatment</td>
</tr>
<tr>
<td>DF</td>
<td>Dark field</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>HAADF</td>
<td>High angle annular dark field</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection high energy electron diffraction</td>
</tr>
<tr>
<td>RSM</td>
<td>Reciprocal space mapping</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SN</td>
<td>Surface energy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>WCA</td>
<td>Water contact angle</td>
</tr>
<tr>
<td>WSA</td>
<td>Water sliding angle</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRR</td>
<td>X-ray reflectivity</td>
</tr>
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</table>
## List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$C_b$</td>
<td>Bulk concentration</td>
</tr>
<tr>
<td>$d$</td>
<td>Grain size</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$f$</td>
<td>Pulse frequency</td>
</tr>
<tr>
<td>$f_1$</td>
<td>Fraction of component 1</td>
</tr>
<tr>
<td>$f_2$</td>
<td>Fraction of component 2</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>$g$</td>
<td>Force due to gravity</td>
</tr>
<tr>
<td>$H$</td>
<td>Hardness</td>
</tr>
<tr>
<td>$H_0$</td>
<td>Hardness at large grain size</td>
</tr>
<tr>
<td>$i_{avg}$</td>
<td>Average current density</td>
</tr>
<tr>
<td>$i_L$</td>
<td>Limiting current density</td>
</tr>
<tr>
<td>$i_{peak}$</td>
<td>Peak current density</td>
</tr>
<tr>
<td>$k$</td>
<td>Hall-Petch constant for strength</td>
</tr>
<tr>
<td>$k'$</td>
<td>Hall-Petch constant for hardness</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
</tr>
<tr>
<td>$n$</td>
<td>Electron transfer</td>
</tr>
<tr>
<td>$q$</td>
<td>Scattering vector</td>
</tr>
<tr>
<td>$R_f$</td>
<td>Roughness factor</td>
</tr>
</tbody>
</table>
\( R_{rms} \)  
Roughness root mean square

\( t \)  
Time

\( T_{on} \)  
Time period when current is on

\( T_{off} \)  
Time period when current is off

\( V_{gb} \)  
Grain boundary volume fraction

\( V_{ic} \)  
Intercrystalline volume fraction

\( V_{tj} \)  
Triple junction volume fraction

\( w \)  
Width

\( 2\theta \)  
Angle between X-ray source and detector

\( \alpha \)  
Sliding angle

\( \gamma_{lv} \)  
Liquid – vapour interfacial surface tension

\( \gamma_{sl} \)  
Solid - liquid interfacial surface tension

\( \gamma_{sv} \)  
Solid – vapour interfacial surface tension

\( \Delta \)  
Grain boundary thickness

\( \delta \)  
Thickness of Nernst diffusion layer

\( \theta \)  
Angle of measurement

\( \theta_{cr} \)  
Critical angle for total reflection

\( \theta_C \)  
Cassie contact angle

\( \theta_{CB} \)  
Cassie-Baxter contact angle
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_W$</td>
<td>Wenzel contact angle</td>
</tr>
<tr>
<td>$\theta_Y$</td>
<td>Young contact angle</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Zeta potential</td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>Yield strength at large grain size</td>
</tr>
<tr>
<td>$\sigma_{UTS}$</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>$\sigma_y$</td>
<td>Yield strength</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Sample rotation angle</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Sample tilt angle</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Duty cycle</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angle between X-ray source and sample</td>
</tr>
</tbody>
</table>
Chapter 1
Introduction

1 Introduction

Exploring nature provides new ideas and inspirations for daily activities in society, as well as science. In the past two decades, there has been growing attraction in the materials science and engineering community to explore various biological species for the design of new, functional materials. Three particular examples of bio-inspired functional materials design currently of great interest are colour, anti-reflectivity, and non-wetting.

The first example deals with colour. In biological tissues, colours can be introduced in many different ways. The most common case involves the incorporation of pigments. For instance, the yellow in the American Gold Finch feather and the red of the Northern Cardinal feather originate from pigments. However, this is not the case for the blue colour observed in the Blue Jay feathers. Here, the colour is due to a structural effect. Cross-sectional analysis of feather barbs of the Blue Jay has revealed nanometre scale air pockets in keratin matrix. In a sense, this structure in similar to a photonic crystal but with less structural order. The result is that the feather structure scatters short wavelength light, producing a vivid, brilliant blue that changes in intensity with the angle of incident light. Structural colour can also be produced by layered structures of materials with different refractive indices (e.g. the rainbow colours of the horsefly eye) or the fine-scale structure of wing scales (e.g. the blue–violet colour of some morpho butterflies). The structural colour found in nature have already been mimicked in man-made materials. Examples are Chroma (air-light interference “pigments”) by JDSU Uniphase and Morphotex fibre by Teijin Fibers Limited.

The second example looks at anti-reflective surfaces. When light shines onto the surface of a transparent material (e.g. PMMA, glass) most of the light is transmitted and some is reflected. The ratio of transmitted to reflected light depends on the difference between the refractive indices of the material and air. However, when there is a nanostructure on the surface of the material (e.g. pyramids, cones) the percentage of the reflected light is significantly reduced due to a gradual instead of abrupt changes in the refractive index. In other words, more light is transmitted instead of reflected on the nanostructured surface. In nature, this effect was first
observed on the surfaces of moth eyes. For this reason, this effect is often referred to as the moth eye effect. The reason why the moth eye is covered with millions of cone-shaped nano chitin protrusions (also called nanonipples) is to provide better night vision because more light can enter the moth eye under low light conditions if there is no reflection loss. The moth eye effect has also been mimicked in man-made materials. Anti-reflective polymer films with nanoprotrusion surfaces by Mac Derrmid Autotype or reflection reducing lenses made by camera manufacturers are just two examples.

The third case, and most relevant to this study, is water repellent, (super)hydrophobic or non-wetting surfaces. In nature, this phenomenon was first observed on the surfaces of certain plants, insects, and animals and is caused by a combination of surface structure and chemistry. Since the lotus leaf is one of the most famous examples of non-wetting surfaces, this phenomenon is often referred to as the Lotus effect and is of critical importance to the current thesis and will therefore be explained in more detail in section 2.2 of the literature review. However, it should be pointed out here that this effect has already been mimicked in engineered materials such as self-cleaning STO Lotusan house paint or spill resistant fabrics by Nano-Tex. Another example is NeverWet by Rust-Oleum, a spray-on coating that can be applied to many different surfaces, including wood, metal, and concrete. This material will be used in parts of this thesis and described in more detail in Chapter 6. By looking at the structure – property relationships, the mechanism of the non-wetting phenomenon on the lotus leaf can be understood; dual-scale hierarchical surface roughness with intrinsically hydrophobic material (wax crystals). Currently, many researchers focus on designing new materials and processes to mimic the remarkable non-wetting property of the lotus leaf. The potential applications of these materials can have a significant impact on society; e.g. self-cleaning windows and walls.

One of the main obstacles to overcome with applying non-wetting surface concepts observed in nature in many industrial applications is the question of long term mechanical stability of the surface. In nature, this is often not a concern. For example, the lotus effect on leaves only has to last for the growing season of the leaf, typically less than one year. Then the leaf is replaced with a fresh leaf and the entire cycle from leaf development to maturity and finally leaf abscission begins with the next generation of leaves. The same is true for some of the already existing man-made applications. For example, the long term stability of non-wetting fabrics such as Nano-Tex
is limited to a certain number of (approximately 10) regular washes. After that, the structure that gives rise to the original non-wetting properties is destroyed and cannot be restored.

What is needed for many applications of non-wetting surfaces in numerous industrial applications is reliable anti-wetting behaviour of surfaces over extended periods of time. In industrial applications, surfaces are exposed to numerous degradation processes including wear, erosion, corrosion, and oxidation. Early failure in service due to any of these degradation processes will make a new anti-wetting technology less likely to survive in widespread industrial applications. This study deals primarily with the mechanical (i.e. wear) robustness of non-wetting surfaces.

This thesis is comprised of an applied part (Part I) and a more fundamental study (Part II) on robust, water non-wetting / (super)hydrophobic surfaces. The objective of the applied study (Part I) in this thesis is to develop a low cost, industrially viable electrochemical process to produce mechanically robust, wear stable non-wetting composite surfaces for a diverse range of large scale and industrial applications. The target applications include anti-icing surfaces for infrastructure such as power transmission and telecommunication towers, condensers and boilers in energy generation, desalination, and chemical processing. This thesis addresses some of the drawbacks of current engineered non-wetting surfaces: insufficient hardness, wear resistance, and stability to elevated temperature excursions that are required for many industrial applications. On the fundamental side (Part II), the objective is to understand the wetting properties of rare earth oxide ceramics, one of the materials studied in part I, by studying single crystal / highly oriented epitaxial films in order to provide new insights on this highly controversial debate in the community on this type of non-wetting surfaces.

First, a general literature review on the wetting fundamentals, natural and artificial superhydrophobic surfaces is included in Chapter 2. The hypothesis and design philosophy for Part I of the thesis are described in Chapter 3. In Chapter 4, the general characterization techniques utilized in this thesis are described. The literature review concerning the experiments involved in Part I of the thesis is included in Chapter 5. Afterwards, the applied studies on the synthesis and characterization of non-wetting composites are described in Chapter 6 and Chapter 7 for Ni-PTFE and Ni-CeO₂ composites, respectively. In Chapter 8, the fundamental study on the wettability of rare earth oxide ceramics is reported. In Chapter 9, surface contamination, which
seems to hinder our current understanding of wetting phenomena in general, is discussed in a
broader context. Finally, conclusions of this thesis and recommendations for future work are
provided in Chapter 10 and 11, respectively.
Chapter 2
Literature Review – Wetting of Surfaces

2 Literature Review

In this chapter, the fundamentals of wettability of surfaces are reviewed in order to understand the mechanism of non-wetting surfaces. Subsequently, natural non-wetting surfaces and current engineered non-wetting surfaces are described.

2.1 Surface Wetting Fundamentals

The fundamental equation that describes a liquid droplet at rest on an ideal, smooth surface is Young's equation, given by:

\[ \gamma_{sv} = \gamma_{lv}\cos\theta_Y + \gamma_{sl} \quad [1] \]

Where \( \gamma_{sv}, \gamma_{lv}, \gamma_{sl} \) are the interfacial surface tensions for solid-vapour, liquid-vapour, and solid-liquid interfaces, respectively, and \( \theta_Y \) is the contact angle of the liquid droplet. For water, when the contact angle is less than 90°, the surface is said to be hydrophilic. Between 90° and 150°, the surface is hydrophobic. There are two other extreme cases. If the water contact angle (WCA) is greater than 150°, the surface is defined to be superhydrophobic. If the WCA is 0°, it is termed superhydrophilic. A table summarizing the wetting states and their respective applications is presented in Table 2-1. However, the largest WCA \( \theta_Y \) reported for smooth solid surfaces is about 120° [ref 1]. In order to achieve superhydrophobicity, surface roughness is also required.
Figure 2-1 (a) Young equation; (b) Wenzel state; (c) Cassie-Baxter state; (d) water droplet on an incline, showing advancing and receding contact angle and sliding angle.

Table 2-1. Water contact angle and wetting states

<table>
<thead>
<tr>
<th>Water Contact Angle $\theta_Y$</th>
<th>Wetting State</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_Y = 0^\circ$</td>
<td>Superhydrophilic</td>
<td>Fast drying surface</td>
</tr>
<tr>
<td>$0^\circ &lt; \theta_Y &lt; 90^\circ$</td>
<td>Hydrophilic</td>
<td>Anti-fogging</td>
</tr>
<tr>
<td>$90^\circ &lt; \theta_Y &lt; 150^\circ$</td>
<td>Hydrophobic</td>
<td>Heat transfer</td>
</tr>
<tr>
<td>$\theta_Y &gt; 150^\circ$</td>
<td>Superhydrophobic</td>
<td>Self-cleaning, anti-icing</td>
</tr>
</tbody>
</table>

There are two main theories that describe wetting of rough surfaces, namely the Wenzel and Cassie-Baxter models. A schematic diagram of a liquid droplet on a rough surface, according to the Wenzel model is shown in Figure 2-1b. The Wenzel model describes homogeneous wetting where the liquid droplet is in contact with the peaks and valleys of the rough surface with the following equation:

$$\cos \theta_W = R_f \cos \theta_Y \quad [2]$$

where $\theta_W$ is the Wenzel contact angle and $R_f$ is the roughness factor which is defined as the surface area ratio between the rough surface and its projection on a 2D plane. For a surface that is intrinsically hydrophilic, $\theta_Y < 90^\circ$, increasing roughness factor renders the surface more hydrophilic, i.e. a decrease in $\theta_W$ is observed. Similarly, hydrophobicity can be enhanced with increased roughness for a surface that is intrinsically hydrophobic. However, increases in roughness also increases the solid-liquid interface, hence, the surface in the Wenzel state is “sticky”.
The Cassie-Baxter model describes heterogeneous wetting, where the liquid droplet is suspended by the peaks and does not penetrate into the valleys filled with air \(^3\), as shown in Figure 2-1c. The Cassie-Baxter equation is derived from Cassie’s law, which describes wetting for a two component surface \(^4\):

\[
\cos \theta_C = f_1 \cos \theta_1 + f_2 \cos \theta_2 \tag{3}
\]

where \(f_1\) and \(f_2\) are the area fractions of components 1 and 2, respectively, \(\theta_1\) and \(\theta_2\) are the contact angles of components 1 and 2, respectively, and \(\theta_C\) is the apparent contact angle of the composite. Air trapped in the valleys between the solid and liquid can be treated as one component with a water / air contact angle of 180°. Equation (3) can then be rewritten to form the Cassie-Baxter equation \(^3\):

\[
\cos \theta_{CB} = f_1 (\cos \theta_1 + 1) - 1 \tag{4}
\]

where \(f_1\) is the area fraction of the solid surface in contact with the liquid droplet and \(\theta_{CB}\) is the contact angle of liquid droplet according to Cassie-Baxter. In this case, increasing the area fraction of air \(1 - f_1\) will increase the contact angle and reduce the adhesion of the liquid droplet to the surface, thus the surface is “slippery”.

An irreversible transition from the Cassie-Baxter to the Wenzel state is observed for many surfaces, where the composite interface of trapped air pocket in the valleys of the rough surface is destroyed and the valleys are filled with the liquid to form a homogenous solid-liquid interface and a decrease in the apparent contact angle \(^5\). The transition from the Cassie-Baxter to the Wenzel state can be caused by many factors, including chemical and surface roughness inhomogeneity, geometry and profile of surface roughness \(^5\).

Adhesion of a liquid droplet to a surface can be related to the contact angle hysteresis, \(\Delta \theta\). Contact angle hysteresis is the difference between the advancing contact angle \(\theta_A\) and the receding contact angle \(\theta_R\). For a liquid droplet on an inclined surface, the advancing contact angle is the contact angle on the lower side (advancing side) and the receding contact angle is the contact angle on the upper side (receding side) just before the droplet slides off when the incline reaches a critical angle, known as the sliding or roll off angle \(\alpha\). A schematic diagram of a liquid
Contact angle hysteresis can be related to the sliding angle by the following equation:\(^6\):

\[
mg \sin \frac{\alpha}{w} = \gamma_{lv} (\cos \theta_R - \cos \theta_A) \quad [5]
\]

where \(g\) is the force due to gravity, \(m\) and \(w\) are the mass and width of the droplet, respectively. According to this equation, the sliding angle \(\alpha\) is minimized when the contact angle hysteresis \(\Delta\theta\) is small. Surface roughness also has a significant effect on the contact angle hysteresis. For instance, when the surface is in the Wenzel wetting state, the liquid droplet will remain on the surface even with a high tilt angle due to surface roughness providing pinning points for the liquid droplet\(^7\). On the other hand, when the rough surface is in the Cassie-Baxter wetting state, a droplet will roll off the surface with a small tilt angle due to the low area fraction of the solid-liquid interface and hence the high area fraction of the liquid-air interface. In addition to high contact angle, the water sliding angle (WSA) should be less than 10° for superhydrophobic surfaces\(^8\). When the sliding angle is low, the liquid droplet has low adhesion and the self-cleaning effect is achieved; water droplets will easily roll off the surface and will carry dirt and contaminants along the way.

### 2.2 Natural Non-wetting Surfaces

Non-wetting surfaces were first discovered on natural species, with the lotus leaf being the most well-known example. The lotus leaf achieves its non-wetting property (WCA = 160°) by a combination of specific chemical and microstructural characteristics: nanoscale hydrophobic epicuticular wax crystals superimposed on microscale papillae\(^9\), as shown in Figure 2-2. Due to its high water repellency, the lotus leaf also has the self-cleaning mechanism, known as the Lotus-Effect, where contaminating particles on the leaf surface can be easily removed by rainwater droplets\(^9\).
Figure 2-2. Secondary electron micrograph of adaxial leaf surface of *Nelumbo nucifera* (Sacred Lotus) with nanoscale epicuticular waxes superimposed on microscale papillose epidermal cells. Scale bar is 20 µm.

Closer to home, quaking aspen tree leaves that are native to Southern Ontario also demonstrate non-wetting behaviour as described by Victor et al.\textsuperscript{10}. They reported that quaking aspen tree leaves also have a WCA of about 150° and WSA less than 5°. However, the surface morphologies of the quaking aspen leaves are slightly different. As shown in Figure 2-3, the height of the microscale features is shorter than that of the Sacred Lotus, but the overall structure and mechanism are still quite similar; hydrophobic, low surface energy material / substance (wax) with dual scale hierarchical surface roughness that allows trapped air pockets which reduce the contact area of water with the surface of the leaves (Cassie-Baxter wetting).
Another example of biological species that exhibit non-wetting behaviour are the wings of some butterflies, for example, *Morpho aega*, commonly known as the morpho butterfly. The WCA of the wing surface is 152°, however, the water droplet can only roll off the surface easily in only one direction (~ 10°), radially outward from the centre of the body, but is pinned tightly in the opposite direction due to its distinct overlapping, flexible scale microstructure and lamella nanostructure as shown in Figure 2-4.

The study of biological species has contributed to the development of artificial materials that mimic the functional properties found in nature. In the next section, artificial non-wetting surfaces inspired by these phenomenal species are reviewed.
Figure 2-4. Directional adhesion of water droplet on Morpho butterfly wing. Water droplet can slide off easily along the radially outward (RO) direction, but not opposite to it. The scale and lamella features of the wings can be observed in the secondary electron micrographs, along with the AFM images showing the overlapping micro and nano scale features.

2.3 Artificial Non-wetting Surfaces

Over the past decade, there have been many studies that replicated the non-wetting properties found in nature on engineered materials. As described earlier, the mechanism behind superhydrophobicity is a combination of low surface energy/hydrophobic material with a specific surface roughness. In the literature, there are many different fabrication techniques to create the desired surface roughness for non-wetting behaviour, including lithography, templating, femtosecond laser pulsing, etching, sol-gel techniques, thermal chemical vapor deposition, and electrochemical processes.

2.3.1 Lithography

Lithography is a great technique for fundamental investigation as the technique allows precise control of surface feature on silicon and polymers. However, lithography lacks practical significance as it is an expensive process and is not easily scalable for large surfaces.
2.3.2 Femtosecond Laser Patterning

Various metal surfaces, such as copper, platinum and titanium can be made superhydrophobic by femtosecond laser pulsing to create hierarchical micro- and nano-scale roughness and with 30 or without 22 any subsequent treatment with low surface energy material. For the case of structured metallic surfaces that were not treated with low surface energy substances, superhydrophobicity developed after adsorption of low surface energy carbon species from the exposure of the surface to ambient air. Similar to lithography, there are drawbacks with femtosecond laser pulsing to fabricate non-wetting surfaces, namely expensive process equipment and difficult scalability for industrial applications. Furthermore, this class of superhydrophobic material is not expected to have good resistance to degradation of non-wetting properties when exposed to physical wear since they rely on surface chemical treatment or the adsorption of airborne carbon species to render the water repellent properties, any surface wear will expose the “bulk” hydrophilic metal. Although the bulk material is metallic with a relatively high melting point compare to polymers, these non-wetting materials may not retain their non-wetting properties when exposed to elevated temperature excursions as desorption of low surface energy carbon species and degradation of the coating from the chemical surface treatment are likely.

2.3.3 Templating

Large polymer surfaces can be made superhydrophobic by a simple, templating process described by Victor et al18. In this case, the reusable template (negative) is a shot-peened and acid etched nanocrystalline nickel with hierarchical roughness. The template is pressed against a heated, softened polymer to transfer the desired hierarchical surface roughness for superhydrophobicity. Although the process is simple and industrially scalable, the materials choice is limited to polymers only, which are usually mechanically soft.
In a study by Gong et al., a templating approach was developed to produce high transparency superhydrophobic polydimethylsiloxane (PDMS) surfaces. First, femtosecond laser processing was used to fabricate a stainless steel template with microgrooves and microholes array. The templating of the PDMS consisted of three main steps, i) a mixture of PDMS, silicone elastomer, and hardening agent were poured into the template, ii) followed by curing at 80°C for 3 hours, and ii) releasing the cured PDMS from the template. The structured PDMS is composed of a microwall array with microcones positioned in the middle of each microwall enclosure, as shown in Figure 2-6. The results of various characterization techniques, including abrasive wear and thermal stability demonstrated that the structured PDMS retained superhydrophobicity even after abrasion with sandpaper and elevated temperature exposure up to 350°C. The authors proposed the intended application of this material is for microfluid channels as this application would benefit from the non-wetting properties for efficient fluid transport, as well as its transparent properties. However, this material would not be suitable for industrial applications as the template fabrication process requires specialized laser processing equipment that is not easily scalable.
2.3.4 Electrochemical Processing

On the other hand, electrodeposition is a promising approach to fabricate metallic non-wetting surfaces due to its simplicity, low cost, and ease of scalability. In addition electrodeposits can be applied on a wide range of materials including metals, composites, and polymers. In general, superhydrophobic surfaces made by electrodeposition can be classified into 3 main categories, as shown in Figure 2-7. Superhydrophobicity is achieved by i) surface roughness alone, ii) surface roughness and surface chemical modification with low surface energy material, and iii) co-deposition of hydrophobic particles with a metal matrix.

Figure 2-7. Cross-sectional schematic diagrams of (i) rough superhydrophobic surface; (ii) rough surface modified by low surface energy material to achieve superhydrophobicity; (iii) metal matrix composite with hydrophobic particles.

Since the superhydrophobic surfaces produced by electrochemical processing are mostly metal based, it is expected that these surfaces have sufficient mechanical robustness for demanding industrial applications. However, for the case of i) and ii), the wetting behaviour of the “bulk” material is not hydrophobic and only the surface is non-wetting. Therefore, when these types of electrodeposits are subjected to surface wear, it is expected that the non-wetting properties will be significantly compromised. On the other hand, for the case of iii), as the surface is subjected to wear, the underlying hydrophobic particles will be exposed, leading to the potential of long lasting non-wetting characteristics even with surface wear.

Extensive tables showing examples of previous studies on these three types of surfaces are presented in Appendix A, which are extracted from an in-depth literature review regarding superhydrophobic electrodeposits.
3 Hypothesis / Design Philosophy for Part I

As noted in the previous chapter, the main drawbacks of artificial non-wetting surfaces reported previously are namely low/unknown mechanical robustness and wear stability, as well as expensive and difficult to scale up processes. In this study, a composite approach was adopted to produce mechanically robust, wear resistant (super)hydrophobic metal matrix composite coatings for two potential classes of applications: (i) infrastructure including power transmission and telecommunication towers, and (ii) industrial condensation / boiling systems. Specific examples are described in Appendix B. The target material properties include: good mechanical performance (strength, hardness, and wear resistance) and highly stable non-wetting behaviour even with exposure to abrasive wear and high temperature excursions. In order to achieve these properties, a composite approach is employed and the design philosophy is as follows (Figure 3-1): First, refine the crystal size of the metal matrix from conventional polycrystalline to ultra-fine grain or the nanocrystalline range. By refining the crystal size of the metal matrix, increased strength, hardness, and wear resistance can be realized according to the Hall-Petch relationship \(^{34}\) and Archards law \(^{35}\), respectively. Secondly, when second phase hydrophobic particles are incorporated into the ultra-fine grain / nanocrystalline metal matrix, a composite with all the attributes of grain size reduction and non-wetting properties can be achieved. Another critical feature of this composite is that the hydrophobic second phase particles are uniformly distributed throughout the entire thickness.

![Figure 3-1](image_url)

Figure 3-1. Cross-section schematic diagram of various metals and composites. (a) Polycrystalline metal. (b) Ultra-fine grain / nanocrystalline metal with refined grain size and high density of grain boundaries. (c) Ultra-fine grain / nanocrystalline metal matrix composite with hydrophobic particles.
The hydrophobicity of the second phase particles should be a bulk, inherent property rather than just a surface effect (for example, fluorinated particles $^{36-38}$, silane treated particles $^{39,40}$, sodium dodecyl sulfate $^{41}$). In other words, many of the numerous surface modified particles currently available $^{36-41}$ that only function because of surface modifications are not suitable for this approach. This could potentially create long lasting non-wetting surfaces as new hydrophobic particles will be continually exposed at the surface when the original surface is worn away during service and new surface roughness is introduced because of wear action (Figure 3-2). In a sense, this is similar to the self-repair capability previously observed on quaking aspen leaves which show a continuous re-growth throughout the growing season of worn off wax crystals on top of papillae responsible for the non-wetting properties of these leaves $^{42}$.

To fabricate this class of composite material, a simple, easily scalable electro-codeposition technique was developed. Further information on the electro-codeposition will be described in Chapters 5 and 6.

![Figure 3-2. Cross-section schematic diagram of non-wetting composite (a) before and (b) after abrasive wear. Hydrophobic particles will be continually exposed with increasing wear roughness.](image_url)
Chapter 4
Characterization Techniques

4 Characterization Techniques

Many different characterization techniques were employed to study the material properties of interest. A summary of all the characterizations techniques is shown in Table 4-1. In this chapter, some of the general characterization techniques that were commonly used in most chapters of this thesis are described in detail. Characterization techniques that are specific to particular parts of the thesis will be described in detail in their corresponding chapters.

Table 4-1. Summary of characterization techniques employed in this thesis.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Surface, Chemical or Structural Information?</th>
<th>Raw Data Acquired</th>
<th>Qualitative / Quantitative</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acoustic particle size measurement</td>
<td>-</td>
<td>Size distribution curves</td>
<td>Quantitative</td>
<td>To determine size of particles in a dispersion.</td>
</tr>
<tr>
<td>Atomic force microscopy (AFM)</td>
<td>Surface</td>
<td>Image</td>
<td>Quantitative</td>
<td>To evaluate surface roughness.</td>
</tr>
<tr>
<td>Contact angle</td>
<td>Surface</td>
<td>Image</td>
<td>Quantitative</td>
<td>To quantify the wettability of surfaces.</td>
</tr>
<tr>
<td>Cross-cut tape test</td>
<td>-</td>
<td>Image</td>
<td>Qualitative</td>
<td>To determine adhesion of a coating on a substrate.</td>
</tr>
<tr>
<td>Energy dispersive X-ray spectroscopy (EDS)</td>
<td>Chemical</td>
<td>X-ray energy spectrum</td>
<td>Quantitative</td>
<td>To determine surface chemical composition of specimens.</td>
</tr>
<tr>
<td>Focused ion beam (FIB)</td>
<td>Surface</td>
<td>Image</td>
<td>Qualitative / Quantitative</td>
<td>To prepare site-specific TEM specimens and to perform cross-section analysis.</td>
</tr>
<tr>
<td>Laser particle size measurement</td>
<td>-</td>
<td>Size distribution curves</td>
<td>Quantitative</td>
<td>To determine particle size.</td>
</tr>
<tr>
<td>Reciprocal space mapping (RSM)</td>
<td>Structural</td>
<td>Reciprocal space map</td>
<td>Qualitative / Quantitative</td>
<td>To evaluate lattice stress / strain, lateral coherent length, and quality of thin films.</td>
</tr>
<tr>
<td>Reflection high energy electron diffraction (RHEED)</td>
<td>Surface and structural</td>
<td>Diffraction pattern</td>
<td>Qualitative</td>
<td>To evaluate the surface roughness and structure of thin films.</td>
</tr>
<tr>
<td>Scanning electron microscopy (SEM)</td>
<td>Surface</td>
<td>Image</td>
<td>Qualitative / Quantitative</td>
<td>To produce images of surfaces.</td>
</tr>
<tr>
<td>Scanning / transmission electron microscopy (STEM / TEM)</td>
<td>Structural</td>
<td>Image, diffraction pattern</td>
<td>Qualitative / Quantitative</td>
<td>To determine grain size of materials, microstructure analysis, and atomic structure of materials.</td>
</tr>
<tr>
<td>Sliding angle</td>
<td>Surface</td>
<td>Angle</td>
<td>Quantitative</td>
<td>To quantify the wettability of surfaces.</td>
</tr>
<tr>
<td>X-ray diffraction (XRD)</td>
<td>Structural</td>
<td>Diffraction pattern, rocking curves</td>
<td>Qualitative / Quantitative</td>
<td>To analyze phases present, epitaxial relationships of thin films, crystallite tilting, determination of lattice parameter.</td>
</tr>
<tr>
<td>X-ray reflectivity (XRR)</td>
<td>Surface and structural</td>
<td>Reflectivity curves</td>
<td>Quantitative</td>
<td>To calculate thin film thicknesses and roughness.</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>Chemical</td>
<td>Binding energy spectrum</td>
<td>Qualitative / Quantitative</td>
<td>To determine surface chemistry of materials.</td>
</tr>
</tbody>
</table>
4.1 Wetting Properties

The wetting behaviour of surfaces are quantified by measuring the water contact angle (WCA) and the water sliding angle (WSA); i.e. $\theta$ and $\alpha$ as shown in Figure 2-1. For WCA measurements, 5 µL of deionized (DI) water droplets were dispensed on the specimen surface by using an adjustable volume pipette. A digital single lens reflex camera with a macro lens attached was used to capture images of the side view of the water droplets. The WCAs were determined by analyzing the images using ImageJ software. For WSA measurements, the sample is placed on a levelled tilting stage. 25 µL of DI water droplets were placed on the specimen surface. The stage was then slowly titled until the water droplet moves and the angle when the droplet began to slide was recorded. At least 4 measurements were made and the averages of the measurements were reported.

4.2 Electron Microscopy

4.2.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a highly versatile technique so study surfaces and chemical compositions of solid materials. In this thesis, SEM and energy dispersive X-ray spectroscopy (EDS) were employed to obtain morphology and chemical information of the specimens studied. Multiple microscopes were used throughout the study; Hitachi SU3500 thermionic emission SEM, Hitachi SU5000 Schottky field emission SEM, and Hitachi SU8230 cold field emission SEM. In a SEM, a focused, electron beam (probe) is scanned across the specimen and the interaction between the incident electron beam and the specimen generates different signals for imaging and spectroscopy. Typically, two types of signal can be collected in a SEM to form images; secondary electrons (SE) and backscattered electrons (BSE).

SE are low energy electrons that are generated as a result of inelastic scattering interaction of the incident beam electrons with the specimen. SE images provide rich morphology and surface topography contrast making them ideal to analyze surface roughness and texture of the specimen. The contrast mainly depends how many SE reach the SE detector; a recessed area or valley on the specimen will appear dark as some of the SE may be prevented from reaching the detector, whereas a protrusion on the specimen will appear brighter due to a clear path for the SE to reach to the detector.
BSE are electrons that have been ejected from a specimen by elastic scattering through an angle greater than 90°. The contrast arising from the BSE image is due to the atomic number of the elements present in the specimen. Heavier elements (or higher atomic number) have greater positive charges on the nucleus, hence, more electrons are backscattered and the resulting image is brighter. On the other hand, elements with lower atomic number will yield a lower number BSE and the resulting image appears darker.

In addition to the electron signals generated when the primary electron beam interacts with the specimen, characteristic X-rays are also produced. Characteristic X-rays are emitted when the incident electron beam knocks out an inner shell electron from the atoms in sample (ionization of atom). An outer shell electron subsequently fills in the vacancy and releases a characteristic X-ray energy whose energy is the differences in the energy level of the 2 electron orbitals. Characteristic X-rays can be used for elemental analysis in the SEM by energy dispersive X-ray spectroscopy, where a silicon drift detector collects the x-ray signal and passes the information to an analyzer to process and display the composition of elements present in the sample.

4.2.2 Focused Ion Beam

Similar to SEM, focused ion beam (FIB) refers to a technique where a focused Ga⁺ ion beam / probe is rastered across a specimen. Since Ga⁺ ions are larger and heavier than electrons, they are able to cut and mill any material at the micro- and nano-scale. In this thesis, a Hitachi NB5000 focused ion beam system was used to perform site-specific cross-section analysis and to prepare thin foil specimens of some materials for transmission electron microscopy analysis. Furthermore, the FIB can be used as the imaging incident probe to acquire secondary electron images with exceptional topography, compositional, and channeling contrast.

4.2.3 Transmission Electron Microscopy

Unlike SEM and FIB, transmission electron microscopy (TEM) provides information not only at the surface of the specimen, but also the bulk interior structure. In this thesis, Hitachi HF-3300 and JEOL ARM-200 Cs-corrected transmission electron microscopes were used to study the microstructure of various materials.

Typically, TEM can be operated in the conventional parallel beam mode or scanning (STEM) mode with a focused electron probe. In conventional parallel beam mode, diffraction contrast
bright field and dark field images, as well as high resolution phase contrast images can be obtained. In addition, selected area electron diffraction (SAED) can be performed to understand the crystallography and structure of the specimen. For the STEM mode, high angle annular dark field (HAADF) and bright field (BF) images can be acquired. At high magnification, HAADF images provide directly interpretable images with clear position of the atomic columns.
Part I: Applied Study
Chapter 5
Literature Review for Part I: Electro-codeposition of Composites

5 Literature Review for Part I - Electro-codeposition of Composites

Chapter 3 described the design philosophy to make robust non-wetting composite materials by an electro-codeposition approach. Figure 3-1 explained the various material design aspects of this approach which include i) Hall-Petch strengthening through grain size refinement, ii) electrodeposition of a metal matrix, and iii) co-deposition of non-wetting particles. The necessary background information on these aspects is summarized in-depth in this chapter.

5.1.1 Hall-Petch Relationship

As first reported in the 1950’s by Hall and Petch, metals and alloys can be strengthened by reducing the grain size from micron size polycrystal to submicron size ultra-fine grain (UFG) due to greater volume fraction of grain boundaries, which act as barriers to dislocation motion. This phenomenon is also known as the Hall-Petch strengthening, as demonstrated by the following equation:

\[ \sigma_y = \sigma_0 + k d^{-0.5} \] \[ H = H_0 + k' d^{-0.5} \]

In these equations, \( \sigma_y \) and \( H \) are the yield strength and hardness of the material, \( \sigma_0 \) and \( H_0 \) are the yield strength and hardness at large grain size, \( k \) and \( k' \) are constants, and \( d \) is the average grain size of the material. A Hall-Petch plot showing the hardness of electrodeposited nickel as a function of grain size down to 11 nm is shown in Figure 5-1; hardness increases as the grain size is decreased.
5.1.2 Nanocrystalline Metals and Alloys

On the extreme end of grain size reduction, nanocrystalline materials refer to a class of materials with grain size less than 100 nm. According to Gleiter, the idea of nanocrystalline materials is to introduce a high density of defects such as grain boundaries where a large percentage of atoms are situated in these defects, as shown in Figure 5-2. To quantify the percentage of atoms in the intercrystalline region of a 3-D nanocrystalline material, Palumbo et al. developed a set of mathematical equations based on the 14 sided tetrakaidecahedron (Figure 5-3) as the grain shape:

\[ V_{ic} = 1 - \left[ \frac{d - \Delta}{d} \right]^3 \]  \[ 8 \]

\[ V_{gb} = \frac{3\Delta(d - \Delta)^2}{d^3} \]  \[ 9 \]

\[ V_{tj} = V_{ic} - V_{gb} \]  \[ 10 \]
where $V_{ic}$ is the total volume fraction of intercrystalline region, $V_{gb}$ and $V_{tj}$ are the grain boundary and triple junction volume fraction components respectively, $d$ is the grain size, and $\Delta$ is the grain boundary thickness. A plot of these three equations is shown in Figure 5-4, where the grain boundary thickness $\Delta$ is assumed to be 1nm. From the graph, it is clear that the volume fraction of the intercrystalline region increases significantly with decreasing grain size from 1000 nm to 2 nm.

![Figure 5-2. 2-D model of nanocrystalline material. Crystals are represented by the black atoms, while grain boundaries are represented by the white atoms.](image)

Figure 5-2: 2-D model of nanocrystalline material. Crystals are represented by the black atoms, while grain boundaries are represented by the white atoms.

![Figure 5-3: A group of tetrakaidecahera to form a multi-grain structure showing grain boundaries and triple junctions.](image)

Figure 5-3: A group of tetrakaidecahera to form a multi-grain structure showing grain boundaries and triple junctions.
Figure 5-4: The effect of grain size (d) on volume fractions of intercrystal region, grain boundaries, and triple junctions. The grain boundary thickness Δ is assumed to be 1nm.

Owing to the high volume fraction of grain boundaries in nanocrystalline materials, structure-dependent properties are expected to be different compared to conventional polycrystalline materials\textsuperscript{45}.

As described previously, the enhanced yield strength and hardness are expected according to the Hall-Petch relationship. There are other properties that are strongly affected by grain refinement in electrodeposited Ni, as listed in Table 5-1.
Table 5-1. Grain size dependent properties of electrodeposited

<table>
<thead>
<tr>
<th>Property</th>
<th>Effect due to grain size reduction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wear resistance</td>
<td>Greatly enhanced</td>
<td>(Erb, 1995)</td>
</tr>
<tr>
<td>Ductility</td>
<td>Reduced from 50% to 10%</td>
<td>(Brooks, Palumbo, Hibbard, Wang, &amp; Erb, 2011)</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td>Reduced by a factor of 2</td>
<td>(Erb, 1995)</td>
</tr>
<tr>
<td>Corrosion</td>
<td>Localized corrosion is greatly reduced or eliminated</td>
<td>(Erb, 2010)</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>Increased by a factor of 3</td>
<td>(Aus et al, 1994)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Decreased by 26%</td>
<td>(Wang, 2011)</td>
</tr>
</tbody>
</table>

5.1.3 Electrodeposition

Electrodeposition is a metallic surface coating technology that has been used for over 200 years. Conventionally, this process is commonly used to coat the underlying metal substrates or metallized (e.g. sputter deposited or chemically plated) insulator materials (ceramics, polymers) for improvements in appearance, wear resistance, corrosion resistance, or erosion resistance. A schematic diagram of lab scale electrodeposition setup with dissolvable anode is shown in Figure 5-5. The system consists of an electrolyte containing ions of the metal to be plated (often referred as the “bath”), external power supply, and electrodes (anode and cathode) submersed into the bath. An electrical current is passed between the electrodes to produce a metal deposit on the cathode.

Figure 5-5. Schematic diagram of the electrodeposition process.
The mechanism of electrodeposition is that the electrical current dissolves the anode metal into ions and drives the reduction of metal ions on the cathode surface to form a metal coating. The simplified anodic and cathodic reactions for nickel plating are shown below. At the anode, metal dissolution is the only reaction. On the other hand, there are two possible reactions at the cathode: metal deposition and hydrogen evolution. The generation of hydrogen is an unwanted process as it lowers the efficiency of the plating process.

Anodic Reaction: \( Ni \rightarrow Ni^{2+} + 2e^- \) \[11\]

Cathodic Reactions: \( Ni^{2+} + 2e^- \rightarrow Ni \) \[12\]
\( 2H^+ + 2e^- \rightarrow H_2 \) \[13\]

In the early 1990’s, electrodeposition of nanocrystalline metals was developed by El-Sherik & Erb\cite{52} by modifying certain plating parameters including: (i) high current density in a pulse square waveform as opposed to direct current (DC) and (ii) the addition of grain refining additives such as saccharin.

High current density promotes nucleation of new grains rather than growth of existing grains due to two reasons: i) the rate of nickel reduction is increased and ii) the critical crystal nucleation radius is reduced\cite{53}. However, for conventional DC plating, there is an upper limit of current density at which metal deposition becomes limited by the transport of metal ions to the cathode. This is known as the limiting current density \( i_L \) which can be represented by the following equation:

\[
i_L = \frac{nFD}{\delta} c_b \quad [14]
\]

Where \( n \) is the number of electrons involved in the reaction, \( F \) is Faraday constant, \( D \) is the diffusion coefficient of metal ions in the electrolyte, \( \delta \) is the thickness of the Nernst diffusion layer, and \( c_b \) is the bulk concentration of metal ions. Figure 5-6 shows the concentration profile
of metal ions close to the surface of the electrode. According to a computer simulation study on electroplating, the typical thickness of the Nernst diffusion layer is on the order of tens of microns.\(^{54}\) In this model, the concentration of metal ions in solution is the bulk concentration \(c_b\) for a distance greater than \(\delta\) from the electrode. When the distance from the electrode is less than \(\delta\), the concentration of metal ions decreases with decreasing distance from the electrode until it reaches zero at the surface of the electrode. There are a few assumptions made in this model: i) the liquid layer between the electrode surface and the distance \(\delta\) away is assumed to be stagnant and not well mixed, ii) for distance greater than \(\delta\), stirring of the solution is assumed to be efficient, hence, the concentration of metal ions is equal to \(c_b\). If the applied current density is greater than the limiting current density, formation of hydrogen gas is the dominant reaction, which can have significant consequences on the quality of the metal coating.\(^{32}\) Pulse current electrodeposition overcomes this problem by cycling the electrical current on and off. A schematic diagram of a current density versus time graph is shown in Figure 5-7. The current density \(i_{peak}\) when the current is on \(T_{on}\) can be significantly higher than the limiting current density in DC electrodeposition. To replenish the metal ions in the Nernst diffusion layer, the current is turned off for a time period \(T_{off}\). Pulse frequency \(f\), duty cycle \(\psi\), and average current density \(i_{avg}\) are the process parameters and can be represented by the following equations:

\[
\begin{align*}
  f &= \frac{1}{T_{on} + T_{off}} \quad [15] \\
  \psi &= \frac{T_{on}}{T_{on} + T_{off}} \quad [16] \\
  i_{avg} &= i_{peak} \cdot \psi \quad [17]
\end{align*}
\]
Figure 5-6. Concentration profile according to Nernst diffusion layer model

Figure 5-7: Schematic diagram of current waveform for pulse electrodeposition

Typical values for $T_{on}$, $T_{off}$, and $i_{peak}$ for nanocrystalline nickel plating are 45ms, 5ms, and 1900 mA/cm$^2$ respectively.

According to El-Sherik, grain size reduction resulting from addition of additives such as saccharin to the bath is due to the combined effects of i) decreasing the overpotential for nickel ion reduction, ii) increasing the frequency of nucleation by blocking crystal growth, and iii) reducing the surface diffusion of nickel adsorbed adatoms on the cathode surface.

Electrodeposition offers many advantages compared to other synthesis techniques for nanocrystalline metals. First, it is a simple, inexpensive, and scalable process to produce large
volume of nanocrystalline metals. Second, there are very few size and shape limitations with this process. Third, the resulting material is fully dense and does not require additional processing such as compaction and consolidation 51.

5.1.4 Electro-codeposition

Metal matrix composite coatings and films can be produced by adding secondary inert particles and often combined with surfactants into the plating electrolyte. The properties of conventional electrodeposited coatings can be modified by the choice of the secondary particles. In the following sub-sections, theoretical models for electro-codeposition and important process parameters are described.

5.1.4.1 Guglielmi’s Model

One of the most important models in the mechanism of electro-codeposition of particles was developed by Guglielmi 55 in the early 1970’s. He proposed a mechanism that consists of two consecutive adsorption steps. In the first step, the particles are loosely adsorbed to the cathode and are still surrounded by a cloud of adsorbed ions and solvent molecules. In the second step, adsorption is field assisted and the ionic cloud around the particles is lost, producing a strong adsorption of the particles on the cathode. The strongly adsorbed particles are then covered by the growing metal. A schematic diagram of the two-step adsorption process is shown in Figure 5-8.

![Two step codeposition process according to Gugliemi](image)

Figure 5-8: Two step codeposition process according to Gugliemi 55.
Guglielmi used a modified Langmuir adsorption theorem to describe the loose adsorption coverage $\sigma$ in the first adsorption step:

$$\sigma = \frac{kC}{1+kC} (1 - \varepsilon) \quad [18]$$

In this equation, $\varepsilon$ is the strong adsorption coverage, $k$ is a constant and depends on the intensity of the interaction between the particles and electrode and $C$ is the concentration of suspended particles in the electroplating.

The second adsorption step depends on $\sigma$ and it is considered to be a linear dependence $^{55}$. Since it is assumed the electric field has an impact on the strong adsorption, the rate of volume of particles strongly adsorbed on the cathode surface $\frac{dV_p}{dt}$ can be represented by the product of loose adsorption coverage and an exponential term $v_0 e^{B\eta}$. $v_0$ and $B$ are constants while $\eta$ is the overpotential. Therefore, the strong adsorption rate can be written as:

$$\frac{dV_p}{dt} = \sigma v_0 e^{B\eta} = \frac{kC}{1+kC} (1 - \varepsilon) v_0 e^{B\eta} \quad [19]$$

The constants in equations [18] and [19] can be determined experimentally by relating particle concentration in the electrolyte to particle content in the deposit at varying overpotential $^{55}$. Although Guglielmi successfully verified his model with experiments on nickel-titanium dioxide and nickel-silicon carbide composites, the model does not take into account other critical electrodeposition parameters such as bath agitation, bath pH, bath constituents, and particle size.

**5.1.4.2 Celis’ Model**

In 1987, Celis et al. proposed a mechanism for electro-codeposition that is based on two processes: i) adsorption of ionic species around the inert particles at the time when the particles are added to the plating electrolyte, ii) reduction of these adsorbed ionic species at the cathode is required for incorporating the particles in the metal matrix $^{56}$.

According to Celis et al.’s model, there are 5 steps for the codeposition of an inert particle as shown in Figure 5-9 $^{56}$.

1. The particles in the bulk electrolyte accumulate an ionic cloud by adsorption
2. Particles are transported by forced convection towards the hydrodynamic boundary layer at the cathode
3. Diffusion of particles through the diffusion double layer
4. Adsorption of the particles with the ionic cloud at the cathode surface
5. Some of the adsorbed ionic species are reduced and the particles become incorporated into the deposit

Based on this 5 stage codeposition mechanism, Celis et al. formulated a mathematical model to determine the percentage of embedded particles. The primary hypothesis of the mathematical model is that a particle will only be embedded when a certain amount $k$ out of $K$ adsorbed ionic species, is reduced $^{56}$. The expression for the model is:

$$\text{wt}_{\text{particle}}\%\text{ embedded} = \frac{W_p N_p P}{M n e + W_p N_p P} \times 100\% \quad [20]$$

$W_p$ is the weight of a particle, $N_p$ is the number of particles crossing the diffusion layer at the cathode per unit time and surface area, and $P$ is the probability for a particle to become incorporated in the cathode at a current density $i$, $M$ is the atomic weight of the electrodeposited metal, $n$ is the number of valence electrons of the metal, and $F$ is the Faraday’s constant. The effect of bath agitation is also included in the probability term $P$. Celis et al. applied their model to the co-deposition of copper with alumina and gold with alumina and found that the theoretical model was in good agreement with their experimental results $^{56}$.

Figure 5-9: Stages of co-deposition of an inert particle according to Celis et al. $^{56}$ (1) formation of ionic cloud, (2) convection, (3) diffusion, (4) adsorption at cathode surface, (5) reduction and deposition.
5.1.4.3 Bercot’s Model

The model proposed by Bercot et al. is a refinement of Guglielmi’s model; they applied a corrective factor based on hydrodynamic conditions (magnetic stirring) that Guglielmi did not account for. Bercot et al.’s model is based on an experiment on electrolytic co-deposition of polytetrafluoroethylene (PTFE) and nickel composite with varying PTFE concentration in the electrolyte and varying magnetic stirring speed. It was determined that there is an optimum PTFE particle incorporation rate, which is based on the particle concentration in the electrolyte and stirring speed.

5.1.4.4 Zeta Potential

In electro-codeposition, the suspension of particles in the electrolyte needs to be stable and free of agglomeration in order to achieve a composite coating with uniform distribution of particles. The zeta potential, \( \zeta \), is a parameter that can be used in characterizing the stability of particles in a suspension.

When a particle is immersed in an electrolyte, it gains a surface charge by specific adsorption of charge-determining ions. As a result, an electric double layer is formed around the particle as presented in Figure 5-10. The two layers of importance are the Stern layer and diffuse layer. In the Stern layer, counter ions are firmly adsorbed to the surface of the charged particle. Additional counter ions are still attracted to the colloid, but they are also repelled by the counter ions in the Stern layer. This layer of loosely adsorbed counter ions is the diffuse layer. In the diffuse layer the concentration of counter ions gradually decreases with increasing distance away from the particle until it reaches bulk concentration. The diffuse layer also contains a low concentration of co-ions (ions that have the same charge as the particle surface charge) and gradually increases with increasing distance away from the particle.
The zeta potential is defined as the electrical potential in the interfacial double layer at the location of the so-called slipping plane, located at the edge of the diffuse layer, versus a point in the bulk fluid away from the interface. The magnitude of the zeta potential of the particles can be used to predict the stability of a suspension. For instance, if particles in suspension have a large positive or negative zeta potential, they will tend to repel each other due to electrostatic repulsion between particles. Consequently, aggregation of particles will not occur. On the other hand, when the zeta potential is low and close to zero, there are no repelling forces between particles and agglomeration of particles becomes likely. In general, when the zeta potential of particles in suspension is greater than +30mV or less than -30mV, the suspension is considered stable. The zeta potential can be affected by the pH or additives of the colloidal system. As the pH increases in a colloidal system, the surface of the particle will become more negative (or less positive), leading to a more negative zeta potential. At low pH, the particles will have a more positive zeta potential. Additives such as a surfactant can also influence the zeta potential. Further discussion regarding the effect of surfactant on zeta potential will be presented in the subsequent section.
5.1.4.5 Effect of Surfactants

Surfactants are often used to disperse hydrophobic particles and to alter the zeta potential of particles in a suspension. Surfactants are compounds that lower the surface tension between a solid and liquid. In other words, they allow wetting of hydrophobic particles (i.e. PTFE) in a solution. They are amphiphilic organic compounds that have a hydrophilic head and hydrophobic tail. In addition, some surfactants carry a net positive or negative charge on the head. If the charge is negative, the surfactant is called anionic, likewise, if the charge positive, it is called cationic surfactant.

The dispersing effect of a surfactant is due to steric stabilization and electrostatic repulsion. Steric stabilization is attributed to the bulky nature of the adsorbed surfactant molecule on the particle and this is likely the case for non-ionic surfactant. For cationic and anionic surfactants, the surface charge and zeta potential of a particle is modified by the adsorbed surfactant (positive or negative), therefore, particles tend to repel each other and agglomeration of particles will be reduced. Cationic surfactants provide a favourable charge to the particle for electro-codeposition as the positively charged particle would be attracted to the negatively charged cathode where the deposit forms.
Chapter 6
Ni-PTFE Composites

6 Ni-PTFE Composites

In this chapter, a novel electrochemical process to produce non-wetting composite coatings comprised of nanocrystalline metal matrix with embedded hydrophobic particles is described. For proof of concept, nanocrystalline nickel was chosen as the metal matrix and polytetrafluoroethylene (PTFE or Teflon) was chosen as the second phase, inert, hydrophobic particles. A broad range of characterization techniques were employed to develop a better understanding of this composite coating and to evaluate its potential in various engineering applications.

The experiments to make these composite coatings are a continuation of earlier experiments carried out by a M.A.Sc. student (Mr. Daniel Iacovetta) in this department which provided the basis for the materials synthesis 65.

The experiments involving the wear and thermal degradation of the Ni-PTFE composites were done in collaboration with two undergraduate students (Zhonghui Jiao and Jonathan Lau) and a Master of Engineering student (Jonathan Lau), also from the Department of Materials Science and Engineering.

6.1 Literature Review

Electrodeposition offers many advantages compared to other synthesis techniques for nanocrystalline metals. First, it is a simple, inexpensive, and scalable process to produce large volume of nanocrystalline metals. Second, there are very few size and shape limitations with this process. Third, the resulting material is fully dense and does not require additional processing such as compaction, consolidation, or sintering 51.

6.1.1 Ni-PTFE Composites in Previous Studies

Ni-PTFE composite is not a new coating system; it has been developed in the past for low friction coatings 66, corrosion resistant coatings 67, and electrode materials for fuel cell applications 68,69. The synthesis processes to fabricate these coatings include electrodeposition 66,67,70 (current applied between the anode and cathode) and electroless deposition 68,69 (no
external power source). There was one previous study on electrodeposition of non-wetting Ni-PTFE composites. In that study, the embedded PTFE particles had a unimodal size distribution (i.e. 300 nm) and the surface morphology did not have a hierarchical roughness to mimic natural superhydrophobic leaves. Further, unlike in the present study, the mechanical properties, wear and thermal stability, and adhesion of the composites to the substrate were not described.

In prior work, Daniel Iacovetta, performed a systematic study to determine the effect of PTFE and saccharin concentration in a Watts type electrolyte on the structure and properties of the Ni-PTFE composites. The PTFE concentration in the electrolytes was varied from 5 g/L, 10, 20, 30, and 40 g/L and the corresponding volume fraction in the Ni-PTFE composites were 41, 45, 58, 70, and 63 vol. %. At Ni-70vol.% PTFE, a WCA of 152° was observed. The addition of saccharin into the composite plating electrolyte was to achieve the nanocrystalline metal matrix structure. However, it was determined that the addition of saccharin reduced the non-wetting behaviour due to lower PTFE particles co-deposited.

6.1.2 Wear on Superhydrophobic Surfaces

As indicated earlier, commercialization of non-wetting surfaces remains rather limited due to the high costs of many fabrication processes and the poor understanding of the long-term stability of their non-wetting properties, specifically when the surface is subjected to wear. Since the specific surface roughness plays an important role in non-wettability, if the surface morphology is lost in service, the non-wetting property is expected to degrade. Therefore, it is important to develop a better understanding on the effect of abrasive wear on the non-wetting properties.

Currently, there are no standards to evaluate the durability of non-wetting surfaces when they are exposed to wear. There are number of studies that evaluated the wear stability of various superhydrophobic surfaces which are summarized in Table 6-1. As shown in the table, the wear tests can be categorized into 5 groups: linear abrasion with abrasive media, stainless steel block as the abradant, Taber linear abrader, reciprocating friction test, and sand drop abrasion. Among the techniques summarized, the most common wear test for superhydrophobic materials is linear abrasion with abrasive media. The specimen is dragged across the abrasive media and WCAs are measured as a function of abrasion length. In most cases, the abrasive medium is silicon carbide abrasive paper. Other media include cotton fabric and Technicloth (laboratory wipes).
linear abrasion is the most common technique in the literature, it was adapted in the present study to evaluate the wear stability of the newly developed non-wetting composites.

Table 6-1. Abrasive wear techniques for superhydrophobic surfaces.

<table>
<thead>
<tr>
<th>Wear Test</th>
<th>Superhydrophobic Material</th>
<th>Abrasive Medium</th>
<th>Pressure</th>
<th>Abrasion Length (mm)</th>
<th>Initial WCA (°)</th>
<th>Final WCA (°)</th>
<th>Initial WSA (°)</th>
<th>Final WSA (°)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Abrasion</td>
<td>Co + Stearic Acid</td>
<td>#800</td>
<td>1500</td>
<td>1100</td>
<td>156</td>
<td>148</td>
<td>32</td>
<td></td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>CuO, Cu(OH)₂; with</td>
<td>800 mesh</td>
<td>1200</td>
<td>700</td>
<td>156-163</td>
<td>140-145</td>
<td>-</td>
<td>-</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Stearic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microstructured</td>
<td>P1500</td>
<td></td>
<td></td>
<td>4500 (15 cycles of 30 cm, one direction)</td>
<td>152</td>
<td>147</td>
<td>11</td>
<td>18</td>
<td>75</td>
</tr>
<tr>
<td>PTFE film, 100 µm thick</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper sulfide film +</td>
<td>Cotton fabric</td>
<td>5000</td>
<td>250</td>
<td>152</td>
<td>143</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>76</td>
</tr>
<tr>
<td>steearic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hierarchical Si + PFOS</td>
<td>Technicloth</td>
<td>3450</td>
<td>250</td>
<td>168</td>
<td>167</td>
<td>2</td>
<td>14</td>
<td></td>
<td>77</td>
</tr>
<tr>
<td>UHMWPE substrate with silver + fluorinated surface</td>
<td>1500 mesh</td>
<td>10000</td>
<td>3000 (10 cycles of 30 cm)</td>
<td>163</td>
<td>160</td>
<td>5</td>
<td>15</td>
<td></td>
<td>78</td>
</tr>
<tr>
<td>Polyester fabric with silver + fluorinated surface</td>
<td>1200 mesh</td>
<td>13000</td>
<td>?</td>
<td>158</td>
<td>153</td>
<td>5</td>
<td>18</td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>Fluorinated silica nanoparticles / TiO₂ nanocomposite</td>
<td>1500 mesh</td>
<td>20000</td>
<td>225 (10 cycles)</td>
<td>155</td>
<td>139</td>
<td>5</td>
<td>70</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>Cotton fabric with structured co-polymer</td>
<td>1000 mesh</td>
<td>3920</td>
<td>8000 (40 cycles of 20 cm)</td>
<td>158</td>
<td>150</td>
<td>3</td>
<td>18</td>
<td></td>
<td>81</td>
</tr>
<tr>
<td>SiO₂ nanoparticle / epoxy composite + fluoroalkyl silane</td>
<td>Technicloth</td>
<td>3450</td>
<td>3000</td>
<td>169</td>
<td>165</td>
<td>2 (CAH)</td>
<td>40 (CAH)</td>
<td></td>
<td>82</td>
</tr>
<tr>
<td>Stainless Steel block</td>
<td>MoO₂ / polyurethane nanocomposite</td>
<td>Stainless steel abraded with 900 grit</td>
<td>700000</td>
<td>100000</td>
<td>167</td>
<td>152</td>
<td>5 (CAH)</td>
<td>40 (CAH)</td>
<td></td>
</tr>
<tr>
<td>Taber Linear Abrader</td>
<td>ABS</td>
<td>Crocking cloth</td>
<td>20500</td>
<td>1270 (25 cycles of 5.08 cm)</td>
<td>159</td>
<td>140-158</td>
<td>2-5</td>
<td>8-35</td>
<td></td>
</tr>
<tr>
<td>Titanium + fluoroacrylic polymer</td>
<td>H-18 0.25* taber abradant</td>
<td>10800-433700</td>
<td>165</td>
<td>105</td>
<td>7 (CAH)</td>
<td>60 (CAH)</td>
<td></td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Polymer-silica nanocomposite</td>
<td>Crocking cloth</td>
<td>20500</td>
<td>304.8 (60 cycles of 5.98 cm)</td>
<td>152</td>
<td>140-152</td>
<td>10</td>
<td>70</td>
<td></td>
<td>86</td>
</tr>
<tr>
<td>Reciprocating Friction Test</td>
<td>Polyurethane elastomer</td>
<td>Polished</td>
<td>2945</td>
<td>(1000 cycles)</td>
<td>165</td>
<td>158</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sand Abrasion</td>
<td>Hierarchical Si + PFOS</td>
<td>140 mesh sand</td>
<td>Sand dropped from 30cm for 30 s</td>
<td>165</td>
<td>161</td>
<td>1</td>
<td>70</td>
<td></td>
<td>77</td>
</tr>
</tbody>
</table>
6.1.3 Thermal Degradation of Non-Wetting Surfaces

Just as important as abrasive wear stability, thermal degradation of non-wetting surfaces needs to be well understood in order to determine the operating temperature window for these surfaces in industrial settings. To date, there are few studies that have investigated the thermal degradation of these materials. For instance, Gong et al. studied the thermal stability of electrospun fluorinated polyimide mat and demonstrated it retained superhydrophobic properties even after exposure to 300°C for 1 h. The comparison material of that study, electrospun polystyrene, had a similar initial WCA but lost the non-wetting properties when heated about 100°C, due to its low glass transition temperature, leading to change in surface morphology. In another study, Cha et al. investigated the thermal stability of nanostructured Si coated with silicon oxide (SiOx) - diamond like carbon film. WCAs were measured with varying annealing temperature. It remained superhydrophobic behaviour up to 300°C for 24 h. Beyond that, the WCA decreased to less than 90° after annealing at 400°C and became nearly superhydrophilic at 500°C.

Since the types of non-wetting material are quite diverse, the parameters (annealing temperature, time) used for the study of thermal degradation can be quite different, depending on the decomposition / melting / glass transition temperature of the material. Similar to abrasive wear stability, there are no standards to evaluate the thermal stability of non-wetting surfaces.

6.2 Experimental Details

6.2.1 Synthesis Process Development

Electro-codeposition was chosen as technique to fabricate the nanocrystalline metal matrix composite proposed in Figure 3-1. As noted in the literature review, electro-codeposition is an industrially scalable technique and allows good control of grain size and particles size deposited.

6.2.1.1 Metal Matrix Selection

Nickel was chosen as the metal matrix for the non-wetting composite due to its excellent mechanical properties, high thermal stability and good corrosion resistance. Furthermore, electrodeposition of nickel is well-established and the grain size can be easily tuned by the use of bath additives and adjusting the current waveform.
6.2.1.2 Hydrophobic Particle Selection and Characterization

As noted earlier, the mechanism of superhydrophobicity is a combination of intrinsically low surface energy hydrophobic material with hierarchical surface roughness. In order to meet these criteria, the inert particle to be co-deposited should have a bimodal particle size distribution in order to form hierarchical surface roughness when co-deposited. In this study, polytetrafluoroethylene (PTFE) particles were chosen for number of reasons: (i) highly hydrophobic with WCA = 116° (for a flat sheet of PTFE), (ii) chemical inertness; i.e. it will not dissolve or decompose in the acidic plating electrolyte, and (iii) high melting point. The PTFE particles used in this study were supplied by AGC Chemicals (product name: FL1710). According to the manufacturer, the average particle size is 3μm.

In addition, the PTFE particles were characterized by an acoustic technique to quantify the particle size distribution (Dispersion Technology DT-1200). To do so, the PTFE particles (30 g/L) were dispersed in deionized water containing 1 g/L cationic surfactant: cetyltrimethylammonium bromide (CTAB). Mechanical and ultrasonic agitation were applied to disperse the hydrophobic PTFE particles in water.

6.2.2 Electro-codeposition of Ni-PTFE

Electro-codeposition of Ni-PTFE was performed in a beaker setup containing 200 mL of electrolyte. A schematic diagram of the synthesis process is shown in Figure 6-1. The DC power supply provides electrical current to dissolve the anode (Ni rounds held in an inert titanium basket) and to reduce Ni$^{2+}$ in solution to solid Ni on the cathode. The cathode is the substrate onto which the coating is deposited. In this study, the cathodes were 2 cm × 2 cm × 0.16 cm Cu coupons. Prior to deposition, the coupons were ground to 1200 grit fine SiC abrasive paper and ultrasonically cleaned in ethanol. A magnetic stir bar was used to maintain agitation in the electrolyte. Furthermore, the temperature of the electrolyte is maintained by the hot plate.
Figure 6-1. Schematic diagram of the electro-codeposition setup for Ni-PTFE composites.

The electrolyte used to fabricate the non-wetting composite coatings is a modified Watts bath containing dispersed PTFE particles. The composition of the electrolyte is based on Iacovetta’s study\textsuperscript{65}. The details of the plating electrolyte is listed in Table 6-2. The goal was to produce composite coatings of about 70 vol.% PTFE on the surface.

Table 6-2. Electrolyte for the co-deposition of Ni-PTFE.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO\textsubscript{4}·6H\textsubscript{2}O</td>
<td>300 g/L</td>
<td>Main source of Ni\textsuperscript{2+} ion</td>
</tr>
<tr>
<td>NiCl\textsubscript{2}·6H\textsubscript{2}O</td>
<td>45 g/L</td>
<td>Promotes anode dissolution, secondary source of Ni\textsuperscript{2+} ion</td>
</tr>
<tr>
<td>H\textsubscript{3}BO\textsubscript{3}</td>
<td>45 g/L</td>
<td>pH buffer</td>
</tr>
<tr>
<td>PTFE</td>
<td>30 g/L</td>
<td>Hydrophobic inert particles to be co-deposited</td>
</tr>
<tr>
<td>CTAB</td>
<td>1 g/L</td>
<td>Wetting agent for the hydrophobic PTFE particles. Also provides positive surface charge to the PTFE particles to assist co-deposition</td>
</tr>
</tbody>
</table>

Electro-codeposition was performed at a current density of 100 mA/cm\textsuperscript{2} for 20 minutes to achieve coatings with thickness between 60 – 80 μm. The electrolyte was continuously agitated at 250 rpm and the temperature and pH were maintained at 60°C and 3.5 – 4.0, respectively. The electrodeposition parameters were based on Iacovetta’s study and were slightly modified. While Iacovetta initially started with an electrolyte containing saccharin (Ni grain size refiner) and CTAB (PTFE dispersion agent), it was shown in the TEM characterization of the present study (6.3.3) that CTAB actually takes on a dual role during electro-codeposition. It dispersed the hydrophobic PTFE particles and refines the Ni grain size at the same time. Therefore, no
saccharin was added to the plating bath in this study. After deposition, the samples were rinsed with DI water and ultrasonically cleaned in ethanol to remove loosely attached PTFE particles.

### 6.2.3 Microhardness Measurements

Before microhardness measurements, the specimen was ground with SiC abrasive paper, up to 1200 grit fine papers to achieve a suitable, smooth surface. Microhardness testing was performed using a 50 g load (Buehler Micromet 5103). In addition, EDS was performed on each microhardness indent to determine the local PTFE concentration.

### 6.2.4 Wear Stability

In this study, a simple abrasion wear testing apparatus based on linear abrasion (Table 6-1), as depicted in Figure 6-2 was developed to evaluate the wear stability of Ni-PTFE composites. The sample was pushed in a reciprocating motion at a rate of 10 cm/s across the surface of SiC paper (400 and 800 grit) under a constant applied pressure of 2000 Pa perpendicular to the surface. The abrasion stroke length was 15 cm. For each sample, a fresh SiC paper was used in order to compare the results with previous studies. The chosen parameters, including applied pressure and grit size of SiC papers were similar to several past studies on the abrasive wear of electrodeposited superhydrophobic surfaces, so that a comparison was possible.

In addition, a commercially available superhydrophobic spray treatment (CSHST) was tested for wear performance under the same conditions. This product is called NeverWet™, made by Rust Oleum. The purpose of these experiments was to compare the Ni-PTFE composite coatings made in this study with a non-wetting technology that is already available on the market today. The CSHST coatings were also applied on the surface of 2 cm × 2 cm × 0.16 cm Cu coupons according to the manufacturer's instructions.

![Figure 6-2. Schematic diagram of the abrasion wear test apparatus.](image-url)
6.2.5 Coating Adhesion Testing

A robust coating for practical application also requires strong adhesion to the underlying substrate. In addition to abrasive wear testing, the adhesion of both non-wetting coatings (Ni-PTFE and CSHST) on the substrate was also evaluated by a cross-cut tape test per ASTM D3359-09 standard using square grid cross-cuts all the way down to the substrate at 1 mm spacings. An optical microscope was employed to analyze the coatings before and after the adhesion test. The adhesion was rated by comparing with the classification figure in the ASTM D3359-09 document, shown in Figure 6-3.

![Classification of adhesion test results according to ASTM D3359-09](image-url)

Figure 6-3. Classification of adhesion test results according to ASTM D3359-09 [ref 97].
6.2.6 Thermal Degradation

To evaluate the stability of the Ni-PTFE under high temperature excursions, Ni-PTFE composites were annealed in a furnace at 150°C, 200°C, 250°C, 300°C, 350°C, and 400°C for 60 minutes. These selected parameters were based on previous studies on thermal degradation of non-wetting surfaces. The samples were cooled in the furnace and were subsequently removed when room temperature was reached. For comparison purpose, this experiment was also performed on the CSHST coatings.

6.3 Results and Discussions

6.3.1 PTFE Powder

Secondary electron micrographs of the as-received PTFE powder are shown in Figure 6-4. The low magnification image (Figure 6-4a) shows micron size PTFE. Many of the micron size particles are agglomerates of submicron size particles, as shown in Figure 6-4b. In the high magnification image, it can be observed that the submicron size particles (~ 300 nm) have a nearly spherical shape.

![Figure 6-4. Secondary electron micrographs of as-received PTFE powder mounted on silver paste. (a) Low magnification, (b) medium magnification, (c) high magnification.](image)

As noted in the experimental section, the particles size of the PTFE was also characterized by the acoustic technique. The results are shown in Figure 6-5. The PTFE particles have a bimodal particle size distribution showing micron sized particles with an average size of about 8 μm and sub-micron particles with an average size of 0.6 μm. About 60vol.% of all particles have size less than 1μm (Figure 6-5b). These measurements are in good agreement of the SEM image presented in Figure 6-4, where two distinct particles sizes were observed.
Figure 6-5. (a) Particle size distribution (PSD) and (b) cumulative volume fraction of 30 g/L PTFE particles in solution of DI water containing 1 g/L CTAB.

6.3.2 Surface Morphology and Wetting Properties of Ni-PTFE

Optical image of the Ni-PTFE composite coating electro-codeposited on Cu substrate is shown in Figure 6-6. The composite coating has a uniform, dark grey appearance on the entire plated area. Representative secondary electron micrographs of the Ni-PTFE composite coatings with about 70vol% surface PTFE are shown in Figure 6-7. As shown in the low magnification image (Figure 6-7a), micron size and submicron size PTFE particles were co-deposited into the nickel matrix. The surface morphology of the Ni-PTFE composite resembles natural superhydrophobic leaves with dual scale hierarchical roughness. As depicted in the high magnification image (Figure 6-7b), the submicron size PTFE particles are embedded in the fine grain structure of the
Ni matrix. The composition of the composite coating was determined to be Ni-70vol.% PTFE by energy dispersive X-ray spectroscopy technique. Between specimens that were produced under the same electro-codeposition parameters, there can be variations in the chemical composition of +/- 5vol.%.

The geometry of the specimen is not ideal for EDS measurements as the PTFE particles protrude out of the surface. Therefore, the chemical composition data obtained by EDS may “over-report” the PTFE content since the e⁻ beam – specimen interaction will be biased towards the protruding PTFE particles.

Figure 6-6. Optical image of Ni-PTFE coating on copper substrate.

![Optical image of Ni-PTFE coating on copper substrate.](image)

Figure 6-7. Secondary electron micrographs of as-deposited Ni-70vol.% PTFE composites. (a) Low magnification image. Hierarchical roughness formed by the biomodal PTFE particles can be observed. (b) High magnification image. Submicron size PTFE particles are well embedded in the nickel matrix.

The Ni-70vol.% PTFE composite coatings exhibit superhydrophobic behaviour: WCA = 156° and WSA of about 5°. An optical image of 5 μL deionized water droplet at rest on the surface is
shown in Figure 6-8. For the rest of the discussion in this thesis, the Ni-70vol.% PTFE composite specimens will simply be referred to as Ni-PTFE.

Figure 6-8. 5 μL deionized water droplet at rest on the surface of Ni-70vol.% PTFE composite coating.

6.3.3 Cross Sectional FIB and TEM Characterization

To develop the structure – property relationships of the Ni-PTFE composite coatings, cross-section microstructure analysis was performed by FIB and TEM techniques. Cross-section of the Ni-PTFE prepared by FIB milling is shown in Figure 6-9. Two different scanning probes were used to acquire the micrographs; electrons (Figure 6-9a) and Ga+ ions (Figure 6-9b). The signal collected for both cases were secondary electrons. However, the contrast between them is slightly different. In Figure 6-9a, the dominant contrast is topographical contrast; the surface morphology of the Ni-PTFE composite coating can be clearly observed. At the cross-section surface, it is clear that micron and submicron size PTFE particles are well embedded in the Ni matrix, as hypothesized in Figure 3-1. The vertical “scratches” observed on the cross-section surface are due to differential milling of the hard metal phase and soft polymer phase. Compositional and topographical can be observed from Figure 6-9b. The dark layer (thickness: 1.5 μm) on top of the cross-section window is a tungsten coating to protect the area of interest from ion beam damage. Similar to Figure 6-9a, topographical features of the composite coating can also be observed. On the cross-section surface, it appears that the PTFE particles were preferentially milled out, leading to the holes observed.
As noted earlier, thin TEM samples of Ni-PTFE were prepared by FIB. Snapshots of the process are shown in Figure 6-10. First, a site of interest was located and trenches around the site of interest were milled out by FIB, followed by a bottom cut (Figure 6-10a). Second, a micromanipulator was bonded to the microsample by depositing tungsten. After bonding the micromanipulator, the microsample was lifted out (Figure 6-10b). The microsample was transferred to the TEM grid and was attached by tungsten deposition (Figure 6-10c). The micromanipulator was detached from the sample by FIB milling. Finally, the specimen was thinned by FIB, as shown in the cross-section image on Figure 6-10d.
Figure 6-10. TEM thin sample preparation by FIB processing. (a) Trenches around the site of interest were created, followed by a bottom cut. (b) The micromanipulator was bonded to the microsample and was lifted out. (c) Microsample was bonded to the TEM support grid. (d) Cross-section of the microsample after thinning.

Representative selected area electron diffraction (SAED) pattern, bright field (BF) and dark field (DF) images of the Ni-PTFE are shown in Figure 6-11. The ring-like pattern of the SAED confirms that the Ni matrix is composed of many small crystals. This is further supported by the diffraction contrast BF and DF images where nanosize grains can be directly observed. The size of one crystal / grain was measured by taking the average length of major axis and minor axis. In addition, sub-grains that are separated by low angle grain boundaries are considered as an individual grain in this study. Multiple BF and DF images were studied to determine the grain size distribution, as shown in Figure 6-12. The Ni matrix has a lognormal grain size distribution with an average grain size of 27 nm. Even without the use of pulse current waveform during electro-codeposition and the addition of grain refining additive such as saccharin, grain
refinement was achieved due to the use of CTAB to disperse the PTFE particles in the electrolyte. It was demonstrated in a previous study that the addition of CTAB in Ni plating electrolyte increases the hardness of the Ni electrodeposit \(^{98}\), which indirectly infers that grain refinement was achieved. In this case, the CTAB serves 2 functions: (i) to disperse the hydrophobic PTFE particles in the electrolyte, and (ii) grain refiner. Furthermore, as the PTFE co-deposits with the Ni, the cathode surface area decreases. Therefore, the effective current density of the plating process was likely to be higher than 100 mA/cm\(^2\). Higher current density is known to promote nucleation of new crystals rather than growth of existing crystals on the electrodeposit.

![Figure 6-11](image)

Figure 6-11. (a) Selected area electron diffraction pattern, (b) bright field image, and (c) dark field image of Ni-PTFE composite.

![Grain Size Distribution](image)

Figure 6-12. Nickel matrix grain size distribution of Ni-PTFE composite coatings.
6.3.4 Microhardness of Ni-PTFE Composite Coatings

Based on over 25 indentations, the average microhardness of the Ni-PTFE composite coatings after the surface was polished was determined to be 145 ± 45 HV. In addition, each of the indentations were located in the SEM to determine the local chemical composition by EDS (Figure 6-13a, b). The results of these measurements are presented in Figure 6-13c, where indentation local PTFE vol% is plotted with the corresponding microhardness. The result also rationalizes the large standard deviations of average microhardness for the composites as microhardness is very sensitive to the local microstructure. Due to the limitations of the microhardness testing, the PTFE vol% values shown in Figure 6-13c are notability lower than 70 vol.% on the as-deposited surface. EDS measurements were performed on the polished surface at multiple locations, each with a scan area of approximately 200 × 150 µm and the average PTFE content was 48 ± 8 vol.%. Indentations can only be made on regions of the sample where the relative volume fraction of PTFE was relatively low or at regions away from the micron size particles in order to avoid ambiguity in determining the boundary of the indentation.

The rule of mixture is frequently applied for composite materials to predict the theoretical upper- and lower-bound properties, such as elastic modulus and tensile strength. In this case, the rule of mixture equation for composite hardness is: 

\[ H_{comp}^n = f_{Ni} H_{Ni}^n + f_{PTFE} H_{PTFE}^n, \]

where \( f_{Ni}, f_{PTFE} \) are the volume fractions and \( H_{Ni}, H_{PTFE} \) are the hardness values for nickel and PTFE. For the upper bound composite hardness, the value for exponent \( n = 1 \), while \( n = -1 \) applies for the lower bound case. The upper bound represents the iso-strain condition, where the constituents of the composite are aligned parallel to the loading direction and the strain of the constituents are identical under loading. The lower bound depicts iso-stress condition. In this case, the constituents are stacked in series and aligned perpendicular to the loading direction. Therefore, the constituents must experience the same stress upon loading. Since the average grain size of nickel is about 27 nm, the hardness \( H_{Ni} \) is about 500 HV according to El-Sherik et al.’s study. Although there is no available hardness value for PTFE, an estimation for \( H_{PTFE} \) was made using the relation \( H = 3\sigma_{UTS} \). This relation is a reliable approximation for nanocrystalline metals and is assumed to hold true for PTFE. According to the manufacturer, the tensile strength of PTFE ranges from 20.6-34.4 MPa, which translates to an average of about 8 HV using the above relation. Using these parameters, the theoretical upper and lower bound curves of composite hardness are plotted with the experimental results in Figure 6-13c. The experimental data lies
well within the two extreme limits which suggest that the rule of mixture model is applicable for the microhardness of Ni-PTFE composites. Furthermore, this result also indicates that the composite is in a mixture of iso-strain and iso-stress conditions, which agrees with the geometry of the particulate composite. It can also be seen that there was a greater contribution of iso-stress as the trend of the microhardness measurements is similar to the shape of the lower bound curve. A similar observation was also reported in a finite element study on the indentation of silver matrix composite containing nickel inclusions where the dominant stress state was iso-stress.

![Figure 6-13. Microhardness measurements of Ni-70vol.% PTFE composites. Representative optical image (a) and SE image (b) of an indent. (c) Effect of local PTFE content on the microhardness of Ni-PTFE composites.](image)
6.3.5 Wear Stability of Ni-PTFE

Secondary electron micrographs of the as-prepared Ni-PTFE composite and CSHST coatings are shown in Figure 6-14a, d. As described previously, the Ni-PTFE composite has a dual scale surface roughness with lotus leaf-like morphology. The high magnification image of as-prepared Ni-PTFE composite (Figure 6-14a, inset) shows smaller PTFE particles embedded in the fine grain structure of the nanocrystalline Ni matrix. On the other hand, nanoparticles bonded together forming a porous structure were observed on the CSHST coating (Figure 6-14d). According to the material safety data sheet, the CSHST coating contains silicone and silica. Based on this finding, it can be speculated that the nanoparticles observed in the micrographs are silica nanoparticles that are held in clusters by hydrophobic silicone.

![Figure 6-14. SE micrographs of non-wetting coatings. (a) As-prepared Ni-PTFE, showing dual scale roughness. Inset shows submicron PTFE particles embedded in the nanocrystalline Ni matrix, scale bar: 500 nm. (b) Ni-PTFE after 3 m of wear on 400 grit SiC paper. Wear grooves generated from the SiC abrasive can be observed. (c) Ni-PTFE after 24 m on 800 grit, showing finer wear grooves and deformed PTFE particles. No evidence for particle pull-out was found. (d) As-prepared CSHST with porous structure. Inset shows clusters of nanoparticles forming the porous structure, scale bar: 250 nm. (e) CSHST after 3 m on 400 grit. Patches of delaminated coating can be observed. (f) CSHST after 24 m on 800 grit, showing fine wear grooves and smaller patches of exposed Cu substrate.](image-url)

As shown in Figure 6-15, WCA of Ni-PTFE composites remained above 150° and WSA was below 15° for about 3 m of abrasion length on 400 grit SiC. The WCA gradually decreased to about 130° and WSA converged to 50° after 18 m of abrasion length. On the other hand, the
CSHST specimens were no longer superhydrophobic when the surface was abraded for only 0.75 m and the mobility of water droplets was strongly reduced as shown by the rapid rise in WSA from 3° to 70° (Figure 6-15a, c). Furthermore, water droplets did not slide off the surface even when the samples were turned upside down for abrasion lengths greater than 3 m.

![Figure 6-15](image)

Figure 6-15. Effect of abrasive wear on WCA (a, b) and WSA (c,d) of Ni-PTFE composite coatings and CSHST coatings. (a, c): 400 grit SiC. (b, d): 800 grit SiC. Error bars show the standard deviation of the measurements.

Micrographs of the specimens after 3 m of abrasive wear are shown in Figure 6-14b, e. Wear tracks and deformed micron size PTFE particles caused by the abrasion can be observed for the Ni-PTFE composite (Figure 6-14b). No evidence for pull-out of PTFE particles was found. Due to the hierarchical surface roughness, submicron size PTFE particles in the recessed areas were undamaged which allowed for a stable Cassie-Baxter wetting state to be maintained even with
some larger scale surface damage. In contrast, delamination wear was observed for the CSHST specimens (Figure 6-14e); portions of the coating were stripped off, exposing the underlying copper substrate. As a result of the surface inhomogeneity, large standard deviations of WCA and WSA measurements were observed after abrasive wear (Figure 6-15) as the water droplets come in contact with both the hydrophilic Cu substrate (Cu WCA: 52°) and the superhydrophobic CSHST coating.

On 800 grit SiC, extended stability of superhydrophobic properties was observed for Ni-PTFE composite; WCA remained above 150° after 48 m of abrasion (Figure 6-15b). In contrast, durability of the CSHST was limited as the WCA dropped to 141° after only 3 m of abrasive wear. Moreover, water droplets did no longer slide off the surface after 24 m of abrasion (Figure 6-15d). At the conclusion of the wear test, CSHST specimens were barely hydrophobic as the WCA dropped to 92°.

Micrographs of both specimens after 24 m of abrasive wear are shown in Figure 6-14c, f. Fine wear groves and deformed micron size protrusions were observed on the Ni-PTFE composite (Figure 6-14c). Although top portions of the large scale roughness were damaged, superhydrophobic properties were retained and trapped air pockets can still form within the submicron-scale roughness that was protected from abrasion by the larger PTFE particles and the hard nanocrystalline Ni matrix of the coating. Similar to the observation made with the coarser SiC abrasive medium, patches of exposed hydrophilic copper substrate were observed on the CSHST following 24 m of wear (Figure 6-14f). These hydrophilic spots act as pinning points for water droplets, which led to the high WSA (Figure 6-15d).

Furthermore, the wear stability of electrodeposited Ni-PTFE on 800 grit SiC was compared to other superhydrophobic electrodeposits that were previously tested under similar conditions. As shown in Table 6-3, the total abrasion length before the loss of superhydrophobicity for the Ni-PTFE composite is significantly higher than for the other electrodeposited coatings studied to date owing to i) the hierarchical surface roughness and the continual exposure of new hydrophobic PTFE particles as the surface is exposed to wear and ii) the hard nanocrystalline Ni matrix. The non-wetting state (WCA > 90°) of Ni-PTFE was maintained even after extensive surface wear which demonstrates the hypothesis for generating long lasting and robust non-wetting surface by the composite approach.
Table 6-3. Abrasion lengths leading to the loss of superhydrophobic properties. Abrasive medium: 800 grit SiC.

<table>
<thead>
<tr>
<th>Material</th>
<th>Pressure</th>
<th>Abrasion Length</th>
<th>Initial WCA</th>
<th>Final WCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-PTFE composite [this study]</td>
<td>2000 Pa</td>
<td>50 m</td>
<td>156°</td>
<td>150°</td>
</tr>
<tr>
<td>CSHST [this study]</td>
<td>2000 Pa</td>
<td>3 m</td>
<td>155°</td>
<td>141°</td>
</tr>
<tr>
<td>Fluorinated Ni 96</td>
<td>6000 Pa</td>
<td>1 m</td>
<td>162°</td>
<td>148°</td>
</tr>
<tr>
<td>Co with stearic acid 73</td>
<td>1500 Pa</td>
<td>1.1 m</td>
<td>156°</td>
<td>148°</td>
</tr>
<tr>
<td>CuO with stearic acid 74</td>
<td>1200 Pa</td>
<td>0.7 m</td>
<td>163°</td>
<td>140°</td>
</tr>
</tbody>
</table>

6.3.6 Coating Adhesion

Optical images of the Ni-PTFE composite coating, as well CSHST coating before and after the cross-cut tape test is shown in Figure 6-16. Based on the result, none of the squares of the lattice were detached for both Ni-PTFE composite and the CSHST coating indicating excellent adhesion for both coatings to the copper substrates. Therefore, the classification of the results for both materials is 5b according to the ASTM D3359-09 standard, which is the highest classification; i.e. the coating has good adhesion to the metal substrate and did not detach from the test.

Figure 6-16. Cross-cut tape test of superhydrophobic coatings. (a, b) Ni-PTFE composite before and after the tape test. (c, d) CSHST before and after the tape test.
6.3.7 Thermal Degradation

The wetting behaviours of the Ni-PTFE composites and CSHST coatings after the elevated temperature treatment are presented in Table 6-4 and Figure 6-17. Even after temperature excursion up to 400°C for 1 hour, no significant changes were observed for the wetting behaviour of Ni-PTFE composites. On the other hand, the CSHST coatings degraded after exposure to temperature above 350°C. To understand the changes in wetting properties, scanning electron microscopy was employed to determine the changes in surface morphology. As expected, no significant changes were observed for the Ni-PTFE after exposure to 200°C for 60 minutes since the melting point of PTFE is 340°C (Figure 6-18a, b). On the other hand, microcracks were observed on CSHST coatings and the underlying hydrophilic substrate was exposed (Figure 6-18c), leading to the decrease in WCA (144°). In the high magnification image (Figure 6-18d), the nanoscale feature of the silica particles remained unchanged. A possible explanation for the formation of microcracks of the CSHST coatings is the difference in coefficient of thermal expansion (CTE). The CTE of the constituents of the non-wetting surfaces studied are summarized in Table 6-5. The difference between the CTE of silicone rubber, which is most likely the polymer binder that holds the SiO\textsubscript{2} nanoparticles together and copper is over an order of magnitude. Therefore, it is expected that heating to high temperature and cooling down to room temperature can cause compressive stress in the CSHST coating, leading to formation of cracks.

Table 6-4. WCA of Ni-PTFE composites and CSHST coatings after 60 minutes exposure to elevated temperature.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Ni-PTFE</th>
<th>CSHST</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 (as-prepared)</td>
<td>153° ± 6°</td>
<td>154° ± 4°</td>
</tr>
<tr>
<td>150</td>
<td>151° ± 2°</td>
<td>146° ± 4°</td>
</tr>
<tr>
<td>200</td>
<td>152° ± 5°</td>
<td>144° ± 3°</td>
</tr>
<tr>
<td>250</td>
<td>151° ± 3°</td>
<td>150° ± 4°</td>
</tr>
<tr>
<td>300</td>
<td>153° ± 4°</td>
<td>148° ± 3°</td>
</tr>
<tr>
<td>350</td>
<td>150° ± 3°</td>
<td>115° ± 1°</td>
</tr>
<tr>
<td>400</td>
<td>148° ± 4°</td>
<td>104° ± 7°</td>
</tr>
</tbody>
</table>
Figure 6-17. WCA of Ni-PTFE composite and CSHST coating after 60 minutes of annealing at various temperature. Insets show water droplet on Ni-PTFE (*) and CSHST (#) after exposure to 400°C for 60 minutes.

Figure 6-18. SE images of superhydrophobic surfaces after exposure to 200°C for 1 h. (a, b) Ni-PTFE composite coating. No significant changes were observed. (c, d) CSHST coating, microcracks were observed.
Table 6-5. Coefficient of thermal expansion for the constituents of the non-wetting surfaces

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient of Thermal Expansion at 20° C [$10^{-6}$ K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>17</td>
</tr>
<tr>
<td>Nickel</td>
<td>13</td>
</tr>
<tr>
<td>PTFE</td>
<td>120</td>
</tr>
<tr>
<td>Silica</td>
<td>0.5</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>250</td>
</tr>
</tbody>
</table>

After exposure to 350°C, changes in the surface morphology of Ni-PTFE can be observed, as shown in Figure 6-19a, b. Since 350°C is higher than the melting point of PTFE, the nearly spherical submicron size PTFE particles transformed into elongated, thorn-like shape due to partial melting. Hierarchical surface roughness can still be seen, allowing the composite coating to maintain excellent non-wetting behaviour. However, the feature size of the small-scale roughness increased to about 1 μm (thorns) from the submicron size spheres. For the CSHST, the size and network of the microscale cracks on the coating increased, contributing to the rapid decrease in non-wetting behaviour.

Figure 6-19. SE images of superhydrophobic surfaces after exposure to 350°C for 1 h. (a, b) Ni-PTFE composite coating. Thorn-like morphology can be observed, likely due to melting and re-solidification of
the PTFE particles. (c, d) CSHST coating, larger microcracks were observed. In the high magnification, most of the nanoscale features remain intact.

Furthermore, the abrasion wear stability of the coatings was evaluated by the simple abrasion test after the high temperature (400°C) excursion experiments. The wear stability test was conducted using the same experimental setup and parameters described in 6.2.4. The result of this experiment is summarized in Figure 6-20. The Ni-PTFE maintained WCA close to 150° even after 30 m of abrasion on 800 grit SiC abrasive paper. The result is comparable to the Ni-PTFE composite that was not subjected to any high temperature treatment (Figure 6-15b). For the CSHST coating, after 15 m of abrasion, the surface became hydrophilic (WCA < 90°).

Figure 6-20. Effect of abrasive wear on WCA of Ni-PTFE composite and CSHST coating after exposure to 400°C for 1 h. Abrasive medium is 800 grit SiC abrasive paper. Insets show water droplet on Ni-PTFE (*) and CSHST (#) after exposure to 400°C for 60 minutes and abrasive wear on 800 grit SiC abrasive for an abrasion length of 60 m and 15 m, respectively.

6.4 Summary

In this chapter, it was demonstrated that an electro-codeposition process is a low cost and viable technique to produce robust non-wetting, metal matrix composite coatings with embedded hydrophobic particles (preliminary cost estimate is included in Appendix C). The Ni-PTFE composite coatings exhibit exceptional hardness, coating adhesion, abrasive wear stability and thermal stability that is of interest in the community for industrial implementation of mechanically robust, superhydrophobic surfaces. The observed properties of the Ni-PTFE
composites can be traced back to their structure. Through the various microscopy technique, the structure (crystal, surface) of Ni-PTFE composites were analyzed from the nm scale to μm scale. The hierarchical surface roughness formed by the co-deposited bimodal size PTFE particles contributed to the highly non-wetting behaviour as well as excellent wear stability. Despite the high volume fraction of soft PTFE particles, the remarkable hardness of the composite was largely attributed to the nanocrystalline Ni matrix.

6.5 Published Work Based on Findings of This Chapter


Chapter 7
Ni-CeO$_2$ Composites

7 Introduction

In the previous chapter, a simple electro-codeposition process was demonstrated as a viable surface coating technique to produce non-wetting metal matrix composites. Extensive characterization results have shown that not only the Ni-PTFE composite has excellent water repellency in the as-prepared state, the non-wetting properties remained even after abrasive wear and elevated temperature excursions. However, since one of the constituents of the composite was a polymer, the mechanical properties of the coating, such as hardness was slightly compromised. Therefore, there may be a need to replace the soft hydrophobic PTFE particles with high hardness, hydrophobic particles.

Recently, Azimi et al. described that rare earth oxides (REO) are hydrophobic ($98^\circ < \text{WCA} < 112^\circ$) due to their unique electronic structure $^{103}$. Since the hard REOs have a similar WCA compared to PTFE ($\sim 116^\circ$), they are excellent candidate materials to replace the soft polymer particles in the composite coatings. In this chapter, a summary of Azimi's work will be given, followed by the experimental details on the synthesis of Ni-CeO$_2$ composites and the characterization results.

7.1 Hydrophobicity of Rare Earth Oxide Ceramics

The first systematic study on the wettability of rare earth oxide ceramics was performed by Azimi et al. in 2013 $^{103}$. In this study, wettability of all oxides of the lanthanide series (except for radioactive promethium oxide) were examined. The ceramics were fabricated by compacting the oxide powders into disk pellets, followed by sintering in air at elevated temperature (1400 - 1650$^\circ$C). After sintering, the ceramic pellets were polished, cleaned with acetone, ethanol, and water. Prior to water contact angle measurements, the samples were stored in a vacuum desiccator. All rare earth oxides exhibited hydrophobic behaviour with WCA between $98^\circ$ to $112^\circ$. In addition to WCA measurements, contact angle of two other probe liquids, namely ethylene glycol and diiodomethane were measured to quantify the polar component of the surface energy.
The mechanism of hydrophobicity of REOs proposed in this study is that the metal atoms in REOs have a different electronic structure compared to common ceramics such as aluminum oxide, resulting in different orientation of the water molecules on the surface. Aluminum oxide has a large number of polar sites originating from unsaturated aluminum and oxygen atoms that behave as Lewis acid and base sites, respectively. At the surface, the aluminum atoms are electron deficient and in order to achieve full octet of electrons, hydrogen bond formation with interfacial water molecules will occur, resulting in the clathrate or hydrophilic hydration structure (Figure 7-1). On the other hand, the full octet outer shell of the metal atoms of REOs shields the unfilled 4f orbitals from interacting with the surrounding. Therefore, the metal atoms are expected to have a lower tendency to form hydrogen bonds with water molecules, resulting in the anti-clathrate or hydrophobic hydration structure, as schematically shown in Figure 7-1.

![Diagram](image)

Figure 7-1. Schematic diagram of wetting properties and orientation of water molecules on oxide surfaces. On the left, hydrophilicity associated with common metal oxide such as aluminum oxide. On the right, hydrophobicity associated with rare earth oxides. In this case, the 4f orbitals are shielded by the full octet orbitals, therefore, there is no tendency for the unfilled 4f shell to interact with water molecules. Only 1 of the 4 hydrogen bond vectors points towards the surface interacting with the surface oxygen atoms on REO, leading to the hydrophobic behaviour.

The robustness of the hydrophobic REOs was demonstrated with various experiments. For instance, it was demonstrated that even with extensive abrasive wear, CeO$_2$ remained hydrophobic with a WCA of 103°. Also, REOs have a high thermal stability; after exposure to 1000°C for 2 h, CeO$_2$ remained hydrophobic with no significant changes to the WCA (WCA = 105°).
The study also highlighted the practical potential of hydrophobic REOs. Steam condensation experiments show that REOs have sufficient hydrophobic properties to promote dropwise condensation. This property is highly beneficial in condensation applications including power generation and desalination, where conventional polymer-based materials lack the robustness for extended service.

### 7.2 Experimental Details

In this study, the REO chosen for electro-codeposition was cerium oxide. for several reasons: CeO$_2$ is the most widely studied REO for wettability, CeO$_2$ powders are low cost and readily available in different particle sizes, and has similar WCA to PTFE. A comparison of PTFE and CeO$_2$ is shown in Table 7-1.

Table 7-1 Comparison of hydrophobic particles utilized for non-wetting metal matrix composite coatings

<table>
<thead>
<tr>
<th></th>
<th>Polytetrafluoroethylene (PTFE)</th>
<th>Cerium Oxide (CeO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material Type</strong></td>
<td>Polymer</td>
<td>Ceramic</td>
</tr>
<tr>
<td><strong>Melting Temperature</strong></td>
<td>340 °C</td>
<td>2400 °C</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>2.2 g/cm$^3$</td>
<td>7.22 g/cm$^3$</td>
</tr>
<tr>
<td><strong>Water Contact Angle</strong></td>
<td>116°</td>
<td>103° ~ 103°</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td>8 HV</td>
<td>636 HV</td>
</tr>
<tr>
<td><strong>Cost per volume</strong></td>
<td>$4.20/cm^3$</td>
<td>$4.98/cm^3$</td>
</tr>
</tbody>
</table>

The CeO$_2$ particles chosen for this study has a bimodal particle size distribution (more details in the results/discussion). Similar to Ni-PTFE composites, Ni-CeO$_2$ composites were electrodeposited onto polished copper substrates in a modified Watts bath electrolyte containing 300 g/L NiSO$_4$·6H$_2$O, 45 g/L NiCl$_2$·6H$_2$O, 45 g/L H$_3$BO$_3$, and 50 g/L CeO$_2$ particles. No surfactants were used in this system.

Since the density of CeO$_2$ is significantly higher than PTFE (Table 7-1), the particles tend to sink quickly in the plating electrolyte even with agitation. A modification to the electroplating setup was implemented to ensure the heavy ceramic particles to co-deposit with the Ni matrix. As

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$^1$ Pricing was obtained from Sigma Aldrich for 100 g quantity.
shown in the process schematic diagram (Figure 7-2), the cathode was oriented horizontally to allow settling CeO₂ particles to be co-deposited (gravity or sedimentation plating).

The volume fraction of co-deposited CeO₂ particles was controlled by the agitation rate. The pH of the electrolyte was 3.5 – 4.0 and the temperature was maintained at 60°C. Electrodeposition was performed at a current density of 50 mA/cm² for 20 minutes. The resulting coating thickness is about 50 - 70 μm. After deposition, the deposits were rinsed with deionized water and ultrasonically cleaned in ethanol to remove loosely attached CeO₂ particles.

Figure 7-2. Schematic diagram of the electroplating setup for Ni-CeO₂ composites. The cathode is oriented perpendicular to the anode.

7.3 Results and Discussion

7.3.1 CeO₂ Powder Characterization

Surface and particle size characterization of the as-received CeO₂ ceramic particles (Matheson Coleman & Bell, USA) were characterized by scanning electron microscopy and laser diffraction particle size analysis. Figure 7-3a shows a low magnification topographical contrast secondary electron (SE) image of the as-received ceramic powder. The particles are in irregular shape with some flat faces. From the high magnification SE image and electron channelling contrast backscattered electron (BSE) images (Figure 7-3b, c); it is apparent that the large particles observed in the low magnification image are not loose agglomerates of small particles. Instead, they have a three-tier hierarchical structure; the large particles (≥ 10 μm) are made of sub-particles (2 – 3 μm) sintered together. Furthermore, the sub-particles are composed of CeO₂
nanocrystals with average grain size less than 100 nm (Figure 7-3c), this hierarchical structure is providing significant surface roughness that is desirable for highly non-wetting properties in the composite coating.

Figure 7-3. (a) Low magnification and (b) high magnification SE images of as-received CeO$_2$ particles. The particles are in random shape, many with relatively flat surfaces. The high magnification image shows that the larger particles are made up of several sub-particles with flat faces. (c) Electron channeling contrast BSE image of the same area as (b). Each sub-particle is composed of sintered nanocrystals.

The ceramic particle size distributions as determined by the laser diffraction technique are presented in Figure 7-4. As shown in the histogram (Figure 7-4a), the particles are in a wide, bimodal distribution, with peaks at ~ 9 µm and ~ 50 µm. Therefore, the as-received CeO$_2$ particles have an average particle size of 15.8 µm with a relatively large standard deviation of 17 µm due to the bimodal distribution. The bimodal particle size distribution allows for a high packing factor of the particles when they are co-deposited with the metal matrix. Further discussion regarding this matter will be presented in section 7.3.2. Due to the broad distribution, the measured number frequencies are dominated by small particles below 10 µm, as depicted in Figure 7-4a. However, the low magnification SE micrograph (Figure 7-3a) shows that there is a substantial fraction of larger particles. To illustrate this quantitatively, cumulative undersize %
plot (Figure 7-4b) is included to provide another perspective on the particle size analysis. From this curve, particles with diameter less than 10 µm make up 50% of the particle frequency, i.e., \( d_{50} = 9.8 \) µm. In addition, the figure further shows that a large frequency (approximately 20%) of particles have a diameter greater than 20 µm.

Figure 7-4. (a) Particle size distribution and (b) cumulative undersize % of the as-received CeO\(_2\) powder.

The crystal size of the ceramic particles was determined by direct measurements from electron channeling contrast BSE images (i.e. Figure 7-3c) and the results are presented in a histogram and cumulative volume plot (Figure 7-5). The crystals are in a lognormal distribution with an average grain size of 52 ± 18 nm. The distribution is relatively narrow, as 50% of the volume within the ceramic particles is composed of crystals 52 nm or less, and 90% of the volume contained crystals that are 81 nm or less.

Figure 7-5. (a) Grain size distribution and (b) cumulative volume fraction of the as-received CeO\(_2\) powder.
7.3.2 Surface Characterization of Ni-CeO$_2$ Composites

To explore the effect of CeO$_2$ incorporation on the wetting properties, Ni-CeO$_2$ composites with varying surface volume fractions of co-deposited particles were fabricated by varying the agitation of the plating electrolyte during electro-codeposition. Optical images of composite coating containing 55vol.% and 97vol.% CeO$_2$ are shown in Figure 7-6 a and b, respectively. The 55vol.% specimen has a grey finish, while the 97vol.% specimen has a white / grey finish.

![Figure 7-6. Optical images of a) Ni-55vol.% CeO$_2$ and b) Ni-97vol.% CeO$_2$.](image)

The findings of the surface and chemical characteristics of two of the composite coatings with 55vol.% and 97vol.% CeO$_2$ on the surface are presented in Figure 7-7. CeO$_2$ particles of various size are uniformly co-deposited on the surface of the Ni-55vol.% CeO$_2$ coating, as shown in the SE micrograph and the energy dispersive X-ray spectroscopy (EDS) elemental map (Figure 7-7a, b). The bimodal particle size distribution (Figure 7-4) allows high coverage of the ceramic particles deposited on the surface; small particles fill the space between the larger particles. By modifying the agitation rate of the plating electrolyte, the deposition process can be transitioned from electrodeposition dominated (movement and reduction of metal ions under the influence of the applied electric field) to higher contribution of electrophoretic dominated deposition (movement and deposition of particles under the influence of the applied electric field). Hence, the incorporation of CeO$_2$ particles on the surface of the composite coating increases, up to 97vol.%.

As shown in the SE micrograph (Figure 7-7c), the surface of the Ni-97vol.% CeO$_2$ is very rough and is densely packed with CeO$_2$ particles and regions of Ni cannot be easily identified from the image. The EDS elemental map (Figure 7-7d) indicates that there are regions...
of Ni-rich area on the surface of the composite between the particles. Based on this analysis, the Ni phase does not percolate. In other words, the matrix of the composite is not Ni and the composite coating is expected to be highly brittle (more details in 7.3.6) as the dense surface layer of CeO$_2$ particles is not mechanically interlocked by a metal matrix.

Figure 7-7. SE images and EDS elemental maps of (a,b) Ni-55vol.% CeO$_2$ and (c,d) Ni-97vol.% CeO$_2$.

Quantitative analyses of the surface roughness for Ni-55vol.% CeO$_2$ and Ni-97vol.% CeO$_2$ coatings are shown in Figure 7-8a, b, respectively. The micrometer sized CeO$_2$ protrusions on the Ni-55vol.% CeO$_2$ have an average diameter and average height of 10 µm and 4.5 µm, respectively. On the other hand, the same features on the Ni-97vol.% CeO$_2$ are nearly twice as large; where the average protrusion diameter and height are 18.2 µm and 8.1 µm, respectively. Compared to the micro papillae protrusions on the surface of the lotus leaf (diameter: ~6 µm, height: ~10 µm [ref 104]), the aspect ratio (diameter : height) of the micro protrusions of these composites are wider and less slender.
7.3.3 Crystal Structure Characterization

The X-ray diffraction patterns of pure electrodeposited Ni, as-received CeO$_2$ powder, and the Ni-55vol.% CeO$_2$ composites are shown in Figure 7-9. All specimens are crystalline as indicated by the sharp peaks. The diffraction pattern of the composite contains both sets of diffraction peaks from the Ni phase (A1, cF4) and the CeO$_2$ phase (C1, cF12) confirming that there are no changes to the phases due to the electro-codeposition process. The minor changes in the relative Ni peak intensities for the composite and pure Ni indicate a small change in the crystal orientation of the Ni grains when co-depositing the ceramic particles with the nickel matrix. Such an effect can be expected in electroplated materials $^{32}$. 
7.3.4 Wetting Properties of Ni-CeO\(_2\) Composites

The water contact angles of the composites are shown on the two plots in Figure 7-10. Water contact angles were also measured on the flat constituents: electropolished Ni and sputter deposited CeO\(_2\) on Si substrate, represented by the red squares on Figure 7-10 at 0 vol.% and 100 vol.% CeO\(_2\), respectively. The predicted WCA based on Cassie equation \(^4\) (Equation 3) is shown by the red dash line.

\[
\cos \theta_C = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad [3]
\]

In the Cassie equation, \(f_1\), \(f_2\) and \(\theta_1\), \(\theta_2\) are the area fractions and contact angles for components 1 (Ni) and 2 (CeO\(_2\)), respectively and \(\theta_C\) is the apparent contact angle of the composite.

Regardless of the volume fraction of CeO\(_2\) particles on the surface of the composite coatings,
complete wetting (WCA ≈ 0°) was observed for the as-plated composite specimens and the as-sputter deposited pure CeO$_2$ coating on Si substrate (Figure 7-10a). The observed WCA of the composite coatings does not obey the rule of mixture as per Equation 3.

Figure 7-10. The influence of volume fraction of CeO$_2$ on the water contact angle. The WCA of pure, flat Ni and CeO$_2$ (sputter deposited on Si substrate) are also included in the plots. Before the vacuum treatment (a), all composite specimens and pure CeO$_2$ were superhydrophilic (WCA ≈ 0°). After the vacuum treatment (b), all Ni-CeO$_2$ coatings demonstrate non-wetting properties with linearly increasing WCA as the co-deposited CeO$_2$ particle concentration increases (linear trend fitted by the black dotted line). The red dash line represents the predicted WCA based on the rule of mixture of the flat constituents (Cassie equation).

After a treatment in vacuum (10$^{-3}$ – 10$^{-4}$ Pa), all composite coatings and the pure CeO$_2$ coating made by sputter deposition became hydrophobic (Figure 7-10b). This observation is similar to a previous study on thermal spray coated superhydrophobic ytterbium oxide surfaces. Cassie equation (Equation 3) was also plotted for the vacuum-exposed materials and the observed WCA is significantly higher by roughly 50°. Interestingly, according to Cassie equation (rule of mixture), a flat composite would remain hydrophilic until the volume fraction of the CeO$_2$ particles exceeds about 60%. However, hydrophobic behaviour was observed even for the composites with about 35vol.% CeO$_2$. This observation suggests that the enhanced hydrophobicity is largely contributed to surface roughness. Wetting behaviour of a rough surface can be described by Wenzel equation (Equation 2); where $R_f$ is the roughness factor; defined as the ratio of the true surface area to the 2D projection and $\theta$ is the intrinsic contact angle of the smooth surface and $\theta_W$ is the Wenzel contact angle. In the Wenzel wetting regime, the liquid droplet is in complete contact with the rough solid surface and the droplet is pinned by the
asperities. As described previously, in the Cassie-Baxter wetting regime, the liquid droplet is not in complete contact with the solid surface. Instead, it is suspended by the trapped air pockets in the troughs of the rough surface. Cassie-Baxter equation (Equation 4) can be derived from the Cassie equation (Equation 3) by substituting one of the components with air ($\theta_{air} = 180^\circ$).

$$cos\theta_W = R_f cos\theta$$

(2)

$$cos\theta_{C-B} = f_1(cos\theta_1 + 1) - 1$$

(4)

With these equations and the surface area determined from Figure 7-8, the expected WCA without trapped air pockets ($\theta_W$) and the area fraction of droplet in contact with air pockets were calculated, as shown in Table 7-2 For the Ni-55vol.% Ni-CeO$_2$ composite, the calculated $\theta_W$ using equations 2 and 3 is lower than the WCA predicted for a flat surface $\theta_C$ since the composite is expected to be hydrophilic at that composition. In this case, hydrophobicity is induced by surface roughness that allows trapped air pockets to minimize the contact of the liquid droplet with the hydrophilic valleys (Ni). For this sample, the calculated fraction of droplet in contact with air pockets is 0.70 (Table 7-2). Since WSA was not observed for this composite (i.e. water droplets remain on surface even when it is upside down), the wetting state is most likely in a mixed state of Wenzel and Cassie-Baxter.

Table 7-2. Analysis of surface and wetting properties of Ni-CeO$_2$ composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>True Surface Area [(\mu m^2)]</th>
<th>2D Projected Area [(\mu m^2)]</th>
<th>Roughness Factor $R_f$</th>
<th>Calculated Cassie Contact Angle $\theta_C$ [°]</th>
<th>Calculated Wenzel Contact Angle $\theta_W$ [°]</th>
<th>Measured Contact Angle [°]</th>
<th>Calculated Solid Fraction $f_1$</th>
<th>Calculated Air Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-55 vol.% CeO$_2$</td>
<td>57337</td>
<td>48300</td>
<td>1.19</td>
<td>85</td>
<td>84</td>
<td>132</td>
<td>0.30</td>
<td>0.70</td>
</tr>
<tr>
<td>Ni-97 vol.% CeO$_2$</td>
<td>76582</td>
<td>48300</td>
<td>1.59</td>
<td>99</td>
<td>104</td>
<td>156</td>
<td>0.12</td>
<td>0.82</td>
</tr>
</tbody>
</table>

A linearly increasing trend in WCA was observed as the volume fraction of the CeO$_2$ particles increased. At very high content of CeO$_2$ (97vol.%), the composite coating exhibited superhydrophobic behaviour with an average WCA of 156° and WSA of 25°. The predicted WCA without the air pockets ($\theta_W$) is 104°. At this composition, the larger area fraction of air
pockets (0.82) highly contributed to the observed superhydrophobicity. The reflected light in the optical micrograph of a water droplet (Figure 7-11) of the Ni-97vol.% composite coating shows the presence of air pockets trapped between a water droplet and the coating surface as small white speckles. This observation further reinforces that the water droplet is in the Cassie-Baxter wetting state; the droplet is not in complete contact with the surface and is partially suspended by the peaks of the rough surface. Therefore, the droplet has low adhesion to the surface as suggested by the relatively low WSA of 25°.

Figure 7-11. Reflected light under the water droplet at rest on Ni-97vol.% CeO₂ coating indicates the presence of trapped air pockets.

7.3.5 Cross-section Microstructure Characterization

In order to verify that co-deposition of CeO₂ particles is not just limited to the surface of the composite coating, focused ion beam (FIB) milling was performed to gain a better insight of the cross-sectional microstructure. FIB milling was carried out on the Ni-55vol.% CeO₂ coating. Figure 7-12a shows the SE image of the studied area before sectioning with FIB. From this micrograph, it appears that the CeO₂ particles are mainly sitting on the surface, rather than being embedded in the Ni matrix. To protect the surface of the region of interest from damage by the ion beam, a thin layer of tungsten was deposited as indicated by the arrows in Figure 7-12b. Topographical contrast SE image of the cross-section after FIB milling and polishing is shown in Figure 7-12c. The image shows that the co-deposited sintered CeO₂ particles have some porosity. Due to the porosity present in the CeO₂ particles, the vertical streaks on the image are a result of differential milling. A compositional contrast backscattered electron (BSE) image of the cross-section surface is depicted in Figure 7-12d. The distribution of CeO₂ particles on the cross-section of the coating can be easily identified in this image. This image provides evidence that
the ceramic particles are not just located on the Ni surface; they are indeed embedded in the nickel matrix and across the thickness of the coating. In addition to topography and compositional information, FIB images also provide information on the crystallographic structure of the composite material (Figure 7-12e). In this case, the incident beam is a focused ion beam and secondary electrons generated from the ion beam – specimen interaction are collected to form the image. Crystals of the Ni matrix and CeO₂ particles can be clearly observed due to ion channeling contrast 106. Furthermore, the distribution of elements in the composite can be identified from the EDS elemental map (Figure 7-12f). The elemental map further reinforces that the co-deposition of CeO₂ particles inside the Ni matrix was indeed achieved.

Moreover, the interface between the metal matrix and ceramic particles and the structure of the two phases were studied by high magnification FIB imaging (Figure 7-13). From the FIB micrographs presented in Figure 7-13, it is clear that the Ni matrix grew around the CeO₂ particles during the plating process. Regardless of particle location, close to the surface Figure 7-13a) or beneath it (Figure 7-13b), the interface between the Ni matrix and CeO₂ particles is free of voids and defects. The observation of well-embedded CeO₂ particles promises that the particles will not be easily removed from the coating when applied in industrial applications that involve wear conditions. As shown in Figure 7-13c, the Ni matrix has a large fraction of twinned grains which can be expected in Ni electrodeposits 32.

The crystal size of the nickel matrix was determined by measuring grain size directly on multiple FIB images. The histogram and cumulative frequency of the grain size are shown in Figure 7-14. The Ni matrix has an ultra-fine grain structure (average grain size: 310 nm) with wide, lognormal grain size distribution, as shown in the histogram.
Figure 7-12. Cross-sectional analysis of Ni-55vol.% CeO₂ composite coating. (a) SE image of the as-deposited surface. (b) Protective tungsten coating (indicated by the arrows) was deposited on to the region of interest before FIB milling. (c) SE image of the cross section after FIB milling; arrows indicated the protective tungsten coating. (d) BSE image of the cross section showing elemental contrast. (e) FIB image of the cross-section topography, compositional, and channeling contrast. (f) EDS elemental map of the cross-section.
Figure 7-13. Cross-sectional FIB images of Ni-CeO$_2$ composite. (a) Interface of the CeO$_2$ particles and Ni matrix near the surface of the coating. (b) Interface of the ceramic particle and metal matrix below the surface of the coating. (c) High magnification image of the Ni matrix.

Figure 7-14. Grain size analysis of the Ni matrix (a) histogram of grain size distribution, (b) cumulative frequency plot.

7.3.6 Ni-CeO$_2$ Composite Coating Adhesion

A robust non-wetting coating for industrial applications demands strong adhesion to the underlying substrate material. Cross-cut tape adhesion test was conducted on 3 materials: pure Ni coating, Ni-55vol.\% CeO$_2$ composite coating, and Ni-97vol.\% CeO$_2$ composite coating. For the Ni and Ni-55vol.\% CeO$_2$ coatings, no noticeable removal of the lattice squares was observed after the tape test, suggesting that these coatings have excellent adhesion to the substrate (classification of 5B, Figure 6-3). Due to the structure and brittle nature of the Ni-97vol.\% CeO$_2$ composite, parts of the coating cracked when the cross-cut square grid was drawn by a sharp knife. Hence, a classification for the coating adhesion was not assigned.
7.3.7 Hardness of Ni-CeO$_2$ Composite Coating

In addition to the enhanced non-wetting properties of Ni coatings by the incorporation of CeO$_2$, the ceramic particles are expected to provide second phase strengthening to the Ni matrix. Vickers microhardness measurements were performed on Ni-CeO$_2$ composite coating, sintered CeO$_2$, copper, and mild steel and compared with conventional large grained Ni$^{107}$ and Ni-PTFE, as shown in Figure 7-15. The average microhardness (over 30 microhardness indentations) of the composite coating containing 55vol.% CeO$_2$ is 366 ± 18 HV, which is in between the pure constituents (Ni: 131 ± 3 HV, CeO$_2$: 636 ± 16 HV).

Since the Ni-CeO$_2$ is a particulate type composite material, it is expected the microhardness to vary depending on the local concentration of ceramic particles. As shown in Figure 7-16, over 30 indentations were made at different locations on the Ni-55 vol.% CeO$_2$ coating and the local ceramic particle concentration at each indentation was determined by EDS. Although there is a variation in the measured microhardness between indents, it appears that measured hardness remains relatively constant despite the differences in local surface CeO$_2$ content at each of the indents. SE images and EDS elemental maps were acquired for 2 indents with similar microhardness; 377 HV (herein, referred as indent A, Figure 7-17a, b) and 379 HV (referred as indent B, Figure 7-17c, d). It is evident from the SE images that the dimensions of the indents are very similar, yet the fraction of CeO$_2$ at the indent is very different, as shown on the EDS elemental maps: 0 vol.% for indent A (Figure 7-17b) and 32 vol.% for indent B (Figure 7-17d).
Figure 7-15. Vickers microhardness of electrodeposited polycrystalline nickel, sintered cerium oxide, Ni-55 vol.% CeO₂ composite, Ni-70 vol.% PTFE, copper, and mild steel.

Figure 7-16. Effect of surface CeO₂ content on measured Vickers microhardness.
Figure 7-17. SE images and EDS elemental maps of (a, b) indent A, 377 HV and (c, d) indent B, 379 HV.

Since EDS only probes the surface chemical composition (typically up to 1 μm deep at an accelerating voltage of 20 kV), FIB milling was employed to determine the presence of ceramic particles in the sub-surface beneath the indentations that may affect the measured hardness. Figure 7-18a-f and g-l are the FIB images and EDS elemental maps of three cuts perpendicular through indent A and indent B, respectively. As observed in Figure 7-18a, d, there are no ceramic particles directly beneath indent A. In the final two cross-section surfaces for indent A (Figure 7-18b, c, e, f), CeO$_2$ particles, which were not probed in the surface EDS elemental map (Figure 7-17b) were found near the periphery of the indent. On the other hand, CeO$_2$ particles were found directly beneath indent B in all 3 cuts (Figure 7-18g-l). Based on the cross-section analysis, there is strong evidence that the local concentration of ceramic particles had little influence on the measured hardness. This result brings the following question: why does the incorporation of hard second phase ceramic particles provide little strengthening in this composite material? According to classical physical metallurgy principles, metals can be
strengthened by the incorporation of finely dispersed, hard second phase particles. In order to effectively impede dislocation movement, in other words, increasing the hardness / strength of the metal matrix, the size of the second phase particles should be 100 nm or less and the distance between particles should be small. In the current study, the CeO₂ particles have irregular shapes and the average size is about 15 μm; more than 2 orders of magnitude larger than the ideal particle size for effective dispersion strengthening. Furthermore, pores, cracks, and voids can be found on the surface and inside the ceramic particles (Figure 7-3, Figure 7-13, and Figure 7-18). The presence of these defects can significantly decrease the fracture strength and hardness of the ceramic particles, thereby lowering the strengthening potential in the Ni matrix. For these reasons, the measured overall microhardness of the Ni-CeO₂ composite coatings is mainly contributed by Hall-Petch strengthening from the ultrafine grain Ni matrix and is insensitive to the local ceramic particle content.

Figure 7-18. Cross-section FIB images and EDS elemental maps of (a-f) indent A, 377 HV and (g-l) indent B, 379 HV.
7.3.8 Wear Stability of Ni-CeO$_2$ Composite Coating

To evaluate the robustness and long-term wear stability of the non-wetting characteristics of the Ni-$55$vol.$\%$ CeO$_2$ composite, abrasion tests using 800 grit silicon carbide (SiC) paper and WCA measurements were performed with the progression of abrasion length and the results are presented in Figure 7-19 and Figure 7-20. SE images of the surface morphology before and throughout the abrasion test, i.e. 0 m, 360 m, and 720 m are shown in Figure 7-19a-c, respectively, along with optical images of the water droplets on the surface. After extended abrasion, the surfaces of the topmost ceramic particles were sheared and flattened by the reciprocating abrasion (Figure 7-19b, c). Wear grooves on the CeO$_2$ particles caused by the abrasive SiC are visible after 720 m of abrasion (Figure 7-19c).

![SE images of the surface morphology before and throughout the abrasion test](Image)

Figure 7-19. Wear stability of Ni-$55$vol.$\%$ CeO$_2$ composite coating on 800 grit SiC abrasive. SE images and the corresponding water contact angle; (a) as-deposited coating, WCA = 132°. (b) After 360 m of abrasion, WCA = 128°. (c) After 720 m of abrasion, WCA = 127°.

As shown in Figure 7-20, negligible reduction of WCA of Ni-$55$vol.$\%$ CeO$_2$ was observed over the course of 720 m of abrasion on 800 grit SiC abrasive paper. The abrasive SiC paper was
replaced with a fresh one after every 72 m of abrasion, as depicted by the vertical lines on the graph. No step drop in the WCA was observed after every replacement of the SiC paper.

The surface profile of the worn coating after 720 m of abrasion is shown in Figure 7-21a. Compared to the as-prepared specimen (Figure 7-8a), the average height (2.1 µm) of the CeO₂ protrusions on the micro scale decreased after extended abrasion, as expected. However, WCA did not decrease significantly owing to the CeO₂ bimodal particle size, whereby the lower lying hydrophobic particles are protected from abrasion by the larger ones as demonstrated in high magnification SE image of the recessed area (Figure 7-21b). This observation is similar to the natural degradation of non-wetting aspen leaves over a growth season. The aspen leaves were able to maintain highly non-wetting properties since the peaks of the micrometer-sized papillae provide significant amount of protection from abrasion to the nanoscale wax crystals in the valleys between papillae. Furthermore, since the ceramic particles are porous, as they are worn down, nano-scale roughness on the surface is continuously exposed, contributing to long lasting, stable non-wetting properties.

![Figure 7-20. The influence of abrasive wear on the WCA. In addition of Ni-55vol.% CeO₂, Ni-PTFE from the previous study is also included in the plot for comparison. The dash-dot black line represents the linear fit of the Ni-55vol.% CeO₂ experimental result. The abrasive paper was replaced with a fresh one after every 72 m, as marked by the red dotted lines.](image-url)
Figure 7-21. (a) Surface profile of Ni-55vol.% CeO$_2$ after 720 m of abrasive wear. (b) High magnification SE image of a recessed region in Figure 7-19c.

7.3.9 Practical Implications

On the synthesis side, industrial electroplating facilities come in different scales and are capable of producing parts of varying sizes, from several millimeters up to tens of meters. These plating systems can be adapted to the composite electro-codeposition technique developed in this study with minimal capital investment and modifications. From the viewpoint of practical applications, the characterization results presented here have demonstrated that the Ni-CeO$_2$ composite coatings are highly robust and suitable for many engineering applications that are normally exposed to some form of mechanical wear. Furthermore, preliminary cost calculations indicate that the cost to manufacture Ni-CeO$_2$ composite coatings is comparable to commercially available coatings (Appendix C).

As described in the introduction, the thermal stability of the non-wetting properties is not fully understood yet. However, it has been shown that CeO$_2$ has sufficient thermal stability $^{103,110}$ and hydrophobic properties to promote dropwise condensation $^{103,111}$. These properties are highly beneficial in condensation applications including power generation and desalination $^{112}$. However, there is a need for simple methods of applying hydrophobic rare earth oxide ceramic onto typical condenser surfaces such as large tubes and plates. The electro-codeposition technique presented in this study has a great potential for the commercial application of incorporating hydrophobic rare earth oxide for such applications. In addition, since thermal conductivity of the metal matrix (Ni: 90 W/m·K [ref $^{113}$]) is approximately an order of magnitude
higher than rare earth oxide ceramics (CeO$_2$: 12 W/m·K [ref 114]), it is expected that dropwise condensation will be further enhanced compared to pure rare earth oxides.

7.4 Summary

In this chapter, it was demonstrated that electro-codeposition is a viable electrochemical technique to produce non-wetting Ni matrix composite with embedded CeO$_2$ ceramic particles. Through extensive characterization, structure-property relationships of the non-wetting composites were established. It was shown that the hierarchical surface roughness formed by the co-deposited bimodal size CeO$_2$ particles and the absence of defects at the particle / matrix interfaces contributed to long lasting non-wetting characteristics, even after extensive abrasive wear. Furthermore, the combination of hard CeO$_2$ ceramic particles and the small grain size of the electroplated Ni matrix contributed to the high hardness of the composite coating.

The findings of this chapter establish the feasibility of applying non-wetting Ni-CeO$_2$ composites coatings in applications that demand high wear stability, such as condenser tubes and plates for power generation and desalination. However, one question that remains to be addressed is the mechanism of hydrophobicity for this material; specifically, why are the Ni-CeO$_2$ composite coatings initially superhydrophilic (WCA ≈ 0°) and became hydrophobic or superhydrophobic after a vacuum treatment? This will be addressed in Part II of this thesis.

7.5 Published Work Based on Findings of This Chapter


Part II: Fundamental Study
Chapter 8
Fundamental Investigation of Rare Earth Oxides Wettability

8 Introduction

In Part I of this thesis, the synthesis and properties of non-wetting metal matrix composite coatings with rare-earth oxide particles were investigated in Chapter 7. Although this chapter established the engineering perspective of this new class of non-wetting composite materials, the fundamental understanding of their wetting properties remained limited. At the end of the chapter, the question that was not addressed was “why are the Ni-CeO$_2$ composite coatings initially superhydrophilic (WCA $\approx 0^\circ$) and become hydrophobic or superhydrophobic after a vacuum treatment?”

During the time when the work for the previous chapter was carried out, a number of publications reported conflicting results on the wettability of rare earth oxides emerged. In this chapter, a thorough literature review on the state of the art related to the controversial topic is presented, followed by the experimental approach performed in the current study in an attempt to develop a better fundamental understanding on the wettability of rare earth oxides.

8.1 State of the Art on the Wettability of Rare Earth Oxides

Following the original work published by Azimi et al. in 2013 [ref 103], there has been a widespread interest in further investigating on the wettability of rare earth oxides. A list of relevant studies and the important information including specimen synthesis technique, WCA, and characterization techniques employed is presented in Appendix D.

The first follow-up study on the wettability of REOs was reported by Preston et al. in 2014 [ref 111]. In this work, the wetting behaviour of cerium oxide and holmium oxide, along with control samples of gold and silicon oxides were investigated. The REO specimens were fabricated in this same way as in the work by Azimi et al.; the oxide powders were pressed and sintered in air at 1560-1600°C for 4 h. Atomic force microscopy data showed that the surface roughness $R_f$ is less than 1.05, which indicates that “surface roughness did not significantly impact wettability.” After the specimens were cooled down, advancing and receding contact angles were measured. Surprisingly, the specimens were superhydrophilic with a contact angle of $\approx 0^\circ$. Samples were then cleaned with argon plasma to remove adsorbed hydrocarbons and the expected
stoichiometric ratios for the oxides were observed by XPS. After cleaning, the specimens were stored in ambient air. The WCA of CeO$_2$ and Ho$_2$O$_3$ increased to about 50° and 70° in 24 h and converged to 90° and 103° after about 100 h, respectively, as shown in Figure 8-1. The change in WCA was also observed on gold and silica control samples. However, the WCA converge to about 60° and 40° respectively. Surface chemistry analysis with XPS was performed at the same time point as the WCA measurements. The results showed that with increasing exposure time to ambient air, the surface atomic percent carbon increased. The study concluded that the hydrophobicity of rare earth oxides is mainly due to the adsorption of airborne hydrocarbon as evident in the increasing WCA and surface carbon percent over time exposed to ambient atmosphere.

Figure 8-1. Advancing water contact angle as a function of time for homia, ceria, and control gold and silica samples exposed to ambient air. Time t = 0 represents the WCA measured right after Ar ion bombardment surface cleaning.

Also in 2014, Oh et al. reported hydrophobicity of rare earth oxide thin films made by atomic layer deposition (ALD). CeO$_2$, Er$_2$O$_3$ and Dy$_2$O$_3$ thin films with thickness up to 50 nm were fabricated by thermal or plasma enhanced ALD processes using organic precursors. Without any post synthesis treatment or storage in ambient air, the WCA of as-deposited REO films were in the range of 97° - 108°, which is comparable with the WCA of sintered REOs reported in Azimi et al.’s work. Since the ALD process involved the use of organic precursors, it is expected that the specimen should contain some surface carbon which may affect the wetting properties. Although XPS characterization was performed in this work, the specimens were cleaned by Ar
sputtering prior to analysis, hence, the results showed no presence of carbon. Structurally, the as-deposited Er$_2$O$_3$ films were amorphous but after the annealing treatment at 600°C, crystalline phase was observed. The authors claimed that there is no significant effect of microstructure on the hydrophobicity. However, the WCA of Er$_2$O$_3$ films decreased from 100° to 80° after annealing. The decrease in WCA was explained by the fact that surface hydroxyl groups were created after annealing. Surfaces with surface hydroxyl groups are known to be hygroscopic, that is the ability to absorb moisture in air. Hydroxyl groups are known to have higher probability to interact with water molecules, hence increased hydrophilicity.

In 2015, Khan et al. proposed that the surface oxygen-to-metal ratio may affect the wetting properties of cerium oxide. In that study, cerium oxide films with a thickness of 300 nm were fabricated by sputter deposition onto silicon substrates, along with aluminum oxide control samples. After fabrication, the specimens were transported to XPS system with a vacuum desiccator and surface compositional analysis was performed. Both CeO$_2$ and Al$_2$O$_3$ had surface carbon content of 15%. Immediately after XPS measurements, the WCAs were measured. Despite both types of ceramics having the same surface carbon content, the WCAs were completely different; CeO$_2$ had a WCA of 104°, while Al$_2$O$_3$ was hydrophilic with a WCA of 45°. In this case, the relationship between surface carbon content and WCA of CeO$_2$ was not in agreement with Preston et al.’s work, where they reported that hydrophobicity was only observed when the surface carbon content exceeded 34% after exposure to ambient air. Therefore, Khan et al. stated that surface hydrocarbon contamination exclusively cannot explain the hydrophobic phenomena of REOs. For sputter deposition, non-stoichiometric transfer of metal and oxygen to the substrate is a known phenomenon. Khan et al. demonstrated that by storing a freshly prepared CeO$_2$ films in ultra-high vacuum (UHV) environment, the surface can undergo relaxation to reach an optimal surface stoichiometry without airborne contamination. XPS results showed that there is a net increase in Ce$^{3+}$ from 10.2% to 27.2% and the contribution of Ce$^{4+}$ decreased from 89.8% to 72.8% with overnight relaxation in UHV. This change suggests that the cerium oxide underwent a partial reduction from Ce$^{4+}$ to Ce$^{3+}$. In other words, there is an overall decrease in the surface oxygen to cerium ratio. When WCA was measured after the relaxation treatment in UHV, the WCA was 104° (O/Ce ratio: 2.2), compared to as-sputtered specimen without being exposed to XPS or post-treatment of 15°, where the O/Ce ratio was 3.0. The study concluded that airborne hydrocarbon contaminants do not exclusively affect the
wetting properties. Surface relaxation, i.e. the O/Ce ratio can also impact the wettability of this class of ceramics.

Cho et al. reported a hydrothermal approach to grow superhydrophobic cerium oxide nanorods on various substrates including aluminum, titanium, stainless steel, and silicon \(^{117}\). The substrates were placed in the growth solution containing cerium nitrate and urea. The growth process took place in an autoclave at 95°C for 24 h. The substrates were then removed from the autoclave, rinsed and dried prior to heat treatment in air at 350°C for 3 h, followed by storage in vacuum environment. WCA was measured afterwards and all substrates were superhydrophobic with WCA = 160°. XPS result showed that after heat treatment, the surface of the substrate is composed of CeO\(_2\). However, the XPS survey scan spectrum did not reveal any evidence of possible carbon adsorption on the surface.

The first computational study on the wettability of REOs was reported by Carchini et al \(^{118}\). In this work, density functional theory (DFT) calculations were performed to explore the interaction between water and CeO\(_2\), Nd\(_2\)O, and Al\(_2\)O\(_3\). For CeO\(_2\), the (111) surface was modelled, and for Nd\(_2\)O\(_3\) and Al\(_2\)O\(_3\), the (0001) surfaces were studied. For the DFT calculation, ice water bilayers were used instead of liquid water as they have similar surface energy and for simplicity in the calculation. The water contact angle was calculated by using the surface energy of ice, the adsorption energy of ice water bilayers to the surface of the ceramics (determined from DFT calculations), and the surface area of the ceramics. The study concluded that REOs are hydrophobic and the calculated WCAs are in agreement with Azimi et al \(^{103}\).

In 2015, Pedraza et al. reported an electrochemical technique to produce superhydrophobic CeO\(_2\) coatings on textured Ni alloy substrates without surface chemical modification \(^{119}\). The process consisted of three major steps: (i) mechanical and electropolishing of the metal substrate, (ii) electrodeposition of CeO\(_2\) from cerium nitrate aqueous electrolyte, and (iii) dehydration and long-term relaxation in UHV. A hierarchical roughness on the coating was achieved from substrate preparation as well as the electrodeposition process. Initially, the as-prepared surfaces were hydrophilic due to excess surface oxygen created arising from the electrodeposition process. After 60 hours of storage in UHV to reduce the excess surface oxygen, the surfaces became superhydrophobic (WCA = 151°).
In 2016, Cai et al. developed an industrially scalable thermal spray technique for fabricating superhydrophic REO surfaces. The specific thermal spray applied was solution precursor plasma spraying (SPPS). In SPPS, a precursor salt of the coating material is dissolved in a solvent and the solution is injected into a plasma instead of solid powder, during which the solution is broken up into micron sized droplets. As the solvent is evaporated by the plasma, nano-sized precipitates are formed and deposited on the substrate as a coating. The advantage of this technique is that nano- and micro-sized features can be generated on the coating. In this study, Cai et al. fabricated ytterbium oxide (Yb$_2$O$_3$) coatings by SPPS from ytterbium nitrate precursor solution. SEM images showed that the coatings had a hierarchical surface roughness that resembles superhydrophobic aspen leaves. Initially, water completely wetted the as-deposited coatings. Similar to other studies, after storage in vacuum environment, superhydrophobicity was observed.

The first study on the wettability of epitaxial REO films was reported by Sarkar et al. in 2016. They fabricated (001) oriented CeO$_2$ and Lu$_2$O$_3$ films on YSZ single crystal substrate by pulsed laser deposition (PLD). The main purpose of this study was to determine the relationship between wettability and oxygen vacancies of different metal oxides: 4f rare earth oxides, and a 3d transition metal oxide, i.e. SrTiO$_3$. The WCA of as-deposited (001) oriented Lu$_2$O$_3$ film, grown at low oxygen partial pressure in the PLD process was about 70°. Due to the film growth conditions, it was expected that the films had significant oxygen vacancies. To reduce the oxygen vacancies, the films were subsequently annealed in atmospheric condition at 900°C and the resulting WCA was 60°. In both cases, WCA measurements were performed 120 h after the specimen preparation process to rule out the possibility of hydrocarbon desorption.

In 2017, Fu et al. also studied the wettability of CeO$_2$ thin films produced by PLD, but on a Si substrate. Although not documented in the study, the film is not expected to be epitaxial due to differences in crystal structures and lattice parameters. The main finding of this work was that there is a time-dependence of WCA after fabrication of the film, as shown in Figure 8-2. XPS analysis showed that there was an increase in the C 1s signal as the specimen aged in ambient air after fabrication and the observation was consistent with Preston et al. The study also demonstrated that after a mild annealing of the film in air at 200°C for 1 h, the WCA decreased from about 95° to 40°. However, the hydrophobicity was recovered by simply storing the surface in ambient air for 3 days. The study also explored the effect of storage in vacuum on the
wettability. After 5 days storage in vacuum, the WCA was about 48° and reached 102° after 1 week in ambient air. The result is somewhat different from the earlier study and the authors suggested that the high WCA observed in the previous study can only be possible if the sample was left in ambient air for several hours after the vacuum treatment.

Figure 8-2. Time-dependent exposure in air to water contact angle of CeO₂ thin film.

Lundy et al. revisited the surface adsorption and wettability of bulk, sintered CeO₂ pellets, along with other oxides including SiO₂, HfO₂, and ZrO₂ [ref]. The objective of the study was to clarify the adsorption mechanism that leads to reduced wettability of REOs by exposing it to vapour phase nonane environment. In addition, time dependent WCA measurements were done by exposing the surfaces to perfluorononane. The samples were plasma cleaned before the initial WCA measurements. All samples were initially hydrophilic and the WCA increased with time exposed to the perfluorononane environment (Figure 8-3b). The results show that the WCAs of all surfaces saturated at about 70 – 85°. However, the WCA of CeO₂ was higher than other oxides for all times studied, due to higher surface coverage of perfluorononane. (Figure 8-3d)
Figure 8-3. Average advancing and receding contact angles as a function of time over a 96 h period for Ce₂O₃, SiO₂, ZrO₂, and HfO₂ (Ar plasma) exposed to nonane (a) and perfluorononane (b) environments in a desiccator (temperature ≈ 21 °C and relative humidity ≈ 40%). The advancing contact angles increase asymptotically over time and saturate after a 96 h period. A reduction in advancing contact angles is evident for all samples when exposed to the perfluorononane environment. (c) and (d) Surface coverage for nonane and perfluorononane (θ max ≈ 119.6° with γ sv ≈ 15.5 mN/m).

In addition to magentron sputter deposited REOs, Kuluh et al. studied the surface modification of rare earth nitrides and fluorides upon exposure to ambient air and correlated with WCA measurements. Similar to other studies, time-depended WCA measurements showed that WCA of Gd₂O₃ films increased rapidly from about 3° for freshly prepared specimen, 60° after 2 days, and converge to about 100 degrees after 10 days. In addition, the study also showed that REO films can dissolve in water due to their ionic nature, based on profilometry and XPS measurements.

Another study on REOs thin films prepared by atomic layer deposition was reported by Lv et al. in 2017. The study showed that with increasing film thickness, up to 26 nm, hydrophobicity was observed with WCA above 100°. After annealing at 500°C, the WCA decreased to about 90°. However, when the specimen was exposed to UHV treatment after annealing, the WCA increased back to the value of the as-deposited specimen. The authors also demonstrated that UHV treatment has no effect on the as-deposited specimen. XPS spectra revealed that for the as-deposited specimen, a prominent C 1s peak was present. After annealing, the intensity of C 1s decreased, which is well related to the slight decrease in WCA. After the UHV treatment, the
intensity of C 1s increased, which is related to the increase in WCA. Since ALD process involved the use of carbon containing precursors, it is not surprising that the spectrum for the as-deposited sample showed an intense C 1s peak.

Shi et al. \textsuperscript{124} reported a study on CeO$_2$ films made by magnetron sputter deposition in Ar and O$_2$ atmosphere on Si (100) substrates. The main objective of the study was mainly on the effect of O$_2$ gas flow during the deposition on the material structure (surface roughness, microstructure) and properties (wetting, hardness, and elastic modulus). After deposition, the specimens were stored in a vacuum desiccator. All specimens were hydrophobic with WCA $> 90^\circ$. The authors acknowledge that even when the specimens were stored in vacuum desiccator, hydrocarbons were easily adsorbed on the CeO$_2$ film surfaces, as shown by XPS measurements.

A simple, electrochemical synthesis process of CeO$_2$ coating was reported by Nakayama et al. \textsuperscript{125} In this study, CeO$_2$ coatings with hierarchical roughness were deposited on to steel plate and mesh substrates. Right after deposition, the CeO$_2$ coatings were hydrophilic with WCA $< 20^\circ$. However, with storage time in ambient air, the WCA increased to about 130° and 160° for plate and mesh substrates, respectively. The authors stated that surface hydrocarbon adsorption was the mechanism of change in non-wetting behaviour when the surfaces are exposed to ambient air. XPS spectra of the C 1s region showed a rapid increase in intensity for the first 12 h of exposure in ambient air, as shown in Figure 8-4. The study also demonstrated the self-healing hydrophobic properties by oxygen plasma cleaning the surface to decompose adsorbed carbon species, followed by WCA measurements with exposure to air. After cleaning, the WCA of the surface was 0° and the superhydrophobicity recovered after 72 h of exposure to air. The transition between superhydrophilic to superhydrophobic behaviour is completely reversible as carbon species can re-accumulate on the surface of CeO$_2$. 
Two follow up applied studies on the superhydrophobic Yb$_2$O$_3$ surfaces made by SPPS were reported by Xu et al.\textsuperscript{126,127}. After coating fabrication, the specimens were exposed to vacuum environment (1 – 15 Pa) for 24 h to “remove moisture and loosely-bound oxygen species from the surface.” However, no surface chemistry analysis data was provided to support this claim. After the vacuum treatment, the coatings were superhydrophobic with WCA up to 163° and sliding angle of 6.5°. In the first study\textsuperscript{126}, the stability of the non-wetting properties was evaluated by leaving water droplets on the surface and monitoring the WCA for a period of 3 minutes. No measurable changes were observed, indicating good stability of the superhydrophobic behaviour and Cassie-Baxter wetting regime. The second study\textsuperscript{127} focused on the effect of process parameters on the structure and wetting properties of the coating; specifically, the geometry of the micro scale roughness on the effect of WCA and WSA. Since the spotlight on both of these studies were on engineering the surface, the underlying mechanism of hydrophobicity was not addressed.

In early 2018, Prakash et al.\textsuperscript{128} fabricated a series of cubic (001) REO epitaxial films on YSZ (001) single crystal substrates by pulsed laser deposition. The REO films studied included CeO$_2$, Sm$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, Dy$_2$O$_3$, Er$_2$O$_3$, Tm$_2$O$_3$, Yb$_2$O$_3$, and Lu$_2$O$_3$. It was also shown that as-deposited (001) REO epitaxial films are hydrophilic with WCA as low as 15°. Afterwards, the WCA of the films increased with exposure time to ambient air due to adsorption of airborne hydrocarbon species, as confirmed by increases in the C 1s intensity from XPS spectra. The effect of vacuum treatment on the wettability of REO surfaces was also investigated. After
sample synthesis, the samples were stored in a vacuum chamber (10^{-5} \text{ Pa}) for 5 days. Carbon species were detected on these samples by XPS and the authors claimed that previous studies that report storage in vacuum can prevent adsorption of hydrocarbon are not correct. Furthermore, the samples were annealed at 300°C to determine the desorption of carbon species on the surface. The off-gas was monitored by selected ion flow tube mass spectrometry (SIFT-MS) and methane, ethane, and propane were determined to be the primary gas species desorbed through annealing. WCA measurements were performed afterwards and a decrease to about 30° was observed. The study concluded that the extrinsic nature of the surface wetting properties of REO (001) epitaxial films have “no relation to the electronic configuration of the rare earth atoms” proposed by Azimi et al.

8.2 Experimental Approach

In the previous investigations on the wettability of rare earth oxides, most of the materials studied were either in bulk form made by high temperature sintering or thin film made by vapour deposition. These materials are usually polycrystalline or nanocrystalline with random crystal orientation parallel to the surface, as shown in Figure 8-5. Furthermore, these materials contain considerable microstructural defects, including surface roughness, porosity and large fractions of high energy intercrystalline regions that may affect the measured wetting properties and may not be suitable for a fundamental study.

![Figure 8-5](image_url)

Figure 8-5. (a) SE image of sintered CeO$_2$ pellet. Considerable amounts of surface roughness and porosity (circled) are present in the material. (b) High angle annular dark field (HAADF) image of a sputter deposited CeO$_2$ thin film with large fractions of grain boundaries and triple junctions.
In addition, unlike conventional hydrophobic polymeric materials such as PTFE, rare earth oxides are crystalline ceramics with long range order and well-defined crystal structure. For instance, CeO$_2$ has a cubic fluorite structure and Er$_2$O$_3$ has a cubic bixbyite structure, as schematically shown in Figure 8-6. Since the arrangement of the metal and oxygen atoms vary between crystallographic orientations (Figure 8-7), surface energies (SN) between orientations are different as reported in previous theoretical studies $^{129-131}$, hence the wetting properties are expected to differ as well.

The experimental approach taken in this chapter is to systematically determine the water contact angle on pristine bulk single crystals or highly oriented epitaxial films with different crystallographic orientation parallel to the surface, i.e. (001), (110), and (111). The influence of crystallographic orientation on the wetting properties of REOs was not considered in any of the previous studies. Hence, the intrinsic wetting behaviour of REOs has not been clarified yet due to the lack of information on the crystallographic orientation – surface energy (SN) – WCA relationships.

Figure 8-6. Unit cells of CeO$_2$ and Er$_2$O$_3$. Oxygen atoms are represented in red, cerium atoms are depicted in white, and erbium atoms are pink.
Figure 8-7. (a) Space filling models of the 3 low index orientations of CeO$_2$. (a) (001) orientation with alternating layers of oxygen anions and cerium cations. The surface can be O or Ce surface termination with a surface dipole moment (Tasker Type III surface $^{132}$). (b) (111) orientation with close packed planes of repeating O, Ce, and O ions. There is no surface charge or dipole moment as charge neutrality is maintained for every O-Ce-O plane (Tasker Type II surface $^{132}$). (c) (110) orientation where the composition and the charges of the Ce cations and O anions in each plane are balanced with no surface charge (Tasker Type I surface $^{132}$).
8.3 Hypothesis

The hypothesis for this part of the study is that atomic arrangement of the REO crystal surface affects both surface energy (SN) and WCA as shown in Figure 8-8. In the case of O–RE–O-terminated (111) REO surface (Figure 8-8a), the surface should show charge neutrality since the positively charged ($\delta^+$) RE$^{n+}$ ions and negatively charged ($\delta^-$) O$^{2-}$ ions compensate each other$^{132}$. Therefore, the attraction of water molecules to the surface is less likely as the electrostatic force would not work at O–RE–O-terminated surface due to its charge neutral surface. On the other hand, in the case of O-/RE-terminated (001) REO surface (Figure 8-8b), the surface should be negatively/positively charged with a dipole moment perpendicular to the surface$^{132}$, which strongly attracts polar molecules such as water. Therefore, we expected that O–RE–O-terminated REO surface (Figure 8-8c) shows larger WCA as compared with O-terminated surface (Figure 8-8d). This difference can be expected due to the differences in SN between orientations. Currently, there are no experimental data on the SN of differently oriented REOs surfaces. However, such data are available from density functional theory – generalized gradient approximation (DFT-GGA) calculations$^{129-131}$. For example, SN of (111) surface of CeO$_2$, which can be considered as a charge neutral O-Ce–O surface, is 0.60 J m$^{-2}$ [ref $^{131}$]. whereas SN of the (001) surface of CeO$_2$, which can be considered as a negatively/positively charged surface, is 1.43 J m$^{-2}$ [ref $^{131}$]. Since the (110) surface of CeO$_2$ can be considered as intermediate between (111) and (001), the SN of (110) is 1.01 J m$^{-2}$ [ref $^{131}$].

In order to confirm this hypothesis, smooth, epitaxial thin films of CeO$_2$ and Er$_2$O$_3$ were grown on yttria stabilized zirconia (YSZ) single crystal substrates by pulsed laser deposition (PLD) and extensive structural and surface chemistry characterizations were performed to better understand the wetting behaviour of rare earth oxides.
Figure 8-8. Hypothesis: Atomic arrangement of REO crystal surfaces and macroscopic water droplets on REO crystal surfaces. (a) O-RE-O-terminated REO surface (charge neutral surface) and (b) O-terminated surface (negatively charged surface). Positively charged H atoms of the water molecules would be attracted by the negatively charged O-terminated surface, whereas such electrostatic attraction does not exist on O–RE–O-terminated surface due to its charge neutrality. Macroscopic schematic pictures of water droplets on (c) O–RE–O-terminated REO surface showing large water contact angle (WCA) and (d) O-terminated surface showing small WCA. This difference can be expected due to the difference of the surface energy (SN). For example, SN of (111) surface of CeO$_2$, which can be considered as a charge neutral O–Ce–O surface, is 0.60 J m$^{-2}$ [ref. 131], whereas SN of (001) surface of CeO$_2$, which can be considered as a negatively charged surface, is 1.43 J m$^{-2}$ [ref. 131]. Since the (110) surface of CeO$_2$ can be considered as intermediate between (111) and (001), the SN of (110) is 1.01 J m$^{-2}$ [ref. 131].
8.4 Background on Experimental Methods

8.4.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a physical vapour deposition technique to produce high quality thin film oxides with good control of surface roughness / flatness\(^{136}\). PLD is performed in high vacuum, similar to other vapor deposition techniques including molecular beam epitaxy and sputter deposition. In a PLD system, schematically shown in Figure 8-2, a pulsed UV excimer laser beam is focused onto the target material. The high energy laser pulses ablate the ceramic target, creating a plasma plume. The vaporized species condenses on the substrate, forming a thin film. Usually, a background gas, such as oxygen is injected to the vacuum chamber to ensure the oxide thin deposited is stoichiometric. By choosing a suitable single crystal substrate material, epitaxial film of metal oxides can be fabricated.

![Schematic diagram of pulsed laser deposition](image)

Figure 8-2. Schematic diagram of pulsed laser deposition\(^{137}\).
8.4.3 Reflection High Energy Electron Diffraction

As the name implies, reflection high energy electron diffraction (RHEED) is a forward scattering electron diffraction technique to determine the crystallinity and the smoothness of the thin film. Depending on the thin film crystallinity and surface structure, the RHEED patterns can differ significantly as schematically shown in Figure 8-9. In addition, this technique can be used to monitor thin film growth by observing the oscillation in the intensity of diffraction spots.

Figure 8-9. RHEED patterns for various structures and surfaces.
8.4.4 High Resolution X-ray Diffraction

High resolution X-ray diffraction (HRXRD) is an important analytical technique to determine the structure of thin film materials. Multiple HRXRD techniques can be applied for thin film materials, including X-ray reflectivity (XRR), out-of-plane and in-plane diffraction, rocking curves, as well as reciprocal space mapping (RSM). A schematic diagram showing the geometry of an X-ray diffractometer is shown in Figure 8-10. The angles related to the diffractometer are described in Table 8-1.

![Schematic diagram of X-ray diffractometer](image)

Figure 8-10. Schematic diagram of X-ray diffractometer (modified from 139).

Table 8-1. Geometry of X-ray diffractometer

<table>
<thead>
<tr>
<th>Angle</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ω</td>
<td>Angle between the X-ray source and the sample</td>
</tr>
<tr>
<td>2θ</td>
<td>Angle between the X-ray source and the detector, θ = ω for synchronized scan</td>
</tr>
<tr>
<td>χ</td>
<td>Sample tilt angle</td>
</tr>
<tr>
<td>φ</td>
<td>Sample rotation angle</td>
</tr>
</tbody>
</table>

XRR is a surface sensitive technique to quantify thickness, roughness, and density of thin films. XRR measurements are performed in symmetric 2θ-ω scan (ω = θ), but with much smaller θ than 2θ-ω diffraction, typically less than 3°. When the X-ray is at a grazing angle incidence to a flat specimen, the wave can undergo reflection and/or refraction. Total reflection occurs when the incident X-ray grazing angle is smaller than the critical angle for total reflection \(θ_{cr}\), as schematically shown in Figure 8-11a. When the incident angle is equal to the critical angle, X-rays propagates along the sample surface (Figure 8-11b). When the incident angle is greater than
the critical angle, incident X-rays penetrate into the specimen and reflectivity decreases significantly (Figure 8-11c).

![Diagram](image)

Figure 8-11. Reflection and refraction of X-ray at the specimen surface with different grazing angle.

Thin film thickness can be extracted from XRR curves by analyzing the period of oscillation in the X-ray intensity. Surface roughness of the thin film can be related to the decay of intensity on a XRR curve. Since roughness causes diffused scattering of X-rays, the intensity decreases significantly with increasing roughness. Density of a thin film can be related to the amplitude of the oscillations and the critical angle for total reflection.

In general, thin films grown on single crystal substrate can be classified into three different microstructures: i) single crystalline film, ii) polycrystalline film with a single out-of-plane orientation and multiple in-plane orientations, and iii) polycrystalline film with multiple out-of-plane orientations. Various X-ray diffraction techniques described below can be applied to effectively characterize such microstructures of thin films.

For a thin film grown on a (hkl) oriented single crystal substrate, the relationship between their out-of-plane orientations, expressed as \((hkl)_f// (hkl)_s\), can be determined from out-of-plane X-ray diffraction. Typically, epitaxial films grown on single crystal substrates contain dislocations to
accommodate the lattice mismatch. As a result, the microstructure of the epitaxial film can be described as a mosaic crystal, as schematically shown in Figure 8-12. Mosaic crystal containing small building crystal blocks that are separated by dislocations. A mosaic crystal resembles a single crystal, but with slight differences. The mosaic crystal is composed of smaller building blocks (sub-crystals, domains, or crystallites) separated by low angle grain boundaries (< 1°) that are composed of series of dislocations.

![Figure 8-12. Mosaic crystal containing small building crystal blocks that are separated by dislocations.](image)

Out-of-plane rocking curves (ω scan) provide information on the spread in orientation of the different crystalline domains of a mosaic crystal. This measurement is performed by fixing 2θ at the (hkl)_f of interest, and “rock” the sample. The full width half maximum (FWHM) of a rocking curve is a good indication on the quality of the thin film. Since the epitaxial film is a mosaic crystal with the building blocks that are slightly misoriented with each other, each block will be in Bragg condition as the sample is rocked during the ω scan, resulting in peak broadening.

Out-of-plane diffraction only reveals orientation of the crystals parallel to the surface; therefore, this technique cannot distinguish the difference between a single crystalline film and a polycrystalline film with the same out-of-plane orientation but multiple in-plane orientation. To determine the differences, in-plane diffraction needs to be performed. The sample needs to be tilted to an angle χ; the reflecting plane of interest, followed by a ϕ scan where the sample rotates...
Depending on the symmetry of the plane selected, the number of diffraction peaks varies. For instance, if (111) was selected for the ϕ scan, 6 peaks that are spaced 60° apart should be observed due to symmetry. The rotation relationship of the film and the substrate can be established by carrying out separate ϕ scan for the film and substrate. If there is no shift in the diffraction pattern, the in-plane orientation relationship can be expressed as [uvw]f // [uvw]s.

Reciprocal space mapping (RSM) is a powerful X-ray diffraction technique to study the structure and quality of thin film and the substrate. RSM maps around a particular reciprocal lattice spot, i.e. for every 2θ, ω is scanned, unlike out-of-plane ω-rocking curve, ω is scanned for only the film. RSM can provide information relating to strain, relaxation, lateral coherent length / size of the mosaic blocks. This information can be used to evaluate the quality of the thin film.

8.4.5 X-ray Photoelectron Spectroscopy

Surface chemistry of a material can be studied by X-ray photoelectron spectroscopy (XPS). It is a highly surface sensitive technique (less than 10 nm) that can determine chemical and electronic states of the elements present in the material. Spectra are acquired by irradiating the specimen with a X-ray beam (usually monochromatic) in a ultra-high vacuum (UHV) chamber. The interaction of the X-ray beam with the specimen generates photoelectrons. The kinetic energy of the photoelectrons is analyzed to form the spectra, usually reported in binding energy. For each element present in the material, there are characteristic peaks that correspond to their electronic configuration. Compared to EDS, XPS can detect light elements including carbon.

8.5 Experimental Details

8.5.1 Substrate Preparation

The single crystal substrates used in this study were commercially available yttria stabilized zirconia (YSZ), purchased from Shinkosha, Japan. The single crystals were grown from a melt and sliced into 1 cm × 1 cm × 0.5 mm substrates with the surface orientation of (001), (110), or (111). The substrates were polished in the as-received condition. YSZ was chosen as the substrate material because it has similar lattice parameter and crystal structure as CeO2 and Er2O3 of interest. A table summarizing the structure of YSZ, CeO2 and Er2O3 is shown in Table 8-2. Before deposition of the desired thin film, YSZ substrates were annealed in a furnace at 1350ºC.
for 30 minutes to acquire atomically flat surfaces\textsuperscript{140}. The flatness of the surfaces was verified with atomic force microscopy.

Table 8-2. Structural information of YSZ, CeO\textsubscript{2}, and Er\textsubscript{2}O\textsubscript{3}

<table>
<thead>
<tr>
<th></th>
<th>Substrate</th>
<th>Film</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>YSZ</td>
<td>CeO\textsubscript{2}</td>
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<tr>
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</tr>
<tr>
<td>Space Group</td>
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<td>Fm-3m (225)</td>
</tr>
<tr>
<td>Lattice Parameter</td>
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<td>5.411</td>
</tr>
<tr>
<td>Lattice Mismatch</td>
<td>+5.3%</td>
<td>+2.6% (a/2)</td>
</tr>
</tbody>
</table>

8.5.2 Pulsed Laser Deposition

Pulsed laser deposition (PLD) was performed in a vacuum chamber with a background pressure of $5 \times 10^{-5}$ Pa. Oxygen was introduced to the chamber and the pressure was maintained a $3 \times 10^{-3}$ Pa. REO films were deposited on the YSZ substrates with different orientations at 900ºC by pulsing a focused KrF excimer laser beam (laser wavelength: 248 nm laser fluence: 1.3 J/cm\textsuperscript{2} for CeO\textsubscript{2} and 2 J/cm\textsuperscript{2} for Er\textsubscript{2}O\textsubscript{3}, laser repetition rate: 5 Hz, pulse width: 20 ns) on a rotating dense ceramic target (CeO\textsubscript{2} and Er\textsubscript{2}O\textsubscript{3}) for 30 minutes. Optical image of a CeO\textsubscript{2} epitaxial film on YSZ (111) substrate is shown in Appendix E, Figure E-1.

8.5.3 Reflection High Energy Electron Diffraction

Reflection high energy electron diffraction (RHEED) was performed in the PLD chamber. The accelerating voltage of the electron beam was 20 kV. For (001) surfaces, RHEED patterns were collected with the electron beam parallel to [110]. For the (110) surface, RHEED patterns were observed along [110]. For (111) surfaces, RHEED patterns were collected along [112].

8.5.4 High Resolution X-ray Diffraction

The crystal structure, thickness, and roughness of the thin films were characterized by a four-circle high resolution X-ray diffractometer (Rigaku ATX-G). The diffractometer is equipped with 4 crystal monochromator and analyzer crystals. The tube voltage was set at 50 kV and a current of 300 mA. The diffractometer can be configured for multiple X-ray characterization techniques: X-ray reflectivity (XRR), out-of-plane and in-plane X-ray diffraction, rocking curves, and reciprocal space mapping (RSM)
8.5.4.1 X-ray Reflectivity

XRR curves were acquired by performing a 2θ-ω scan at grazing angle, 0.3° - 3.0° with a step size of 0.001° and scan rate of 1.0°/min. Rigaku proprietary XRR analysis software was used to fit the experimental data to theoretical reflectivity in order to obtain film thickness, roughness, and density. Details of the technique is presented in Appendix F.

8.5.4.2 Out-of-Plane X-ray Diffraction and Rocking Curves

Out-of-plane XRD was performed by a symmetrical 2θ-ω scan from 5° to 80° with a step size of 0.005° and a scan rate of 5°/min. In addition, narrow scans around the film and substrate peaks were performed with a step size of 0.002° and a scan rate of 2°/min. Out-of-plane rocking curves were acquired by fixing 2θ at the position of maximum film peak and performing a ω scan, -2° to 2° relative to the set 2θ with a step size of 0.002° and 2°/min scan rate.

8.5.4.3 In-Plane X-ray Diffraction and Rocking Curves

In-plane XRD was performed by 2θχ/ϕ scan. Depending on the orientation of the sample, in-plane XRD can be performed at 2 different azimuth directions. For instance, (001) and (110) oriented samples can be positioned such that [100] or [110] is parallel to the incident X-ray, hence, (200) or (110) can be detected by the 2θχ/ϕ scan, respectively. 2θχ/ϕ scans were performed from 5° to 80° with a step size of 0.006° and a scan rate of 5°/min. In-plane rocking curves were obtained by performing ϕ scans with 2θχ fixed at the position that give rise to maximum intensity from the thin film. The scanning parameters are as follow: scan range of -180° to 180°, step size of 0.05°, and a scan rate of 50°/min.

8.5.4.4 Reciprocal Space Mapping

Reciprocal space mapping was performed by 2θ-ω and ω scans around a diffraction spot of the YSZ peak, depending on the orientation of the film and the structure factor. For (001) substrate, RSM was performed around (113). For (110) substrate, the scan was performed around (240). For (111) substrate, the scan was performed around (331). For all RSM measurements, 2θχ was fixed at 0°.
8.5.5 Atomic Force Microscopy

Surface topography of the substrates and thin films were studied with a Hitachi Nanocute atomic force microscope and Oxford Instruments Asylum MFP-3D. The scan area of the specimens was 2 μm × 2 μm. Roughness root mean square ($R_{\text{rms}}$) and surface area of the scanned region were calculated by the instrument software.

8.5.6 Scanning Transmission Electron Microscopy

The atomic structure of the REOs thin films were characterized by scanning transmission electron microscopy (STEM). Thin specimens of the REO cross-sections were prepared by mechanical grinding and ion milling. An aberration corrected JEOL ARM-200 STEM operated at 200kV was used to acquire atomic resolution images.

8.5.7 X-ray Photoelectron Spectroscopy

Surface chemistry of the REO thin films was studied by a JEOL JPS-9200 and Thermofisher Scientific K-alpha X-ray photoelectron spectrometers. The X-ray source for both systems is monochromated Al K-α. Since the specimens were insulators, a flood gun operated at 2 kV, 5 mA was used to prevent charging artifacts that can lead to energy shift. The base vacuum of the chamber was $1.0 \times 10^{-6}$ Pa. Survey scans were performed with an energy step of 1.0 eV, 100 ms dwell time, and pass energy of 50 eV. At least 5 scans were performed to acquire sufficient signal. For the high resolution narrow scans, the energy step was 0.1 eV, dwell time of 100 ms, and pass energy of 10 eV. At least 30 – 50 scans were performed to obtain acceptable signal to noise ratio.
8.6 Results and Discussion

8.6.1 Structural Characterization

Multi-scale structural characterization techniques were employed to verify the REO thin films produced by PLD are structurally (crystal structure, surface structure) optimal for wetting property measurements.

8.6.1.1 Reflection High Energy Electron Diffraction

Reflection high energy electron diffraction (RHEED) patterns of CeO$_2$ and Er$_2$O$_3$ epitaxial films grown on YSZ substrates are shown in Figure 8-13 and Figure 8-14, respectively. Interpretation of the RHEED patterns can be performed by comparing with Figure 8-9. In all RHEED patterns, intense elongated spots with some streaks were observed. This result is comparable with Figure 8-9b, which suggests that the films have flat surfaces with a mosaic structure; i.e. some small crystalline domains that are slightly tilted with respect to each other. Further discussion on tilting of crystalline domains will be presented in 8.6.1.2.
Figure 8-13. RHEED patterns of CeO$_2$ epitaxial films grown on (a): (001), (b): (110), and (c): (111) YSZ substrates.
Figure 8-14. RHEED patterns of Er$_2$O$_3$ epitaxial films grown on (a): (001), (b): (110), and (c): (111) YSZ substrates.
8.6.1.2 X-ray Characterization

8.6.1.2.1 X-ray Reflectivity

The X-ray reflectivity curves for CeO$_2$ and Er$_2$O$_3$ are presented in Figure 8-15 and Figure 8-16. By fitting the reflectivity curves with the Rigaku software, the thicknesses of the CeO$_2$ films were determined to be 63 – 71 nm. In addition, the decay in reflectivity intensities are higher for (001) and (111) than (110), therefore, the surface of (110) is expected to be smoother. Since the reflectivity curves for Er$_2$O$_3$ specimens have similar oscillation and decay, the thicknesses of the films are quite similar (59 – 61 nm) and the surface roughness is expected to be the same.

![Figure 8-15](image1.png)

Figure 8-15. XRR curves of CeO$_2$ film on YSZ single crystal substrate, (a) 001 oriented, (b) 110 oriented, and (c) 111 oriented. Film thickness is listed on the corner of each reflectivity curves.

![Figure 8-16](image2.png)

Figure 8-16. XRR curves of Er$_2$O$_3$ film on YSZ single crystal substrate, (a) 001 oriented, (b) 110 oriented, and (c) 111 oriented. Film thickness is listed at the top of each reflectivity curve.

8.6.1.2.2 Out-of-Plane Diffraction and Rocking Curves

Out-of-plane diffraction patterns of CeO$_2$ deposited on low-indexed oriented YSZ single crystals are shown in Figure 8-17. For all orientations, only the expected peaks from the single crystal
substrate and the corresponding CeO$_2$ film peaks were present. Therefore, the films and the substrates have a crystal relationship of (hkl)$_{CeO_2}$ // (hkl)$_{YSZ}$.

![X-ray diffraction patterns of CeO$_2$ films deposited onto (001), (110), and (111) YSZ substrates. Peaks labelled with the suffix “s” denote diffraction from the YSZ substrate.](image)

Figure 8-17. Out-of-plane X-ray diffraction of CeO$_2$ films deposited onto (001), (110), and (111) YSZ substrates. Peaks labelled with the suffix “s” denote diffraction from the YSZ substrate.

Fine features of the diffraction patterns can be observed in the narrow scans, as shown in Figure 8-18, Figure 8-19, and Figure 8-20 for (001), (110), and (111) orientations, respectively. For the (001) and (111) films, Pendellesung fringes are clearly visible, indicating good crystal quality and film flatness$^{141,142}$. Furthermore, interplanar spacing of the film can be extracted from the narrow scan diffraction patterns and the results are presented in Table 8-3. The differences between the measured and theoretical out-of-plane d-spacings for CeO$_2$ are minimal which suggest that there are no distortion to the lattices along the axis perpendicular to the film surface.
Figure 8-18. Out-of-plane X-ray diffraction (narrow scan) of CeO\textsubscript{2} films deposited onto (001) YSZ substrate.

Figure 8-19. Out-of-plane X-ray diffraction (narrow scan) of CeO\textsubscript{2} films deposited onto (110) YSZ substrate.
Figure 8-20. Out-of-plane X-ray diffraction (narrow scan) of CeO$_2$ films deposited onto (111) YSZ substrate.

Table 8-3. Interplanar spacing of CeO$_2$ and YSZ calculated from narrow scan out-of-plane X-ray diffraction.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Scattering Vector (nm$^{-1}$)</th>
<th>Measured d-spacing (Å)</th>
<th>Theoretical d-spacing (Å)</th>
<th>Difference (Å)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>001</td>
<td>3.698</td>
<td>2.704</td>
<td>2.706</td>
<td>-0.001</td>
<td>-0.055</td>
</tr>
<tr>
<td>110</td>
<td>5.227</td>
<td>1.913</td>
<td>1.913</td>
<td>0.000</td>
<td>0.004</td>
</tr>
<tr>
<td>111</td>
<td>3.172</td>
<td>3.152</td>
<td>3.124</td>
<td>0.028</td>
<td>0.900</td>
</tr>
<tr>
<td>YSZ</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>001</td>
<td>3.874</td>
<td>2.581</td>
<td>2.570</td>
<td>0.012</td>
<td>0.4644</td>
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<tr>
<td>110</td>
<td>5.492</td>
<td>1.821</td>
<td>1.817</td>
<td>0.004</td>
<td>0.2178</td>
</tr>
<tr>
<td>111</td>
<td>3.357</td>
<td>2.979</td>
<td>2.967</td>
<td>0.012</td>
<td>0.4081</td>
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</tbody>
</table>

The out-of-plane $\omega$ rocking curves for the CeO$_2$ films are shown in Figure 8-21. The crystallite tilting or misorientation of the mosaic building blocks that made up the epitaxial film is insignificant for the (001) and (111) oriented films, as indicated by the low full width half maximum (FWHM) of 0.02° and 0.03°, respectively. On the other hand, the FWHM of the $\omega$ rocking curve of CeO$_2$ (110) oriented film is about 0.5°. It can be speculated that the (110) film contains greater number of dislocations between the mosaic building blocks.
Figure 8-21. Out-of-plane ω rocking curve of CeO$_2$ film deposited onto (001), (110), and (111) YSZ single crystal substrates.

For the Er$_2$O$_3$ specimens, similar results were observed for the out-of-plane diffraction, as shown in Figure 8-22. Epitaxial growth of Er$_2$O$_3$ film on single crystal YSZ substrates was achieved as only the expected peaks from the single crystal substrate and the corresponding Er$_2$O$_3$ film peaks were observed. Again, the films and the substrates have a crystal relationship of 2(hkl)$_{Er_2O_3}$ // (hkl)$_{YSZ}$. Narrow scans of the Er$_2$O$_3$ specimens do not reveal any special features. Similarly, the out-of-plane interplanar spacing can be extracted from the narrow scan XRD patterns. Based on the calculation, lattice distortion for the Er$_2$O$_3$ film in the direction perpendicular to the surface of the specimen is minimal as shown by the small differences between the experimental and theoretical d-spacings as shown in Table 8-4.
Figure 8-22. Out-of-plane X-ray diffraction of Er$_2$O$_3$ films deposited onto (001), (110), and (111) YSZ substrates. Peaks labelled with the suffix “s” denotes diffraction from the YSZ substrate.
Figure 8-23. Out-of-plane X-ray diffraction (narrow scan) of Er$_2$O$_3$ film deposited onto (001) YSZ substrate

Figure 8-24. Out-of-plane X-ray diffraction (narrow scan) of Er$_2$O$_3$ film deposited onto (110) YSZ substrate
Figure 8-25. Out-of-plane X-ray diffraction (narrow scan) of Er$_2$O$_3$ film deposited onto (111) YSZ substrate

Table 8-4. Interplanar spacing of Er$_2$O$_3$ and YSZ calculated from narrow scan out-of-plane X-ray diffraction.

<table>
<thead>
<tr>
<th></th>
<th>Orientation</th>
<th>Scattering Vector (nm$^{-1}$)</th>
<th>Calculated d-spacing (Å)</th>
<th>Theoretical d-spacing (Å)</th>
<th>Difference (Å)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$_2$O$_3$</td>
<td>001</td>
<td>3.769</td>
<td>2.653</td>
<td>2.637</td>
<td>0.016</td>
<td>0.607</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>5.307</td>
<td>1.884</td>
<td>1.865</td>
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<td>1.060</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>3.240</td>
<td>3.086</td>
<td>3.045</td>
<td>0.041</td>
<td>1.362</td>
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<tr>
<td>YSZ</td>
<td>001</td>
<td>3.885</td>
<td>2.574</td>
<td>2.570</td>
<td>0.004</td>
<td>0.174</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>5.493</td>
<td>1.820</td>
<td>1.817</td>
<td>0.004</td>
<td>0.197</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>3.357</td>
<td>2.979</td>
<td>2.967</td>
<td>0.012</td>
<td>0.402</td>
</tr>
</tbody>
</table>

Finally, crystallite tilting on all Er$_2$O$_3$ specimens were more significant than on CeO$_2$ films, as indicated by the wider FWHM of 0.7 – 0.8° (Figure 8-26).
Figure 8-26. Out-of-plane ω rocking curve of Er₂O₃ film deposited onto (001), (110) and (111) YSZ single crystal substrates.

8.6.1.2.3 In-Plane Diffraction and Rocking Curves

In-plane diffraction patterns of CeO₂ deposited onto YSZ single crystal substrates are shown in Figure 8-27. For the (001) and (110) orientations, the azimuth can be along <100> or <110> to probe for {100} or {110} perpendicular to the surface. For the (111) oriented specimen, the azimuth was <110>. In all cases, only the expected substrate peaks and the film peaks of the same (hkl) were detected. These results further reinforce that epitaxial film growth was achieved for all 3 low index orientations.
Figure 8-27. In-plane X-ray diffraction of CeO$_2$ films deposited onto (001), (110), and (111) YSZ substrates. 2 different azimuths were chosen for (001) and (110) films.
In addition, narrow in-plane diffraction scans can shed some light whether there is any in-plane lattice strain or distortion of the film due to the lattice mismatch between CeO$_2$ and YSZ. Narrow scan in-plane diffraction patterns for all 5 cases are presented in Figure 8-28 to Figure 8-32. Due to the low intensity inherent in this technique, these diffraction patterns are noisier than the out-of-plane counterparts. Interplanar spacing extracted from these measurements are listed in Table 8-5. The percent difference between the theoretical and calculated d-spacing is about 0.4% or less, which indicates that the CeO$_2$ lattice of the thin films are relaxed and there is no in-plane strain.

![Graph](image-url)

Figure 8-28. In-plane X-ray diffraction (narrow scan) of CeO$_2$ film deposited onto (001) substrate, azimuth: [100].
Figure 8-29. In-plane X-ray diffraction (narrow scan) of CeO$_2$ film deposited onto (001) substrate, azimuth: [110].

Figure 8-30. In-plane X-ray diffraction (narrow scan) of CeO$_2$ film deposited onto (110) substrate, azimuth: [001].
Figure 8-31. In-plane X-ray diffraction (narrow scan) of CeO$_2$ film deposited onto (110) substrate, azimuth: [\overline{1}10].

Figure 8-32. In-plane X-ray diffraction (narrow scan) of CeO$_2$ film deposited onto (110) substrate, azimuth: [1\overline{1}0].
Table 8-5. In-plane interplanar spacing of CeO₂ and YSZ calculated from narrow scan in-plane X-ray diffraction.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Azimuth</th>
<th>Scattering Vector (nm⁻¹)</th>
<th>Measured d-spacing (Å)</th>
<th>Theoretical d-spacing (Å)</th>
<th>Difference (Å)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>001</td>
<td>100</td>
<td>3.681</td>
<td>2.716</td>
<td>2.706</td>
<td>0.011</td>
</tr>
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<td></td>
<td></td>
<td>110</td>
<td>5.206</td>
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<td>1.913</td>
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<tr>
<td></td>
<td>110</td>
<td>001</td>
<td>3.684</td>
<td>2.714</td>
<td>2.706</td>
<td>0.009</td>
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<td></td>
<td></td>
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<td>1.916</td>
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<td>0.003</td>
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<td></td>
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<td>5.219</td>
<td>1.916</td>
<td>1.913</td>
<td>0.003</td>
</tr>
<tr>
<td>YSZ</td>
<td>001</td>
<td>100</td>
<td>3.876</td>
<td>2.580</td>
<td>2.570</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>110</td>
<td>5.484</td>
<td>1.823</td>
<td>1.817</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>001</td>
<td>3.889</td>
<td>2.571</td>
<td>2.570</td>
<td>0.002</td>
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<td></td>
<td></td>
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<td>5.503</td>
<td>1.817</td>
<td>1.817</td>
<td>0.000</td>
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<td>110</td>
<td>5.483</td>
<td>1.824</td>
<td>1.817</td>
<td>0.007</td>
</tr>
</tbody>
</table>

In-plane rocking curves of CeO₂ films are shown in Figure 8-33. For the (001) oriented film, (110) planes were chosen for the φ scan and intense peaks were observed every 90°, which signifies 4-fold rotational symmetry. For the (110) oriented film, 2-fold symmetry was observed when the (001) planes were chosen for the φ scan. Finally, (110) planes were chosen for the φ scan of the (111) oriented film and intense peaks were separated by 60°, or 6-fold symmetry. These results clearly demonstrate that heteroepitaxial growth of CeO₂ on single crystal YSZ was successful.

Due to the close proximity of the diffraction peaks of Er₂O₃ and YSZ, in-plane diffraction cannot clearly separate them (Figure 8-34). Hence, in-plane diffraction and rocking curves were not performed for all Er₂O₃ specimens.
Figure 8-33. In-plane $\phi$ rocking curves of CeO$_2$ films deposited onto (001), (110), and (111) YSZ substrates.
Figure 8-34. In-plane X-ray diffraction of Er$_2$O$_3$ films deposited onto (001) YSZ single crystal substrate, azimuth: [100]. 400 peak of the Er$_2$O$_3$ cannot be clearly resolved.

8.6.1.2.4 Reciprocal Space Mapping

Reciprocal space mapping results of CeO$_2$ and Er$_2$O$_3$ on YSZ single crystal substrates are shown in Figure 8-35 and Figure 8-36, respectively. For (001) oriented specimens mappings were performed around the ($\overline{1}$13) diffraction spot from the substrate. For the (110) oriented specimen, mappings were performed around (240) diffraction spot from the substrate. Finally, for the (111) oriented specimens, mappings were performed around the (331) diffraction spot from the YSZ. The dotted lines on the maps represent relaxation lines.

As shown in Figure 8-35a, b, the maximum intensities from the film for the (001) and (110) oriented CeO$_2$ specimens is well aligned with the relaxation line. Based on this observation, these CeO$_2$ films are fully relaxed and free of lattice strain that may be caused by lattice parameter mis-match with the YSZ substrate. For the CeO$_2$ (111) specimen, there is a slight deviation on the observed maximum intensity on the in-plane direction from the expected spot on the relaxation line (marked by x), indicating the film lattice structure is partially relaxed; there is some compressive strain.

On the other hand, different observations were made for the Er$_2$O$_3$ films. Based on the mapping, the (001) oriented film is partially relaxed as the maximum intensity on the observed around ($\overline{2}$26) is shifted towards the left (marked by +), indicating there is compressive strain on the
planes perpendicular to the surface. For the (110) and (111) oriented films, deviations from the expected bulk position (marked by X) are significantly greater; film lattice strain is present in both the in-plane and out-of-plane directions, most likely due to lattice mismatch between YSZ and Er$_2$O$_3$.

Figure 8-35. Reciprocal space mapping of CeO$_2$ on YSZ single crystal substrates (a) 001 orientation, (b) 110 orientation, and (c) 111 orientation.

Figure 8-36. Reciprocal space mapping of Er$_2$O$_3$ on YSZ single crystal substrates (a) 001 orientation, (b) 110 orientation, and (c) 111 orientation.
8.6.1.3 Atomic Force Microscopy

Surface morphology of annealed YSZ substrates are shown in Figure 8-37. All substrates are nearly atomically flat. Since the single crystal substrates have a mis-cut tolerance up to 0.5°, after annealing, low energy step and terrace structures are observed for (001) and (111). On the other hand, the (110) substrate remained featureless after annealing, which suggest the substrate was cut almost perfectly during the manufacturing process. Numerical data on the AFM results, including roughness root mean square $R_{\text{rms}}$, and surface area ratio ($R_s$) are shown in Table 8-6.

Figure 8-37. AFM images of annealed YSZ single crystal substrates (a) 001 orientation, (b) 110 orientation, and (c) 111 orientation.

AFM images of CeO$_2$ and Er$_2$O$_3$ thin films deposited on YSZ substrates are shown in Figure 8-38 and Figure 8-39, respectively. For the (001) and (111) CeO$_2$ specimens, the underlying step and terrace morphology of the YSZ substrate remained visible (Figure 8-38a, c). Furthermore, grain-like feature can be observed on the surface for these orientations. On the other hand, the (110) CeO$_2$ specimen remained smooth and featureless as indicated by the low z-value (Figure 8-38b) and low $R_{\text{rms}}$ (Table 8-6). On the other hand, the AFM images (Figure 8-39) and the numerical data (Table 8-6) of Er$_2$O$_3$ specimens indicate the surfaces are featureless with very low roughness. These results indicate the YSZ substrates and the REO thin film specimens produced by PLD are suitable for water contact angle measurements as they have very little roughness, which otherwise may affect the observed water contact angle.
Figure 8-38. AFM images of CeO$_2$ films deposited on YSZ single crystal substrates. (a) 001 orientation, (b) 110 orientation, and (c) 111 orientation.

Figure 8-39. AFM images of Er$_2$O$_3$ films deposited on YSZ single crystal substrates. (a) 001 orientation, (b) 110 orientation, and (c) 111 orientation.

Table 8-6. Roughness root mean square and surface area ratio of YSZ, CeO$_2$ films, and Er$_2$O$_3$ films.

<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation</th>
<th>$R_{rms}$ (nm)</th>
<th>Surface Area Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>(001)</td>
<td>0.62</td>
<td>1.0005041</td>
</tr>
<tr>
<td></td>
<td>(110)</td>
<td>0.09</td>
<td>1.0005853</td>
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<tr>
<td></td>
<td>(111)</td>
<td>0.99</td>
<td>1.0007407</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>(001)</td>
<td>0.80</td>
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</tr>
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<td>(110)</td>
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<tr>
<td></td>
<td>(111)</td>
<td>0.41</td>
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</tr>
<tr>
<td>Er$_2$O$_3$</td>
<td>(001)</td>
<td>0.13</td>
<td>1.00288</td>
</tr>
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<td></td>
<td>(110)</td>
<td>0.10</td>
<td>1.00231</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>0.17</td>
<td>1.00253</td>
</tr>
</tbody>
</table>
8.6.1.4 Scanning Transmission Electron Microscopy

Cross-section high angle annular dark field (HAADF) images of CeO$_2$ films are shown in Figure 8-40. Based on the low magnification images, the thickness of the films is about 65 - 70 nm which is somewhat comparable with XRR. Faint contrast can be observed on the films in the low magnification images, which can be attributed to misfit dislocations and slightly mis-oriented crystallites that make up the mosaic structure. Furthermore, it is visible that the surface of the (001) CeO$_2$ film is not truly atomically flat. Instead, there are some roughness on the surface of about 1.5 – 2 nm in height that are separated laterally by about 30 – 50 nm. This observation is in good agreement with the AFM images where the island-like features were observed (Figure 8-38a). The observation suggest that the growth mode of the thin film can be a combination of Volmer-Webber and Stranski-Krastanov. For the (110) and (111) CeO$_2$ epitaxial films, the surfaces were relatively smooth with negligible roughness which is in good agreement with AFM data. Atomic resolution images clearly indicate that the surface of the films maintains the orientation of the YSZ single crystal substrate, i.e. (001), (110) and (111).

HAADF-STEM images of Er$_2$O$_3$ epitaxial films are shown in Figure 8-41. Similar to CeO$_2$, weak contrast on the film can be observed, most likely due to small misorientation between crystallites. Based on the low magnification images, the thicknesses of the films are about 50 nm and the surface of the films are relatively flat without observable roughness. This finding is consistent with the AFM images (Figure 8-39), where the surfaces appear featureless. Atomic resolution images show that the films are epitaxial, i.e. (hkl)$_{YSZ} \parallel 2(hkl)_{ErO_3}$. 
Figure 8-40. Cross-sectional HAADF-STEM images of the CeO$_2$ epitaxial films grown on YSZ single crystals. (a, b) (001) oriented CeO$_2$ epitaxial film on (001) YSZ single crystal. The incident direction of the electron beam is [100]. (c, d) (110) oriented CeO$_2$ epitaxial film on (110) YSZ single crystal. The incident direction of the electron beam is [001]. (e, f) (111) oriented CeO$_2$ epitaxial film on (111) YSZ single crystal. The electron beam direction is [110]. Atomic resolution images (b, d, f) clearly show that the CeO$_2$ films are epitaxial as the surfaces maintain the crystallographic orientation of the underlying YSZ single crystal substrate; i.e. (001), (110), and (111) planes can be clearly observed.
Figure 8-41. Cross-sectional HAADF-STEM images of the Er$_2$O$_3$ epitaxial films grown on YSZ single crystals. (a, b) (001) oriented Er$_2$O$_3$ epitaxial film on (001) YSZ single crystal. The incident direction of the electron beam is [100]. (c, d) (110) oriented Er$_2$O$_3$ epitaxial film on (110) YSZ single crystal. The incident direction of the electron beam is [110]. (e, f) (111) oriented CeO$_2$ epitaxial film on (111) YSZ single crystal. The electron beam direction is [112]. Atomic resolution images (b, d, f) clearly show that the Er$_2$O$_3$ films are epitaxial as the surfaces maintain the crystallographic orientation of the underlying YSZ single crystal substrate; i.e. (001), (110), and (111) planes can be clearly observed.

8.6.1.5 Summary of Structural Characterizations

Through the multiple structural characterization techniques that probe from the millimetre scale to sub-nanometre scale, the results clearly demonstrate that high quality CeO$_2$ and Er$_2$O$_3$ thin films were heteroepitaxially grown on YSZ single crystal substrates with low lattice defects and negligible surface roughness. Therefore, these specimens are highly suitable for the establishment of crystal orientation – wetting property relationships.
8.6.2 Wetting Properties

8.6.2.1 Wetting Properties of Fresh Surfaces

After pulsed laser deposition, the specimens were removed from the deposition chamber when the substrate holder temperature was about 50°C. Within 2 minutes of exposing the specimen to ambient condition, water contact angles were measured to minimize the potential effect of airborne contamination. The water contact angles for fresh CeO$_2$ and Er$_2$O$_3$ films, along with annealed YSZ substrates are presented in Figure 8-42 and Figure 8-43. All fresh surfaces are hydrophilic; WCA ranges from 1° to 5° for YSZ, 37° to 57° for CeO$_2$, and 31° to 58° for Er$_2$O$_3$. For all 3 materials, the order of increasing WCA for the 3 low index orientation is as follows: (001) < (110) < (111). It is established that there is an inverse relationship between surface energy and water contact angle, that is for lower surface energy, the water contact angle is usually greater. Indeed, by plotting the experimental WCA with computed surface energy of low index orientations for CeO$_2$ and Er$_2$O$_3$ from the literature$^{129,130}$, an inverse relationship was observed (Figure 8-44).
Figure 8-42. 5 µL water droplet at rest on fresh YSZ, CeO$_2$, and Er$_2$O$_3$ low index orientation surfaces.
Figure 8-43. Water contact angle – crystallographic orientation relationship of pristine YSZ, CeO₂, and Er₂O₃ surfaces. All water contact angles are the average of at least 4 measurements.

Figure 8-44. Water contact angle - surface energy relationship of fresh CeO₂ and Er₂O₃ surfaces.
8.6.2.2  Time-dependent Wetting Behaviour

As demonstrated in the previous section, hydrophilicity was observed for both as-deposited, pristine rare earth oxide surface; unlike what was reported in some of the previous studies. Following the first WCA measurements after preparation, the specimens were kept in a cabinet under ambient conditions (25°C, 30% relative humidity).

As noted in the literature review, several studies demonstrated that wetting properties of REO surfaces change after storage in ambient air. In the current study, WCA of YSZ, CeO₂, and Er₂O₃ low index surfaces were also measured as a function of storage time in ambient air. The results of these experiments are presented in Figure 8-45, Figure 8-46, and Figure 8-47.

For YSZ surface (Figure 8-45), initially, the WCA is below 10° and there is a monotonic increase in WCA with time elapsed. The most significant change occurs within the first 24 h; WCA increased to about 30-40° after 2 h exposure to air. After 168 h, the WCA ranges from 60 - 80° and the orientation dependence still remains.

On the other hand, the behaviour is slightly different for rare earth oxides surfaces. As shown in Figure 8-46 and Figure 8-47, the most significant change in WCA also occurs within the first 24 h. However, after 48 h, WCA of all REO surfaces converge to about 80° and the orientation relationship was no longer observed. Here, there is an indirect evidence that the surface chemistry has changed significantly so that the crystal orientation effect is no longer observed. The results of this experiment do indeed support that the adsorption of airborne hydrocarbons is responsible for the high WCA.

In addition, Al₂O₃ single crystals were also studied for their time-dependent WCA and the results are presented in Appendix G. Similar time dependence was observed as well.
Figure 8-45. Water contact angle behaviour of YSZ single crystals stored in ambient air.

Figure 8-46. Water contact angle behaviour of low index orientation CeO$_2$ epitaxial films stored in ambient air.
8.6.2.3 Effect of Vacuum Treatment on the Wettability of Smooth REO Epitaxial Films

As noted in the literature review, hydrophobicity of REOs can be achieved by the so-called vacuum treatment. In the present study, REO epitaxial films were subjected to different vacuum treatment experiments to observe changes in the wetting behaviour. In the first experiment, WCA of freshly prepared CeO$_2$ (111) was measured (WCA = 58°), and then the specimen was placed in a high vacuum environment (10$^{-4}$ Pa) for 4 days. The WCA increased to about 80°, which is about the same as for the specimen stored in ambient after 2 days. In the second experiment, WCAs of low index oriented Er$_2$O$_3$ specimens were measured after storage in ambient for 1 month, followed by a vacuum treatment (10$^{-4}$ Pa) for 2 days. The results are presented in Figure 8-48. There were no significant changes to the WCA and the specimens remained hydrophilic. Based on these experiments, it is not possible to achieve hydrophobicity (WCA > 90°) for smooth REO epitaxial films, even with vacuum treatment. Therefore, the trend observed in previous studies that claimed hydrophobicity of “smooth” REO surfaces can be achieved by a vacuum treatment does not apply for near-atomically smooth epitaxial film surfaces investigated in the present work.
Figure 8-48. Effect of vacuum treatment on Er₂O₃ (001), (110), (111) specimens that were stored in ambient air for 1 month.

8.6.2.4 Effect of Vacuum Treatment on the Wettability of Rough REO Epitaxial Films

A similar experiment described in the preceding section was also performed on a CeO₂ epitaxial film with a rough and porous surface. To obtain a rough (001) epitaxial film, the film deposition parameters were modified. The substrate heating temperature was decreased from 900°C to 400°C and oxygen flow into the deposition chamber was increased to achieve a chamber vacuum of 6.7 Pa (from 3 × 10⁻³ Pa). An AFM image of the film is shown in Figure 8-49. It is clear that the surface roughness is significant compared to the smooth epitaxial films (Figure 8-38). The WCA of the as-deposited, rough film is about 15°. After a vacuum treatment, hydrophobicity was observed (WCA of 110°). Therefore, in the previous studies that reported hydrophobicity of REOs, it is likely the surfaces studied were not smooth and dense.
8.6.3 Surface Chemistry of Freshly Prepared REO Epitaxial Films

In order to develop a better understanding of the time-dependent wetting behaviour of REO epitaxial films, X-ray photoelectron spectroscopy was employed to study the change in surface chemistry of a selected REO surface as a function of exposure time to ambient air, and specifically the build-up of carbon species on the surface. For this experiment, only the Er$_2$O$_3$ (001) surfaces were studied for number of reasons: (i) There are no peaks in the vicinity of the C 1s at 284.5 eV (region of interest), unlike CeO$_2$, where Ce 4s at 291 eV overlaps with the C 1s; (ii) the largest change in WCA was observed for the (001) Er$_2$O$_3$ orientation.

8.6.3.1 XPS Survey Scans of Er$_2$O$_3$ (001)

The XPS survey scan spectra of Er$_2$O$_3$ (001) acquired as a function of time exposure to ambient air after pulsed laser deposition are shown in Figure 8-50. Technically not measured instantaneously after the PLD process, 0 h represents the first measurement after film fabrication and there was some transfer time (approximately 5 min) from the PLD chamber to the XPS chamber. All the expected peaks from erbium and oxygen are present in the spectra. Even from the first measurement, carbon can be detected although the film surface was expected to be “clean”. Adventitious carbon, which contributes to the C 1s peak, is present everywhere,
including high vacuum environment. A noticeable increase in the C 1s intensity can be observed with increasing exposure time in ambient air, especially the first 48 h. These results provide the evidence that the Er$_2$O$_3$ epitaxial film surfaces underwent surface chemistry change when they were exposed to ambient condition, contributing to the increase in the measured WCA.

Figure 8-50. Survey scan X-ray photoelectron spectra of Er$_2$O$_3$ (001) epitaxial films as a function of exposure time in ambient air.
8.6.3.2 High Resolution XPS Scans of Er\textsubscript{2}O\textsubscript{3} (001)

Although the survey scans provided evidence that carbon adsorbed on the surfaces of Er\textsubscript{2}O\textsubscript{3} (001), it cannot be simply deduced that hydrocarbons were the primary carbon species present as reported in some of the previous studies \textsuperscript{111,121,128}. High resolution scans around the C 1s region were performed to better identify the form of carbon species present Figure 8-51.

![High resolution XPS scans](image)

Figure 8-51. High resolution scans around C 1s of Er\textsubscript{2}O\textsubscript{3} (001) as a function of storage time in ambient.

From these spectra, the C 1s can be resolved into 3 characteristic binding energies at 284.5 eV, 286.6 eV, and 288.7 eV, which correspond to C=C and C-H (hydrocarbon), oxidized carbon and oxidized hydrocarbon, respectively. It is clear that with increasing storage time in air, the intensity of the hydrocarbon peak increases, which can be related to the adsorption of airborne hydrocarbon on the surface. This observation can be correlated with the higher water contact angle of rare earth oxides after exposure to ambient conditions.
8.6.4 Surface Chemistry of Sputter Cleaned REO Epitaxial Films

At the time when the fabrication of REO epitaxial films was done in summer of 2017, surface chemistry analysis was not performed due to unavailability of XPS instrumentation. However, two XPS experiments were later performed on CeO$_2$ (001) films that were stored in plastic container for 5 months in ambient condition.

In the first experiment, a spectrum was collected on the specimen without any cleaning and it is labelled as “as-received” in Figure 8-52. Afterwards, the same specimen was cleaned by sputtering using Ar ion clusters at 2 keV until the C 1s peak (285 eV) was no longer visible (Figure 8-52, labelled “cleaned”). Subsequently, the specimen was removed from the XPS chamber and left in ambient air for 30 minutes intervals. After every 30 minutes, the sample was transferred back to the XPS chamber to collect a new spectrum. Narrow scans around Ce 4s and C 1s peaks are shown in Figure 8-53. From these spectra, it is clear that when the CeO$_2$ was exposed to ambient air, carbon (most likely airborne hydrocarbon) was adsorbed on the surface as indicated by the increase in C 1s intensity. Due to the proximity of the Ce 4s peak (291 eV) to the C 1s peak (284 eV), it is difficult to determine the type of carbon species adsorbed on the surface, i.e. C-C, C=C, C-O, C-H, COOH.
Figure 8-52. Survey scans of CeO$_2$ 001 surface kept in ambient air after cleaning. The spectra show as-received CeO$_2$ 001 surface (left in air for about 5 months), after cleaning with Ar cluster sputtering, and after exposure to ambient air for 30, 60, and 120 minutes. Details of the rectangle box in dashed line are shown in Figure 8-53. Take-off angle was 90°.

Figure 8-53. Narrow scans around Ce 4s and C 1s of cleaned CeO$_2$ (001) surface and after exposure to ambient air.
In the second experiment, the CeO$_2$ (001) specimen was cleaned with Ar cluster sputtering until the C 1s peak was no longer present. The specimen then remained in the ultra-high vacuum (UHV) environment ($1.5 \times 10^{-7}$ Pa) inside the XPS system to determine the influence of vacuum treatment on a “clean” sample. All the sub-systems were turned off, including the X-ray source and ion gun to avoid the possibility of introducing contamination. Spectra were collected at different times, as shown in Figure 8-54, along with narrow scans shown in Figure 8-55. For this set of experiments, the take-off angle was 20° to increase surface sensitivity. Similar to the specimen that was exposed to air, there is an increase in the C 1s signal with increasing time in vacuum. Although the increase in intensity is not as rapid as for the surface stored in ambient condition, adventitious carbon is adsorbed on the surface, even in a “clean” UHV environment. Therefore, previous studies that performed a vacuum treatment to uncover the “intrinsic” hydrophobic nature of REOs may not have considered this effect.

Figure 8-54. Survey scans of CeO$_2$ 001 surface kept in UHV after cleaning. The spectra show the CeO$_2$ 001 surface after cleaning with Ar cluster sputtering, and after 30, 60, 90, 120, and 4320 minutes in the UHV chamber. Details of the rectangle box in dashed line are shown in Figure 8-55. Take-off angle was 20°.
Figure 8-55. Narrow scans around Ce 4s and C 1s of cleaned CeO$_2$ 001 surface and after exposure to UHV environment.

### 8.7 Summary

In this part of the study, it was demonstrated experimentally that there is a clear relationship between the crystallographic orientation, surface energy, and the water contact angle of the fresh surfaces of CeO$_2$ and Er$_2$O$_3$ epitaxial films prepared by a PLD technique. Extensive structural characterization was performed to confirm the specimens were near-perfect for such fundamental work. By studying the wetting properties of REOs with different crystallographic orientations, their differences in wetting behaviour was addressed. All fresh surfaces of REO epitaxial films were hydrophilic and the WCA strongly depended on the crystallographic orientations, WCA$_{(111)} >$ WCA$_{(110)} >$ WCA$_{(001)}$, which reflects the differences in the surface energy, SN$_{(111)} <$ SN$_{(110)} <$ SN$_{(001)}$ reported in theoretical studies. Moreover, the WCA on REOs increased rapidly and converged to about 80° (technically still hydrophilic) upon exposure to ambient air, regardless of the crystallographic orientation, due to surface adsorption of airborne carbon species. This was supported by XPS data, where the intensity for hydrocarbons (284.5 eV) on Er$_2$O$_3$ (001) surface increased rapidly with increasing storage time in ambient air. It was determined that REO
surfaces can be rendered hydrophobic (WCA > 90°) after a vacuum treatment only if surface roughness is present.

The results presented in this chapter are consistent with the wetting behaviour of Ni-CeO₂ composites described in Chapter 7. As-plated Ni-CeO₂ composites (with significant surface roughness) and as-deposited, rough epitaxial films described in this chapter were both hydrophilic (Figure 7-10 and Figure 8-49b). After vacuum treatment, both types of specimens became hydrophobic with WCA > 90°. In both cases, the hydrophobicity observed was an extrinsic property. The vacuum treatment induced hydrocarbon adsorption on these surfaces, as evident in the XPS data (Figure 8-55), where the C 1s intensity of CeO₂ (001) epitaxial film that was cleaned by argon cluster sputtering increases with increasing storage time in a “clean” vacuum environment. The convergence of the wetting properties of REO epitaxial films, regardless of orientation with increasing hydrocarbon contamination to a common water contact angle indicates that for the practical applications of REOs for non-wetting characteristics, such as the Ni-CeO₂ composite materials described in Chapter 7, the crystallographic orientation of REOs is likely not of significant importance.

8.8 Published Work Based on Findings of This Chapter

Chapter 9
On the Bigger Picture of Surface Contamination

9 On the Bigger Picture of Surface Contamination

9.1 Hydrocarbon Contamination and Wettability on Other Materials

Controversial debates on the influence of hydrocarbon contamination on wettability are not new nor just limited to rare earth oxide ceramics discussed in this thesis. A well-known classical example is gold, where a similar controversy regarding wetting / non-wetting started in the 1930s. In the 1960’s, gold was reported to be “hydrophobic” in several studies, where the advancing WCA was about 60 - 65° [ref 143–146]. Note that the definition of hydrophobic was somewhat different in the past; i.e. a surface was considered hydrophobic when the WCA around 60°. Currently, hydrophobic surfaces are defined to have WCA > 90°. Following the initial reports on “hydrophobicity” of gold, there were numerous follow-up studies 147,148 that demonstrated water spreads spontaneously on polished, clean gold surfaces after heat treatment in high purity gas; i.e. WCA = 0° and high contact angles were only achieved when adsorbed organic films were present on the surface. At the same time, there were studies (i.e. 149) that insisted gold is hydrophobic by demonstrating that dropwise condensation occurred on gold surface even after 20,000 h of continuous condensation in a chamber. It was thought that hydrocarbon contamination cannot form / remain on the surface of gold in the condenser environment (temperature > 101°C). From about 1970 to 1980, the debate on the wettability of gold remained active. In the 1970s, Gardner and Woods 150 conducted a series of experiments to clean gold surfaces chemically or electrochemically. Immediately after polishing the surface with diamond paste, a finite WCA was observed 150. However, it was found that after cleaning gold surfaces electrochemically after polishing, in the absence of inorganic and organic contaminants, WCA of 0° was observed, consistent with earlier studies 147,148. In 1980, Smith 151 measured WCA of vapour deposited gold surfaces in ultra high vacuum system that was backfilled with argon. Auger electron spectroscopy was performed prior and after the WCA measurements to demonstrate the gold surfaces had minimal surface contamination. The study also concluded that water spreads completely on the surface of the clean, vapour deposited gold and a partial monolayer of carbon contamination will transform the surface to “hydrophobic” (WCA ~ 65°). In 1981, Gaines 152 reported when clean gold surfaces are exposed to air, the surface becomes
non-wettable due to “the arrival of hydrophobic contamination from the air.” Ever since, it has been accepted that gold is hydrophilic with a WCA = 0° in a clean state and hydrophobicity (WCA ~ 65°, technically hydrophilic in today’s terminology) is observed due to adsorption of airborne hydrocarbon species.

One of the more recent example is graphene. In this community, it was accepted that graphene is slightly hydrophobic with WCA > 90° [ref 153,154] and is similar to the wetting properties of graphite. Li et al. 155 demonstrated that freshly prepared graphene on copper substrate (cm scale), fabricated by a chemical vapor deposition technique is hydrophilic with a WCA of 44°. After exposure to air for 20 minutes, the WCA increased to 60°, and finally plateaued at 80° after 1 day. The study also investigated multilayer graphene on Ni substrate and highly ordered pyrolytic graphite (HOPG); similar behaviour was also observed. XPS and ATR-FTIR confirmed that the increase in WCA is related to adsorption of lower surface energy airborne hydrocarbons. To partially clean the surface, thermal annealing and brief UV-ozone cleaning techniques were employed and the WCA decreased from 80° to 55°. The surface energies of monolayer graphene and HOPG were determined to be 0.085 J/m² and 0.125 J/m². The study concluded that clean graphitic surfaces adsorbed hydrocarbon species from ambient air very rapidly and the WCA increased as a result.

There are a few parallels between the graphene study and the present study on REO epitaxial films. In both cases, the crystallographic orientations are well-defined and the surfaces are atomically smooth (or nearly atomically smooth). Secondly, the convergent WCA after extended exposure to ambient air is similar (~ 80°), which suggest the same extrinsic mechanism (hydrocarbon adsorption) affecting the wettability of theses surfaces. Furthermore, the initial WCA are similar and calculated surface energies are within the same order of magnitude ii.

Other materials that showed similar wettability behaviour include electrodeposited metals and alloys. However, these surfaces were not atomically smooth, surface roughness was intentionally introduced to induce the Cassie- Baxter wetting state to obtain superhydrophobicity. However, since metals and alloys are known to be intrinsically hydrophilic, the WCA of as-prepared

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ii The surface energies of CeO₂ (001), (110), and (111) are 1.51, 1.05, and 0.68 J/m², respectively 131.
electrodeposited metals and alloys with specific surface roughness are typically < 10° (hydrophilic) \(^\text{156–160}\). In these studies, the wettability of the surfaces was found to transform from hydrophilicity to superhydrophobicity with WCA >150° by leaving the specimen in air \(^\text{156,158–160}\) or after drying in a vacuum furnace at mild temperature (65°C) \(^\text{157}\). The change in the wettability was due to adsorption of airborne hydrocarbons, which was evident in the XPS data presented in these studies. Furthermore, it was confirmed that when these surfaces were exposed to UV-ozone treatment, wettability was increased (lower WCA) and XPS analysis confirmed partial removal of hydrocarbons and the conversion of hydrocarbons to hydrophilic oxidized carbon species \(^\text{157}\). However, the wetting properties can be reversed; by storing the surfaces in dark, ambient environment for few weeks, superhydrophobicity will re-emerge, accompanied by an increase in hydrocarbons on the surface. It was noted that the recovery rate of non-wetting properties can be expedited by storing the surface in vacuum drying furnace at 65°C.

### 9.2 Surface Contamination on Other Materials

Surface carbon adsorption from hydrocarbons in the environment is not limited to the type of surfaces (REO thin films) considered here. In fact, hydrocarbon adsorption is reported in many seemingly unrelated areas including i) organic geochemistry \(^\text{161,162}\), ii) environmental hazards and human health \(^\text{163,164}\), iii) analytical vacuum equipment technology \(^\text{165,166}\), iv) XPS analysis \(^\text{167}\), or v) the general assessment of surface cleanliness in manufacturing industries \(^\text{168}\).

In the field of geochemistry hydrocarbons on rock surfaces are used as biomarkers on Archean sediments to obtain information about the earliest life on Earth \(^\text{161}\). In a recent study \(^\text{162}\), it was shown that airborne hydrocarbon contamination of rock samples stored at various locations inside an analytical laboratory can show significant differences in the type and quantity of hydrocarbons present on these samples. Even events such as the waxing of the laboratory floor was found to produce changes in the fingerprint of the hydrocarbons which can lead to erroneous conclusions \(^\text{162}\). For similar reasons it was recently recommended that astronomical samples such as meteorites and interplanetary dust particles should be analyzed as quickly as possible and not stored in containers that could potentially be contamination sources for hydrocarbon emissions and surface hydrocarbon contamination \(^\text{169,170}\).
Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that exist in various concentrations in the environment \(^\text{163}\). They contain two or more benzene rings and can occur as small particles in the air or in the vapor phase depending on the number of benzene rings \(^\text{164}\). They originate mainly from incomplete combustion of carbonaceous material in various industrial processes, internal combustion engines, biomass burning, natural occurrences like volcanic eruptions or forest and savannah fires, etc. Several of these compounds are known carcinogens and therefore pose a risk to human health \(^\text{164}\). While the heavier PAHs are in particle form, the lighter gaseous ones can be readily adsorbed on other atmospheric particles such as pollens and dust \(^\text{164}\).

Contamination due to hydrocarbons on samples or detection systems in modern analytical equipment based on vacuum technology can be of significant concern. For example, in scanning electron microscopes, this contamination comes from polymerization in the electron beam of stray hydrocarbon molecules which deposit on the surface and affect image quality and resolution \(^\text{165}\). The main sources of the stray hydrocarbons are pump oils, o-rings, stage lubricants, or the sample itself. Even though there have been enormous efforts by high vacuum equipment manufacturers over the years to reduce hydrocarbon contamination e.g. reference \(^\text{166}\), to date, there is no technical solution to create a 100% hydrocarbon-free environment. In the XPS community, this layer of carbonaceous material (referred to as adventitious carbon) which builds up on the surface of the material either during exposure to air or even inside the XPS chamber is actually used as a convenient reference and calibration material by setting the C 1s peak at 285 eV \(^\text{167}\). It has been reported that virtually all types of surfaces show adventitious carbon \(^\text{171}\).

Perhaps the most relevant technology branch where hydrocarbon adsorption is of great concern is in the manufacturing of components which require extreme clean surfaces, e.g. in the electronics or aerospace industries. As discussed in reference \(^\text{168}\), the cleanliness of surfaces can be monitored by measuring their wettability. In fact, there is even an ASTM standard to test hydrophobic surface films by the so-called atomizer test \(^\text{172}\). While not quantitative, this test is inexpensive, rapid, and non-destructive and is claimed to be able to detect even fractional molecular layers of hydrophobic organic surface contaminants. The test involves the spraying of a surface with a mist of fine water droplets. In the absence of hydrophobic surface contaminants, the water droplets will wet the surface, while they will bead up when contaminants are present.
The example shown in this ASTM standard is for the case of metal surfaces. The WCA of nickel reported in the literature is typically $70 - 80^\circ$ \cite{102,173}. However, if a nickel surface is made completely free of contaminants the wetting behaviour is superhydrophilic, i.e. complete wetting. However, with increasing surface contamination the water begins to bead up, the picture presented in the ASTM standard (Figure 9-1) clearly showing the break-up of an initially continuous water film into individually separated water droplets with increasing contamination.

![Figure 9-1. Atomizer test of nickel specimen showing hydrophobic contaminants, causing water to bead up into droplets.](image)

Summarizing these observations from quite diverse fields, it is clear that hydrocarbon adsorption on a wide range of materials (metals, oxides, glass, graphene, pollens) is actually the norm rather than the exception. And this hydrocarbon build-up can occur in air as well as in vacuum. What is needed in this area is a better analysis of the exact nature of these films as well as adsorption rates for different types of materials as can be determined, for example, from water contact angle versus time curves such as presented here for CeO$_2$ and Er$_2$O$_3$ (Figure 8-46, Figure 8-47), or in previous studies of metals\cite{156}, graphene\cite{155}, and metal oxides\cite{174}. It may well be that the nature of the hydrocarbon contaminant on the surface and the build-up rates depend on the type and nature of the substrate material, including crystal structure and crystallographic orientations, as well as electronic structure \cite{103}. Perhaps the latter could explain the much more rapid increase in WCA for REO compared to YSZ. The build-up rates and final coverage also depend on the partial pressure of the hydrocarbon source as previously shown, for example, metal oxide surfaces exposed to either paraffin alone or a mixture of paraffin and water \cite{174}. 
9.3 Summary

Based on the analysis described in this chapter, the current controversy regarding hydrocarbon contamination on rare earth oxides almost appears to be a déjà vu when comparing with the gold controversy example. Surface contamination has been known for decades, yet, the knowledge is somewhat lost in modern research in various fields, not just surface wettability. In any study that deals with very surface-sensitive properties, hydrocarbon adsorption in air or in vacuum cannot be ignored or overlooked.
Chapter 10
Conclusions

10 Conclusions

In this thesis, contributions were made for the overall theme of robust, hydrophobic surfaces. On the applied / engineering front, a process was developed to fabricate non-wetting metal matrix composite coatings with different hydrophobic particles, namely PTFE and CeO₂. Results from various characterization techniques supported that the composite approach addressed the drawbacks of current non-wetting materials: low hardness and excellent resistance to the degradation of non-wetting behaviour as the surface is subjected to abrasive wear. The major findings of this work include:

1. Ni-PTFE composites; nanocrystalline matrix with embedded PTFE particles with a bimodal particle size distribution was fabricated by a simple, electro-codeposition technique.

2. The surface morphology of Ni-PTFE composites resembles that of natural superhydrophobic leaves.

3. Stability of the non-wetting properties was evaluated by a simple abrasion test. Compared to a commercially available superhydrophobic spray treatment, Ni-PTFE composites retained highly non-wetting behaviour for significantly longer abrasion length due to the composite structure and nanocrystalline Ni matrix.

4. The synthesis process developed for Ni-PTFE was modified for co-depositing CeO₂ particles instead.

5. As-deposited Ni-CeO₂ composites were hydrophilic and there was no dependence on the volume fraction of CeO₂ in the coating on wetting properties.

6. After a vacuum treatment, all Ni-CeO₂ composites became hydrophobic or superhydrophobic, depending on the vol. % of CeO₂.

7. A negligible decrease in the non-wetting behaviour of Ni-CeO₂ was observed, even after 700 m of abrasion due to the high hardness of the CeO₂ particles and the ultra-fine grain Ni matrix.
On the fundamental front, basic materials science principles were applied to understand the wetting behaviour of REO ceramics. The significant findings of this portion of the thesis include:

1. Crystal orientation – surface energy – wetting property relationships were established for REO epitaxial film made by a PLD process.

2. Fresh REO epitaxial films are hydrophilic.

3. The crystal orientation dependence of the water contact angle diminished when the specimens were exposed to ambient conditions for more than 48 hours, due to the adsorption of low surface energy hydrocarbons on the surface of REOs.
Chapter 11
Suggested Future Work

11 Suggested Future Work

11.1 Suggested Future Work (Part I)

11.1.1 Process Scale Up Feasibility

In this thesis, various characterization techniques have demonstrated that the non-wetting composites are robust and have the attributes that suggest the materials can be used in industrial applications. Before doing so, the scalability of the electro-codeposition process needs to be investigated. In the present study, flat 2 cm × 2 cm specimens were fabricated from a 200 mL beaker setup. As a first step in a scale up process, one should consider fabricating larger samples (e.g. 20 cm × 20 cm specimens from 100 L plating setup) and determine if the properties of the composite materials are consistent with the present work.

Furthermore, electro-codeposition with complex geometry parts should be studied as some of the potential applications of the non-wetting composite coatings could include condenser parts in various forms and shapes (tubes, pipes, etc.).

11.1.2 Explore Different Hydrophobic Particles and Metal Matrix

Two non-wetting Ni-based composites were developed on this thesis, namely Ni-PTFE and Ni-CeO$_2$. One should consider co-deposition with other REOs and determine if the non-wetting behaviour remains the same as for Ni-CeO$_2$. For heat transfer applications, higher thermal conductivity is preferred. Therefore, it would be insightful to change the metal matrix from Ni (90 W/m·K) to Cu (368 W/m·K).

11.2 Suggested Future Work (Part II)

11.2.1 Hydrocarbon Adsorption Rate and Mechanism

Although the inherent wetting behaviour of REOs was addressed in this study, the mechanism of hydrocarbon adsorption remains unknown. For instance, the adsorption rate of hydrocarbon on YSZ was significantly slower than for REOs as indicated by the WCA measurements. The question is, what is the mechanism of hydrocarbon adsorption for these ceramics and what can
account for their differences in hydrocarbon adsorption rate / time-dependent wetting behaviour? In a broader scope, are their differences in the adsorption mechanism of airborne hydrocarbons for different materials; metals, graphene, and other 2D materials? Does electronic structure have an influence on hydrocarbon adsorption rate?

Furthermore, the structure of the hydrocarbon contamination film on the surface of the REOs is not known. Does hydrocarbon develop and grow islands on the specimen surface until the islands coalesce (Figure 11-1) or does the contamination develops by a more layer-by-layer growth mode? Also, a better clarification on the effect of surface roughness and adsorption rate of hydrocarbon should be explored.

![Figure 11-1. Hypothesis: hydrocarbon film growth mode on a surface that is initially clean.](image)

11.2.2 Convergence Water Contact Angle

As noted in 9.1, the WCA of REO epitaxial films converged to about 80°, similar to that of graphene reported in previous studies. It would be of interest to determine if the “equilibrium” WCA on other materials with a very smooth surface is also ~ 80°. If that is the case, a WCA of 80° could of significance in determining the cleanliness of a surface.
11.2.3 Surface Energy of REO Epitaxial Films

In this study, the relationship between water contact angle and surface energy of fresh REO epitaxial films was established using surface energies calculated in previous theoretical studies. Currently, there is no information on experimental surface energy of low index oriented REO surfaces. It would be beneficial to determine surface energy of fresh and aged REO epitaxial films by contact angle measurements with different probe liquids and apply models that relate contact angle to surface energy, such as Neumann model \(^{175}\), Fowkes model \(^{176}\), and Owens-Wendt model \(^{177}\).
References


(65) Iacovetta, D. Synthesis of Superhydrophobic Nanocomposite Coatings Using Electrodeposition, University of Toronto, 2014.


## Appendices

### Appendix A. Literature of Superhydrophobic Electrodeposits

<table>
<thead>
<tr>
<th>Electrodeposit Category</th>
<th>Material</th>
<th>Bath Type</th>
<th>Bath Constituents</th>
<th>Voltage/Current Density</th>
<th>Morphology (H: Hierarchical)</th>
<th>WCA (°)</th>
<th>SA (°)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ni</td>
<td>Aqueous</td>
<td>NiCl₂, H₃BO₃, ethylenediamine dihydrochloride</td>
<td>20–50 mA/cm²</td>
<td>Nano-micro-cone array (H)</td>
<td>154–156</td>
<td>–</td>
<td>173,178</td>
<td></td>
</tr>
<tr>
<td>(a) Ni</td>
<td>Ionic</td>
<td>Ethylene glycol, choline chloride, NiCl₂·6H₂O</td>
<td>1.0 V</td>
<td>Nanosheets, nanostrips, cauliflower-like (H)</td>
<td>110–164</td>
<td>3</td>
<td>179</td>
<td></td>
</tr>
<tr>
<td>(a) Ni</td>
<td>Organic</td>
<td>Ethanol, NiCl₂·6H₂O, myristic acid</td>
<td>30 V</td>
<td>Cauliflower-like (H)</td>
<td>163</td>
<td>2</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>(a) Cu</td>
<td>Aqueous</td>
<td>CuSO₄, H₂SO₄</td>
<td>10–120 mA/cm², 0.1–1.3 V</td>
<td>Lotus leaf-like, cauliflower-like (H)</td>
<td>153–160</td>
<td>8, 5</td>
<td>181,182</td>
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<tr>
<td>(a) Cu</td>
<td>Organic</td>
<td>Ethanol, myristic acid</td>
<td>5 V</td>
<td>Spiky, flower-like with nanosheets (H)</td>
<td>154</td>
<td>–</td>
<td>183</td>
<td></td>
</tr>
<tr>
<td>(a) Co</td>
<td>Aqueous</td>
<td>CoCl₂, Na₂SO₄</td>
<td>−1.0 V vs. SCE</td>
<td>Hierarchical flower-like (H)</td>
<td>162</td>
<td>3.5</td>
<td>184</td>
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<tr>
<td>(a) Zn</td>
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<td>Zn(CH₂CO₂)₂, KCl, NH₄OH</td>
<td>−1.35 V vs. SCE</td>
<td>Scaly sheets, willow leaf-like with submicron features (H)</td>
<td>170</td>
<td>&lt;1</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>(a) Bi</td>
<td>Aqueous</td>
<td>BiCl₃, HCl</td>
<td>−1.5 to −2.5 V vs. SMSE</td>
<td>Micron size dendrites with nanoplates (H)</td>
<td>164</td>
<td>–</td>
<td>188</td>
<td></td>
</tr>
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<td>(a) Mn</td>
<td>Organic</td>
<td>Ethanol, MnCl₂, myristic acid</td>
<td>30 V</td>
<td>Cauliflower-like (H)</td>
<td>163</td>
<td>&lt;3</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>(a) La</td>
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<td>Ethanol, LaCl₂·6H₂O, myristic acid</td>
<td>30 V</td>
<td>Spiky, flower-like with nanorods</td>
<td>165</td>
<td>&lt;2</td>
<td>190</td>
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</tr>
<tr>
<td>(a) Ce</td>
<td>Organic</td>
<td>Ethanol, CeCl₂·6H₂O, myristic acid</td>
<td>30 V</td>
<td>Spiky, flower-like with interpenetrating network</td>
<td>163</td>
<td>2</td>
<td>190</td>
<td></td>
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<tr>
<td>(a) Ce</td>
<td>Organic</td>
<td>Ethanol, Ce(NO₃)₃·6H₂O, myristic acid</td>
<td>30 V</td>
<td>Micro-nano papillae (H)</td>
<td>160</td>
<td>1, &lt;2</td>
<td>191,192</td>
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</tr>
<tr>
<td>(a) Ni-Cu-P alloy</td>
<td>Aqueous</td>
<td>NiSO₄, CuSO₄, NaH₂PO₄, Na₂SO₄, citric acid, sodium dodecyl sulfate</td>
<td>200 mA/cm²</td>
<td>Cauliflower-like (H)</td>
<td>153</td>
<td>–</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>(b) Ni + stearic acid</td>
<td>Aqueous</td>
<td>NiCl₂, H₃BO₃, crystal modifier</td>
<td>20 mA/cm²</td>
<td>Nanocone array</td>
<td>148–154</td>
<td>0–90</td>
<td>194</td>
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<tr>
<td>(b) Ni + (heptadecafluoro-1,1,2,2,6,6-tetrahydrodecyl)-1,1,2-trithiolsilane</td>
<td>Aqueous</td>
<td>NiSO₄, NiCl₂, H₃BO₃</td>
<td>750 mA/cm²</td>
<td>Needle-like leaf structure, pine cone-like hierarchical structure (H)</td>
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<td>96</td>
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<td>(b) Ni + perfluoropolyether</td>
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<td>NiSO₄, NiCl₂, H₃BO₃, saccharin</td>
<td>50 mA/cm²</td>
<td>Lotus leaf replica with conical protuberance (H)</td>
<td>156</td>
<td>–</td>
<td>195</td>
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<td>(b) Cu + lauric acid</td>
<td>Aqueous</td>
<td>CuSO₄, KNaC₆H₄O₇, NaOH, H₃BO₃</td>
<td>5 mA/cm²</td>
<td>Microcone with nanoroughness (H)</td>
<td>154</td>
<td>2</td>
<td>196</td>
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<td>(b)</td>
<td>Cu + n-dodecanethiol</td>
<td>Aqueous</td>
<td>Cu(NO₃)₂</td>
<td>−0.25 V vs. Ag/AgCl</td>
<td>Micro spheres with submicron roughness (H)</td>
<td>152</td>
<td>–</td>
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<tr>
<td>(b)</td>
<td>Cu + fluorocarbon</td>
<td>Aqueous</td>
<td>CuSO₄, H₂SO₄</td>
<td>200 mA/cm²</td>
<td>Micro-nano-scale spheres (H)</td>
<td>160</td>
<td>&lt;2</td>
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<tr>
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<td>Cu + n-octanoic acid</td>
<td>Aqueous</td>
<td>CuSO₄, H₂SO₄</td>
<td>−0.8–2.5 V vs. SCE</td>
<td>Microclusters with nano-protruberances (H)</td>
<td>153</td>
<td>–</td>
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<tr>
<td>(b)</td>
<td>Zn + polypropylene</td>
<td>Ionic</td>
<td>choline chloride, urea, thiourea, ZnCl₂</td>
<td>2.5 mA/cm²</td>
<td>Porous, submicron sheet structure</td>
<td>170</td>
<td>–</td>
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<td>Zn + silicone</td>
<td>Aqueous</td>
<td>ZnCl₂, Zn(NO₃)₂, HNO₃</td>
<td>−1.4 V vs. Ag/AgCl</td>
<td>Micro-nano-fractal morphology (H)</td>
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<td>2 *</td>
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<tr>
<td>(b)</td>
<td>ZnO + stearic acid</td>
<td>Aqueous</td>
<td>ZnCl₂, Zn(NO₃)₂, KCl</td>
<td>−0.5–1.5 V vs. Ag/AgCl</td>
<td>Flower-like with nanorods (H)</td>
<td>170</td>
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<tr>
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<td>Co + stearic acid</td>
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<td>CoCl₂, Na₂SO₄</td>
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<td>156</td>
<td>1</td>
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<tr>
<td></td>
<td></td>
<td>Aqueous</td>
<td>CoCl₂, H₃BO₃, crystal modifier</td>
<td>12.5 mA/cm², 100 mA/cm²</td>
<td>Nanocore array, hierarchical nanocore/shell structure (H)</td>
<td>154–160</td>
<td>4–10</td>
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<tr>
<td>(b)</td>
<td>Ag + n-dodecanethiol</td>
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<td>AgNO₃</td>
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<td>Micron size dendrites with nanocrystals (H)</td>
<td>155</td>
<td>&lt;2</td>
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<td>Au + 1-dodecanethiol</td>
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<td>Au₂S₃, EDTA, Na₂SO₃</td>
<td>1–15 mA/cm²</td>
<td>Nanoleaf structure on micro-aggregates (H)</td>
<td>179</td>
<td>–</td>
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<tr>
<td>(b)</td>
<td>Au + 1-dodecanethiol</td>
<td>Aqueous</td>
<td>HAuCl₄, Na₂SO₄</td>
<td>−0.6 V vs. SCE</td>
<td>Hierarchical dendritic structure (H)</td>
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<tr>
<td>(b)</td>
<td>Au + fluoroalkyl silane</td>
<td>Aqueous</td>
<td>HAuCl₄, polyvinylpyrrolidone</td>
<td>1.0 V</td>
<td>Cauliflower-like (H)</td>
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<td>–</td>
<td></td>
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<tr>
<td>(b)</td>
<td>Au + thiols</td>
<td>Aqueous</td>
<td>HAuCl₄, H₂SO₄</td>
<td>−0.2 V vs. Ag/AgCl</td>
<td>Dendritic structure with nanobranches (H)</td>
<td>154</td>
<td>–</td>
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<tr>
<td>(b)</td>
<td>Pd + n-dodecanethiol</td>
<td>Aqueous</td>
<td>K₂PdCl₆, H₂SO₄</td>
<td>−0.3 to 0.25 V vs. Ag/AgCl</td>
<td>Spiky, nanoflake structure (H)</td>
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<td>3</td>
<td></td>
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<tr>
<td>(b)</td>
<td>Pt + fluoroalkyl silane</td>
<td>Aqueous</td>
<td>H₂PtCl₆, HCl</td>
<td>0 V vs. SCE</td>
<td>Nanowire bundles (H)</td>
<td>158</td>
<td>&lt;3</td>
<td></td>
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<tr>
<td>(b)</td>
<td>Ni-Cu alloy</td>
<td>Aqueous</td>
<td>Ni(NH₂SO₄)₂, CuSO₄, H₂BO₃</td>
<td>−0.9 to −1.5 V vs. Ag/AgCl</td>
<td>Microspheres with nano-protrusions (H)</td>
<td>158</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>CuO-Cu-Zn alloy + lauric acid</td>
<td>Aqueous</td>
<td>CuSO₄, ZnSO₄, KNaC₆H₇O₆</td>
<td>6 mA/cm²</td>
<td>Multi-scale feather-like structure (H)</td>
<td>155</td>
<td>3</td>
<td></td>
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<tr>
<td>(b)</td>
<td>Zn-Co alloy + stearic acid</td>
<td>Ionic</td>
<td>Choline chloride, urea, ZnCl₂, CoCl₂</td>
<td>3.5 mA/cm²</td>
<td>Micro- and nano-particles in clusters (H)</td>
<td>152</td>
<td>–</td>
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<td>(c)</td>
<td>Ni-TiO₂ composite + fluoroalkyl silane</td>
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<td>Aqueous</td>
<td>NiSO₄, NiCl₂, H₂BO₃, sodium dodecyl sulfate, TiO₂</td>
<td>60 mA/cm²</td>
<td>Micro- and nano-particles (H)</td>
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<td>NiSO₄, NiCl₂, H₂BO₃, Polysorbate 80, TiO₂</td>
<td>14–50 mA/cm²</td>
<td>Hierarchical thorn-like structure (H)</td>
<td>175</td>
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<td>Aqueous</td>
<td>Ni(SO₂NH₂)₂, NiCl₂, H₂BO₃, TiO₂</td>
<td>2.3–54 mA/cm²</td>
<td>Nanoparticles in micron size agglomerates (H)</td>
<td>157</td>
<td>–</td>
</tr>
<tr>
<td>(c)</td>
<td>Ni-PTFE composite + fluoroalkyl silane</td>
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<td>Aqueous</td>
<td>Ni(NH₂SO₄)₂, NiCl₂, H₂BO₃, cationic surfactant, PTFE</td>
<td>30 mA/cm²</td>
<td>Microscale fractal morphology</td>
<td>156</td>
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<td>Aqueous</td>
<td>NiSO₄, NiCl₂, H₂BO₃, cationic fluorosurfactant, PTFE</td>
<td>50–100 mA/cm²</td>
<td>Submicron roughness</td>
<td>155</td>
<td>–</td>
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<td></td>
<td></td>
<td>Aqueous</td>
<td>NiSO₄, NiCl₂, H₂BO₃, cetyltrimethylammonium bromide, PTFE</td>
<td>100 mA/cm²</td>
<td>Lotus leaf-like (H)</td>
<td>152</td>
<td>–</td>
</tr>
</tbody>
</table>

* Contact angle hysteresis. †SCE: Saturated calomel electrode. ‡SMSE: Saturated mercury sulfate electrode. §PTFE: Polytetrafluoroethylene.
Appendix B. Potential Applications of the (Super)Hydrophobic Composite Coatings Developed in the Current Study

As described in the introduction, there are two potential classes of applications for the (super)hydrophobic composite coatings developed in this study: (i) infrastructure including power transmission and telecommunication towers and (ii) industrial condensation and boiling systems.

In the event of an ice storm, power transmission and telecommunication towers are susceptible to collapse due to additional load from the ice build-up. Non-wetting surfaces have been shown to resist or delay ice formation \(^{201,218}\). Therefore, the Ni-PTFE composites developed in the present study can be an excellent coatings for these structures to prevent ice build-up and have sufficient abrasive wear resistance. Furthermore, the electro-codeposition process to produce the coating is capable for such large parts.

Efficiency of industrial condensation and boiling systems for heat exchangers, energy generation, thermal management, desalination, and chemical processing can be greatly improved by increasing the heat transfer coefficient and heat flux. For the case of condensation, it is known that the heat transfer coefficient for dropwise condensation is significantly higher than that of filmwise condensation (accumulation of liquid film on the surface) \(^{112}\). Typically, dropwise condensation can be promoted by the use of non-wettable or superhydrophobic surface since the condensed droplets are isolated and can be easily removed (Cassie-Baxter wetting state). However, droplet nucleation on superhydrophobic surface is reduced compared to that on a hydrophilic surface since the nucleation energy barrier is higher. Therefore, a mixture of hydrophobic and hydrophilic material may be beneficial in enhancing the overall heat transfer coefficient in condensers. The Ni-PTFE and Ni-CeO\(_2\) composites developed in this thesis contain both hydrophilic phase (Ni matrix) and hydrophobic phase (PTFE, CeO\(_2\) particles). Having a combination of both hydrophilic and hydrophobic phases can lead to a balance of increased droplet nucleation density and reduced droplet departure size for efficient heat transfer \(^{219}\).

Similar to condensation, there are primarily two modes of boiling: film boiling and nucleate boiling, while the latter is analogous to dropwise condensation \(^{220}\). Film boiling occurs if the
heating surface is significantly hotter than the liquid, where a layer of vapor is formed between the liquid and the solid. In this case, the layer of vapor film between the solid and liquid acts as an insulator and significantly reduces the heat transfer coefficient and heat flux. In nucleate boiling, the surface temperature is slightly higher than the fluid. Bubbles form at the heat transfer surface, break away, and are carried into the bulk of the fluid. Heat transfer is more efficient in the nucleate boiling as the bubbles flowing in the fluid causes agitation, which can effectively carry away the energy created at the boiling surface (higher heat transfer coefficient) \[^221\]. It is known that hydrophobic surfaces promote nucleation of bubbles. However, if the entire heat transfer surface is non-wetting, the bubbles coalesce with neighboring bubbles \[^220\]. Film boiling would result and the blanket of vapor on the surface would not depart \[^220,222\]. On the other hand, bubble nucleation on hydrophilic surface is poor. However, bubbles are more likely to retain spherical shape and would depart as the surface has high affinity for water rather than vapor.

According the patent published by Hummel \[^222\] in 1965, it is desirable to have a heterogeneous surface; that is a major part of the surface is hydrophilic with dispersed parts of hydrophobic spots (Figure B-1, #2). The heterogeneous surface would promote bubble nucleation the hydrophobic spots and the hydrophilic surround would prevent transition to boiling film. As the bubbles grow in size and come in contact with the hydrophilic surrounding, they would transition from hemisphere bubbles to spherical bubbles and eventually depart from the surface (Figure B-1, #2b).

The mechanical robust Ni-PTFE and Ni-CeO\(_2\) composite coatings developed in this study contain both hydrophobic and hydrophilic phases that satisfy the design requirements for efficient heat transfer in boiling applications. In addition, the electro-codeposition process to make these coatings can be adapted to various geometries, including pipes and tubes that are common in boilers.
Figure B-1. Schematic diagram of bubble formation on (1) hydrophilic surface, (2) hydrophobic spot with hydrophilic surround, (2a) bubble growth on hydrophobic surface, (2b) bubble growth on hydrophobic spot with hydrophilic surround, (3) pitted spot on a hydrophilic surface filled with hydrophobic material.
Appendix C. Cost Analysis of (Super)Hydrophobic Composite Coatings Developed in the Current Study

A preliminary cost estimate for making the electro-codeposited composite coatings developed in the current study is described in this section. Typically, the costs of electrodeposited materials can be broken down into 3 components: material costs, equipment costs, and labour costs. In an article by Mazzilli and Lenau, the costs of various electrodeposited metals are described. For instance, the total cost to produce electrodeposited gold is approximately 1.1 times the raw material cost, as gold is a very expensive metal. On the other hand, the total cost to produce a multilayer chromium coating is about 100 times the cost of the raw metal. Chromium is a relatively low cost metal, however, the complexity of the process involve significant labour resources. Another example described in the article is silver; the total cost is approximately 4 times the raw material cost. The material cost and the electrodeposition process of silver are intermediate between gold and chromium.

Based on Mazzilli and Lenau’s article, the estimated total cost of electrodeposited (super)hydrophobic composite coatings is estimated to be 10 times the material costs as the process is slightly more complex than electrodeposition of pure metals (dispersing hydrophobic particles, gravity / sedimentation plating). The detailed calculations of the total cost (in USD) for the electrodeposited composites coating, with an area of 1 m² and a thickness of 50 µm are listed below.

Table C-1. Density and cost of Ni, PTFE, and CeO₂.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>PTFE</th>
<th>CeO₂</th>
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<tbody>
<tr>
<td>Density</td>
<td>8908 kg/m³</td>
<td>2200 kg/m³</td>
<td>7220 kg/m³</td>
</tr>
<tr>
<td>Cost  iii</td>
<td>$13/kg</td>
<td>$1/kg</td>
<td>$10/kg</td>
</tr>
</tbody>
</table>

Calculation for Ni-70% PTFE

Volume of PTFE: \((70\%) (5 \times 10^{-5} \text{ m}^3) = 3.5 \times 10^{-5} \text{ m}^3\)

Mass of PTFE: \((3.5 \times 10^{-5} \text{ m}^3)(2200 \text{ kg/m}^3) = 7.7 \times 10^{-2} \text{ kg}\)

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iii Cost of Ni was obtained from London Metal Exchange. Cost of PTFE and CeO₂ powder were obtained from Alibaba.
Cost of PTFE: $(7.7 \times 10^{-2} \text{ kg})(\$1/\text{kg}) = \$0.077$

Volume of Ni: $(30\%)(5 \times 10^{-5} \text{ m}^3) = 1.5 \times 10^{-5} \text{ m}^3$

Mass of Ni: $(1.5 \times 10^{-5} \text{ m}^3)(8908 \text{ kg/m}^3) = 1.34 \times 10^{-1} \text{ kg}$

Cost of Ni: $(1.34 \times 10^{-1} \text{ kg})(\$13/\text{kg}) = \$1.742$

Total cost of raw material for Ni-70% PTFE: $\$1.819/\text{m}^2$, 50 µm thick

Total cost, including equipment and labour cost to produce Ni-70% PTFE: $\$18.19/\text{m}^2$, 50 µm thick

**Calculation for Ni-55vol% CeO$_2$**

Volume of CeO$_2$: $(55\%)(5 \times 10^{-5} \text{ m}^3) = 2.75 \times 10^{-5} \text{ m}^3$

Mass of CeO$_2$: $(2.75 \times 10^{-5} \text{ m}^3)(7220 \text{ kg/m}^3) = 1.99 \times 10^{-1} \text{ kg}$

Cost of CeO$_2$: $(1.99 \times 10^{-1} \text{ kg})(\$10/\text{kg}) = \$1.986$

Volume of Ni: $(45\%)(5 \times 10^{-5} \text{ m}^3) = 2.25 \times 10^{-5} \text{ m}^3$

Mass of Ni: $(2.25 \times 10^{-5} \text{ m}^3)(8908 \text{ kg/m}^3) = 2.00 \times 10^{-1} \text{ kg}$

Cost of Ni: $(2.00 \times 10^{-1} \text{ kg})(\$13/\text{kg}) = \$2.606$

Total cost of raw material for Ni-55vol% CeO$_2$: $\$4.592/\text{m}^2$, 50 µm thick

Total cost, including equipment and labour cost to produce Ni-55vol% CeO$_2$: $\$45.92/\text{m}^2$, 50 µm thick

In addition, the estimated cost to produce 1 m$^2$ of the commercially available superhydrophobic coating NeverWet™ is described below:

Cost of raw material: $\$12.15/\text{m}^2$

No specialized equipment is required for the application of NeverWet™ to the substrate is required, therefore, there will not be equipment cost. To produce 1 m$^2$ of the coating, approximately 1 h of labour ($\$30$) would be required to apply the two recommended coatings. The total cost to produce 1 m$^2$ of NeverWet™ is estimated to be about $\$42.15$.

In conclusion, the costs of manufacturing the coatings developed in this thesis are either comparable (Ni-CeO$_2$) or lower (Ni-PTFE) than currently available commercial coatings. Their main advantage is their enhanced durability in service.
The following table summarizes the performance and cost of the 3 (super)hydrophobic coatings.

Table C-2. Performance and cost comparison of (super)hydrophobic coatings.

<table>
<thead>
<tr>
<th></th>
<th>Ni-70% PTFE</th>
<th>Ni-55vol% CeO$_2$</th>
<th>NeverWet™</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water Contact Angle</strong></td>
<td>156°</td>
<td>132°</td>
<td>155°</td>
</tr>
<tr>
<td><strong>Water Sliding Angle</strong></td>
<td>~ 5°</td>
<td>-</td>
<td>~ 3°</td>
</tr>
<tr>
<td><strong>Vickers Microhardness</strong></td>
<td>145 HV</td>
<td>366 HV</td>
<td>-</td>
</tr>
<tr>
<td><strong>Wear Resistance</strong></td>
<td>Good</td>
<td>Best</td>
<td>Poor</td>
</tr>
<tr>
<td><strong>Total Cost, per 1 m$^2$</strong></td>
<td>$18.19</td>
<td>$45.92</td>
<td>$42.15</td>
</tr>
</tbody>
</table>
Appendix D. Literature on the Wettability of Rare Earth Oxide Ceramics

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Ref.</th>
<th>REO Studied</th>
<th>Material Form</th>
<th>Synthesis Technique(s)</th>
<th>Microstructure</th>
<th>Hydrophilic / Hydrophobic</th>
<th>WCA</th>
<th>Grain Size</th>
<th>Characterization</th>
<th>Vacuum Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>Azimi</td>
<td>103</td>
<td>All</td>
<td>Sintered pellets, thin film</td>
<td>Sintering, sputter deposition</td>
<td>Polycrystalline</td>
<td>Hydrophobic</td>
<td>98-115</td>
<td>&gt; 10 μm for sintered pellets</td>
<td>SEM, XPS, XRD</td>
<td>Yes</td>
</tr>
<tr>
<td>2014</td>
<td>Preston</td>
<td>111</td>
<td>CeO₂, Ho₂O₃</td>
<td>Pellet</td>
<td>Sintering</td>
<td>Polycrystalline</td>
<td>Hydrophilic</td>
<td>0</td>
<td>&gt; 10 μm</td>
<td>SEM, XPS, AFM</td>
<td>No</td>
</tr>
<tr>
<td>2014</td>
<td>Oh</td>
<td>113</td>
<td>CeO₂, Er₂O₃, Dy₂O₃</td>
<td>Thin film</td>
<td>Atomic Layer Deposition</td>
<td>?</td>
<td>Hydrophilic</td>
<td>100-105</td>
<td>?</td>
<td>SEM, TEM, XPS, No</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>Khan</td>
<td>115</td>
<td>CeO₂</td>
<td>Thin Film</td>
<td>Sputtering</td>
<td>Nanocrystalline</td>
<td>Hydrophobic</td>
<td>104</td>
<td>?</td>
<td>XPS</td>
<td>Yes</td>
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<tr>
<td>2015</td>
<td>Cho</td>
<td>117</td>
<td>CeO₂</td>
<td>Nanorods</td>
<td>Hydrothermal</td>
<td>Nanocrystalline</td>
<td>Hydrophobic</td>
<td>160</td>
<td>10-300 nm</td>
<td>SEM, XPS, XRD</td>
<td>Yes</td>
</tr>
<tr>
<td>2015</td>
<td>Carchini</td>
<td>118</td>
<td>CeO₂, Nd₂O₃</td>
<td>DFT Study</td>
<td>-</td>
<td>Single Crystal</td>
<td>Hydrophobic</td>
<td>103</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2016</td>
<td>Pedraza</td>
<td>119</td>
<td>CeO₂</td>
<td>Coating</td>
<td>Electrochemical</td>
<td>Nanocrystal / Amorphous like</td>
<td>Hydrophobic</td>
<td>151</td>
<td>3 nm</td>
<td>SEM, XRD, XPS, Raman spectroscopy</td>
<td>Yes</td>
</tr>
<tr>
<td>2016</td>
<td>Cai</td>
<td>105</td>
<td>Yb₂O₃</td>
<td>Coating</td>
<td>Solution precursor plasma spray</td>
<td>?</td>
<td>Hydrophobic</td>
<td>161</td>
<td>?</td>
<td>SEM, XRD</td>
<td>Yes</td>
</tr>
<tr>
<td>2016</td>
<td>Sarkar</td>
<td>126</td>
<td>CeO₂, Lu₂O₃</td>
<td>Thin film</td>
<td>Pulsed laser deposition</td>
<td>Epitaxial (001)</td>
<td>Hydrophilic</td>
<td>71</td>
<td>?</td>
<td>AFM, XRD, XPS, RBS</td>
<td>No</td>
</tr>
<tr>
<td>2017</td>
<td>Fu</td>
<td>121</td>
<td>CeO₂</td>
<td>Thin film</td>
<td>Pulsed laser deposition</td>
<td>?</td>
<td>Hydrophilic</td>
<td>20</td>
<td>?</td>
<td>XPS</td>
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<td>2017</td>
<td>Lundy</td>
<td>122</td>
<td>CeO₂</td>
<td>Sintered pellets</td>
<td>Sintering</td>
<td>Polycrystalline</td>
<td>Hydrophilic</td>
<td>6</td>
<td>10 μm</td>
<td>SEM, XPS, AFM</td>
<td>Yes</td>
</tr>
<tr>
<td>2017</td>
<td>Kulah</td>
<td>123</td>
<td>CeO₂, Sm₂O₃, Ho₂O₃, Er₂O₃, Tb₂O₃</td>
<td>Thin film</td>
<td>Magnetron sputtering</td>
<td>Nanocrystalline</td>
<td>Hydrophilic</td>
<td>4</td>
<td>50-100 nm</td>
<td>XPS, AFM</td>
<td>No</td>
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<tr>
<td>2017</td>
<td>Lv</td>
<td>118</td>
<td>CeO₂</td>
<td>Thin film</td>
<td>Atomic Layer Deposition</td>
<td>?</td>
<td>Hydrophobic</td>
<td>96</td>
<td>?</td>
<td>XPS, AFM</td>
<td>Yes</td>
</tr>
<tr>
<td>2017</td>
<td>Shi</td>
<td>124</td>
<td>CeO₂</td>
<td>Thin film</td>
<td>Magnetron sputtering</td>
<td>Nanocrystalline</td>
<td>Hydrophobic</td>
<td>100</td>
<td>20 nm</td>
<td>TEM, XPS, AFM</td>
<td>No</td>
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<tr>
<td>2017</td>
<td>Nakayama</td>
<td>125</td>
<td>CeO₂</td>
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<td>Electrochemical</td>
<td>Nanocrystalline</td>
<td>Hydrophilic</td>
<td>19.7</td>
<td>20 nm</td>
<td>SEM, TEM, XPS</td>
<td>No</td>
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<tr>
<td>2018</td>
<td>Xu</td>
<td>126</td>
<td>Yb₂O₃</td>
<td>Coating</td>
<td>Solution precursor plasma spray</td>
<td>?</td>
<td>Hydrophobic</td>
<td>163</td>
<td>?</td>
<td>SEM</td>
<td>Yes</td>
</tr>
<tr>
<td>2018</td>
<td>An</td>
<td>224</td>
<td>CeO₂</td>
<td>Thin film</td>
<td>Magnetron sputtering</td>
<td>Nanocrystalline</td>
<td>Hydrophobic</td>
<td>143</td>
<td>20 - 200 nm</td>
<td>SEM</td>
<td>No</td>
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<tr>
<td>2018</td>
<td>Prakash</td>
<td>128</td>
<td>CeO₂, Sm₂O₃, Eu₂O₃, Gd₂O₃, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃</td>
<td>Thin film</td>
<td>Pulsed laser deposition</td>
<td>Epitaxial (001)</td>
<td>Hydrophilic</td>
<td>10-30</td>
<td>-</td>
<td>XRD, AFM, XPS, RBS</td>
<td>No</td>
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<td>Current</td>
<td>Current</td>
<td>Current</td>
<td>CeO₂, Er₂O₃</td>
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<td>Pulsed Laser Deposition / Epitaxial</td>
<td>Hydrophilic</td>
<td>31-58</td>
<td>-</td>
<td>-</td>
<td>RHEED, XRD, AFM, STEM, XPS</td>
<td>No</td>
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</table>
Appendix E. Optical Image of CeO$_2$ Epitaxial Film on YSZ (111) Single Crystal Substrate

Figure E-1. Optical image of CeO$_2$ epitaxial film on YSZ (111) single crystal substrate. The corners of the specimen were masked by the specimen holder during deposition.
Appendix F. Details of X-ray Reflectivity Calculations

Thin film thickness, density, and surface roughness can be determined by non-linear least-squares fitting of experimental X-ray reflectivity curve to a theoretical reflectivity curve. The calculation procedure for the theoretical curve applied in the Rigaku GXRR software package is described below.\(^{225}\)

X-ray reflection occurs at all interfaces in a multilayer film. The X-ray reflectivity of a multilayer film as a function of \(\theta\) can be theoretically calculated using the following recursion formula (Equation E1). The gas phase or vacuum on top of a film with \(n\) layers is defined as the 1st layer, i.e. \(j = 1\). Each layer in the multilayer film is labeled in sequence. For instance, the first film layer is \(j = 2\) and the substrate is \(j = n + 1\). The reflection coefficient at the interface between the \(j^{th}\) layer and \((j + 1)^{th}\) layer is defined as \(R_{j,j+1}\).

\[
R_{j,j+1} = \frac{R_{j+1,j+2} + F_{j,j+1}}{(R_{j+1,j+2})(F_{j,j+1})+1} a_j^{\frac{1}{2}} \quad [E1]
\]

where

\[
F_{j,j+1} = \frac{g_j - g_{j+1}}{g_j + g_{j+1}} \exp \left( \frac{-8\pi^2 g_j g_{j+1} \sigma_{j+1}^2}{\lambda^2} \right) \quad [E2]
\]

\[
a_j = \exp \left( -\frac{i\pi g_j d_j}{\lambda} \right) \quad [E3]
\]

\[
g_j = \sqrt{n_j^2 - \cos^2 \theta} \quad [E4]
\]

\(\lambda\) is the wavelength of the X-ray, \(\theta\) is the X-ray incidence angle, \(d_j\) and \(a_j\) are the \(j^{th}\) layer thickness and roughness, respectively, and \(n_j\) is the refractive index of material in layer \(j\). The calculation starts from the interface on top of the substrate, and then the next upper interface up to the surface layer \(R_{1,2} = \frac{l}{l_0}\). For each layer, there are 4 parameters: \(d_j\) layer thickness, \(a_j\) layer roughness, and parameters that are related to the refractive index \(n\) of a material, which can be calculated using the following equations:

\[
n = 1 - \delta - i\beta \quad [E4]
\]
\[ \delta = \left( \frac{r_e \lambda^2}{2\pi} \right) N_0 \rho \sum_k x_k (Z_k + f'_k) / \sum_k x_k M_k \]  \[ \text{[E5]} \]

\[ \beta = \left( \frac{r_e \lambda^2}{2\pi} \right) N_0 \rho \sum_k x_k (Z_k + f''_k) / \sum_k x_k M_k \]  \[ \text{[E6]} \]

\[ i: \text{ imaginary number} \]

\[ r_e: \text{ classical radius of an electron (2.818\times10^{-15} \text{ m})} \]

\[ N_0: \text{ Avogadro number} \]

\[ \rho: \text{ density (kg/m}^3\text{)} \]

\[ Z_k: \text{ Atomic number of the material } k \]

\[ M_k: \text{ Atomic weight of material } k \]

\[ x_k: \text{ atomic ratio of material } k \]

\[ f'_k, f''_k: \text{ atomic scattering factors of material } k \]
Appendix G. Time Dependent Wetting Behaviour of Al$_2$O$_3$ Single Crystals

Al$_2$O$_3$ (0001) and (01-12) oriented single crystals were also studied for their time-dependent wetting behaviour. Bulk single crystals (1 cm × 1 cm × 0.5 mm) were annealed in air at 1400°C for 30 minutes to obtain the step and terrace morphology as shown in Figure G-1. Similar to other oxides studied, upon cooling down to about 50°C room temperature, the first WCA measurement was performed to avoid the potential of airborne hydrocarbon adsorption. Additional WCA measurements were carried out subsequently as a function of storage time in ambient air, as shown in Figure G-2. Similar to other oxides studied in this thesis, WCA – crystallographic orientation relationships were only observed for a certain period of time. With exposure time in ambient air, the WCA increased and converged to a common WCA between orientations.

Figure G-1. AFM image of Al$_2$O$_3$ (0001) after annealing. Low energy step and terrace morphology can be observed.
Figure G-2. Time-dependent water contact angle of Al₂O₃ single crystals.