Tuned sustainable anodic coatings for reduced ice adhesion

Thirza Poot

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Herein, the effects of the anodizing voltage, electrolyte temperature and anodizing time on the morphology and wettability of TSA-anodized aluminum alloy 2024-T3 were studied by scanning electron microscopy (SEM) and contact angle (CA) measurements. The morphology in relation to wettability and ice adhesion strength as well as the use of posttreatments such as hydrothermal sealing and silanization was investigated. SEM images show a clear influence by the anodizing conditions on the porosity, interpore distance and pore diameter of the porous alumina. The morphology has influence on the wettability although the relationship needs further investigation. A superhydrophobic surface obtained by silanization of a surface anodized at high voltage characterized by a rod-like morphology has potential as a passive anti-icing surface. Future work may include additional polishing pretreatments, testing of additional parameters, investigating the CA hysteresis and roll-off angle as well as measuring the adhesion strength of high-impact ice. By tuning the morphology of sustainable anodic coatings, the research area is one step closer to implementing passive anti-icing materials in aircrafts.
Abstract

Aluminum alloys are widely used materials in the aircraft industry due to their high specific strength and durability. The natural corrosion resistance of aluminum can be improved through an electrochemical anodizing process. Due to recent restrictions in the use of chromic acid with toxic hexavalent chromium as electrolyte, the industry has shifted towards the use of the functional comparable tartaric sulfuric acid (TSA). TSA anodizing provides a porous alumina layer with good corrosion resistance, yet there is a desire to tune the process to fit other purposes. For instance, ice accretion to aircraft surfaces implies a safety risk and reduced energy efficiency. Due to insufficient active anti-icing systems, aircraft manufacturers are in the search for passive anti-icing materials. The ice adhesion properties of a material are thought to be affected by wettability. In turn, the wettability is affected by the morphology of the alumina influenced by the anodizing conditions.

Herein, the effects of the anodizing voltage, electrolyte temperature and anodizing time on the morphology and wettability of TSA-anodized aluminum alloy 2024-T3 were studied by scanning electron microscopy (SEM) and contact angle (CA) measurements. The morphology in relation to wettability and ice adhesion strength as well as the use of posttreatments such as hydrothermal sealing and silanization was investigated. SEM images show a clear influence by the anodizing conditions on the porosity, interpore distance and pore diameter of the porous alumina. The morphology has influence on the wettability although the relationship needs further investigation. A superhydrophobic surface obtained by silanization of a surface anodized at high voltage characterized by a rod-like morphology has potential as a passive anti-icing surface. Future work may include additional polishing pretreatments, testing of additional parameters, investigating the CA hysteresis and roll-off angle as well as measuring the adhesion strength of high-impact ice. By tuning the morphology of sustainable anodic coatings, the research area is one step closer to implementing passive anti-icing materials in aircrafts.

Key words: aluminum alloys, tartaric-sulfuric acid anodizing, ice adhesion, silanization, hydrothermal sealing, contact angle, SEM, corrosion
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First of all, I would like to express my gratitude to Saab Aeronautics and the research team of Molecular Surface Physics and Nanoscience at Linköping University for giving me the opportunity to gain this tremendous amount of knowledge about a fascinating topic. This thesis has been worthwhile for my personal development. I have learned so much about conducting research and about my possibilities.

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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CA</td>
<td>Contact angle</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>IFM</td>
<td>Department of Physics, Chemistry and Biology</td>
</tr>
<tr>
<td>HTS</td>
<td>Hydrothermal sealing</td>
</tr>
<tr>
<td>IADS</td>
<td>International Alloy Designation System</td>
</tr>
<tr>
<td>LIU</td>
<td>Linköping University</td>
</tr>
<tr>
<td>PBR</td>
<td>Pilling-Bedworth ratio</td>
</tr>
<tr>
<td>REACH</td>
<td>Registration, Evaluation, Authorization and Restriction of Chemicals</td>
</tr>
<tr>
<td>RISE</td>
<td>Research Institutes of Sweden</td>
</tr>
<tr>
<td>ROA</td>
<td>Roll-off angle</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SHS</td>
<td>Superhydrophobic surface</td>
</tr>
<tr>
<td>WCA</td>
<td>Water contact angle</td>
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## Chemical denotations

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>(CH₃)₂CO</td>
<td>Acetone</td>
</tr>
<tr>
<td>CH₃(CH₂)₇SiCl₃</td>
<td>Tri(chloro)octylsilane</td>
</tr>
<tr>
<td>C₃H₆OH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminum oxide, alumina</td>
</tr>
<tr>
<td>AlO(OH)</td>
<td>Boehmite</td>
</tr>
<tr>
<td>C₄H₆O₆</td>
<td>Tartaric acid</td>
</tr>
<tr>
<td>Ce</td>
<td>Cerium</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>Trivalent chromium</td>
</tr>
<tr>
<td>Cr(IV)</td>
<td>Tetravalent chromium</td>
</tr>
<tr>
<td>Cr(V)</td>
<td>Pentavalent chromium</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>Hexavalent chromium</td>
</tr>
<tr>
<td>Cr₂O₇²⁻</td>
<td>Dichromate</td>
</tr>
<tr>
<td>CrO₄²⁻</td>
<td>Chromate</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>H₂CrO₄</td>
<td>Chromic acid</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>Mn</td>
<td>Manganese</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen (gas)</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>TSA</td>
<td>Tartaric Sulfuric Acid</td>
</tr>
<tr>
<td>W</td>
<td>Tungsten</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Zirconium</td>
</tr>
<tr>
<td>Zn</td>
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### 1 Introduction

A high specific strength, i.e. strength-to-weight ratio, and durability is desired for materials used in aerospace and aircraft industries. Aluminum (Al) alloys are the most widely used materials that meet these requirements. [1] When employing Al alloys in aircrafts, corrosion [1] and paint adhesion [2] properties of the used material need to be considered for economical, safety and environmental reasons.

Al exhibits a natural corrosion protective layer consisting of Al oxide (alumina, Al₂O₃) that is formed on the surface upon exposure to oxygen [3]. However, alloys containing elements such as copper (Cu) often exhibit insufficient corrosion resistance, creating a need for additional surface treatments [4]. Anodizing is a simple, cost-effective and versatile electrochemical process which improves corrosion and wear resistance by thickening the natural oxide film into a layer with porous morphology [1, 5]. Chromic acid (H₂CrO₄) is one of most widely used anodizing electrolytes in the aircraft industry [6] but has become strictly regulated due to the toxicity of hexavalent chromium (Cr(VI)) to humans and the environment. The use of Cr(VI) is controlled by a regulation of the European Union (EU) called REACH, which stands for Registration, Evaluation, Authorization and Restriction of Chemicals. [7] For this reason, Saab AB Business Area Aeronautics ("Saab Aeronautics") has replaced chromic acid with a functional comparable but non-toxic electrolyte mixture of tartaric acid (C₄H₆O₆) and sulfuric acid (H₂SO₄) denoted TSA [8]. When anodizing in acidic electrolytes such as TSA, the alumina film consists of a porous oxide layer which rests upon a compact barrier layer [9]. The morphology of the porous layer, often discussed in terms of porosity, pore diameter, pore wall thickness and interpore distance, is affected by anodizing conditions such as voltage [6], electrolyte temperature and anodizing time [10, 11].

In addition to issues that arise from insufficient corrosion resistance and paint adhesion, ice accretion on aircraft surfaces such as wings and wind turbine blades implies a safety risk and reduced energy efficiency [12]. The ice adhesion properties of a surface are influenced by the wettability of a surface [13]. In turn, the wettability is thought to be changeable with the morphology of the porous alumina formed when anodizing [14]. Furthermore, posttreatments such as hydrothermal sealing (HTS) [15] and silanization [16] of the alloys after anodizing can be applied for further control of the morphology, corrosion resistance, paint adhesion and ice adhesion.

#### 1.1 Purpose

The purpose of this project is to further investigate the influence of anodizing conditions on the morphology of the porous alumina on Al alloys used in aircrafts. The relation between ice adhesion and morphology-dependent wettability is enlightened and additional post-treatments are applied to obtain tuned sustainable anodic coatings for reduced ice adhesion.

#### 1.2 Expected impact of work

The anodizing process could be adjusted to suit a specific application if the influence of post-treatments as well as anodizing conditions on the morphology of porous alumina is investigated. When aircraft parts are anodized by Saab Aeronautics, the process could be customized for improved corrosion resistance, paint adhesion or ice adhesion properties.
Furthermore, by replacing chromic acid with TSA Saab Aeronautics contributes to a more environmental-friendly and less toxic industry.

Tunable anodic coatings can help to improve the aircraft industry in terms of cost-efficiency, safety and environmental sustainability. With improved corrosion resistance, which may be achieved by sufficient paint adhesion, the need of maintenance and replacement of aircraft parts can be minimized. With no or less ice adhesion, the risk for fatal accidents and fuel consumption is reduced. Furthermore, extensive anti-icing systems on aircrafts will become redundant leading to a decrease in construction costs and a less negative impact on the environment.

1.3 Project objectives

The process and main objective of this master’s thesis is initially defined in the planning report written during the first few weeks of this thesis (Appendix I - Planning Report). The main objective is to illuminate the effects of parameters such as voltage, electrolyte temperature and anodizing time on the anodizing process of Al alloys. Furthermore, surface morphology, wettability and adhesion properties will be investigated, including the use of additional posttreatments. The main objective can be divided into the following sub-objectives:

1. The effect of anodizing voltage on the morphology of anodic Al coatings is investigated.
2. The effect of electrolyte temperature on the morphology of anodic Al coatings is investigated.
3. The effect of anodizing time on the morphology of anodic Al coatings is investigated.
4. The effect of anodizing conditions and the morphology of anodic Al coatings on wettability and ice adhesion of Al alloys is investigated.
5. The effect of the posttreatment methods silanization and HTS of anodized Al coatings on wettability and ice adhesion properties is investigated.

The morphology and wettability of the anodized alloys are characterized using scanning electron microscopy (SEM) and goniometry, respectively. Ice adhesion measurements are performed at Research Institutes of Sweden (RISE). The first step of this master’s thesis is to perform a literature study, found in Chapter 2, which lays the foundation for the experimental study conducted in this project.

1.4 Boundary conditions

This master’s thesis is written on behalf of the research team of Molecular Surface Physics and Nanoscience at the department of Physics, Chemistry and Biology (IFM) at Linköping University (LiU) and conducted in collaboration with Saab Aeronautics as well as RISE Surface, Process and Formulation.

In 1975, LiU was the 6th university to be founded in Sweden. Today, LiU has 4 000 employees and 32 000 students divided at four faculties: Arts and Sciences, Medicine and Health Sciences, Educational Sciences and Science and Engineering. The faculties are further divided into 14 multidisciplinary departments where the actual education and research is conducted. [17] IFM is one of the departments at the Faculty of Science and Engineering and has approximately 420 employees. The department is organized in several scientific areas, one being Applied Physics. [18] The research team of Molecular Surface Physics and Nanoscience is active in the field of Applied Physics, more specifically nanomaterial and molecular thin film
1.4. Boundary conditions

physics and spectroscopy. [19] The research team and IFM provides laboratory facilities, materials and equipment as well as the examiner and two supervisors.

Saab AB is a Swedish defense and security company with over 16,000 employees and business areas such as aeronautics, kockums, surveillance, support and services, industrial products and dynamics. The company was founded in 1937 with the mission to maintain Sweden's security in terms of military aircrafts during World War II. Today, Saab operates on every continent to serve the global market in areas ranging from military defense to civil security with world-leading products, services and solutions. [20, 21] Saab Aeronautics cooperates closely with LiU and provides the problem of this master's thesis as well as laboratory material. One of the supervisors provided by LiU is partly employed at Saab Aeronautics.

RISE is an independent research institute and innovation partner owned by the Swedish state. The mission of RISE is to work for sustainability and innovation in the Swedish industry while the competitiveness is strengthened. [22] RISE was founded in 2009 when IRECO Holding AB, a holding company founded in 1997 by the Swedish Government, changed their name. Between 2009 and 2016, the institutes Swedish ICT, Innventia and SP Technical Research Institute of Sweden merged together with RISE to create a uniform institute. A majority of the shares in research group Swerea were bought in 2018. [23] The 2,700 employees at RISE today are divided into six divisions: Bioeconomy, Bioscience and Materials, Built Environment, Information and Communication Technology (ICT), Materials and Production, and Safety and Transport [24]. The division of Bioscience and Materials, more specifically the department of Surface, Process and Formulation, provides this master's thesis with knowledge and equipment for ice adhesion measurements.
2 Theory

In this chapter, the scientific background for this master’s thesis is presented. A description of Al and its alloys following by surface treatments such as anodizing, HTS and silanization will be presented. Furthermore, the relevance of this master’s thesis will be discussed in terms of environmental aspects, corrosion resistance, ice adhesion and wettability.

2.1 Aluminum and aluminum alloys

Al is the most abundant metallic element in the earth’s crust although it never occurs in the metallic form in nature due to its chemical activity. During the late 19th century, commercial methods for producing Al became available and in the 1960s, Al exceeded Cu in the world production of nonferrous metals. [25] Today, only steel surpasses Al in its use as structural material [3]. However, metals are rarely used in commercial applications in their pure state. Metals are often alloyed with one or several other elements to adjust the material properties to specific applications. Al has a density approximately one-third of that of steel resulting in a light weight metal with high strength when alloyed with other materials. [26] The high strength-to-weight ratio (also called specific strength) and durability has made the Al alloys the most widely used materials in aerospace and aircraft industries [1].

Al alloys are divided into two major categories: cast compositions and wrought compositions. The main difference between the categories is the primary mechanism of property development. [26] Cast products are produced using several casting techniques whereas wrought products are produced by forging, rolling or extrusion [27]. Wrought Al alloys are in many countries designated by a four-digit numerical system developed by the Aluminum Association called the International Alloy Designation System (IADS). IADS categorizes Al alloys in series, represented by the first digit, depending on their composition as presented in Table 2.1. [28]

<table>
<thead>
<tr>
<th>Series</th>
<th>Alloy composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1xxx</td>
<td>Aluminum (Al), at least 99.00 % purity</td>
</tr>
<tr>
<td>2xxx</td>
<td>Copper (Cu)</td>
</tr>
<tr>
<td>3xxx</td>
<td>Manganese (Mn)</td>
</tr>
<tr>
<td>4xxx</td>
<td>Silicon (Si)</td>
</tr>
<tr>
<td>5xxx</td>
<td>Magnesium (Mg)</td>
</tr>
<tr>
<td>6xxx</td>
<td>Magnesium (Mg) and Silicon (Si)</td>
</tr>
<tr>
<td>7xxx</td>
<td>Zinc (Zn)</td>
</tr>
<tr>
<td>8xxx</td>
<td>Other elements</td>
</tr>
<tr>
<td>9xxx</td>
<td>Unused series</td>
</tr>
</tbody>
</table>

Table 2.1: Al alloy series and their compositions according to IADS [28].

In this project, the Al alloy 2024-T3, of which the composition is shown in Table 2.2, is investigated due to the common use of this alloy in Saab Aeronautics’ aircraft production. Cu-rich alloys exhibit improved mechanical properties [29] and can for example be used in parts such as shear webs in aircraft wings and the main body of the aircraft (fuselage) where toughness, fatigue and mechanical strengths are important properties [6]. T3 represents the temper designation used to heat treat the alloy. The letter T describes that the alloy is solution heat treated whereas the digit indicates a specific sequence of basic treatments. In this case, the
alloy is cold worked and naturally aged to a substantially stable conditions improving the strength of the material. [3]

**Table 2.2:** Al alloy 2024-T3 is composed (%) of elements such as Copper (Cu), Magnesium (Mg), Manganese (Mn), Silicon (Si), Iron (Fe), Zinc (Zn), Titanium (Ti), Chromium (Cr) and others. [28].

<table>
<thead>
<tr>
<th>Aluminum Alloy</th>
<th>Cu</th>
<th>Mg</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Zn</th>
<th>Ti</th>
<th>Cr</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>2024-T3</td>
<td>3.8-4.9</td>
<td>1.2-1.8</td>
<td>0.3-0.9</td>
<td>0.5</td>
<td>0.5</td>
<td>0.25</td>
<td>0.15</td>
<td>0.1</td>
<td>0.15</td>
</tr>
</tbody>
</table>

### 2.2 Corrosion resistance

Al alloys are widely used in aircraft industry due to their high specific strength and durability. The specific strength is said to be an intrinsic property of the alloy, while durability largely depends on interactions between the alloy surface and its surrounding environment. [1] Corrosion influences an alloy’s durability by a slow, progressive or rapid deterioration of the material’s properties such as its appearance, surface or mechanical properties. The deterioration is caused by the electrochemical reaction between the surface and an aqueous phase. [4] The mechanisms of corrosion are not completely understood but in order for corrosion to proceed, five criteria need to be met: (i) an anode, (ii) a cathode, (iii) continuous electrical contact between the anode and cathode, (iv) an electrolyte with free ions and (v) a cathodic reactant (e.g. H₂O, or H₂ or O₂). [2]

Vargel [4] describes the corrosion of Al as follows. Two simultaneous reactions that are in equilibrium are responsible for the corrosion of a metal. Firstly, the loss of electrons of the metal at an anodic site, called oxidation. Secondly, The gain of electrons at a cathodic site, called reduction. For Al, oxidation occurs as described by Equation 2.1.

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad (2.1)
\]

For nearly neutral solutions, two reduction reactions that balance the oxidation can occur. The reduction of H⁺ (Equation 2.2), and the reduction of oxygen dissolved in water (Equation 2.3 for alkaline or neutral media, or 2.4 for acidic media).

\[
3\text{H}^+ + 3e^- + \frac{3}{2}\text{H}_2 \quad (2.2)
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (2.3)
\]

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad (2.4)
\]

The dissociation of water molecules (Equation 2.5) and the corrosion of Al in the presence of H₂O can be summarized by Equation 2.6, where Al(OH)₃ precipitates as a white gel.

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad (2.5)
\]

\[
\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \frac{3}{2}\text{H}_2 \quad (2.6)
\]

One advantage of Al is the formation of a natural inert alumina film on a surface upon exposure to the atmosphere due to a high affinity for oxygen [3, 26, 30]. The colorless, transparent, thin film protects the metal of further oxidation which causes other metals like steel to corrode. Additionally, instant resealing occurs upon damage to the protective layer, unlike iron
rust which easily flakes off. [26] The self-protecting alumina layer gives Al a high corrosion resistance. When alloyed and treated correctly, Al can resist corrosion by environmental factors such as salt and water as well as by many other physical and chemical substances [3, 26]. However, when Al is alloyed with Cu, such as in the 2024-T3 alloy, the anodic and cathodic sites (Al and Cu, respectively) are in constant contact making these alloys particularly prone to corrosion. The only way to inhibit corrosion is to avoid contact with an electrolyte and cathodic reactant. [2] This can be done by applying surface treatments such as anodizing which aims to enhance the corrosion resistance of alloys.

2.3 Anodizing

Anodizing is a cost-effective and simple electrochemical process which thickens the natural alumina film formed on an Al alloy in order to improve corrosion and wear resistance. [1, 5]. When anodizing Al in aqueous electrolyte solutions, two different alumina films can be formed: barrier and/or porous oxide films, as shown in Figure 2.1 [31]. When anodizing Al in neutral solutions [31] or solutions of pH 5-7 [30] such as borate, phosphate and adipate electrolytes, a non-porous barrier layer is formed. The barrier layer consists of a thin, dense amorphous oxide layer with a uniform thickness proportional to the applied voltage. [31]

When anodizing in acidic electrolyte solutions such as sulfuric acid, phosphoric acid and chromic acid, a porous oxide film is formed on top of the barrier layer [9]. A well-organized porous layer is characterized by a honeycomb cell structure with nanopores separated by cell walls perpendicular to the Al surface. [1, 31]

![Diagram of Barrier oxide film and Porous oxide film](image)

Figure 2.1: Depending on the electrolyte, two types of alumina films can be formed. The barrier oxide film consists of a thin, dense barrier layer and the porous oxide film consists of a porous layer grown upon the barrier layer.

In the aircraft industry, chromic acid is a commonly used electrolyte when anodizing Al [6]. However, due to the toxicity to humans and the environment, the use of chromic acid is strictly regulated by REACH.

2.4 REACH

REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) is a regulation of the EU adopted in 2007 to protect the environment and humans from risks due to chemical exposure. The regulation applies to all substances used in industrial processes as well as in everyday lives. It has to be demonstrated how a substance can safely be used before it can be manufactured and marketed in the EU. The use of a substance can be restricted if the chemical cannot be handled safely and the goal is to substitute hazardous substances with those being safer to use. [32]
The need of replacements for chromic acid anodizing has largely increased since, as of September 2017, the usage of hexavalent chromium (Cr(VI)), is restricted for industrial purposes due to its carcinogenic and mutagenic properties [7].

2.5 Chromium

Chromium (Cr) is a naturally occurring heavy metal and one of the most abundant elements of the earth's crust. Heavy metals are metallic elements with a relatively high density (4 g/cm$^3$) and are known for their toxic effects even at low concentrations. Due to a fast industrialization of countries, environmental contamination by heavy metals has become a huge issue. [33] Besides anodizing processes, Cr and chromic acid is widely used for metal decoration, inks, anticorrosive coating agents, paints and fuels [34]. Cr mainly exists in the form of Cr compounds such as the ore chromite (FeO$\text{Cr}_2\text{O}_3$), but is also distributed in air, soil, water and food. [33]

Cr exists in several oxidation states ranging from -II and +VI, whereof Cr(VI) and trivalent Cr (Cr(III)) are the most stable oxidation states in nature. [34] The remaining states are metastable and do therefore not occur naturally. Cr(III) is the most common form and is found in soil and aquatic environments due to its ability to interact with organic matter. Cr(VI) has a strong oxidizing potential and often forms chromate (Cr$\text{O}_4^{2-}$) or dichromate (Cr$\text{O}_7^{2-}$) ions, making Cr(VI) more water soluble than Cr(III). [35] The two stable oxidation states further differ in their bioavailability, solubility, mobility and toxicity [33] and their effects on humans, animals and the environment need to be thoroughly considered.

2.5.1 Toxicity to humans

Cr(III) and Cr(VI) do not only differ in their oxidation states and chemical properties, but also in toxicity [36]. Cr(III) is considered to play an essential role in lipid and glucose metabolism and is even used as a dietary supplement [34]. For instance, Cr(III) has beneficial effects on regulation of glucose levels [37]. However, Cr(III) causes negative effects on cellular structures at high concentrations [34]. On the other hand, Cr(VI) causes cell injuries to DNA, chromosomes and epigenome [36] by interacting with nucleic acids and other cellular components [33]. Cr(VI) is a hundred times more toxic than Cr(III) and exposure to Cr(VI) has been linked to epithelial irritation, cancers, degenerative diseases and inflammatory diseases. Cr(VI) enters the human body by ingestion, inhalation or absorption by the skin and is able to act directly at the site of contact or by transported to other tissues. For instance, Cr is absorbed through the lungs and transported to kidney and liver through the blood system upon inhalation. Upon dermal exposure, Cr(VI) can directly act as an oxidant or be absorbed through the skin.

Less water soluble compounds containing Cr(III) may be taken up by prokaryotic and some phagocytically active eukaryotic cells by endocytosis causing genotoxic effects. Furthermore, research has shown that kinetically inert octahedral Cr(III) anions can cross cell membranes of erythrocytes (red blood cells), hepatocytes (liver cells) and thymocytes (thymus cells) slowly by diffusion. However, cells are still relatively impermeable to Cr(III) while Cr(VI) readily enters cells. Erythrocytes, hepatocytes and thymocytes can take up Cr(VI) in the form of tetrahedral chromate anions (Cr$\text{O}_4^{2-}$) via non-selective anion transporters since Cr(VI) compounds are structurally similar to phosphate (PO$_4^{3-}$) and sulfate (SO$_4^{2-}$) anions [38]. After entering the cell, Cr(VI) is reduced to Cr(III) after a series of metabolic reductions of the intermediate pentavalent (Cr(V)) and tetravalent (Cr(IV)) oxidation states [36]. During the production of Cr intermediates, reactive oxygen species (ROS) are released. The reduction of Cr(VI) to Cr(III) together with the production of ROS results in oxidative stress, protein damage, cell proliferation, inflammation, DNA damage and tumor formation in humans and animals. [33] Due to the use of the anion transport system together with the metabolic reduction reactions, Cr
is able to accumulate to higher intracellular concentrations than extracellular concentrations [37]. The reduction of Cr(VI) in cells and the toxic effects are summarized in Figure 2.2.

**Figure 2.2:** Chromium is released into the environment by the industrial use of chromium compounds. Chromium exists in oxidation states ranging from -II to +VI whereof Cr(VI) is toxic to humans, animals and plants. Cr(VI) is able to enter cells in the form of chromate (CrO$_4^{2-}$) through non-selective anion transporters due to the structural similarity to sulfate (SO$_4^{2-}$) and phosphate (PO$_4^{3-}$) anions. In the cytoplasm of a cell, hexavalent chromate is reduced to Cr(III) which may cause DNA and protein damage. During the reduction, the formation of the intermediate compounds Cr(IV) and Cr(IV) leads to the formation of reactive oxygen species (ROS) and oxidative stress. Overall, the reduction leads to cell proliferation, inflammation and tumor formation.

Besides the carcinogenic effect, Cr(VI) compounds are genotoxic due to their solubility in water. The genotoxicity can be expressed as gene mutation, sister chromatid exchange, chromosomal aberration, DNA damage and cell transformation. During the reduction of Cr(VI) to Cr(III) after cellular uptake, highly mutagenic DNA adducts that inhibit DNA replication are produced, causing the genotoxic effect. [33] The gene mutations are induced by interference with DNA protein cross-links leading to single-strand breakage [35]. Cr(VI) may also cause respiratory effects upon inhalation whereas cardiovascular or reproductive and developmental effects in humans are less understood. [33]

### 2.5.2 Environmental hazards

Besides humans, Cr compounds do also have genotoxic, mutagenic, carcinogenic and toxic effects on plants and microorganisms. Plants do not have specific mechanisms for uptake of Cr since it is a nonessential element. Instead, the uptake of the heavy metals occurs through carriers normally used to for the uptake of elements essential to the plant metabolism. [39] In plants, Cr(VI) is more toxic than Cr(III) due to its solubility and permeability to cross the cell membrane [33]. The uptake of Cr(VI) involves carriers of essential anions such as sulfate...
which are structurally similar to Cr anions [39]. The toxic effects to plants include retardation of their growth and development (phytotoxicity), degradation of pigments, nutrient imbalance and oxidative stress. [33]

Cr is an essential nutrient for living organisms such as microbes although they are sensitive to a deficiency or redundancy of the heavy metal. Cr(VI) is mutagenic and toxic to most bacteria, inhibiting cell growth. Similar to the Cr metabolism in humans, animals and plants, Cr(VI) crosses biological membranes through the sulfate uptake pathway and is readily reduced into Cr(V) and Cr(III), resulting in toxic effects in the cytoplasm. Also in bacteria, the reduction process of Cr(VI) causes the formation of ROS leading to DNA damage and genotoxic effects. [33]

As Cr(VI) is relatively soluble and can move through groundwater and soil. Soil contamination alters microbial communities reducing their growth by retarding enzymatic activities. [33] In turn, Cr can enter the human food chain due to accumulation in crops grown in contaminated soils, causing health effects [40]. Furthermore, concentrations of the heavy metal in the environment continue to increase drastically due to its use in many industrial processes, especially in developing countries [33]. Today's technologies to take care of Cr in industrial waste water often involve the aqueous reduction of Cr(VI) using reducing agents and pH adjustments in order to precipitate the less soluble Cr(III). This treatment requires enormous amounts of energy and chemicals making it insufficient and costly. Other available treatments are adsorption, membrane separation and ion exchange but their disadvantages include incomplete removal, secondary pollution and high-energy requirements. However, research has focused on finding better alternatives, such as bioremediation. Bioremediation refers to the use of the metabolic capacities of microorganisms to transform pollutants, contaminants and toxins into less dangerous or harmless compounds. Bioremediation of Cr(VI) to Cr(III) is possible due to the Cr(VI)-reducing ability found in some bacteria, allowing for a more cost-effective green treatment of Cr(VI)-contaminated waste. [34]

2.5. Replacements for chromium in aircraft industry

The restrictions for using Cr(VI) compounds due to toxicity and environmental reasons has largely affected the aerospace and aircraft industry. As mentioned, chromic acid with Cr(VI) is commonly used in aircraft industry to improve the corrosion resistance of Al alloys through anodizing. [2] For the anodizing process, there are several electrolytes that can serve as replacement for chromic acid. To form the porous anodic oxide film on the substrate, acidic electrolytes such as oxalic acid, phosphoric acid, and sulfuric acid can be used. Sulfuric acid is favored for several reasons including low cost, the ability to anodize at relatively low voltage (15-40 V) compared to other acidic electrolytes, the fabrication of pores at nanoscale and the possibility to improve the mechanical properties of the alloys when anodizing at low temperature (≤ 0°C). [31]

Sulfuric acid can be used for anodizing with or without the addition of a modifier, such as tartaric acid. Tartaric acid is an organic acid which produces alumina films with self-ordered porosity [41]. Tartaric sulfuric acid (TSA) is a less toxic and more environmentally-friendly alternative to chromic acid [6]. While the hazards of chromic acid are many and the substance is strictly regulated [42], neither sulfuric acid or tartaric acid are classified as hazardous to humans or the environment [43, 44]. Furthermore, TSA produces anodic alumina layers comparable to those formed when using chromic acid anodizing [45]. Surfaces anodized in TSA have superior corrosion resistance when compared to surfaces anodized in only sulfuric acid [41, 46]. It is suggested that the superior corrosion resistance is due to the presence of tartaric acid residues in the pores, influencing the pH stability associated with corrosion [47]. It is also discussed that the addition of tartaric acid, which is a weaker acid than sulfuric acid, reduces
the aggressiveness and dissolution effect of the electrolyte, favoring the growth of the anodic oxide layer [46, 48].

Although the TSA anodizing process is very similar to chromic acid anodizing, TSA anodizing has a reduced process time (20-25 min) and anodizing voltage (13-15 V) compared to chromic acid anodizing (45 min and 40 V or 21 V). These differences improve the eco-efficiency by increasing the process capacity and decreasing the energy consumption. [49] TSA is used by Saab Aeronautics as electrolyte when anodizing Al parts for corrosion protection [8] and is therefore used in this master’s thesis as well. Observations have been made by Saab Aeronautics that the strength of Al alloys is less affected when using TSA compared to using sulfuric acid only [50]. In addition to the electrolyte, there are several other parameters influencing the morphology of the anodic alumina layer.

2.6 Morphology of anodic alumina

When anodizing in acidic solutions such as TSA, the formed anodic alumina consists of a thin barrier layer and a thick porous oxide layer [9]. The porous oxide layer is formed as a result from two competitive reactions: the formation and dissolution of alumina. The reaction mechanism of anodic oxidation of Al can be described by the total chemical reaction shown in Equation 2.7 and two partial reactions, Equations 2.8 and 2.9. [51]

$$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \quad (2.7)$$

$$2\text{Al} \rightarrow 2\text{Al}^{3+} + 6\text{e}^- \quad (2.8)$$

$$3\text{H}_2\text{O} \rightarrow 6\text{H}^+ + 3\text{O}^{2-} \quad (2.9)$$

The two partial reactions shown above describe the formation of alumina due to migration of Al$^{3+}$ ions from the metal substrate into the electrolyte solution, while to movement of O$^{2-}$ occurs in the opposite direction. The porous morphology is the result from an electrochemical and chemical dissolution of alumina. A local increase in H$^+$ concentration (Equation 2.7) and an electric field in the barrier layer causes the dissolution effect. A local increase in temperature is caused during the anodizing process, and this also enhances the dissolution reaction. The pores are formed due to impurities and defects such cracks in the metal substrate. When the barrier layer reaches a critical thickness, pores are initiated in these impurities and defects. Just a fraction of the pores initially formed will compose the final honeycomb cell arrangement. [51]

The morphology of anodic coatings is often discussed in terms of the distance between pores (interpore distance), pore diameter and pore wall thickness, as described by Figure 2.3. The morphology and topography of a surface can further be described by the term porosity. Porosity is a quantitative parameter that either can be expressed as the area fraction [%] occupied by pores [11, 52, 53], or as a function of the pore diameter and interpore distance (Equation 2.10) [54, 55]. The morphology of the anodic layer can be modified and tuned by the selection of anodizing conditions such as applied voltage, electrolyte temperature [6, 10] and anodizing time [11].
The morphology of the porous layer grown upon the barrier layer is often described in terms of pore wall thickness, pore diameter and interpore distance.

\[
\frac{\pi}{2\sqrt{3}} \cdot \left( \frac{\text{Pore diameter}}{\text{Interpore distance}} \right)^2
\]

(2.10)

2.6.1 Voltage

There are a number of studies that describe the effect of anodizing voltage on the morphology of the porous alumina layer. Kikuchi et al. [31] states that the interpore distance of the porous alumina increases with the anodizing voltage when anodizing in acidic solutions. Tomassini and Buczko [51] as well as O’Sullivan and Wood [56] confirm that the barrier layer thickness, interpore distance and pore diameter are proportional to the applied voltage.

Belwalkar et al. [11], anodized Al substrates at 12.5 V, 15 V or 20 V in sulfuric acid and at 30 V or 50 V in oxalic acid. The results show that the pore size increases with increasing voltage and that the interpore distance is linearly proportional to the voltage irrespective of the used electrolyte. The author further describes that the formation of pores occurs simultaneously with a volume expansion during the alumina formation at the metal-oxide interface, expressed by the Pilling-Bedworth ratio (PBR). PBR is defined as the ratio between the volume of the oxide produced and the volume of metal consumed. Due to the volume expansion, the oxide is pushed upwards and in tangential direction increasing the thickness of the layer. A higher voltage results in a higher volume expansion, decreasing the pore wall thickness and thus forming larger pores.

In a study conducted by Debuyck et al. [10], where substrates were anodized in sulfuric acid and a voltage between 3-18 V, it was concluded that increasing the voltage results in a decreased porosity. Costenaro et al. [6] also investigated the influence of voltage on the morphology of the alumina layer when anodizing Al substrates alloyed with Cu (2524-T3). Anodizing was performed using TSA as electrolyte and voltages between 8-16 V. Similarly to Debuyck et al. [10] the results show that the pore diameters increase while the porosity slightly decreases. This could be explained by an increase in interpore distance and that a higher voltage favors the growth of the layer compared to its dissolution. Similar results were obtained by Sulka et al. [57], who anodized high-purity Al sheets in sulfuric acid.

2.6.2 Electrolyte temperature

Besides the finding that the voltage influences the porosity of anodized alumina, Debuyck et al. [10] also concluded that a rise in electrolyte temperature from 0 to 28 °C results in an increase in the porosity. Aerts et al. [53] studied the influence of the anodizing temperature
on the porosity of the anodic oxide film formed on 1050 Al alloys using sulfuric acid as electrolyte. Electrolyte temperatures between 5 and 55 °C were tested with a constant voltage and an anodizing time adjusted to obtain equal alumina thickness for all substrates. The authors observed that an increasing temperature leads to increasing pore diameters and declining pore wall thicknesses. These observations concur with the calculated porosity which increased with increasing temperature and are in line with the conclusion of Debuyck et al. [10].

Furthermore, Ma et al. [46] studied the influence of temperature on anodizing of a lithium containing Al alloy (2099-T8) in TSA. When anodizing at temperatures from 22 to 47 °C, film growth rate and current density increased with increasing temperature. The pore diameter, which is proportional to the applied voltage, should theoretically be the same for all temperatures. However, the pore diameters increased slightly with increasing temperature, motivated with a more pronounced dissolution of the anodic film. One study performed by Mubarok et al. [29], in which 2024-T3 samples were anodized in TSA, indicates that a lower temperature, in this case 20 °C, results in a more compact layer with fewer pores, compared to a higher temperature, 40 °C. In line with Ma et al. [46], Mubarok et al. [29] discusses that the more compact layer is most likely to be caused by a slower dissolution of the oxide layer at lower temperatures.

### 2.6.3 Anodizing time

Although the anodizing time often is related to the thickness of the oxide layer [11, 29, 51, 53, 55], the effect on the morphology, especially when using TSA as electrolyte, is so far not fully investigated. Ilango et al. [55] investigated the relation of pore diameter and interpore distance to anodizing time in a two-step anodizing process of high purity Al samples in oxalic and orthophosphoric acid, respectively. The anodizing time of the second step was increased from 1 to 3 min for which the pore diameter increased linearly. The pore cell diameter, which is the sum of pore diameter and pore wall thickness also increased linearly with anodizing time. However, the porosity seemed to be maximized at a certain time point, above which the porosity was saturated.

Both Buijsters et al. [14] and Vidyasagar et al. [54] studied the pore arrangement and surface porosity as a function of anodizing time when anodizing high-purity Al in phosphoric acid. In the case of Buijsters et al. [14], Al alloy 1050 substrates were anodized in two steps in phosphoric acid. The second step was varied from 15-300 min to achieve different thickness. In accordance to the findings of Ilango et al. [55], the surface porosity was found to be nearly constant. Also, the pore arrangement was somewhat disorganized, with a wide distribution of pore diameters. As for Vidyasagar et al. [54] an increase in pore diameter and porosity together with a decrease in pore wall thickness was observed when increasing the anodizing duration from 5 to 30 minutes with pores well distributed over the surface. The authors argued that the arrangement of the pores can be significantly improved by adjusting the anodizing time while keeping the concentration, temperature and voltage static. The pore diameters were larger at the oxide surface than at the metal-oxide interface where the oxide is being most recently formed (the pore-base). Both Vidyasagar et al. [54] and Aerts et al. [53], who also observed this phenomena, state that the widening of the pores may occur due to increasing time of exposure to the electrolyte and its dissolving action.

The morphology of the anodic alumina layer may influence the properties of the anodized alloy. Properties as wettability, ice and paint adhesion as well as corrosion resistance are of importance in aircraft and aerospace industry and are therefore important to consider when tuning the anodizing conditions.
2.7 Ice adhesion

The adhesion of ice to aircrafts is a threat to flight safety and the environment. When ice is formed on aircraft surfaces, it may increase weight and change the weight distribution leading to the loss of control of the aircraft. [58] Ice shedding from fan blades may enter the engine and cause damage [59]. Anti-icing systems are often implemented to remove ice that has formed on a surface. However, frequent application is required and the systems are expensive. [60] The anti-icing protocols often have a negative impact on the environment due to the use of freeze retarding chemicals and energy consumption for heating [61]. Additionally, the increase in weight due to the anti-icing systems themselves reduce fuel efficiency. Due to the safety and environmental issues with ice adhesion and in combination with insufficient active anti-icing systems, it is necessary to develop new methods to reduce ice adhesion. [62] The use of passive anti-icing technologies based on the physical and/or chemical properties of a material could be the solution [12]. One property thought to influence ice adhesion is the wettability of a surface [13, 60, 63].

2.7.1 Wettability

Wettability can be described by the behavior of liquid droplets on a solid surface. The interfaces that arise between the solid (S), liquid (L), and gas (G) will establish an equilibrium between the three interfacial tensions (γ_{LS}, γ_{GL} and γ_{GS}). The wettability of substrates is distinguished by measuring the contact angle (CA), θ, which is the angle between the tangent to the liquid surface and the solid surface, as shown in Figure 2.4A). [64] The CA is related to the interfacial tensions by the Young's equation shown in Equation 2.11 [63]. On hydrophobic surfaces with lower surface energy, the liquid droplet rolls up into a ball, represented by a CA of θ > 90°. In contrast, the liquid droplets spread on a hydrophilic surface, indicated by θ < 90°. [64]

$$\cos(\theta) = \frac{\gamma_{GS} + \gamma_{LS}}{\gamma_{GL}}$$

(2.11)

The Young’s equation describes the equilibrium CA for ideal surfaces. However, for non-ideal surfaces that exhibit surface roughness the Cassie-Baxter and Wenzel states can instead be used to describe the CA. [12] In the Wenzel state it is assumed that a liquid droplet on a rough surface penetrates the surface irregularities, as indicated by Figure 2.4B). [65] The apparent CA, θ*, introduced in this state is related to the Young’s CA, θ, as described by Equation 2.12 [62].

$$\cos(\theta^*) = r \cos(\theta)$$

(2.12)

The Wenzel equation includes a roughness factor, r, which refers to ratio of the actual and apparent solid-liquid interface contact area (r > 1). Under hydrophilic conditions, θ* decreases with increasing roughness and increases with increasing roughness under hydrophobic conditions. However, the Wenzel state is not able to explain phenomena such as the rolling water droplets on surfaces when the apparent CA exceeds 150°. Therefore, the Cassie-Baxter state is introduced where it is assumed that the liquid droplet does not penetrate surface irregularities but rather entraps air pockets reducing the solid-liquid contact area (Figure 2.4C)). [62] The Cassie-Baxter state is represented by Equation 2.13 where ϕ_s is the solid area fraction in contact with the droplet [12].

$$\cos(\theta^*) = 1 + \phi_s[\cos(\theta) + 1]$$

(2.13)
2.7. Ice adhesion

Figure 2.4: The wettability of a surface is described by the behaviour of a liquid droplet on a solid. A) The wettability can be described by the contact angle, \( \theta \). The Young's equation describes \( \theta \) as the equilibrium between the interfacial tensions \( \gamma_{LS}, \gamma_{GL} \) and \( \gamma_{GS} \) of an ideal solid (S), liquid (L) and gas phase (G). For a surface with surface roughness, the Wenzel equation assumes that a liquid droplet penetrates the surface irregularities. C) The Cassie-Baxter equation assumes that a liquid droplet entrap air pockets reducing the solid-liquid contact area.

As the solid-liquid contact area in the Cassie-Baxter state is reduced compared to the Wenzel state, the apparent CA can reach values of \( \geq 150^\circ \). The wettability of a solid surface changes from the Wenzel state to the Cassie-Baxter state beyond a critical roughness factor. [62]. The apparent CA for a liquid droplet on a rough surface is not unique but can range between the receding (minimum) and advancing (maximum) CA, \( \theta_{\text{rec}} \leq \theta \leq \theta_{\text{adv}} \). The difference between these two angles is known as contact angle hysteresis (CAH). [66, 67] CAH reflects the dynamic movements of liquid droplets on a surface and is measured by increasing or decreasing the volume of the droplet to determine the maximum and minimum CA. As a droplet does not easily roll of a rough surface in the Wenzel state, the CAH is high. On the other hand, a smaller CAH is explained by the Cassie-Baxter state. Besides the CAH, another way to characterize the wettability of a hydrophobic surfaces with large CA is to measure the roll-off angle (ROA), \( \alpha \). The ROA is defined as the minimum inclination angle for which a liquid droplet rolls of the surface. Naturally, \( \alpha \) is higher for the Wenzel state than for the Cassie-Baxter state. [62]

2.7.2 Wettability, ice adhesion and morphology of anodic alumina

The common hypothesis is that hydrophobic surfaces, i.e. with high contact angle, also will have weak ice-adhesion properties [58]. Especially superhydrophobic surfaces (SHS's), with a water contact angle (WCA) larger than 150° and low CAH (\( \leq 5^\circ \)), are hypothesized to have proper water repellent and self-cleaning properties [63]. SHS's are a result of a low surface energy, generally obtained by modifying the surface chemistry, and a micro-nanoscale surface roughness conforming to the Cassie-Baxter state. SHS's are thought to have the ability to avoid supercooled water droplets (below 0 °C) from freezing completely before they are removed from the substrate. Even if droplets manage to adhere and freeze to the surface, the smaller solid-liquid interface contact area resulting from the Cassie-Baxter wetting state results in an easy removal of the ice before accumulation occurs. [62]

However, the effectiveness of SHS's as passive anti-icing method is widely debated. For instance, Chen et al. [68] studied the ice adhesion on silicon wafers with various wettability ranging from superhydrophilic to superhydrophobic. It was found that SHS's could not reduce ice adhesion in comparison to other surfaces which is explained as follows. SHS's are in...
the Cassie-Baxter state with air pockets entrapped inside the surface texture. When the temperature of the surrounding environment is lowered, water molecules adsorb to the walls of the surface texture and the water droplet starts to partially or completely penetrate the surface texture. This results in a more hydrophilic surface no longer in the Cassie-Baxter state. When the droplet freezes, the large contact area between the ice and the surface results in increased ice adhesion strength. Furthermore, it is suggested that the ice adhesion on SHS’s correlates to the CAH [60, 63, 69] and ROA [60] of the surfaces rather than just the static CA.

The morphology of anodic alumina is influenced by the anodizing conditions. This provides a great potential for tuning the wettability as well. Although alumina itself is considered hydrophilic, SHS have been obtained by surface chemistry and/or structure. [14] Besides the correlation between anodizing time and morphology, Buijnsters et al. [14] aimed to investigate the correlation between the wettability and structural characteristics of two-step anodized Al. It was found that the wettability is dependent on the surface porosity and that the WCA increases linearly with increasing porosity. However, the WCA drastically decreased when a specific porosity was exceeded, most likely due to pore walls so thin they failed to support the liquid droplet. To this author’s knowledge, Buijnsters et al. [14] is one of few who relates the morphology of anodic oxide to wettability. In combination with the uncertainty amongst researchers whether SHS’s are suitable for anti-icing purposes, it therefore is of interest to further investigate this relation in correlation to ice adhesion properties.

### 2.8 Other surface treatments

In addition to anodizing, other posttreatments can be applied to Al alloys. Firstly, hydrothermal sealing (HTS) aims to enhance corrosion resistance. Secondly, silanization can be used to change the wettability properties of a surface.

#### 2.8.1 Hydrothermal sealing

Anodized Al surfaces are especially prone to attacks from the environment. Due to the porosity of anodized oxide films, the porous structures are able to absorb water and aggressive substances from solutions. These aggressive substances may penetrate the thin barrier layer and cause structural and physical damages to the surface. For this reason, anodized Al is often sealed post anodizing to enhance the corrosion resistance. [15] Sealing can be performed in aqueous solutions of certain salts above 90°. Commonly, the Cr(VI) compound potassium dichromate has been used as salt. [30] However, due to the toxicity and environmental hazards of Cr(VI), other chromate-free sealing methods are preferred. Instead, anodized surfaces can be sealed by immersion in hot or boiling deionized water without salt, called hydrothermal sealing (HTS). [41] No toxic chemicals are involved in the HTS process. The sealing results in a blockage of the pores and production of hydrated alumina, mainly boehmite (AlO(OH)), from alumina (Al₂O₃) as described by Equation 2.14. [15]

\[
\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \text{AlO(OH)}
\]  

Equation 2.14

During HTS, the pore walls start to dissolve following by the precipitation of aluminum hydroxide plugging the upper part of the pores [41]. Arenas et al. [70] suggests that 2024-T3 alloys anodized with TSA and hydrothermally sealed obtain increased corrosion resistance due to tartaric acid residues in the pores. The proposed mechanism involves dissociation of the residues and the formation of chelate complexes of tartrate and Cu ions. Cu²⁺ are removed from the pore walls reducing the heterogeneity of the porous layer and thus increasing corrosion resistance.
2.8.2 Silanization

The wettability can, after anodizing and optional sealing, be changed by modifying the surface chemically. SHS can be created by the use of silanes. [14, 16]. Silanes are compounds consisting of silicon and hydrogen atoms, where the hydrogen atoms can be replaced by other atoms such as halogens [71]. Silanes deposited on many solids and oxides (e.g. Al₂O₃), form a self-assembled monolayer (SAMs) that strongly bind to a surface upon a self-organizing process [72]. SAMs can be formed by molecules that have: (i) a functional group that chemically binds to surfaces, (ii) an aliphatic chain responsible for the self-organization and (iii) a functional group on the top of the layer. [73]

Organosilanes, i.e. silanes containing carbon-silicon bonds, possess the three parts mentioned above needed to form a SAM [74]. These silanes can covalently bind to the surface of native anodized Al to control its wettability and adsorption properties. The wettability can be decreased by silanes with hydrophobic terminal groups such as perfluoroalkyl-silanes and alkyl-trichloro-silanes. [75] In addition to the possible effect on ice adhesion due to tunable wettability, SAMs consisting of silanes enhance the corrosion resistance of Al alloys by minimizing contact between the surface and the corroding species [73].
3 Methodology

In this chapter, the theory behind the used characterization methods, i.e. goniometry, scanning electron microscopy (SEM) and ice adhesion measurements, is explained. Firstly, goniometry is used for CA measurements to determine the wettability of a sample. Secondly, SEM is used to characterize the morphology of the porous anodic surface. Lastly, ice adhesion measurements are performed on anodized and silanized surfaces.

3.1 Goniometry

The wettability of a surface can be determined by measuring the CA between a solid compound and a liquid using a goniometer, as explained in Section 2.7.1 [52]. The sessile drop technique is one of the most common techniques for directly measuring the CA between the three phases (solid, liquid and gas) [76]. The set-up used for the sessile drop technique often consists a horizontal stage on which a substrate can be placed, a syringe with liquid used to deposit a drop on the substrate, a camera used to take photographs of the drop, an illumination source and a magnifying lens, see Figure 3.1. The drop shape and CA can be analyzed using a computer. The sessile drop technique can also be used for measuring the advancing and receding CA to determine the CAH by slowly increasing and decreasing the volume of the deposited drop. Alternatively, the horizontal stage can be tilted to measure the advancing and receding angles at the lowest and the highest point of the drop just before the drop begins to move. [77]

Figure 3.1: The set-up for the sessile drop technique commonly used for measuring the contact angle of a drop deposited on a substrate.

The sessile drop technique is a direct optical method which is simple and does not require large samples or amounts of liquid. However, the method suffers from some limitations. Firstly, the small size of the liquid drop and substrate increases the impact of impurities. Secondly, the reproducibility and accuracy of the measurements is operator-dependent. Due to the asymmetry of a drop, it is recommended to use the average of measured CAs on both sides of the liquid drop profile, i.e. \( \theta_{\text{left}} \) and \( \theta_{\text{right}} \). Small CAs (\( \lesssim 20^\circ \)) have a large uncertainty due to the flat profile of the drop. Additionally, the contact angle is dependent on the drop size causing a systematic issue. Despite of these limitations, the sessile drop method is widely used when a high accuracy (\( < \pm 2^\circ \)) is not required. [77] In this project, the sessile drop technique is used to determine the wettability of anodized surfaces by measuring the static CA.
3.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is a versatile method which can be used to examine the microstructure of a substrate. SEM delivers images with high resolution, i.e. in the order of 10 nm for commercial instruments. Furthermore, SEM has a large depth focus which allows for a three-dimensional appearance of the studied specimen. [78] As the name suggests, images are produced by scanning a focused high-energy electron beam across the specimen. When the incident primary electrons collide with the specimen, a signal containing information about the substrate's surface topography and specific features is registered. [79] The volume of the specimen which is able to interact with the primary electrons is called the interaction volume. On the other hand, the maximum depth at which interactions can occur is called the penetration depth. [80] As illustrated by Figure 3.2A), several types of emission are produced upon interaction of the incident primary electrons with the specimen, e.g. low-energy (< 50 eV) secondary electrons (SEs), backscattered electrons (BSEs), characteristic X-ray emission and photon emission. [79] The type of emissions can be detected using several SEM imaging modes. The two most common imaging modes are the secondary-electron imaging mode and the backscattered-electron imaging mode. [80] The difference between SEs and BSEs is further illustrated in Figure 3.2B).

![Figure 3.2: The principles of SEM. A) The primary electrons from the incident beam penetrate into a sample and interact with specimen electrons. The interactions produce emission of secondary electrons, backscattered electrons, characteristic X-rays and photons. B) Two common SEM imaging modes register the signal from secondary electrons or backscattered electrons that are inelastically and elastically scattered, respectively.](image)

In the secondary-electron imaging mode, SEs are ejected from the specimen as a result of inelastic scattering meaning that the kinetic energy of the incident electron is lost. The ejected SEs will in turn interact with other atomic electrons and lose kinetic energy due to inelastic scattering. Therefore, SEs are only able to travel very small distances (1-2 nm) in a solid meaning that a limited number of SEs lying close to the surface (< 2 nm depth) are able to escape into the surrounding vacuum. The escaped SEs can be detected to create a topographical image of the specimen surface. The average number of SEs that escape into the vacuum per incident primary electron is called the secondary-electron yield, $\delta$, and decreases with increasing primary-electron energy. The yield also depends on the angle between the incident electron and the surface with increasing yield when the angle between the electron beam and the surface-normal increases. For this reason, the SE detector is located on one
side of the specimen rather than directly above it. Due to the position of the detector, raised and depressed features of a surface can be distinguished by contrast giving a SEM image a three-dimensional appearance. [80]

In the backscattered-electron imaging mode, the contrast is a result of variations in chemical composition of the studied specimen rather than the surface topography such as when detecting SEs. BSEs are primary electrons that are reflected from the solid upon elastic scattering through an angle > 90°. While SEs have low kinetic energy, the kinetic energy of the BSEs is preserved allowing for separate detection of SEs and BSEs. The preserved energy allows the BSEs to leave the specimen and re-enter the surrounding vacuum. The fraction of incident primary electrons that turn into BSEs is called the backscattering coefficient, \( \eta \), and increases with atomic number and thus depends on the chemical composition of the specimen. [80]

The specimens studied with SEM need to be conductive. If not conductive, the specimen may undergo negative electrostatic charging when exposed to the electron beam causing fluctuations in image intensity and/or image distortion. Although conducting specimens do not require any special preparations, insulating materials can be covered with a thin film (10-20 nm) of metal. [80] Commonly used coating materials include heavy metals or heavy metal compounds such as gold, platinum, tungsten and graphite which can be deposited by high-vacuum evaporation or low-vacuum sputtering techniques [79]. In the secondary-electron imaging mode, the SEs detected come from the coating rather than the specimen since the coating thickness is larger than the escape depth. However, since the coating closely follows the original surface a proper representation of the surface topography is still provided. [80] In this project, the secondary-electron imaging mode is used to capture topographical images of anodized aluminum surfaces with varying morphology.

### 3.3 Ice adhesion measurements

High quality ice adhesion measurements performed in laboratory conditions, useful for comparison to industrial conditions, are complicated due to the many factors involved. Factors affecting ice adhesion include the crystal structure of ice, interface morphology, temperature and water salinity. [81] While liquid CA easily can be measured using goniometry, there are no analogous instruments that are commercially available to measure adhesion strengths between two solids such as that between ice and a substrate [60]. Instead, various methods for measuring ice adhesion have emerged over the years leading to data covering a wide range of adhesion strengths. The two most popular methods are the centrifuge tests and mechanical tests. [82]

When performing centrifuge tests, centripetal forces are used to shear adhered ice from a substrate. One simple centrifuge approach is to spin a weighed ice sample at a constantly increasing rate until it separates from the substrate. [82] The ice can be deposited on a surface by spraying supercooled water droplets on a test substrate. However, the centrifuge test set-up often requires a complex centrifuge apparatus and an icing chamber usually not practical for academic laboratories. [60] The shear strength, \( \tau \), of the ice to the surface can be presented as force \( F \) divided by the interfacial area \( A \), as shown in Equation 3.1 [82].

\[
\tau = \frac{F}{A}
\]  
(3.1)

The equation above assumes a uniform stress distribution although shear stresses predominantly act at the sample edges. Other issues with centrifuge tests include the lack of testing at varying parameters, e.g. strain rate. The strain rate is dependent on the mass or growth
rate of the ice and has a strong effect on the ice adhesion strength. Furthermore, to perform quantitative measurements that can be used for the design of aircraft components, the adhesion strength of high-speed impact ice should be tested. However, high-speed wind tunnels are rare and expensive and the cost-saving alternatives are only able to provide qualitative comparisons between surfaces. [82]

One of the most common mechanical test methods is the push/pull test. In a push/pull test, the ice adhesion strength is measured as the force required to break the solid-ice interface when applying a load on one side of the sample. In this case, the stress applied to the interface is nonuniform. The push/pull tests can be performed for nonimpact or impact ice. When testing with nonimpact ice, the test is simple. Ice can be frozen to a substrate using a mold, commonly a cuvette. A force sensor can then be used to push or pull the ice until the solid-ice interface is broken. Again, the shear strength is calculated as indicated by Equation 3.1. As with the centrifuge tests, the adhesion strength of impact ice should be measured to be able to apply the results to the aircraft industry. Using a push/pull test on impact ice is a much more complicated process but is not further discussed in this master's thesis. Work and Lian [82]

In this master's thesis, pull tests are performed as described in Cherny et al. [12] to measure ice adhesion strength on surfaces anodized under varying conditions and treated with HTS and silanes. A cuvette is used as a mold to freeze ice on the substrate. Prior to measurements, the substrate is transferred to a cooling plate on a movable platform. The transducer arm of the force sensor is placed around the cuvette and the movable platform slowly moves the sample until the solid-ice interface is broken. [12] The resulting force is measured by the sensor and a force-time curve is recorded [81]. The measured force [kN] is normalized with respect to the interface area [m²] and the ice adhesion strength is expressed in kilopascal [1 kPa = 1 kN m⁻²] [12]. The measurement set-up and an example of the resulting force-time curve is shown in Figure 3.3A) and 3.3B), respectively.

**Figure 3.3:** The principles of ice adhesion measurements. A) In a push/pull test, a cuvette with ice can be frozen upon a substrate. The substrate is mounted on a cooling stage and a movable platform. A force transducer arm is mounted around the cuvette and the force required to break the solid-ice interface is registered using a sensor. B) During a measurement, a force-time curve is obtained indicating the force at which the break occurs.
3.3. Ice adhesion measurements

When measuring ice adhesion strength on textured surfaces, such as anodic aluminum, both adhesive and cohesive forces need to be taken into account. The force needed to remove the ice from a substrate needs to overcome the adhesive strength between the ice and substrate as well as the cohesive forces within the ice. [68] For instance, when traces of the ice remain on the substrate after removing the cuvette in a push/pull test, it shows that the break (partially) occurred within the ice as a cohesive failure rather than at the solid-ice interface. A cohesive failure measures the strength of the ice rather than the interfacial ice adhesion strength, and such measurements should therefore be carefully considered. A cohesive failure can occur on a microscopically rough surface if the micropores are filled with water upon freezing. The water in the pores increases the true solid-ice interfacial contact area, increasing the ice adhesion strength. If the micropores of a substrate are hydrophobic and thus not filled with water, the contact area can be reduced. [81]
4 Experimental

Herein, the materials used for the experiments, procedures and conditions are described.

4.1 Material

The chemicals used in this master’s thesis during the anodizing process and posttreatments are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone ((CH₃)₂CO)</td>
<td>Degreasing of sample, anodizing pretreatment</td>
</tr>
<tr>
<td>Alkaline degreasing solution</td>
<td>Alkaline degreasing, anodizing pretreatment</td>
</tr>
<tr>
<td>Ammonia (25 % NH₃·H₂O)</td>
<td>TL-1 washing procedure of goniometer needle</td>
</tr>
<tr>
<td>Ethanol (95 % C₂H₅OH)</td>
<td>Rinsing after silanization</td>
</tr>
<tr>
<td>Hydrogen peroxide (25 % H₂O₂)</td>
<td>TL-1 washing procedure of goniometer needle</td>
</tr>
<tr>
<td>Milli-Q Ultrapure H₂O₂, 18.2 MΩ-cm at 25 °C</td>
<td>Rinsing of samples, CA liquid, TL-1 washing procedure of goniometer needle</td>
</tr>
<tr>
<td>Nitrogen (N₂, gas)</td>
<td>Blow drying of samples</td>
</tr>
<tr>
<td>Pickling solution</td>
<td>Pickling of sample, anodizing pretreatment</td>
</tr>
<tr>
<td>Tri(chloro)octylsilane (97 % CH₃(CH₂)₇SiCl₃)</td>
<td>Silanization</td>
</tr>
<tr>
<td>TSA</td>
<td>Anodizing electrolyte</td>
</tr>
</tbody>
</table>

The pickling solution, alkaline degreasing solution and TSA used for the laboratory scale anodizing process were retrieved directly from the production scale treatment baths at Saab Aeronautics. Remaining chemicals were provided by IFM, LiU.

Samples of Al alloy 2024-T3 of different sizes were provided by Saab Aeronautics and used in this master’s thesis. For the anodizing procedure, two different set-ups were used requiring different shapes and sizes of the samples. For the smaller set-up, samples of the size 10 x 20 mm with a handle were used. When using the second set-up, larger samples without handle of the size 15 x 25 mm or 15 x 30 mm were anodized. The size and shape of the samples are illustrated in Figure 4.1.

![Figure 4.1: The shapes and sizes of the Al alloy 2024-T3 samples used in this master’s thesis.](image-url)
4.2 Method

The essential method used in this master’s thesis was anodizing including pretreatment steps. The wettability and morphology of the samples were characterized using goniometry and SEM, respectively. Additional posttreatments such as HTS and silanization were used in combination with ice adhesion measurements.

4.2.1 Anodizing

Anodizing was the fundamental process of all experiments. Therefore, a thorough description of the process, the set-ups used and the tested conditions can be found in this section.

4.2.1.1 Process

Anodizing is a simple electrochemical process which enhances the thickness of the natural alumina film formed on an Al alloy upon exposure to oxygen. The process steps are shown in Figure 4.2. Prior to immersing the sample in an alkaline degreasing bath, the Al surface was degreased with acetone. The two degreasing steps were applied to remove grease from fingerprints and other contaminants. Before moving on to the pickling bath, the surface was rinsed in ultrapure Milli-Q water at room temperature (RT). The pickling step aimed to remove the alumina layer naturally formed on the alloy. After a second rinsing step, the sample was immersed in the TSA electrolyte. During the anodizing process, the Al sample served as anode and stainless steel served as cathode. The anode and cathode were connected to a direct current (DC) power supply. In agreement to the Saab process standard [8], the voltage was increased in steps of 1.4 V per 30 seconds to avoid overheating. The current limit of the power supply was set to maximum. The anodizing voltage, temperature and time was adjusted to the experiment. An ammeter was connected to ensure the plausibility of the current running through the circuit, which is dependent on the anodizing conditions and the number of samples run simultaneously. After the final rinsing step, the sample was air dried or dried with nitrogen (N\textsubscript{2}) gas blow and stored in a petri dish. As an initial inspection of the quality and characteristics of the sample, the sample was visually examined for any visible defects or discoloration. Waste from the anodizing process was carefully collected in separate waste cans for each chemical.

Figure 4.2: The anodizing process. Degreasing, rinsing and pickling steps are applied as pretreatment before anodizing in TSA under desired voltage, temperature and duration.
4.2.1.2 Set-up

In this project, two different anodizing set-ups were used. Both set-ups consisted of four glass boxes with plastic lids containing alkaline degreasing solution, pickling solution, Milli-Q water and TSA. The boxes of the first set-up were smaller than those of the second set-up. Hence, the smaller set-up was used to anodize the smaller samples of 10 x 20 mm whereas the larger samples of 15 x 25 or 15 x 30 mm were anodized in the larger set-up. Further differences between the two set-ups regard the shape and size of the cathode as well as the way of connecting the surfaces to the DC power supply, as shown in Figure 4.3. For the smaller set-up, one of the lids was modified to hold a wooden board with small holes at equal distances. A rectangular cathode (50 x 100 mm) of stainless steel was attached to the underside of the lid and connected to a screw on the top side of the lid. To prepare for the anodizing process, thin Al thread was twined tightly around the handle of the 10 x 20 mm surface, threaded through the holes of the lid and twined around a screw attached to the lid. If several surfaces were anodized simultaneously, the Al threads were twisted tightly together after each thread had been individually twined around the screw. Using this set-up, seven surfaces with the dimensions 10 x 20 mm could be anodized at the same time. The wires connected to the plus and minus poles of the DC power supply were attached to the two screws connected to the anode and cathode, respectively.

The second set-up was designed and fabricated for the purpose of this master’s thesis to allow a larger number of the 15 x 25 or 15 x 30 mm samples to be anodized simultaneously. The surfaces were clamped tightly between two metal plates to improve the current flow from the DC power supply through the electrodes of the electrochemical cell. A number of screws placed through the two metal plates were tightened to further increase the contact between the surface and the metal plates. Using this set-up, ten surfaces could be anodized simultaneously. One of the lids was adjusted to be able to hold the device with the two metal plates in place during anodizing but in such way that it could be easily removed for rinsing and other purposes. In this set-up, an U-shaped cathode of stainless steel was attached to the lid to enable a more homogeneous anodizing process on all sides of the anodized surface. The U-shaped cathode had the dimensions 150 x 80 x 90 mm. Two screws served as connection points for the DC power supply, in the same way as for the first set-up.

**Figure 4.3:** For the anodizing experiments, two different set-ups were used. The smaller set-up consisted of a rectangular cathode and each anodized surface was connected to the DC power supply using Al thread twined tightly around the surface. The larger set-up instead consisted of an U-shaped cathode and the connection between the anodized surface and the power supply was established by clamping one or more surfaces tightly between to metal plates. Figure not drawn to scale.
4.2.1.3 Conditions

The main objective of the project included studying the effect of anodizing voltage, electrolyte temperature and anodizing time on the morphology of anodic Al coatings. Therefore, a number of experiments were performed under varying anodizing conditions while the pretreatment steps were kept the same. The reference point was the standard process implemented by Saab Aeronautics, where Al alloys are anodized in TSA at 14 V, a temperature of 36-39 °C and for 20 minutes. In this master’s thesis, several parameter values above and below the standard conditions were tested, as shown in Table 4.2. The table also indicates which set-up that was used for a certain parameter value. One parameter was changed at the time while the other parameters were kept at standard conditions. Two surfaces were anodized simultaneously for each parameter value in order to study the homogeneity of the anodizing process and to yield mean values from CA measurements.

Table 4.2: The anodizing conditions tested in this master’s thesis using the smaller or larger set-up. The standard conditions (14 V, 36-39, 20 min) were tested with both set-ups for comparison.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Smaller set-up</th>
<th>Larger set-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodizing voltage [V]</td>
<td>5, 14, 28</td>
<td>9, 14, 19, 24</td>
</tr>
<tr>
<td>Electrolyte temperature [°C]</td>
<td>2 (on ice), 36-39, 66</td>
<td>20 (RT), 36-39, 50</td>
</tr>
<tr>
<td>Anodizing time [min]</td>
<td>20, 100</td>
<td>5, 20, 40, 60</td>
</tr>
</tbody>
</table>

4.2.2 Ice adhesion

Ice adhesion measurements were performed at RISE using the pull method on surfaces anodized under varying conditions and treated with additional posttreatments, as earlier described in Section 5.3. The equipment used is a Imass SP-2000 Slip/Peel tester equipped with a force sensor with a force sensitivity of 12 kg. A plastic cuvette (10 x 10 mm) filled with 1 mL sonicated Milli-Q water was frozen on the sample surface over night at -18 °C using a lab jack. Prior to the measurement, the sample was quickly transferred from the freezer to the cooling stage with a temperature of -18 °C. Due to the relatively small size of the sample, it was fixed to the stage by freezing Milli-Q water around the edges. After placing the force transducer arm at the right position, the movable platform was moved at a speed of 0.3 mm/s and the ice adhesion strength was registered by the force sensor. Figure 4.4 shows the measurement set-up with a cuvette frozen to the sample which in turn is frozen to the cooling stage. The force-time data points were exported to Microsoft Excel and the peak stress was extracted. The break type, i.e. adhesive or cohesive break, was noted for each measurement. The measured force [N] was transformed to ice adhesion strength [kPa] by normalizing the force to the solid-ice interface area, i.e. 10 x 10 mm = 1 x 10⁻⁴ m². Before loading a new sample onto the cooling stage, the temperature of the stage was raised to 4 °C to be able to remove the previous surface.
Ice adhesion measurements were performed for surfaces anodized at 5, 14 or 28 V. The choice of parameters was based on initial SEM experiments which showed different morphologies for the three voltages. The surfaces were posttreated as shown in Table 4.3. Ten surfaces were anodized simultaneously using the larger set-up. Five out of ten surfaces were HTS treated and all surfaces were silanized according to the procedures described below. The averages and standard deviations of the five measured ice adhesion strengths for each type of surface were calculated using Microsoft Excel and plots were created using MATLAB.

**Table 4.3:** The anodizing conditions and posttreatments used for the ice adhesion measurements.

<table>
<thead>
<tr>
<th>Anodizing voltage [V]</th>
<th>posttreatment (number of surfaces)</th>
<th>Total number of surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silane</td>
<td>HTS + silane</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>28</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

### 4.2.3 Hydrothermal sealing

HTS was performed by immersing the anodized samples in a titration flask with hot Milli-Q water for 30 minutes. The water temperature was kept between 85 °C and 95 °C to avoid boiling.

### 4.2.4 Silanization

Silanization was performed to hydrophobize anodized samples prior to ice adhesion measurements. Prior to silanization, the samples were dried in a vacuum chamber for 4-5 hours to remove all excess water residing in the anodic porous structure. The samples were silanized in vapor phase (vacuum) with 200 µl trichloro(octyl)silane overnight (approximately 15 hours) at 25 °C. Thereafter, the temperature of the vacuum chamber was increased to 115 °C and the samples were baked for 10 minutes. After releasing the vacuum, the samples were sonicated in ethanol for 1 minute to remove excess silanes from the surface. The samples were dried prior to CA measurements.
4.2.5 Goniometry

Goniometry was used to characterize the wettability of a sample by measuring the static CA. In this case, the Cam 200 Optical Contact Angle Meter, KSV Instruments LTD, found at IFM, was used (Figure 4.5). This instrument utilizes the sessile drop technique previously explained in Section 3.1. Prior to performing CA measurements, the goniometer needle that is used to deposit liquid drops on a sample surface and the tweezers used to handle the needle and the substrates underwent a washing procedure referred to as TL-1 wash. The TL-1 procedure aims to remove organic matter from the needle to avoid contamination. The solution used in the TL-1 procedure consists of a 1:1:5 mixture of ammonia, hydrogen peroxide and Milli-Q water, respectively. The needle and tweezers were washed in the solution in separate beakers at 85 °C before being thoroughly rinsed with Milli-Q water and blow dried with N₂. The needle was washed until bubbles were formed in the solution (approximately 2-3 minutes) while the tweezers remained in the solution for 10-15 minutes. After the TL-1 washing procedure the goniometer needle was again carefully attached to the syringe and attached to the instrument.

![Figure 4.5: The Cam 200 Optical Contact Angle Meter, KSV Instruments LTD used for CA measurements. Drops are deposited on a surface sample using a syringe, photographs of the drop are taken using a camera with magnifying lens and a computer is used for analysis.](image)

The measurements themselves were performed by carefully depositing a liquid drop on the sample surface and capturing a photograph using the KSV Contact Angle Measurement system software complimentary to the instrument. The drop shape and static CA were analyzed using the software by automatically or manually selecting the baseline of the drop. For the experiments shown in Table 4.2, the left ($\theta_{\text{left}}$) and right ($\theta_{\text{right}}$) CA for at least three liquid drops on each of the two anodized surfaces were measured. For the surfaces anodized and posttreated for ice adhesion measurements, the CA for at least six drops deposited on two out of the five prepared surfaces were analyzed. If not all drops could be deposited on the sample surface at once, the sample was blow dried using N₂ before depositing another drop. The CAs were exported to Microsoft Excel in which the mean value and standard deviation were calculated and the values were plotted using MATLAB. In some cases, the CA could not be calculated due to the shape of the drop or a presumed low CA value. In these cases, the standard deviation was manually increased to approximate the true value of the CA. In other cases, none of the CAs were computable and therefore denoted as non-detectable (ND).
4.2.6 Scanning Electron Microscopy

An scanning electron microscope with a secondary-electron imaging mode was used to study the morphology of anodic coatings. More specifically, a Zeiss LEO 1550 SEM with one GEMINI column was used. The electron source of the GEMINI column is a Schottky Field Emission Gun made of tungsten (W) and Zirconium (ZrO₂). Primary electrons of approximately 3 keV were emitted at a working distance of 2 to 6 mm and an InLens detector was used to detect secondary electrons.

Prior to mounting the samples in the SEM instrument, the samples were attached to a holder with copper tape and sputtered with Pt for 10 seconds at a current of 60 mA, a pressure of $5 \times 10^{-2}$ mbar and a distance of 50 mm. The sputtering was performed using a Leica EM SCD 500 instrument to improve the conductivity of the samples. Settings such as the contrast, brightness, scanning rate and magnification were adjusted to obtain clear images of the surface. Topographical images were captured at a magnification ranging from 600 and 8000 times.

The morphology of the anodic coatings was further investigated using the image processing software NIH ImageJ. Pore diameters and interpore distances [nm] were calculated by setting a scale based on a known distance. The scale was used to take measurements of the parameters and averages and standard deviations of ten values were calculated using Microsoft Excel. The porosity was calculated as an area fraction [%] of pores covering the surface by converting the image to a binary image by selecting a threshold and using the "Analyze particles" tool implemented in ImageJ. This was done for three different areas of an image of which averages and standard deviations could be calculated. When selecting the areas, large surface defects not consistent with the porous morphology were avoided. The interpore distance and pore diameter were determined for all images of a certain magnification with sufficient contrast and distinctive pores. The porosity was calculated for images of a certain magnification with sufficient contrast. The results were plotted together with trendlines using MATLAB.
## 5 Results

The project aim was to investigate the effect of anodizing conditions on the morphology of anodic Al coatings. Furthermore, the effect of the morphology on wettability and ice adhesion in combination with post-treatments such as silanization and hydrothermal sealing (HTS) was studied. Herein, the results from the experiments designed to reach these aims are presented.

### 5.1 Anodizing conditions and morphology

The morphology of the porous layer of alumina formed during anodization was investigated as a function of anodizing voltage, electrolyte temperature and anodizing time. Therefore, surfaces were anodized under various conditions (Table 4.2) and the morphology was studied using SEM. As the conditions were tested using two different set-ups, a smaller and a larger one, a comparison between these is given. Thereafter, the effects of the anodizing voltage, electrolyte temperature and anodizing time on the morphology are presented the sections below.

#### 5.1.1 Comparison between set-ups

A smaller and a larger set-up were used to anodize surfaces under various conditions. The two set-ups differ in the size and shape of the cathode as well as the way of establishing a connection between the anodized surface and DC power supply. SEM images of surfaces anodized under standard conditions (14 V, 36-39 °C and 20 min) with the smaller and larger set-up are shown in Figure 5.1A and B), respectively. The porosity, pore diameter, interpore distance and contact angle (CA) for the two surfaces are presented in Table 5.1.

![Small and large set-up SEM images](image)

*Figure 5.1: SEM images of surfaces anodized under standard conditions (14 V, 36-39 °C and 20 min). A) Surface anodized with the smaller set-up. B) Surface anodized with the larger set-up.*

<table>
<thead>
<tr>
<th>Set-up</th>
<th>Porosity [%]</th>
<th>Pore diameter [nm]</th>
<th>Interpore distance [nm]</th>
<th>Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smaller set-up</td>
<td>38 ± 5</td>
<td>13 ± 3</td>
<td>20 ± 5</td>
<td>19 ± 7</td>
</tr>
<tr>
<td>Larger set-up</td>
<td>28 ± 8</td>
<td>7 ± 1</td>
<td>14 ± 2</td>
<td>15 ± 11</td>
</tr>
</tbody>
</table>
The morphology of the anodic coating differs between the set-ups even when anodized under similar conditions, see Figure 5.1 and Table 5.1. There are some minor differences due to the image contrast when comparing the SEM images. Though most importantly, the images and Table 5.1 clearly show that the porosity, pore diameter, interpore distance and contact angle are larger for the surface anodized with the smaller set-up. However, overlapping standard deviations for the porosity, interpore distance and contact angle indicate that the difference may not be significant.

5.1.2 Anodizing voltage

The results from the SEM experiments performed on surfaces anodized with voltages ranging from 5 V to 28 V are shown in Figure 5.2. Due to the use of the two set-ups, the images are separated based on whether the surfaces were anodized using the smaller (Figure 5.2 A-C) or the larger (Figure 5.2 D-G) set-up. The SEM images of the two surfaces anodized under standard conditions (14 V, 36-39 °C and 20 min) previously presented in Figure 5.1 are also included in Figure 5.2.

The electrolyte temperature and anodizing time were kept at the standard conditions 36-39 °C and 20 minutes. However, when anodizing at 28 V, the temperature increased due to a high current and the lack of temperature control. The morphology was studied by measuring the porosity, pore diameter and interpore distance using NIH Imagej, as summarized for both set-ups in Table 5.2. The CAs, measured using goniometry, are also included in Table 5.2.

For all voltages except for 28 V (Figure 5.2 A-B and D-G), pores that have been merged together and are not separated by pore walls can be found in the alumina. These interconnected pores are especially clear for the surfaces anodized with the smaller set-up. However, this could depend on the image contrast. Furthermore, larger defects can be seen as dark cavities resulting from the alloy microstructure prior to anodizing. Stripes of brighter color can be observed especially for the lower voltages and are likely due to topographical height differences of the anodic coating.

The surface anodized at 28 V has obtained a more rod-like porous structure rather than the honeycomb pore organization seen for the other voltages. Although there are no pore diameters and interpore distances to be calculated, the diameter of these rod-like structures is measured to be approximately 24 ± 1 nm. During the anodizing process at 28 V, the current limit of the DC power supply was reached and the current was therefore significantly higher than for the other experiments. As a result of the high current, the electrolyte temperature increased to 66 °C.
Figure 5.2: SEM images of surfaces anodized under different voltage conditions. A-C) Surfaces anodized using the smaller set-up at 5, 14 and 28 V, respectively. D-G) Surfaces anodized using the larger set-up at 9, 14, 19 and 24 V, respectively. The electrolyte temperature and anodizing time were kept at the standard 36-39 °C and 20 minutes.
### Table 5.2: The porosity, pore diameter, interpore distance and contact angle for surfaces anodized with different voltages. The superscript numbers 1 and 2 indicate whether the small or the larger set-up was used for that particular experiment, respectively. The standard conditions (14 V) were tested in both set-ups for comparison.

<table>
<thead>
<tr>
<th>Voltage [V]</th>
<th>Porosity [%]</th>
<th>Pore diameter [nm]</th>
<th>Interpore distance [nm]</th>
<th>Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5(^1)</td>
<td>35 ± 3</td>
<td>9 ± 1</td>
<td>15 ± 3</td>
<td>18 ± 6</td>
</tr>
<tr>
<td>9(^2)</td>
<td>29 ± 3</td>
<td>8 ± 1</td>
<td>17 ± 3</td>
<td>22 ± 6</td>
</tr>
<tr>
<td>14(^1)</td>
<td>38 ± 5</td>
<td>13 ± 3</td>
<td>20 ± 5</td>
<td>19 ± 7</td>
</tr>
<tr>
<td>14(^2)</td>
<td>28 ± 8</td>
<td>7 ± 1</td>
<td>14 ± 2</td>
<td>15 ± 11</td>
</tr>
<tr>
<td>19(^2)</td>
<td>30 ± 4</td>
<td>8 ± 2</td>
<td>18 ± 3</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>24(^2)</td>
<td>28 ± 6</td>
<td>8 ± 1</td>
<td>19 ± 4</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>28(^3)</td>
<td>45 ± 3</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

The interpore distance, pore diameter and porosity of anodic coatings are plotted in relation to anodizing voltage, as presented in Figure 5.3. All voltages regardless of the set-up used are included. Since surfaces were anodized at standard conditions (14 V) using both set-ups, the values for this voltage were averaged.

![Graph showing the effect of anodizing voltage on the morphology of anodic coatings](image)

**Figure 5.3:** The effect of anodizing voltage on the morphology of anodic coatings. The morphology is presented in terms of interpore distance, pore diameter and porosity together with a linear trendline.

According to Figure 5.3, the interpore distance and porosity increase slowly with increased voltage. In contrast, the pore diameter decreases with increased voltage. However, the trendlines deviate from Figure 5.3 when the results are separated based on the set-up used for each voltage. The interpore distance, pore diameter and porosity are plotted separately for each set-up in relation to the voltage in Appendix II - Supplementary material, Figure A.1.

### 5.1.3 Electrolyte temperature

The SEM images from surfaces anodized with electrolyte temperatures from 2 °C and 66 °C. Figure 5.4 A-C shows surfaces anodized with the smaller set-up whereas the surfaces in Figure 5.4 D-G were anodized using the larger set-up. A comparison of surfaces anodized under standard conditions (14 V, 36-39 °C and 20 min) using the two set-ups, previously presented in Figure 5.1, is included. The anodizing voltage and time were kept constant at 14 V and 20
minutes for all electrolyte temperatures. The porosity, pore diameter, interpore distance and CA for all electrolyte temperatures are shown in Table 5.3.

Figure 5.4: SEM images of surfaces anodized under different electrolyte temperature conditions. A-C) Surfaces anodized using the smaller set-up at 2 °C (on ice), 36-39 °C and 66 °C, respectively. D-F) Surfaces anodized using the larger set-up at 20 °C (RT) 36-39 °C and 50 °C, respectively. The other parameters were kept constant at 14 V and 20 minutes.

Table 5.3: The porosity, pore diameter, interpore distance and contact angle for surfaces anodized with different electrolyte temperatures. The superscript numbers 1 and 2 indicate whether the smaller or the larger set-up was used for that particular experiment, respectively. The standard conditions (36-39 °C) were tested in both set-ups for comparison.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Porosity [%]</th>
<th>Pore diameter [nm]</th>
<th>Interpore distance [nm]</th>
<th>Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (on ice)¹</td>
<td>ND</td>
<td>8 ± 1</td>
<td>13 ± 2</td>
<td>7 ± 3</td>
</tr>
<tr>
<td>20²</td>
<td>30 ± 5</td>
<td>7 ± 1</td>
<td>15 ± 2</td>
<td>42 ± 17</td>
</tr>
<tr>
<td>36-39¹</td>
<td>38 ± 5</td>
<td>13 ± 3</td>
<td>20 ± 5</td>
<td>19 ± 7</td>
</tr>
<tr>
<td>36-39²</td>
<td>28 ± 8</td>
<td>7 ± 1</td>
<td>14 ± 2</td>
<td>15 ± 11</td>
</tr>
<tr>
<td>50²</td>
<td>33 ± 5</td>
<td>12 ± 2</td>
<td>24 ± 4</td>
<td>9 ± 3</td>
</tr>
<tr>
<td>66¹</td>
<td>49 ± 2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

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5.1. Anodizing conditions and morphology

The SEM images in Figure 5.4 B) and D-F) show a clear porous structure for electrolyte temperatures between 20 °C and 50 °C. In contrast, the pores are less distinctive for a low electrolyte temperature of 2 °C (Figure 5.4 A)) and the porosity could not be calculated. Low electrolyte temperatures result in topographical height differences shown as thin stripes of brighter color in the SEM images, similar as for low voltages. Another interesting feature of the anodic coatings is the number of interconnected pores formed at a temperature of 50 °C (Figure 5.4 F)), which seems to be larger than for lower temperatures.

An electrolyte temperature of 66 °C was chosen based on the observations from the anodizing process at 28 V. At this specific voltage a large increase in temperature was observed. An experiment where the temperature was set to 66 °C but with the standard 14 V was set to distinct between the effects from a high voltage and the effects from a high temperature. As can be seen in Figure 5.4 F), a rod-like porous structure similar to that of 28 V (Figure 5.2) was formed. However, the diameter of the rod-like structures obtained at high temperature is 12 ± 1 nm and thus smaller than the diameter of the structures obtained at high voltage (24 ± 1 nm).

The interpore distance, pore diameter and porosity of anodic coatings anodized with electrolyte temperatures between 2 °C and 66 °C are presented in Figure 5.5. All experiments regardless of the setup used are included with averaged values for the standard temperature (36-39 °C).

The effect of electrolyte temperature on the morphology of anodic coatings

![Graph showing the effect of electrolyte temperature on the morphology of anodic coatings.](image)

**Figure 5.5:** The effect of electrolyte temperature on the morphology of anodic coatings. The morphology is presented in terms of interpore distance, pore diameter and porosity together with a linear trendline.

Figure 5.5 shows an increase in all three morphology parameters with increasing electrolyte temperature. As for the voltage, the trendlines deviate from Figure 5.5 when the results are separated based on the set-up used for each temperature. The parameters describing the morphology of anodic coatings are plotted separately for each set-up in relation to the temperature in Appendix II · Supplementary material, Figure A.2.
5.1.4 Anodizing time

The results from SEM imaging of surfaces anodized for anodizing times varying from 5 min to 100 min are shown in Figure 5.6. Figure 5.6 A-B) shows surfaces anodized with the smaller set-up whereas the surfaces in Figure 5.4 C-F) were anodized using the larger set-up. A comparison of surfaces anodized under standard conditions (14 V, 36-39 °C and 20 min) with the two set-ups, previously presented in Figure 5.1, is included. The voltage and electrolyte temperature were held constant at 14 V and 36-39 °C. The porosity, pore diameter, interpore distance and CA are shown in Table 5.4.

**Figure 5.6:** SEM images of surfaces anodized for different anodizing times. A-B) Surfaces anodized using the smaller set-up for 20 min and 100 min, respectively. C-F) Surfaces anodized using the larger set-up at 5 min, 20 min, 60 min and 100 min, respectively. The other parameters were kept constant at 14 V and 20 minutes.
5.1. Anodizing conditions and morphology

Table 5.4: The porosity, pore diameter, interpore distance and contact angle for surfaces anodized for different anodizing times. The superscript numbers $^1$ and $^2$ indicate whether the small or the larger set-up was used for that particular experiment, respectively. The standard conditions (20 min) were tested in both set-ups for comparison.

<table>
<thead>
<tr>
<th>Time [min]</th>
<th>Porosity [%]</th>
<th>Pore diameter [nm]</th>
<th>Interpore distance [nm]</th>
<th>Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5^1$</td>
<td>21 ± 2</td>
<td>7 ± 1</td>
<td>14 ± 2</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>$20^1$</td>
<td>38 ± 5</td>
<td>13 ± 3</td>
<td>20 ± 5</td>
<td>19 ± 7</td>
</tr>
<tr>
<td>$20^2$</td>
<td>28 ± 8</td>
<td>7 ± 1</td>
<td>14 ± 2</td>
<td>15 ± 11</td>
</tr>
<tr>
<td>$40^2$</td>
<td>31 ± 2</td>
<td>10 ± 2</td>
<td>21 ± 4</td>
<td>5 ± 2</td>
</tr>
<tr>
<td>$60^2$</td>
<td>35 ± 2</td>
<td>11 ± 2</td>
<td>23 ± 4</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>$100^1$</td>
<td>52 ± 1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

A honeycomb porous structure can be seen for anodizing times ranging from 5 min to 60 min, as seen in Figure 5.6 A)-E). Just as for a high anodizing voltage and electrolyte temperature, a long anodizing time of 100 minutes results in a rod-like porous structure (Figure 5.6 F). In this case, the diameter of the rods is approximately $12 \pm 2$ nm and thus similar to the diameter of the rods obtained at a high temperature.

The surface anodized for 60 min shows a larger number of interconnected pores compared to shorter anodizing times, similar to the SEM image of the surface anodized at 50 °C (Figure 5.2).

The effects of anodizing time on the interpore distance, pore diameter and porosity of anodic coatings are presented in Figure 5.7. The values for surfaces anodized with standard conditions (20 min) are averaged.

![The effect of anodizing time on the morphology of anodic coatings](image)

**Figure 5.7:** The effect of anodizing time on the morphology of anodic coatings. The morphology is presented in terms of interpore distance, pore diameter and porosity together with a linear trendline.

The results presented in Figure 5.7 indicate an increase in interpore distance, pore diameter and porosity with increasing anodizing time. When the results are plotted separated based on the set-up used, the trendlines deviate from Figure 5.7, as presented in Appendix II - Supplementary material, Figure A.3.
5.2 Wettability

The effect of the anodizing conditions on the wettability was studied as well. The CAs for all tested parameters were measured and presented in Table 5.2, 5.3 and 5.4 for the anodizing voltage, electrolyte temperature and anodizing time, respectively. The CAs are plotted in relation to the tested parameters in Figure 5.8. For the parameters for which the CA was non-detectable due to a low angle, the CA is plotted as 0.

![Contact angle vs. Anodizing voltage](image1)

![Contact angle vs. Electrolyte temperature](image2)

![Contact angle vs. Anodizing time](image3)

**Figure 5.8**: Contact angles and standard deviations plotted against anodizing voltage, electrolyte temperature and anodizing time.

Figure 5.8 indicates an initial increase in CA with increasing anodizing voltage and electrolyte temperature. However, the CA decreases again after peaking at a certain value. A similar trend can be seen for the anodizing time with the exception of the CA of the surface anodized for 40 minutes.

The relationship between the morphology and the wettability of anodic coatings was investigated. Therefore, the CA was plotted in relation to the porosity as presented in Figure 5.9. The CA increases with increasing porosity up to a specific value (approximately 30%) thereafter it decreases again, as presented by the 3rd order polynomial curve fitted to the data.
5.3 Ice adhesion

Ice adhesion measurements were performed on silane treated surfaces anodized using the larger set-up at 5, 14 or 28 V. Ten surfaces were simultaneously anodized using the larger set-up for each parameter of which five were hydrothermally sealed (HTS) before silanization. The CAs were measured using goniometry for all surfaces prior to and post silane treatment. The calculated averages and standard deviations are presented in Table 5.5. In some cases, the CA was too small to be calculated for every droplet indicating a very hydrophilic surface. These values were not included in the calculation of the average CA and therefore, the standard deviation was manually doubled for a better representation of the true CA. To facilitate interpretation of the results, the CAs were plotted against voltage in Figure 5.10.

Table 5.5: Contact angles and standard deviations for surfaces anodized under different voltage conditions and treated with different post-treatments. The * indicates a doubled standard deviation to account for non-computable angles.

<table>
<thead>
<tr>
<th>Voltage [V]</th>
<th>Treatment</th>
<th>Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anodized</td>
<td>12 ± 7</td>
</tr>
<tr>
<td>5</td>
<td>Anodized, HTS</td>
<td>7 ± 3*</td>
</tr>
<tr>
<td></td>
<td>Anodized, silane</td>
<td>130 ± 3</td>
</tr>
<tr>
<td></td>
<td>Anodized, HTS, silane</td>
<td>139 ± 9</td>
</tr>
<tr>
<td>14</td>
<td>Anodized</td>
<td>5 ± 2</td>
</tr>
<tr>
<td></td>
<td>Anodized, HTS</td>
<td>15 ± 11</td>
</tr>
<tr>
<td></td>
<td>Anodized, silane</td>
<td>131 ± 4</td>
</tr>
<tr>
<td></td>
<td>Anodized, HTS, silane</td>
<td>128 ± 7</td>
</tr>
<tr>
<td>28</td>
<td>Anodized</td>
<td>4 ± 3*</td>
</tr>
<tr>
<td></td>
<td>Anodized, HTS</td>
<td>6 ± 3</td>
</tr>
<tr>
<td></td>
<td>Anodized, silane</td>
<td>162 ± 9</td>
</tr>
<tr>
<td></td>
<td>Anodized, HTS, silane</td>
<td>134 ± 13</td>
</tr>
</tbody>
</table>
The results shown in Table 5.5 and Figure 5.10 indicate decreasing CAs with increasing voltage for non-silanized surfaces that are not HTS treated. However, overlapping standard deviations indicate that the trend may not be statistically significant. The CAs deviate from the CAs for surfaces anodized using the smaller set-up, previously presented in Figure 5.8, as these surfaces were anodized using the larger set-up. Furthermore, silanization results in hydrophobic surfaces in all cases, i.e. $\text{CA} \geq 90^\circ$. The surfaces anodized at 28 V treated with silanes are the only ones resulting in a super hydrophobic surface (SHS) with a $\text{CA} \geq 150^\circ$. Generally, HTS treatment results in a larger standard deviation compared to surfaces not treated with HTS.

The ice adhesion strength was measured for all silane treated surfaces as presented in Table 5.6 and Figure 5.11. The strength is measured as the force needed to break the solid-ice interface. Low ice adhesion strength is represented by a small force, which is what is desired for aircraft applications.

**Table 5.6**: The ice adhesion strength of silane-treated surfaces anodized at 5, 14 or 28 V with optional hydrothermally sealing (HTS).

<table>
<thead>
<tr>
<th>Voltage [V]</th>
<th>Treatment</th>
<th>Ice adhesion [kPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Anodized, silane</td>
<td>324 ± 42</td>
</tr>
<tr>
<td></td>
<td>Anodized, HTS, silane</td>
<td>267 ± 149</td>
</tr>
<tr>
<td>14</td>
<td>Anodized, silane</td>
<td>209 ± 74</td>
</tr>
<tr>
<td></td>
<td>Anodized, HTS, silane</td>
<td>197 ± 145</td>
</tr>
<tr>
<td>28</td>
<td>Anodized, silane</td>
<td>104 ± 56</td>
</tr>
<tr>
<td></td>
<td>Anodized, HTS, silane</td>
<td>389 ± 138</td>
</tr>
</tbody>
</table>
Figure 5.11: Ice adhesion and standard deviation plotted against contact angle. The contact angles are a result from silane-treated surfaces anodized at different voltages and hydrothermally sealed (HTS).

The standard deviations for ice adhesion strength are larger for HTS treated surfaces than for surfaces not treated with HTS. Furthermore, the ice adhesion strength for non-HTS treated decreases with increasing contact angle. Especially noteworthy, the SHS anodized at high voltage (28 V) results in the lowest ice adhesion strength.
6 Discussion

The purpose of this master's thesis was to investigate the influence of anodizing conditions on the morphology of porous alumina of Cu-alloyed Al obtained when anodizing in the environmentally friendly electrolyte TSA. Since the ice adhesion properties of a material are thought to depend on wettability, the relationship between morphology and wettability was further investigated. In this chapter, the results presented in Chapter 5 will be discussed and related to the literature study in Chapter 2.

6.1 The anodizing process

In this master's thesis, a smaller and a larger set-up were used to anodize surfaces under different conditions. The set-ups differed in the way a connection was established between the surface and the DC power supply as well as the size and shape of the cathode. In general, the anodizing process is delicate and prone to errors. One of the main challenges is to obtain enough current flow through the electrochemical cell for an efficient anodizing process. Therefore, it is important to have a tight contact between the Al wire and the alloy for the smaller set-up and a tight contact with the metal device in the larger set-up. Furthermore, it is important to not immerse the Al wire twined around the handle of the surface anodized using the smaller set-up to avoid the formation of an oxide layer between the Al wire and the surface. The insulating oxide layer would compromise the current flow. For the larger set-up, immersion of the metal device in the electrolyte instead results in an undesired current increase affecting the process. Such errors could lead to discoloration or deterioration of the anodized alloy. However, once a proper contact was established when using the larger set-up, the process produced similar results for all surfaces anodized simultaneously. In the case of the smaller set-up, the results could differ from surface to surface even when anodized at the same time. Note that results could differ between batches for both set-ups. The SEM images and most CAs only originate from one batch for each parameters. Therefore, these results should be verified in future studies.

Another factor that may have influenced the results is the temperature during anodizing. Due to the use of regular heating plate, the temperature was difficult to control. During long anodizing procedures or at high voltage, the temperature could increase several degrees. An attempt was made to regulate the temperature by turning the heating plate on and off when needed. However, this resulted in an unstable temperature instead. A solution to this issue would be the use of a heating plate with a temperature probe for improved temperature control.

Furthermore, other pretreatment steps in addition to degreasing and pickling should be considered. The morphology of porous oxide layer is thought to be affected by the surface roughness of the original alloy [83]. For this reason, large cavities can be observed in the SEM images for most parameters that are natural for the anodizing process. Besides, large-scale production of Al sheets involves a process called rolling [7]. During a master's thesis conducted by Nilsson and Staaf [84], analysis of the morphology of anodic Al alloys suggested that the macrostructure obtained during the rolling process affected the growth direction of the porous oxide layer. To decrease the influence of surface roughness and macrostructures on the growth of the alumina layer, a polishing step of the alloys could be added to the pretreatment. In addition to mechanical polishing methods, e.g. with abrasive paper [29, 48], electropolishing can be used to flatten and smoothen the Al alloys prior to anodizing and to promote the self-ordering of the anodized oxide layer. Similar to anodizing, electropolishing
Involves an electrochemical process where the surface roughness can be tuned by adjusting polishing voltage, time and electrolyte temperature. Al can be electropolished in alkaline or acidic electrolytes although the use of acid usually yields a smoother surface. [83] Commonly, a mixture of perchloric acid and ethanol is used for electropolishing Al [11, 14, 83, 85, 86].

6.2 Comparison between set-ups

As one smaller and one larger set-up were used for the anodizing process, two surfaces were anodized under standard conditions (14 V, 36-39 °C, 20 min) using the two set-ups for comparison. The SEM images for these two surfaces (Figure 5.1) as well as the calculated porosity, pore diameter and interpore distance (Table 5.1), show diverse morphologies for the two set-ups. A tight contact between the anodized surface and the DC power supply is important for a well-functioning anodizing process. The surface anodized under standard conditions with the smaller set-up exhibited an anodic coating of higher porosity with larger pore diameters and interpore distances than the surface anodized with the larger set-up. These differences are likely to be caused by surge currents, i.e. large but short-lived currents, that may occur when using the smaller set-up due to an inadequate contact between the surface and the power supply. The surge currents may speed up the anodizing process in a way that it results in larger pore diameters and interpore distances. As the design of the larger set-up allows for tight contact, surge currents are less likely to occur. Therefore, the morphology of surfaces anodized with the larger set-up is thought to correspond better to a well-functioning anodizing process than for surfaces anodized with the smaller set-up. For future experiments, the current running through the electrochemical cell should be measured, studied and compared between experiments. In this master’s thesis, an ammeter was connected to the circuit to determine the plausibility of the current. However, the absolute currents or current densities were not compared between experiments.

6.3 Anodizing conditions and morphology

The morphology of anodic alumina is affected by parameters such as the anodizing voltage, electrolyte temperature and anodizing time. Firstly, the SEM images for surfaces anodized under various voltage conditions shown in Figure 5.2, indicate that the morphology is clearly affected by the voltage in the range of 5-28 V. Several authors have stated that the interpore distance and the pore size increases with increasing voltage [11, 31, 51, 56] while the porosity decreases [6, 10, 57]. Although Table 5.2 and Figure 5.3 show that interpore distance increases, they also show an increase in the porosity and a decrease in the pore diameter. However, the overall trend of the porosity and pore diameter is arguable. For instance, many of the pore diameter values have overlapping standard deviations and are therefore not significantly different, meaning that an average value of repeated experiments may give other results. Furthermore, the pore diameter and interpore distance for the surface anodized at 28 V could not be calculated due to the formation rod-like structures rather than a hexagonal porous structure. However, the porosity of this surface could be calculated and appeared to be significantly higher than for the other surfaces. This results in a trendline with a different slope than if the porosity value for 28 V would not have been included. In fact, a decrease in porosity with increasing voltage in the range of 5 V to 24 V is indicated by Figure 5.3. Logically, a combination of a decreasing, constant or slowly increasing pore diameter and an increase in interpore distance would result in a decreasing or nearly constant porosity. When separating the results based on the set-up used for anodizing, as shown in Figure A.1, the porosity slowly decreases for the surfaces anodized at 9, 14, 19 and 24 V using the larger set-up. At the same time, the pore diameter is nearly constant whereas the interpore distance increases. Surge currents may occur when using the smaller set-up resulting in a sped up anodizing process and thus increased pore diameters and interpore distances. Therefore, it is possible
that higher voltages are required when using the larger set-up to obtain similar results as for lower voltages using the smaller set-up.

Absolute current densities were not compared nor investigated in this master’s thesis. However, one thing that was noticed about the current was that it reached the current limit of the DC power source when anodizing at 28 V. The current was approximately ten times higher than the current obtained when anodizing at the standard 14 V. The high current resulted in minor visible defects at the edges of the anodized surface. The porous oxide layer is formed as a result from the competitive formation and dissolution reactions [51]. Therefore, it is likely that the porous rod-like structures are formed from a dominant dissolution reaction due to the high voltage and/or high current. However, since the temperature during this experiment increased to 66 °C, the characteristic structure could also depend on a high temperature. Therefore, a surface was anodized at 66 °C but at the standard 14 V (Figure 5.4). SEM images show that the morphology of this surface also features rod-like structures, but with a smaller diameter (12 ± 1 nm) than that of the surface anodized at 28 V (24 ± 1 nm). Additionally, the current did not increase significantly compared to standard conditions when anodizing at a high temperature. For this reason, it is likely that the rod-like structure does not only depend on the temperature but also on the voltage and/or current.

When it comes to the electrolyte temperature, SEM images (Figure 5.4) show a clear difference between the anodized surfaces. Observations have been made in earlier publications where a rise in temperature causes an increase in the porosity [10, 53] as well as the pore diameter. However, the interpore distance is not as thoroughly discussed in published research. In this master’s thesis, the results shown in Table 5.3 and Figure 5.5 show an increase in all three parameters used to describe morphology when the temperature is increased. However, one may argue that a larger increase in interpore distance compared to the increase in pore diameter should not increase the porosity. Also in this case, the interpore distance and the pore diameter could not be calculated for the highest electrolyte temperature (66 °C). Furthermore, the porosity could not be calculated for the lowest temperature (2 °C) due to the small pore diameter and interpore distance. The non-computable values may have resulted in misleading trendlines. Therefore, experiments should be repeated several times to verify or correct these initial results. Results from the two set-ups could not be compared quantitatively and therefore only trends could be discussed. The results were presented separately for each set-up in Figure A.2 as a complement to Figure 5.5. When only taking the results from the larger set-up into account, the porosity remains constant whereas the increase in interpore distance is larger compared to the increase in pore diameter.

When it comes to the pore diameter, an increase is thought to be a result from the chemical dissolution effect of the electrolyte. Since the dissolution occurs from the top of the surface, Aerts et al. [53] showed that the pores obtain a cone-shape and have smaller diameters at the substrate-oxide interface. Future studies are recommended for confirmation of the pore shape, including experiments where the pore diameter is measured cross-sectionally at the substrate-oxide interface and near the surface. For this purpose, transmission electron microscopy could be used.

Another interesting observation for the electrolyte temperature is the increased number of inter-connected pores for the surface anodized at 50 °C. This could indicate the temperature where the alumina transforms from the hexagonal porous structure to the rod-like structures. A similar transition structure is obtained when anodizing for 60 minutes (Figure 5.6). At 100 minutes, the rod-like structure has been formed instead with a diameter of 12 ± 2 nm. There was no significant rise in temperature or current in this case indicating that this morphology is obtained due to the dissolution effect of the electrolyte when exposing the alumina at high voltage, high temperature or for a long time.
Further analysis of the effect of anodizing time on the morphology show similar results as for the electrolyte temperature, i.e. an increase in interpore distance, pore diameter and porosity when increasing the anodizing time. Again, the removal of the porosity data point at 100 minutes would decrease the slope of the porosity trendline. As most of the anodizing times were tested using the larger set-up, the separation of the results (Figure A.3), does not result in as deviating trendlines as previously shown for the anodizing voltage and electrolyte temperature. Additionally, due to the large standard deviations and the use of the two set-ups, experiments would need to be duplicated using only one set-up in the hope of getting a clearer idea of the effect of anodizing time on the morphology of anodic coatings.

6.4 Wettability

The relationship between wettability and morphology is important to establish in order to understand the ice adhesion properties of a surface. Although many researchers relate the morphology in terms of porosity, interpore distance and pore diameter to the anodizing conditions, the effect on the wettability is less widely discussed. In this master's thesis, the wettability was related to both the anodizing conditions and the porosity in Figure 5.8 and Figure 5.9, respectively. All surfaces anodized in this project that are not post-treated with silanes exhibit hydrophilic CAs (≤ 90°). The hydrophilic surfaces are thought to be in the Wenzel states due to the roughness of these surfaces. It could be concluded that the CA increases with increasing anodizing voltage and electrolyte temperature up to a specific point whereafter it decreases again. A similar trend can be seen for the anodizing voltage with the exception of the CA of the surface anodized for 40 minutes. A low or non-detectable CA for the higher values of the three parameters could be explained by a high porosity, as shown by Figure 5.9. A high porosity could be the indication of thin or non-existing pore walls failing to support the liquid droplet, as explained by [14]. This could be especially true for the surfaces anodized at 28 V, 66 °C or for 100 minutes for which a highly porous rod-like structure was formed rather than distinctive pores. Furthermore, many measured CAs have large standard deviations and as explained in Section 3.1, drops with a flat profile (CA ≤ 20°) cannot be accurately measured. The large standard deviations could also be a result of heterogeneously anodized surfaces.

6.5 Ice adhesion

Since the ice adhesion to aircrafts affects both flight safety and the environment while the anti-icing technologies of today are insufficient, it is crucial to find new solutions. Therefore, the ice adhesion properties of surfaces with different morphology and wetting properties were investigated in this master's thesis. The surfaces were anodized at 5 V, 14 V or 28 V and post-treated with hydrothermal sealing (HTS) and silanes. Silanization of surfaces results in hydrophobic wetting properties (≥ 90°), as indicated by Table 5.5 and Figure 5.10. The surface anodized at 28 V and not HTS-treated turned out to be superhydrophobic. It is likely that the high CA can be explained by the Cassie-Baxter state for which the liquid droplet does not penetrate surface irregularities. In future studies, the contact angle hysteresis (CAH) should be measured as another indication of the wetting state. The SHS is probably the result from close interactions between the silanes and the rod-like structures due to the deep penetration of the silane solution into the structure.

In general, HTS results in larger standard deviations both before and after silane treatment. The large standard deviations are likely to be caused by a heterogeneous surface morphology due to the rough boehmite structure. Due to the heterogeneity of the HTS-treated surface, the standard deviations of the ice adhesion measurements are also larger than for the surfaces not HTS-treated, as shown in Figure 5.11. The large standard deviations indicate that the surfaces were prone to cohesive failure giving a false representation of the ice adhesion.
strength. Besides a heterogeneous surface morphology, the cohesive failure may also be caused by a water-filled microscopically rough surface like that of the boehmite structure.

The superhydrophobic surface (SHS) anodized at 28 V and not HTS-treated exhibited the lowest ice adhesion strength. As presented and discussed previously, a surface anodized at such a high voltage using the smaller set-up resulted in a rod-like morphology. The surfaces anodized at 28 V with the larger set-up may also exhibit a rough, rod-like surface texture, although the morphologies of these surfaces were not investigated using SEM. Despite the possible surface roughness, the ice adhesion strength was low. One explanation could be that no or less water resides in the rod-like structure compared to the boehmite structure. Although, all surfaces were dried in a vacuum chamber prior to silane treatment and the treatment itself was also performed under vacuum. Ice adhesion measurements of surfaces for which it is known whether the structure is filled with water or not together with SEM imaging could give more information about this matter.

While these initial experiments indicate that SHS's have the best potential for ice adhesion purposes, more dynamic experiments could be performed to confirm or disprove these results. For instance, it is suggested that the ice adhesion on SHS's does not only correlate to the static CA, but also to the CAH and roll-off angle (ROA). Therefore, additional measurements where the CAH and ROA can be measured should be performed. Furthermore, the ice adhesion tests in this master's thesis were performed using ice frozen to the substrate. For aircraft applications, the adhesion strength of high-speed impact ice should also be tested.
7 Future perspectives

The implementation of passive anti-icing technologies described in this master’s thesis has high potential for aircraft applications. Future studies verifying the preliminary results obtained herein need to be considered before taking the next step towards the use of passive anti-icing technologies. Several suggestions of valuable studies are summarized below.

7.1 The anodizing procedure

The anodizing process is sensitive and challenging as described in this report. In this master’s thesis, a smaller and a larger set-up was used which were different in the way of establishing a connection between the surface and the DC power supply as well as the size and shape of the cathode. By comparing two surfaces under the same conditions, one anodized in each set-up, it was clear that the set-up influences the morphology of the anodic coating. Therefore, the same set-up should be used for all experiments in the future. The use of different set-ups is not be a problem in the Saab production, where all surfaces are anodized using the same production line. However, future work also includes performing similar tests at production scale that can be compared to the laboratory scale results. In addition to using the same set-up, a heating plate with a temperature probe should be used for improved temperature control during the process.

Furthermore, measurements in general should be repeated several times to investigate the reproducibility of the results. Additionally, more parameter values should be tested within the ranges tested in this master’s thesis to investigate the relationship between anodizing conditions, morphology, wettability and ice adhesion strength with more certainty. Especially, values between 50 °C and 66 °C as well as 60 minutes and 100 minutes, where the formation of the rod-like morphology seems to be initiated, may be of interest. Instead of changing one parameter at the time, a factorial experiment could be designed to study the effects of anodizing conditions in a more statistical manner.

The effect of current, or rather current density, should be investigated in addition to or instead of the anodizing voltage. Furthermore, pretreatments such as mechanical polishing and electropolishing to smoothen the alloys prior to anodizing could be added to the process. When it comes to the morphology, the pore size, porosity and interpore diameter could be measured at several depths of the alumina layer. For example, measurements could be performed at the substrate-oxide interface as well as near the surface.

7.2 Wettability and ice adhesion

In this master’s thesis, the static contact angle was measured. However, the ice adhesion properties are thought to be more related to the CAH and ROA. Therefore, these parameters should be measured and taken into account in future measurements. Especially, additional CA and ice adhesion measurements should be performed on the SHS obtained when anodizing at 28 V and after silane treatment. Although the morphology of the surfaces anodized with the larger set-up at 28 V and used for ice adhesion measurements was not studied, it is likely that a rod-like structure similar to that of the surface anodized at high voltage using the smaller set-up, was obtained. Since 66 °C and 100 minutes also resulted in the rod-like structures, ice adhesion measurements should be performed for these anodizing conditions as well. For more certainty, the measurements should be repeated in an attempt to reproduce the results. When a proper relationship has been established between the morphology,
wettability and ice adhesion properties of anodic coatings, other ways of measuring ice adhe-
sion should be applied. For example, the adhesion strength of high-speed impact ice should
be investigated.

Since silane treatment results in hydrophobic or superhydrophobic surfaces, the possibility
to use silanes at production scale should be considered. However, the effect of these silicone
compounds on the environment and human health should be taken into account and other
alternatives should be discussed. In this project, HTS treatment prior to silanization did not
improve the ice adhesion properties of surfaces. However, the effects of HTS treatment after
silanization was not studied herein and could instead be performed in future work.

7.3 General remarks

The ice adhesion properties of anodized Al alloys are of interest to the aircraft industry,
amongst others. However, the material strength, corrosion resistance and paint adhesion
properties of the materials are not to be forgotten. When a surface with sufficient ice ad-
hesion properties has been achieved, the material strength, corrosion resistance and paint
adhesion properties should be tested and optimized.
8 | Conclusions

The aims of this master’s thesis was to investigate the effects of anodizing conditions on the anodizing process of Cu-alloyed Al. More specifically, on the morphology of the formed alumina layer. The commonly used electrolyte chromic acid has been replaced by the functional comparable tartaric sulfuric acid (TSA) for environmental and health reasons. The morphology is related to the wettability of the anodized surfaces in the hope of achieving a surface with improved ice adhesion properties. The ice adhesion properties are of importance to the aircraft industry for environmental and safety reasons. The effect of anodizing conditions, morphology and wettability as well as posttreatments such as hydrothermal sealing (HTS) and silanization on ice adhesion properties were studied.

It can be concluded from this master’s thesis that the morphology in terms of porosity, interpore distance and pore diameter of anodic coatings is influenced by anodizing conditions (see Chapter 5 and Chapter 6). The conditions tested herein were the anodizing voltage, electrolyte temperature and anodizing time. In turn, the morphology affects the wettability of a surface although the relationship needs further investigation. More interestingly, silane treatment of a surface anodized at 28 V results in a superhydrophobic surface (SHS) with a contact angle above 160°. SEM images of another surface anodized under similar conditions but using another set-up showed a rod-like morphology rather than a honeycomb cell structure with nanopores normally obtained through anodizing. The superhydrophobic surface also exhibited the best ice adhesion properties in terms of a low force needed to remove ice frozen to the surface. The HTS posttreatment was shown not to be effective for obtaining desirable ice adhesion properties when performed prior to silanization due to a heterogeneous surface.

To summarize, it is clear that anodic coatings can be tuned by adjusting the anodizing conditions such as voltage, electrolyte temperature and time. The tunable anodic coatings have the potential of reducing ice adhesion. However, results will need to be verified with additional experiments. For instance, the addition of polishing pretreatments, the testing of more parameter values and other parameters (e.g. current density), measuring contact angle hysteresis and/or the roll-off angle and the use of other ice adhesion methods may give results with more certainty. Finally, tuned surfaces exhibiting low ice adhesion strength should also have satisfactory material strength, corrosion resistance and paint adhesion properties. Overall, the ability to tune the morphology of sustainable anodic coatings pushes this research area one step closer to implementing passive anti-icing materials in aircrafts.
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Appendix I - Planning Report
Optimization of sustainable anodic coatings for reduced ice adhesion
Planning Report 2019-01-30

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Abstract
The aim of this thesis is to investigate the influence of parameters such as voltage, temperature and time, on the porous aluminum oxide layer achieved through anodization. The anodization of aluminum alloys aims to improve corrosion resistance as well as ice and paint adhesion properties, which is of importance for aircraft and aerospace industry. The pore size and interpore diameter of the porous oxide layer may be adjusted by varying parameters to tune the wettability of the surfaces. In this thesis it is hypothesized that the porosity decreases with increasing voltage but increases with increasing electrolyte temperature and anodization time. Furthermore, the surfaces may be chemically modified using silanes to decrease the wettability and reduce ice adhesion. Pre-treatment methods such as electropolishing may be used to improve the self-ordering of the anodic aluminum oxide. The porosity of anodized surfaces prepared with varying parameters will be studied using characterization methods such as scanning electron microscopy and atomic force microscopy whereas the wettability will be characterized using goniometric contact angle measurements.
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1. Background and purpose

A high specific strength, i.e. strength-to-weight ratio, and durability is desired for materials used in aerospace and aircraft industries. Aluminum alloys are the most widely used materials that meet this requirement. The specific strength is said to be an intrinsic property of the alloy, while durability largely depends on interactions between the alloy surface and its surrounding environment. (1) An alloy’s durability is affected by a slow, progressive or rapid deterioration of the material’s properties such as its appearance, surface or mechanical properties, a process called corrosion. Corrosion is caused by the electrochemical reaction between the surface and an aqueous phase. (2) Although aluminum is a very reactive metal, it obtains a natural protective oxide layer providing corrosion resistance due to the metal’s high affinity for oxygen. (3) To further improve the alloy’s corrosion resistance and thus minimizing the need for maintenance and repair (1), the naturally formed oxide layer can be thickened through a process called anodizing (4). Anodizing of aluminum is an electrochemical process which typically involves anodic oxidation using an electrolyte. When the anodization is performed with an acidic electrolyte solution, a barrier layer and a layer with a unique porous structure with varying pore size and interpore distance is created. (5) The porosity of the oxide layer is dependent on parameters such as voltage, electrolyte temperature (6), electrolyte (3) and duration of anodizing (7).

Chromate anodizing using hexavalent chromium (Cr(VI)) was a commonly used method due to its efficiency to produce oxide layers with appropriate corrosion resistance and painting adhesion (4). However, Cr(VI) is carcinogenic and toxic to humans and the environment and their use is strictly regulated (4,7,8). A more environmentally friendly alternative to chromate anodizing but with corrosion adhesion and paint adhesion compliable with the requirements is the use of tartaric sulphuric acid (TSA) as electrolyte (4). The use of TSA is widely adapted in the aircraft industry, as for example by Saab AB (9). Saab is a Swedish defense and security company with over 16 000 employees and business areas such as aeronautics, surveillance and dynamics (10).

In addition to corrosion resistance, paint and ice adhesion are important material properties to consider in aerospace and aircraft industries. The ability of paint and ice to stick to an aluminum alloy surface largely depends on its wettability behavior (11). Wettability can be described by the behavior of liquid drops on a solid surface. The liquid drop rolls up into a ball on a hydrophobic surface with lower surface energy, and spreads on a hydrophilic surface with higher surface energy. Wettability is distinguished by measuring the contact angle, \( \theta \), where \( \theta > 90^\circ \) indicates a hydrophobic surface and a \( \theta < 90^\circ \) a hydrophilic surface (12). A more hydrophobic surface thus repels water better than a hydrophilic surface, a property desired to obtain reduced ice adhesion which seems to depend on both wettability and surface roughness (13). By improving ice adhesion properties safety risks are minimized, and anti-icing systems will be redundant reducing the weight of the aircrafts and therefore fuel consumption. However, since many environmentally friendly paints used in aircraft industry are water-based, it is essential to have a proper balance between the hydrophobic and hydrophilic properties of the surface. Therefore, it is of interest to investigate the effects of the porosity of anodized aluminum alloys on the wettability and how this property can be controlled.

Furthermore, the coating of aluminum surfaces may improve corrosion resistance and wettability properties (14), and thus reduce ice adhesion. The surfaces could be coated with paints (15) but also through surface modification with silanes. Silanes are used to create superhydrophobic surfaces, i.e.
surfaces with a contact angle $\theta > 150^\circ$ (16). Hence, the possible use of silanes to further improve ice adhesion properties of anodized aluminum alloys needs to be illuminated.

Large-scale production of aluminum sheets do involve a process called rolling (17). During a thesis conducted by Nilsson and Staaf (18), analysis of anodic aluminum alloys with Scanning Electron Microscopy (SEM) suggested that the macrostructure obtained during the rolling process affected the growth direction of the porous oxide layer. To smoothen the aluminum alloys prior to anodizing and promoting the self-ordering of the anodized oxide layer, electropolishing can be used (19).

This thesis is written on behalf of the research team of molecular surface physics and nano-science at the department of Physics, Chemistry and Biology (IFM) at Linköping University (LiU) and conducted in collaboration with Saab Defense and Security, Linköping. The project will be carried out during the spring semester 2019 and for a period of twenty weeks. The thesis aims to illuminate the effect of voltage, anodization time and temperature on the porosity of anodized aluminum alloys. Moreover, the effect of the porosity on wettability, paint adhesion and ice adhesion will be investigated. Additionally, the aluminum alloys can be electropolished prior to anodization to promote the self-ordering of the oxide layer and modified with silanes to increase the hydrophobicity. The surfaces will be characterized using methods such as goniometry to measure wettability as well as Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) to measure surface topography.
2. **Hypothesis**

The following hypothesis will lay the foundation for this project. The thesis aims to investigate the effects of parameters such as voltage, anodization time and temperature on the porosity of anodized aluminum oxide. The effect of porosity and silanization on wettability and adhesion properties will be considered as well as the potential use of electropolishing to facilitate characterization of anodized surfaces.

2.1. **Voltage**

There are several studies that describe the effect of the anodization voltage on the porosity of aluminum oxide. According to a study conducted by Debuyck et al. (6), increasing the voltage results in a decreased porosity. Anodization was performed with sulphuric acid as an electrolyte and the voltage was varied between 3-18 V. Tomassi et al. (20) stated that the pore diameter is proportional to the applied voltage, although dependent on the type of electrolyte. Furthermore, the interpore distance does also seem to increase with increasing voltage. Also, Belwalkar et al. (21) confirms that the pore size seems to increase in direct proportion and that the interpore distance increases linearly with the applied voltage. The formation of an oxide layer with higher pore diameters and increasing interpore distance decreases the porosity (4).

This thesis aims to further investigate the effect of voltage on the porosity with TSA as electrolyte with constant concentration, with the hypothesis that an increasing voltage decreases the porosity.

2.2. **Temperature**

Besides the finding that the voltage influences the porosity of anodized aluminum oxide, Debuyck et al. (6) also concluded that a raise in the electrolyte temperature results in an increase in the porosity (0-28 °C, sulphuric acid). Aerts et al. (22) obtained results in line with Debuyck et al. where the pore diameter and number of pores increases significantly with increasing electrolyte temperature (5-55 °C, sulphuric acid). However, Aerts et al. discusses that the increase in pore diameter is a result of a dissolving action of the electrolyte upon increasing time of exposure. Newly formed pores at the base of the layer seemed to have a constant pore diameter whereas the diameter increased with the thickness of the layer due to electrolyte exposure. The electrolyte thus becomes more aggressive with increasing temperature.

This thesis aims to further investigate the effect of electrolyte temperature on the porosity with TSA as electrolyte with constant concentration, with the hypothesis that an increasing temperature increases the porosity.

2.3. **Anodization time**

Ilango et al. (23) aimed to investigate the effect of anodization time on pore size, interpore diameter and porosity in a two-step anodization process. In the first anodization step, with oxalic acid, a less ordered pore arrangement was fabricated by decreasing the anodization time. In the second anodization step, in orthophosphoric acid, anodization step was varied from 1-3 minutes and the results show a linear increase of cell diameter (the dimension of the pore diameter including the interpore distance) and pore diameter with anodization time. As mentioned in section 2.2., Aerts et al. (22) stated the electrolyte dissolves the porous structure upon long-time exposure.
This thesis aims to further investigate the effect of anodization time on the porosity with TSA as electrolyte with constant concentration, with the hypothesis that an increases anodization time leads to increased porosity.

### 2.4. Porosity and wettability

Guo et al. (24) studied the dependence of wettability on pore diameter by performing a two-step anodization process with different acidic electrolytes under constant voltage and anodization time. The results showed that the contact angle (40-130°) increases with increasing pore diameter (10-230 nm), altering the wettability of the porous anodized aluminum oxide from hydrophilic to hydrophobic. Guo et al. argues that the decreased wettability is due the enhancement of surface roughness caused by the existence of pores.

This thesis aims to further investigate the effect of the porosity of anodized aluminum oxide on wettability and adhesion properties, with the hypothesis that an increasing pore size decreases the wettability and thus reduces ice adhesion.

### 2.5. Silanization

Silanes can be used to tune the wettability of anodized aluminum oxide (25) so that superhydrophobic surfaces can be obtained (26). Wang et al. (27) created superhydrophobic surfaces by anodizing aluminum surfaces and chemically modifying them by dip-coating in a perfluoroalkyl-silane solution. Furthermore, the surfaces showed good ice-phobicity and corrosion resistance. Other examples of the use of silanes to improve surface wettability of anodized aluminum oxide were demonstrated by Buijnsters et al. (16), who also used a perfluoroalkyl-silane solution, and Capelossi et al. (14), who created a hybrid-film of a tetraethoxy-silane and a trimethoxy-silane.

This thesis aims to further investigate the effect of anodized aluminum surface modification with silanes on wettability and adhesion properties, with the hypothesis that the modification decreases the wettability and thus reduces ice adhesion.

### 2.6. Electropolishing

Electropolishing can be used to smoothen the aluminum surface before anodization. Yu et al. (19) demonstrated that by electropolishing using ethanol-perchloric acid solutions and tuning the voltage and polishing time, highly uniform, self-ordered anodic aluminum oxide can be formed through anodization. There are several other studies that have used electropolishing as pre-treatment of aluminum alloys, although without further discussing the possible effect on the results (16,24,28).

This thesis aims to further investigate whether electropolishing is a suitable pre-treatment step for anodization, with the hypothesis that it affects the self-ordering of the porous oxide layer.
3. Project objective

The main objective of this thesis is to illuminate the effects of parameters such as voltage, electrolyte temperature and anodization time in the anodization process of aluminum alloys. Furtherly, the effects of the porosity on wettability and adhesion properties will be investigated, including the use of silanes.

This main objective can be divided into sub-objectives:

1. The effect of anodization voltage on pore size and interpore diameter of the formed porous oxide layer on aluminum alloys is investigated. Aluminum alloys will be anodized with various anodization voltages and the pore size and interpore diameter will be determined using characterization methods such as SEM and AFM.

2. The effect of electrolyte temperature used for anodizing aluminum alloys on pore size and interpore diameter of the formed porous oxide layer is investigated. Aluminum alloys will be anodized with various electrolyte temperatures and the pore size and interpore diameter will be determined using characterization methods such as SEM and AFM.

3. The effect of anodization time on pore size and interpore diameter of the formed porous oxide layer on aluminum alloys is investigated. Aluminum alloys will be anodized with various anodization times and the pore size and interpore diameter will be determined using characterization methods such as SEM and AFM.

4. The effect of pore size and interpore diameter on the wettability, ice adhesion and corrosion properties of the anodized aluminum alloys is determined. The wettability of aluminum alloy samples anodized with varying parameters will be investigated using contact angle measurements. Ice adhesion measurements will be performed at Research Institutes of Sweden (RISE). Corrosion tests will be performed by immersing samples in a salt solution (NaCl).

5. The effect of silanes adhered to anodized aluminum alloys will be investigated using contact angle measurements.

6. The effect of pre-fabricated macrostructures due to rolling on the growth of the porous oxide layer during anodization of aluminum alloys will be investigated. The aluminum alloys will be electropolished to remove the microstructures and differences will be characterized using methods such as SEM and AFM.

4. Boundary conditions

This thesis will be conducted at IFM. The experiments that will be performed to reach the above states objectives will be executed using instruments and other equipment available at the department. However, some experiments may require experienced individuals to supervise the measurements.

Although there are many parameters that are said to influence the porous structure of the oxide layer formed during anodizing aluminum alloys, this focus of this thesis will mainly lie on the voltage, electrolyte temperature and anodization time. This means that not all parameters are considered when analyzing the results, meaning that further studies may need to be conducted to fully understand which parameters that affect the porous structure.
5. Study model

During the first few weeks of the project a literature study will be conducted to gain basal knowledge regarding the effects of the earlier mentioned parameters on the anodization process of aluminum alloys. Resources made available by the Linköping University library will be used to find books, review articles and studies that are of relevance for the topic of this thesis. Online databases like UniSearch, Scopus, PubMed, Google Scholar, PubMed Central (PMC), ScienceDirect, Wiley Online Library and Springer Nature will be utilized. After the initial literature study, laboratory experiments will be prepared for by designing the experiments based on the literature study, performing relevant risk analysis and laboratory introductions.

The laboratory experiments will involve anodizing aluminum alloys with a simple electrochemical setup with varying experimental conditions. A series of anodization experiments where the voltage, electrolyte temperature and anodization time is varied will performed. Aluminum alloys will be pre-treated and anodized according to the anodization process standard used at Saab (9). Selected samples will be analyzed using complex characterization methods such as SEM and AFM. Contact angle measurements using goniometry will be performed as an indication of the wettability of the samples. The wettability can be related to ice and paint adhesion properties. Ice adhesion will be measured in collaboration with Research Institutes of Sweden (RISE). Corrosion tests may be performed by immersing samples in salt solutions (NaCl) for different time periods.

Further treatments prior and after anodization will be investigated. Prior to anodization, aluminum alloys can be smoothened using electropolishing to improve the self-ordering of the oxide layer. A suitable electropolishing method will be investigated and the surfaces will be characterized using SEM and/or AFM in comparison to surfaces not treated with electropolishing. After anodization, the alloys can be further treated with silanes to increase the surface’s hydrophobicity and thus decrease their ice adhesion properties. The silanized surfaces can be compared to surfaces without silanes using characterization methods such as SEM and AFM.

Since the porosity of the anodized aluminum oxide layers related to properties such as wettability, and parameters such as voltage, electrolyte temperature and anodization time, the laboratory work in this thesis will be an iterative process where more experiments may be performed based on data received from previous experiments. An overview of the study model is presented in Figure 1.

![Figure 1: A graphical presentation of the study model of this thesis.](image-url)
6. Methods
To reach the objectives of this thesis, several methods will be utilized. The following sections will provide short descriptions of these methods.

6.1. Anodization
Anodization is a simple electrochemical anodic oxidation process involving an electrochemical cell with an anode and a cathode. The electrolyte is generally stirred with a magnetic stirrer and heated with a heat plate. Upon an applied voltage the following overall oxidation reaction occurs (5):

\[ 2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \]

The aluminum alloys will first be pretreated through washing with acetone, degreasing in Turco 4215 NC-LT, rinsing in deionized water and etching in Ardrox 295 GD. Tartaric sulphuric acid (84 g/l C₄H₆O₆, 42 g/l H₂SO₄, 0.5 g/l Al) will be used as analyte according to the Saab standard process (9). Anodization time, temperature and voltage will be varied to find a working method of anodization.

6.2. Silanization
Anodized aluminum surfaces can be chemical modified using silanes. Organosilanes, i.e. silanes containing carbon-silicon bonds, can covalently bind to the surface of native anodized aluminum to control its wettability and adsorption properties. The surfaces can be modified by incubating hydroxylated alloys in a silane solution. To decrease the wettability, silanes with hydrophobic terminal groups such as perfluoroalkyl-silanes and alkyl-trichloro-silanes can be used. (25,29)

6.3. Electropolishing
Electropolishing is a pre-treatment method that can be used to promote the self-ordering of aluminum oxide during anodization. Through electropolishing, a flat and smooth surface of aluminum alloys can be obtained affecting the surface roughness. The method involves an electrochemical process, similar to anodization, where the surface roughness depends on polishing voltage and time. (19)

6.4. Goniometry
Goniometry is used to measure the contact angle that indicates the wettability of a substrate. The contact angle can be measured by placing a drop (liquid phase) on a substrate (solid phase) which is in contact with air (gas phase). The contact angle, \( \theta \), is defined as the angle between the solid phase and the tangent to the liquid surface at the line of contact with the solid. The contact angle can be optically measured by using a magnifying lens. (12)

For this thesis, the needle used to place droplets of liquid (water) on a surface will be washed using the TL-1 standard procedure to avoid contamination. The TL-1 standard procedure involves boiling the needle in a mixture of purified Milli-Q water, hydrogen peroxide (H₂O₂) and ammonia (NH₃·H₂O, 25%).

6.5. Scanning Electron Microscopy
Scanning electron microscopy (SEM) is used for topographical studies of surfaces. A low energy electron beam penetrates the sample, causing electrons to be back-scattered elastically, retaining approximately their original energy. Electrons may cause other electrons to lose considerable energy,
referred to as low-energy secondary electrons. The back-scattered and secondary electrons are collected and the number of emitted electrons is proportional to the surface topography. (30,31)

6.6. Atomic Force Microscopy
The atomic force microscopy (AFM) provides topographical images of surfaces by measuring the potential energy or force between a sample and a small force-sensing probe called a cantilever. When the cantilever is carefully pushed to the sample, the interacting force between the sample and a tip attached to the cantilever can be measured. By scanning the cantilever over the sample, information about the topographic height is captured. With this method, the force between atoms and the cantilever separated by a distance as close as 0.1-100 nm, can be measured. (32,33)
7. Materials, equipment and other resources

Anodization of aluminum surfaces will be performed at IFM using a simple electrochemical setup with an anode, cathode, voltage source, heat plate and magnetic stirrer. The TSA electrolyte is provided by SAAB. The experiments are performed in a fume hood. Consumables can be found in storage rooms at the department.

Instruments for determining wettability through contact angle and achieving topographical data through AFM and/or SEM are also available at IFM. Assistance for complicated measurements is provided by personnel at IFM for a reasonable amount of time. For contact angle measurements the needle used to deposit liquid on the samples needs to be wash with a TL-1 standard protocol for which material and chemicals are available at the department. Corrosion tests, silanization and electropolishing will also be performed at Linköping University. Ice adhesion test are performed at RISE. Table 1 presents a list of materials needed and where these are acquired.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Provided by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen peroxide (H$_2$O$_2$) for TL-1</td>
<td>IFM</td>
</tr>
<tr>
<td>Ammonia (NH$_3$) for TL-1</td>
<td>IFM</td>
</tr>
<tr>
<td>Tartaric sulphuric acid (C$_4$H$_6$O$_6$, H$_2$SO$_4$, Al) for anodization</td>
<td>Saab</td>
</tr>
<tr>
<td>Turco 4215 NC-Lt for pre-treatment</td>
<td>Saab</td>
</tr>
<tr>
<td>Ardrox 295 GD for pre-treatment</td>
<td>Saab</td>
</tr>
<tr>
<td>Silane for silanization</td>
<td>IFM</td>
</tr>
<tr>
<td>Electropolishing agent for electropolishing</td>
<td>IFM</td>
</tr>
<tr>
<td>Aluminum alloys</td>
<td>IFM</td>
</tr>
<tr>
<td>Nitrogen gas (N$_2$) for blow drying</td>
<td>IFM</td>
</tr>
<tr>
<td>Salt solution (NaCl) for corrosion tests</td>
<td>IFM</td>
</tr>
<tr>
<td>Consumables (containers, pipette tips etc.)</td>
<td>IFM</td>
</tr>
<tr>
<td>Equipment and material for ice adhesion tests</td>
<td>RISE</td>
</tr>
</tbody>
</table>
8. Frame of references
The following references are especially of importance for this thesis.


9. Milestones

The milestones presented in Table 2 will guide the course of the project.

**Table 2. Milestones.**

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Milestone description</th>
<th>Deliverable</th>
<th>Project week</th>
<th>Calendar week</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Planning report ready</td>
<td>Report</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Risk assessments ready</td>
<td>Report</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Midterm report ready</td>
<td>Report</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>Midterm presentation</td>
<td>Presentation</td>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>Final report – first draft ready to send to opponent and examiner</td>
<td>Report</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>Final presentation at LiU</td>
<td>Presentation</td>
<td>19</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Presentation at Saab</td>
<td>Presentation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Final report – revised version ready to send to examiner for approval</td>
<td>Report</td>
<td>21</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>Reflection document ready</td>
<td>Report</td>
<td>21</td>
<td>24</td>
</tr>
</tbody>
</table>
10. **Time plan**

The GANTT-chart presented in Figure 2 provides an overall planning for this thesis. It gives a clear overview on the activities that are part of this project as well as deadlines and holidays.

<table>
<thead>
<tr>
<th>Number</th>
<th>Activity</th>
<th>Time (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Supervisor meetings</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>Literature study</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>Writing planning report</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Performing risk analysis</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>Laboratory introduction</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Experimental design</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Experimental work on anodic coatings</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>Experimental work on silanization</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>Experimental work on characterization</td>
<td>80</td>
</tr>
<tr>
<td>10</td>
<td>Experimental work on ice adhesion</td>
<td>16</td>
</tr>
<tr>
<td>11</td>
<td>Data analysis</td>
<td>40</td>
</tr>
<tr>
<td>12</td>
<td>Writing midterm report</td>
<td>100</td>
</tr>
<tr>
<td>13</td>
<td>Preparing midterm presentation</td>
<td>20</td>
</tr>
<tr>
<td>14</td>
<td>Writing final report</td>
<td>180</td>
</tr>
<tr>
<td>15</td>
<td>Preparing final presentation</td>
<td>40</td>
</tr>
<tr>
<td>16</td>
<td>Preparing presentation Saab</td>
<td>10</td>
</tr>
<tr>
<td>17</td>
<td>Opposition</td>
<td>40</td>
</tr>
<tr>
<td>18</td>
<td>Writing reflection document</td>
<td>10</td>
</tr>
<tr>
<td>19</td>
<td>Extra time</td>
<td>24</td>
</tr>
</tbody>
</table>

**Deadlines**

- Planning report
- Risk analysis
- Midterm report
- Midterm presentation
- Final report first draft
- Final report second draft
- Final presentation
- Final report - revised version
- Presentation Saab
- Reflection document

**Holidays (short weeks)**

- Easter
- Walpurgis night
- Ascension day
- National day

**Total number of hours:** 800

**Hours available:** 800

*Figure 2. Time plan including planning of experimental work, writing of reports and deadlines.*
11. Budget

The budget presented in Figure 3 is a guideline for the costs of the project.

<table>
<thead>
<tr>
<th>Category</th>
<th>Cost</th>
<th>Quantity</th>
<th>Total Cost (SEK)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Instrumentation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>1000 SEK/hour</td>
<td>15 hours</td>
<td>15 000</td>
</tr>
<tr>
<td>Atomic Force Microscopy (AFM)</td>
<td>1000 SEK/hour</td>
<td>15 hours</td>
<td>15 000</td>
</tr>
<tr>
<td>Goniometry</td>
<td>200 SEK/hour</td>
<td>5 hours</td>
<td>1000</td>
</tr>
<tr>
<td><strong>Personnel</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>SEM operator</td>
<td>750 SEK/hour</td>
<td>15 hours</td>
<td>11 250</td>
</tr>
<tr>
<td>AFM operator</td>
<td>750 SEK/hour</td>
<td>15 hours</td>
<td>11 250</td>
</tr>
<tr>
<td>Laboratory introductions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Chemicals and materials</strong></td>
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<td></td>
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<tr>
<td>Hydrogen peroxide (H2O2)</td>
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<td>1000</td>
</tr>
<tr>
<td>Ammonia (NH3)</td>
<td>1000</td>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>Tartaric sulphuric acid (C4H6O6, H2SO4, Al)</td>
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<td></td>
<td>2000</td>
</tr>
<tr>
<td>Turco 4215 NC-LT</td>
<td>500</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Ardrox 295 GD</td>
<td>500</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Silane</td>
<td>1000</td>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>Electropolishing agent</td>
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<td></td>
<td>1000</td>
</tr>
<tr>
<td>Aluminum alloys</td>
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</tr>
<tr>
<td>Nitrogen gas (N2)</td>
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<td>500</td>
</tr>
<tr>
<td>Salt solution (NaCl)</td>
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<td></td>
<td>200</td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
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<tr>
<td>Ice adhesion measurement at RISE</td>
<td>7 000</td>
<td></td>
<td>7 000</td>
</tr>
<tr>
<td>Consumables (containers, pipette tips etc)</td>
<td>1 000</td>
<td></td>
<td>1 000</td>
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<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td>71 200</td>
</tr>
</tbody>
</table>

Figure 3. An estimation of the costs of this thesis.
12. References


Appendix II - Supplementary material

A.1 Anodizing conditions and morphology

In Chapter 5 and Chapter 6, the effects of anodizing voltage, electrolyte temperature and anodizing time were presented and discussed. Although two different set-ups were used when anodizing surfaces under different conditions, an overall effect regardless of the set-up was discussed. Herein, the results are presented separated based on the set-up used as shown in Figure A.1, A.2 and A.3.

**Figure A.1:** The effect of anodizing voltage on the morphology of anodic coatings separated by the set-up used for the anodizing process. The morphology is presented in terms of interpore distance, pore diameter and porosity with linear trendlines.
Figure A.2: The effect of electrolyte temperature on the morphology of anodic coatings separated by the set-up used for the anodizing process. The morphology is presented in terms of interpore distance, pore diameter and porosity with linear trendlines.
**A.1. Anodizing conditions and morphology**

**Figure A.3:** The effect of anodizing time on the morphology of anodic coatings separated by the set-up used for the anodizing process. The morphology is presented in terms of interpore distance, pore diameter and porosity with linear trendlines.