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A Literature Study of the Etching Process on Nickel- and Titanium-Based Superalloys

The Chemical Reactions at the Metal-Liquid Interface

Master's Thesis in Material Chemistry

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ABSTRACT

In the aerospace industry, the requirement for material properties and product safety are among the most important factors to consider in order to ensure the safety and reliability of the aircrafts. During the manufacturing process, the formation of cracks in the material might occur. For example, polishing of a region in the close vicinity of a crack can smear the metallic material over the cracks. This would result in that the crack could go undetected through quality control. Additionally, the oxides formed during heat treatment were shown to have high chemical stability and would cause trouble during removal.

Therefore, in this literature study, the oxidation behavior of nine highly relevant aerospace materials were examined together with the effect of six common etching solutions. Furthermore, the relationship between etch rate with temperature and concentration of each etching solution was also explored.

The study found that the pure metals, in most cases, were dissolved by the etching solutions with a few exceptions where passive reaction products were formed on the surface. Passive reaction products restricted diffusion of metallic elements out towards the oxidizing environment and vice versa. These would instead have the opposite effect on the etch rate where it would decrease as the reaction progressed due to the growing thickness of the metal oxides. A similar behavior could be seen by the metal oxides, but the oxidizing etching solutions and the acetic acid, weak acid, could not affect the metal oxides. An increased temperature and concentration of etching solution, did in most cases lead to an increased rate. Exceptions from the trend showed that some acids had an optimal concentration at which the reaction could ensue. The primary variable was the acids ability to dissociate which occurs when water is present. Therefore, the etch rate would decrease at very high concentrations due to the lack of water.

Although this literature study can give an insight in the etching process, or more specifically the reactions that occur at the interface between the metallic material and the etching solution, further work is needed to achieve a deeper understanding of the application on a larger scale.

Keywords: Superalloy, Etching, Titanium-based, Nickel-based, Dissolution, Corrosion.

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Henrik Appelqvist, Gothenburg, May 2024

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1. Introduction

In the aerospace industry, the material properties are extremely important. This leads to a continuous need for material and process development, in order to improve performance, longevity and manufacturing of the components. Frequently used materials for aerospace applications are alloys, but some polymer based materials has also been developed for this purpose. The properties that the material need to possess include high strength, heat resistance and resistance to long term fatigue failure. Since this is the case, international process and material standards have been introduced to define and specify the quality and characteristics of the material. Examples of groups of such standards are the Aerospace Material Standard (AMS) and the American Society for Testing and Materials (ASTM) but there can also be costumer specifications [1]. Additionally, when product optimization, with regards to weight and strength, and process development continues, the utilization of additive manufacturing can be a useful tool. With the more widespread implementation of additive manufacturing come new challenges.

Quality control is incredible thorough after mechanical processing. A common way to examine the components for cracks is by using a penetrant process, where a fluorescent solution is applied onto the component for a specific amount of time before it is cleaned with water. The solution trapped inside cracks will not be removed and can be studies under ultra violet light. During many manufacturing processes such as welding and polishing, material is smeared over the cracks which makes them undetectable by the penetrant process. Therefore, etching is a crucial tool to remove the smeared material and reveal the hidden cracks.

The stability of the oxide films is one of the predominant factors for the etching process [2]. It is therefore necessary to gain information about the corrosion behavior of the materials as well as the effect of the etching solutions. An understanding of the dependency of controllable factors such as temperature and solution composition can be used in order to create an etching process suitable for each material to produce a high quality finish with high consistency.

1.1 Aim and Objectives

The aim was to examine the chemical reactions and compile information of how the reaction kinetics are dependent on temperature and concentration. In total, 43 combinations of materials and etching compounds were explored.

The primary objective of this thesis was to investigate the chemical reactions between the components of etching solutions with materials commonly used in the aerospace industry, mainly titanium-based and nickel-based superalloys. The compilation of this information would then be used to strengthen the understanding of the interactions of the materials and etching solutions in the etching process.

1.1.1 Demarcations

The thesis was a literature study and was conducted exclusively by investigating already published scientific articles. After the oxidation behavior of each material had been evaluated, the decision was made to limit the investigation to the three most extensively appearing metal oxides and the four principle constituents of the superalloys. The understanding of the processes becomes exceedingly vital as the transition into production using additive manufacturing occurs and the legislation of chemical usage becomes stricter.

2. Background

In this section, the theoretical background of the materials, a simplified explanation of some key manufacturing steps and the oxidation behavior of the materials in question will be introduced. In this thesis, and for GKN Aerospace, the primary materials of interest are titanium-based and nickel-based superalloys. The titanium-based alloys are Ti-6Al-4V (Titanium 64) and Ti-6Al-2Sn-4Zr-2Mo-0.1Si (Titanium 6242) and the nickel-based alloys Inconel 718, Inconel 718 plus, Inconel 625, Haynes 282, Haynes 230, Waspaloy and René 41. The composition of the oxide layer for these materials will be presented in more detail later. For the nominal composition of the materials, see Appendix A1.

2.1 Titanium-Based Superalloys

The aerospace industry has been a large driver in the development of titanium alloys. This is due to the superior characteristics that these alloys present, such as low specific weight, high mechanical strength and corrosion resistance. Therefore, titanium alloys can be and are used in almost every part in a modern aircraft. The commercial use of titanium and its alloys is very large within many different industries. A few examples of areas where titanium is being used are in the chemical, power and automotive industries as well as in the biomedical field and sports [3].

Titanium alloys generally have very high resistance against corrosion. The underlying reason for this characteristic is the spontaneous formation of stable titanium oxide on the alloy surface. This oxide layer is stable in most environments and restricts further dissolution [4]. Although titanium oxide is the most prevalent oxide scale, other alloying elements can also contribute to the corrosion protection but to varying degrees [5].

2.1.1 Effect of Alloying Elements

The mechanical properties can be affected significantly by addition of alloying elements in different amounts. The alloying elements disturb the equilibrium between microstructures, resulting in new structures that improve the mechanical and structural behavior of the material. For titanium alloys, the microstructure stabilization can be present in either α- or β-phase. The α-phase has a hexagonal close packed structure and can be stabilized using aluminum, carbon, nitrogen and oxygen while the beta phase, which has a body centered cubic structure, can be stabilized by adding hydrogen, silicone, molybdenum, vanadium and chromium among others. Additionally, zirconium and tin are soluble in both phases and can thereby be used for both phases. The inclusion of alloying elements can also lead to solid solution strengthening, which further improves the mechanical strength [6].

2.2 Nickel-Based Superalloys

In most cases, nickel-based superalloys are characterized by high strength and resistance towards corrosion at elevated temperatures. The origin of the development of this category of superalloys is within the power generation industry where it was realized that the thermal efficiency of the gas turbines increase with increased temperature and/or pressure. Later it was applied in many other industries and products such as aircrafts where many of the engine components are made from this material group. Due to the good corrosive properties of nickel-based superalloys, these are also suitable in the chemical industry where highly corrosive environments are commonplace [3].

For nickel-based superalloys, the major alloying elements are commonly nickel, cobalt, chromium and iron. The alloy usually consist mostly of these elements, but also smaller amounts of elements including titanium, aluminum, niobium, tantalum, molybdenum and wolfram. Although the percentage is quite low for the latter mentioned elements, their presence can significantly improve the material properties. The generic nickel-based superalloy consist of roughly 60 wt.% face-centered cubic nickel and the rest compiles of a combination of the other alloying elements. However, it is important to acknowledge that the final composition of the alloy is regulated by the intended application [7].

2.2.1 Effect of Alloying Elements

Addition of multiple components can lead to improvement of the corrosion properties for nickel-based alloys. Addition of chromium will enhance the resistance against corrosion and sulfidation at high temperatures. However, too high amounts of chromium has the opposite effect. It is possible to tune the corrosion characteristics by partially substituting chromium with aluminum which forms a stable aluminum oxide which can be strengthened further with minor additions of yttrium. Corrosion by non-oxidizing acids such as hydrochloric acid (HCl), hydrofluoric acid (HF) and phosphoric acid (H_3PO_4) can be reduced by incorporation of molybdenum. Strength, weldability and local corrosion can be improved by inclusion of tungsten [7].

Titanium, along with aluminum, has the ability to, in some cases, improve mechanical strength through age hardening or precipitation hardening. Titanium can also aid in the reduction of intergranular oxidation together with carbon [7].

2.3 Additive Manufacturing

Additive manufacturing (AM) has in recent years emerged with great application possibilities followed by the introduction and development of advanced energy carriers such as the laser and electron beam. AM allows for great freedom when designing and fabricating three dimensional metal components. The components are first designed in a computer aided design (CAD) program from which the AM software can selectively fuse pre-spread metal powders one layer at the time. Before the fusion of each new layer, the platform is lowered by a specified distance and a new layer of powder is applied. A typical layer thickness is in the range of 20-100 µm [8]. The layer-by-layer fabrication gives the potential to create complex structures, which would be difficult to achieve using machining or casting. During the powder melting, when the high energy beam passes over the focused zone, extraordinarily high temperatures are reached followed by rapid cooling. This results in the formation of non-equilibrium phases which significantly improves the mechanical and structural properties. Additionally, this also allows for microstructures with very small grains and better metallurgical properties, which is very attractive for both academia and industry [9]. The principle layout of AM-printer can be seen in Figure 1.

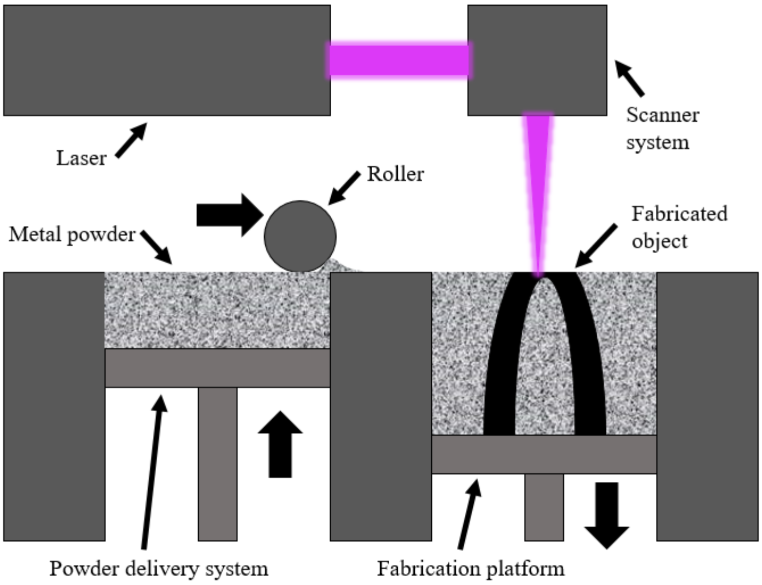

Figure 1: Visual representation of the layout of a generic AM-printer.

At GKN Aerospace, it has been noted that the surface finish of components fabricated using AM is less favorable. The surface roughness is too high which makes it problematic in other processes to differentiate abnormalities on the surface or in the material bulk. Additionally, every single grain in the metallic powder will have an oxide layer before the fabrication has begun which can impact material and corrosion properties.

2.3.1 Laser Beam Melting

Laser beam melting (LBM) is the most common AM method used today. The powder be is melted using a laser beam. This creates the opportunity for the material to form various crystalline structures that are not possible when using conventional machining or casting. The crystalline structures can result in favorable material properties such as higher robustness and strength [8].

The laser beam that is emitted from a high power laser passes through optical components that focuses the beam at a scanning mirror. The mirror redirects the beam onto the powder bed. A computer software controls the placement of the beam by changing the mirror angle and also regulating the width of the beam using optics. To avoid oxidation during the melting, the air is usually exchanged with inert atmospheres such as argon, nitrogen or helium [8].

2.3.2 Electron Beam Melting

In comparison with other AM methods, electron beam melting (EBM) is one of the more mature techniques. It uses a high energy electron beam that sweeps over the powder bed and rapidly melting the powder. EBM has the ability to create a complex structure that is fully dense and free from defects, in a reasonable short time frame. This makes EBM a favorable fabrication method compared to traditional techniques, such as casting or machining, especially for parts with porous structures [10].

In order to use an electron beam as the heat source, the fabrication must take place under vacuum. This is necessary since the surrounding atmosphere interacts with the electrons and affect the heating efficiency. The apparatus typically consist of an electron gun which produces an electron beam with a peak power in the range of 1-10 kW. The electron beam is directed through electromagnetic lenses. The lenses are controlled by a computer software that focuses the beam to have an appropriate size. The electron beam enters into a heat shielded compartment where the powder hoppers, the build tank and the equipment that control the build platform, are placed. The build tank assures that the powder, supplied and spread by the hoppers, remains stationary during the entire fabrication process [10].

2.3.3 Hot Isostatic Pressing

Hot isostatic pressing (HIP) is a commonly used method in metallurgy to densify components and remove porous structures. This is achieved by applying high pressure and elevated temperatures simultaneously within a purpose made compartment. When the elevated conditions are applied, the internal pores and defects inside of the metal body collapse, forming a denser material with increased mechanical properties. The pressure is usually applied in the form of inert gases, although trace amounts of air is usually unavoidable, and is therefore isostatic [11]. The presence of air within the pores and from external sources, can result in metal oxide growth on the surface and internally at the grain boundaries. A visualization of HIP can be seen in Figure 2.

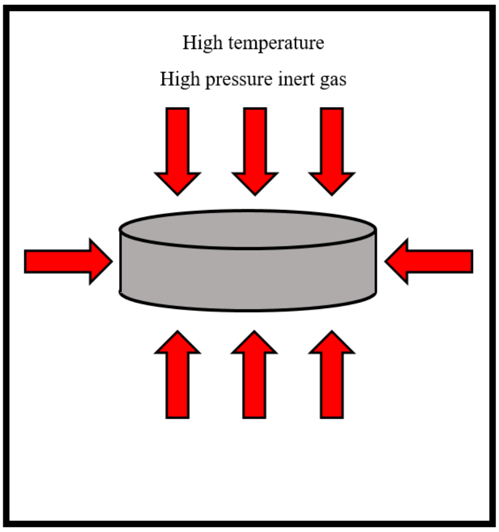

Figure 2: Simplified schematic representation of hot isostatic pressing.

Comparatively to conventional uniaxial pressing, where the pressure is transmitted via a solid surface and a ram or a die, the isostatic pressing applies pressure from all directions through the interaction between the metal surface and the high energy gaseous molecules. When the uniaxial pressing is used, there are friction forces between the metal component and the die resulting in a distorted pressure distribution. This is however avoided when HIP is used [11].

For AM, porosity is one of the major concerns. Porosity and other defects can occur due to process parameters that are not optimized, or powder properties that are not suitable for the specific application. Any factors that affects the layer-by-layer process in a negative way will cause inconsistencies within the final product. The most common types of defects are lack-of-fusion porosity and porosity due to the formation of gas. The distribution of these defects is mostly random. However, there are possibilities for local defects as well. Since the quality control of all components in the aerospace industry is very strict, HIP is suitable technique to achieve a satisfactory result with high consistency [12].

2.4 Oxidation Behavior

The majority of metallic material that are used in practical applications are alloys where the composition of the alloy can be tuned to maximize the important properties. This is also the case regarding oxidation and corrosion resistance. The most common method to reduce the oxidation rate is by the formation of a stable oxide layer which reduces the diffusion of oxygen to the metal.

2.4.1 Oxidation Kinetics

The most stable oxide layer is determined by the thermodynamics wheras the rate at which the layer is formed is controlled by the oxidation kinetics. The oxidation rate is evaluated is by measuring metal or oxygen consumption as a function of time, which relates to a change in weight of the metal sample. If the metal gets dissolved in some sort of oxidizing solution, the consumption will be measured as a weight loss. Alternatively, if the metal is oxidized in for example an oxygen containing gas, then there will be a mass increase as the oxide forms on the surface of the sample. In order to get a plot that depicts the kinetic behavior, the measurement needs to be performed in time intervals. The change in mass divided by the sample surface area can then be plotted as a function of time. In some cases, it is instead plotted as the thickness of the oxide layer as a function of time. The thickness can be measured by examining microscopic images of the sample cross-section. In most cases, the kinetics follow either a linear or a parabolic model [13].

The reaction mechanism can be reflected by formulating an expression for the oxidation rate. This includes two different diffusion mechanisms, transport of metal to and through the metal-oxide interface and transport of oxygen from the gas bulk to the interface between the metal oxide and the surrounding, see Figure 3.

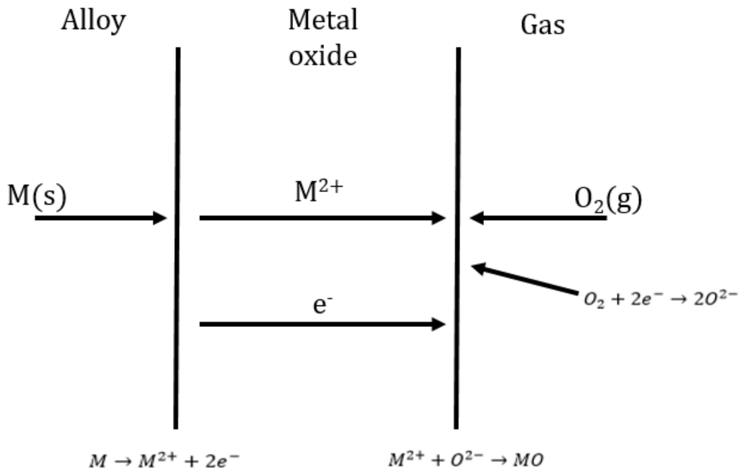

Figure 3: Visual representation of the chemical reactions that take place at the metal-gas interface during external oxidation.

For a generic oxidation reaction

$$\frac{x}{y}M + \frac{1}{2}O_2 \rightarrow \frac{1}{y}M_xO_y \tag{1}$$

the kinetics can in be expressed as Equation 2.

$$\frac{dX}{dt} = f(t) \tag{2}$$

where X represents the thickness of a uniform, flat and single phase oxide layer, which in turn can be calculated by Equation 3,

$$X = \frac{M_{OX}\,\Delta W}{16\,\rho_{OX}\,y\,A} \tag{3}$$

where M_{OX} is the molecular weight of the oxide, ΔW is the change in weight, ρ_{OX} is the density of the oxide, y is a stoichiometric constant and A is the surface area of the sample. Since diffusion is expressed as a function of position, it simplifies the calculation to express the rate as a function of thickness instead of weight gain [13].

2.4.1.1 Linear Kinetics

Considering Figure 3, there are two groups of reactions that take place, those within the oxide scale and those outside the oxide scale. The reactions that take place outside the oxide scale can be considered as independent on the thickness and the rate expression becomes

$$\frac{dX}{dt} = k_l \tag{4}$$

where k_l is the rate constant. This equation will in its integrated form become

$$X = k_l t \tag{5}$$

a linear relationship between the oxide layer thickness and time, which applies to reactions at specific conditions, such as at very high temperatures and containing oxygen. Here, the limiting factor will be the diffusion of oxygen from the bulk to the surface since the diffusion through the oxide layer is very fast in comparison. The rate will therefore be mainly dependent on the gas properties, especially gas pressure and temperature. As long as the delivery of oxygen to the surface is constant, the oxidation rate will follow Equation 4 and 5 [13].

2.4.1.2 Parabolic Kinetics

The diffusion through compact oxide scales are limited and the growth rate will be diffusion controlled. The scale growth will have a parabolic kinetic which can be expressed by Equation 6.

$$\frac{dX}{dt} = \frac{k_p}{X} \tag{6}$$

where k_p is the parabolic rate constant. When this equation is integrated, it becomes Equation 7.

$$X^2 = 2k_p t \tag{7}$$

For materials with parabolic kinetics, the growth rate will initially be very high as the thickness of the scale is thin and the diffusion will not be as significant. However, an increased scale thickness lead to a higher diffusion resistance within the material. Eventually the relationship between the square of weight gain and time becomes more linear [13].

2.5 Oxidation of Titanium-based Superalloys

This section will describe the oxidation behavior of the two titanium-based superalloys Titanium 64 (Ti-6Al-4V) and Titanium 6242 (Ti-6Al-2Sn-4Zr-2Mo-0.1Si) and the metal oxides formed on the respective surfaces. The oxidation products are presented in Table 1.

Table 1: Oxidation products of Titanium 64 and Titanium 6242. The green, orange and red color represents large, low and no presence of the metal oxide respectively.

	Titanium oxide	Aluminum oxide	Tin oxide	Zirconium oxide	Molybdenum oxide
Titanium 64	🟩	🟩	🟥	🟥	🟥
Titanium 6242	🟩	🟩	🟧	🟧	🟧

2.5.1 Titanium 64 (Ti-6Al-4V)

Titanium and aluminum are the two most important alloying elements when considering the oxidative behavior of Titanium 64. In an oxidative environment, these two metals form titanium oxide and aluminum oxide respectively. The titanium oxide and aluminum oxide are both very stable and form compact oxide layers. The oxide layers hinder further transfer of oxygen to the metallic alloy components and stop further metal oxidation. An additional alloying element is Vanadium, but is not contributing to the oxide growth [14]. The chemical reactions are presented in Equation 8 and 9.

$$Ti(s) + O_2(g) \Rightarrow TiO_2(s) \tag{8}$$

$$2Al(s) + \frac{3}{2}O_2(g) \Rightarrow Al_2O_3(s) \tag{9}$$

The oxidation process is controlled both by the diffusion of metal outwards and the diffusion of oxygen in, towards the metal surface. On the metal surface, an internal layer composed mainly of titanium oxide and an external scale of aluminum oxide, is formed. In addition, low quantities of titanium-vanadium oxide is present [14].

At elevated temperatures and with air present, solid solution hardening where oxygen is transferred into the interstitial sites for the titanium lattice will also occur, resulting in a hard region called α-case. This can happen during heat treatment. Before any mechanical or chemical processes can be performed on the material, the α-case needs to be removed [14].

2.5.2 Titanium 6242 (Ti-6Al-2Sn-4Zr-2Mo-0.1Si)

The important components in titanium 6242 are mainly titanium and aluminum, which form a passivating titanium oxide and aluminum oxide layer respectively. The remaining alloying elements can contribute to increased oxidation protection but usually not to a significant degree [15]. The oxidation reactions that take place when the protective layer is formed are Equations 8-12.

$$Sn(s) + \ O_2(g) \Rightarrow SnO_2(s) \tag{10}$$

$$Zr(s) + \ O_2(g) \Rightarrow ZrO_2(s) \tag{11}$$

$$Mo(s) + \frac{3}{2}O_2(g) \Rightarrow MoO_3(s) \tag{12}$$

The oxide scale consists of an internal layer that mainly consists of titanium oxide, followed by an intermediate layer of aluminum oxide. Outside of the aluminum oxide layer, is another layer of titanium oxide [15].

2.6 Oxidation of Nickel-based Superalloys

In the following section, the oxidation behavior of the seven before mentioned nickel-based superalloys will be introduced. For most of the nickel-based superalloys, the major component is nickel alloyed with chromium, cobalt, titanium, aluminum and molybdenum, but small amounts of silicon, sulfur, iron, carbon, boron and manganese are also common. The complete composition of the materials can be found in Appendix A1. The oxidation products for all nickel-based superalloys are presented in Table 2.

Table 2: Oxidation products of the nickel-based superalloys. The green, orange and red color represents large, low and no presence of the respective oxidation product.

	Titanium oxide	Aluminum oxide	Chromium oxide	Nickel oxide	Mn-Cr spinel	Ni-Cr spinel	Ni-Nb complex
Inconel 718	🟩	🟩	🟩	🟥	🟩	🟥	🟩
Inconel 718+	🟩	🟩	🟩	🟥	🟥	🟥	🟥
Inconel 625	🟩	🟩	🟩	🟥	🟥	🟥	🟥
Haynes 282	🟩	🟩	🟩	🟥	🟧	🟥	🟥
Haynes 230	🟩	🟩	🟩	🟥	🟩	🟥	🟥
Waspaloy	🟧	🟧	🟩	🟩	🟥	🟧	🟥
René 41	🟩	🟩	🟩	🟥	🟥	🟥	🟥

2.6.1 Inconel 718

In the case of Inconel 718, the most important parameters in the scale formation is the diffusion of chromium, titanium, manganese and oxygen ions through the chromium oxide scale. At low temperatures the oxide scale consists mainly of a thin layer of chromium oxide but at elevated temperatures, the scale formation becomes rather complex with the presence of three primary layers. Closest to the metal surface, there is a layer of a Ni_3Nb-complex which is rich in niobium, titanium and aluminum oxides. This layer is covered by a layer of chromium oxide and finally the outmost layer is composed of a combination of titanium oxide and a manganese-chromium spinel. The distinct chemical reactions are presented in Equation 8, 9, 13, 14 and 15 [16].

$$3Ni(s) + Nb(s) \Rightarrow Ni_3Nb(s) \tag{13}$$

$$2Cr(s) + \frac{3}{2}O_2(g) \Rightarrow Cr_2O_3(s) \tag{14}$$

$$Cr_2O_3(s) + MnO(s) \Rightarrow MnCr_2O_4(s) \tag{15}$$

As the temperature increases, so does the thickness of titanium oxide layer. The titanium ions from the bulk alloy diffuses through the chromium oxide scale to form titanium oxide at the oxide-gas interface. Simultaneously, oxygen ions diffuse to the alloy-oxide interface where another, internal, titanium oxide layer and aluminum oxide at the grain boundaries are formed. When the temperature approaches the volatilization temperature of chromium, there is a risk for spalling to occur. This means that the surface cracks and unveils the unprotected metal underneath [16].

2.6.2 Inconel 718 plus

The primary difference between Inconel 718 plus and regular Inconel 718 is the higher amount of titanium and aluminum. The oxidation behavior has similarities with the regular Inconel 718, where the base surface is composed of a layer of Ni_3Nb. Likewise, the major component of the oxide scale consists of a layer of chromium oxide. Internally, there will form an aluminum oxide layer. Depending on the alloy composition, the scale formation may vary slightly. The aluminum oxide is thermodynamically more stable than the chromium oxide, but as long as the chromium content is significantly higher than the aluminum content, the scale will mainly consist of chromium oxide [17]. The relevant chemical reactions can be seen in Equation 8, 9 and 14.

On the outside of the chromium scale, there is commonly an increased concentration of titanium. This is an indication that slight formation of titanium oxide occurs at the interphase between the oxide scale and the surrounding gas [17].

2.6.3 Inconel 625

On the surface of the Inconel 625, it has been found that a scale of chromium oxide forms on the outside of a layer consisting of a combination of Ni_3Nb and a niobium-chromium spinel. The two latter do however mainly form internally and do not have as significant impacts on the overall oxidation resistance as the chromium oxide. At the grain boundaries, there were also the formation of titanium oxide and aluminum oxide. But these oxides are not present at the surface [18]. The three major chemical reactions that take place during oxidation are Equation 8, 9 and 14.

When temperatures are increased to above approximately 1000°C, it has also been suggested that a manganese-chromium spinel forms. This layer is usually very thin but the thickness and composition depends heavily on the oxidation temperature and alloy composition [19].

2.6.4 Haynes 282

Oxidation of Haynes 282 results in the formation of a bilayer oxide scale outside of the alloy surface. The external oxide layer consists of titanium oxide. It is very common for nickel-based alloys, that a chromium oxide layer is formed inside of the titanium layer. While the metal ions diffuse from the bulk alloy to the surface, the path of least resistance is by the grain boundaries. This leads to formation of oxide scales at the boundaries as well as the outside surface. For Haynes 282, titanium oxide and aluminum oxide are the prominent oxidation products that form at the boundaries. The three primary oxidation reaction are presented in Equation 8, 9 and 14 [20].

It is also possible that in the presence of high temperature steam that a manganese-chromium spinel is formed but in low concentrations. This reaction follows Equation 15 [21].

2.6.5 Haynes 230

The oxidation protection of Haynes 230 is the formation of chromium oxide on the surface. But, early in the oxidation process, manganese-chromium spinel is formed. As the oxidation progresses, the amount of the spinel increases, restricting diffusion. As temperature increases, this phenomena becomes more prominent. These two reactions can be seen in Equation 14 and 15 [22].

It has also been noted that one reason for the thinning of the chromium layer is due to spalling and volatilization. This is mainly the case at higher temperatures. The spinel is more stable against evaporation than the chromium oxide, which leads to protection against scale thinning. But, when spallation occurs, the underlying chromium oxide gets exposed to the high temperatures and evaporation ensues. The external spinel also moderate internal oxidation due to the previously mentioned restriction of oxygen diffusion [22].

Aluminum oxide does also form internally as islands at the grain boundaries and with time, the islands grow larger and covers an increasing percentage of the grain boundary surface. The primary increase in aluminum oxide growth is after spalling occurs. In the outward regions of the oxide, there is a presence of titanium rich oxides. This is believed to be due to the diffusion of titanium and formation of titanium oxide which appears in combination with the manganese-chromium spinel [22]. The titanium oxide and aluminum oxide are formed according to Equation 8 and 9

2.6.6 Waspaloy

The oxidation behavior of Waspaloy is similar to the other nickel-based alloys regarding the formation of a thick chromium oxide layer. However, nickel rich oxides, such as nickel oxide and nickel-chromium spinel does also form on the outside of the chromium scale. In the early stages of the oxidation, before steady-state has been reached, both chromium and nickel oxide grow on the surface where the oxidation of nickel is much quicker than that of chromium. Due to the difference in oxidation rate, the nickel oxide will form on top along with a nickel-chromium spinel, which is the result of the reaction between the two oxides [23]. These reactions occur according to Equation 14, 16 and 17.

$$Ni(s) + \frac{1}{2}O_2(g) \Rightarrow NiO(s) \tag{16}$$

$$Cr_2O_3(s) + NiO(s) \Rightarrow NiCr_2O_4(s) \tag{17}$$

Additionally, there have been reports stating that small amounts of titanium oxide and aluminum oxide can form at the grain boundaries, equation 8 and 9. This appears to be most common when cracks occur in the material. This region is usually discontinuous but spreads out with time and with increasing temperature, causing slight improvement in corrosion resistance [24].

2.6.7 René 41

In the case of René 41, the most significant oxide formation is in the form of chromium oxide which is formed as a thick continuous layer on the metal surface. Internally, oxidation of aluminum occurs. The aluminum oxide is mainly formed very thinly at the grain boundaries. However, if the sample is exposed to air with higher water content, it has been noted that the continuity of the aluminum oxide layer decreases. In both dry and wet air it has been found that titanium oxide forms in small quantities externally at the oxide-gas interface, but it can also appear as small precipitates internally [25]. The reactions occur in accordance with Equation 14, 9 and 8.

2.7 Chemical Milling

Chemical milling can be defined as the removal of material through chemical corrosion of the surface. It is a machining technique that subtracts material using etching chemicals [26]. The chemical reactions that take place are reduction and oxidation reactions, which transfers the solid metallic material into soluble chemical compounds that are transported away from the surface by diffusion. The rate at which the etching process proceeds, corresponds to the number of metal ions that are produced per unit time at the surface of the solid metal. In addition, the etch rate is proportional to the interchanged anodic partial current divided by the surface area. The rate is dependent on many factors such as reactant concentration and solution convection, temperature and viscosity [27]. Etching can also be used as surface cleaning and pretreatment for surface examination where the underlying metal shall be examined.

The etchant solution is commonly applied in two different ways, swab etching or immersion etching. Swab etching is mostly used when etching on small regions whereas immersion etching is used for larger size scales. The swab etching technique uses a cotton swab which is submerged in the etchant solution prior to application on the surface. The swabbing frequency and etching duration is determined by the etching solution and the desired etch depth [28]. Conversely, immersion etching utilizes a container of etchant solution into which the entire object is immersed, where the main factor is the time duration and stirring in order to achieve the desired material removal [29].

2.7.1 Modes of Corrosion

In corrosion, there are two main modes of which the material gets removed. These two modes are general or uniform corrosion and localized corrosion. In practical applications, general corrosion is usually not seen as too much of a threat to the structural properties of the material on a short timescale, unless the corrosion rate is very high, but is important at longer timescales. General corrosion is recognizable by the relatively even material removal, although not completely smooth, and the absence of small but deep pits. The preference for where the attack occurs does not matter for general corrosion, which leads to the more uniform material removal. On the other hand, localized corrosion leaves the majority of the surface unaffected but at specific positions, the corrosion rate is very high and can cause catastrophic damage to metal components already early in the components lifetime [30]. Localized corrosion will take place when the critical potential for metal dissolution is greater than the passivation potential for the metal. It is however not only related to the potentials but also the concentration of the pit forming component, often halides. When the conditions are appropriate, the halide ion will exchange with the oxygen at the metal surface. It is often the case that the atomic layers closest to the electrolyte consists of metal atoms with adsorbed water molecules, oxygen atoms or hydroxide groups. Therefore, water will be released simultaneously as the halide ions are consumed. This can cause a concentration gradient at locations where corrosion has appeared. Diffusion of halides from the surrounding will thereafter be focused at the specific positions and lead to the formation of pits [31]. A simplified visualization of the interaction between the adsorbed water molecules and the halide, in this case a chloride ion, can be seen in Figure 4.

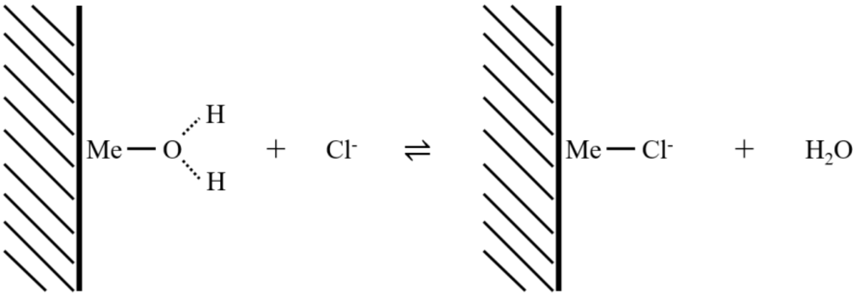

Figure 4: Visualization of the interaction of the adsorbed water molecule and a chloride ion.

It is commonly specific components of the etching solution that determine the corrosion mechanism. Two examples are fluoride and chloride ions. The Hofmeister series is often used to divide anions into two groups depending on the hydration effect. Fluoride ions are so called cosmotropes, water-structure-makers, and will usually lead to general corrosion. Chloride ions are chaotropes, water-structure-breakers, and will typically cause localized corrosion. This is due to the tightness of the hydration shells surrounding the anion. Cosmotropes have tight hydration shells while chaotropes have loose hydration shells [32].

3. Method

The literature study was conducted during the time period of early February to the middle of May 2024. The search for sources was mainly performed through Google Scholar, Elsevier, Springer Link and Wiley Online Library.

Subject specific terms and keywords were identified beforehand but more general searches were also executed for terms corresponding to more general information. During the search, the keywords were adjusted to give more precise results.

No limitations to the searches were made, but the age and relevance was controlled thoroughly before the use of any information. Very old sources were discarded unless in cases where no other trustworthy or relevant sources could be found. The search strategy can be found in Appendix A2.

In addition to the searches in Google Scholar, the reference lists of relevant articles were also manually inspected both in order to find supplementary sources but also to investigate the relevance of the article.

4. Results and Discussion

In this section, the theoretical results will be presented. The results involve the chemical reactions that take place between the alloy surface and the etchant solution during the etching process. From the theoretical background, section 2.5 and 2.6, it is shown that the overwhelming majority of the components of the oxide scales on the separate materials consist of titanium oxide, aluminum oxide or chromium oxide and therefore, only these three oxides will be taken into consideration. However, the typical etching process removes far more material than the thickness of the oxide films, it is therefore also important to investigate the effect with regards to the pure metals as well. In titanium-based and nickel-based alloys, the composition mainly consists of titanium, aluminum, chromium and nickel metal, so these are the four pure metals that will be investigated in addition to the metal oxides. The results will be presented based on the material with a section for each etching solution sorted by relevance. For the titanium-based superalloys, only titanium oxide, aluminum oxide, titanium and aluminum are relevant but all seven metal oxides and metals are relevant for the nickel-based superalloys.

4.1 Choice of Etching Solutions

In the current production, multiple different compositions of the etching solutions are being used depending on which process and which standards are relevant. Therefore, the main interest was to investigate the effect of the etching components that are used or are planned to be used in the future.

From previous experience by the employees at GKN Aerospace and from costumer specifications, the solutions of interest are hydrofluoric acid, hydrochloric acid, sulfuric acid, nitric acid, ferric chloride and acetic acid. For titanium-based superalloys, the primary solutions are hydrofluoric acid and a combination of hydrofluoric acid and nitric acid. For nickel-based superalloys, it is common to use a solution called Schantz etchant which contains hydrochloric acid, sulfuric acid, nitric acid, ferric chloride and acetic acid. A compilation of key solutions for the two groups of superalloys are presented in Table 3. Although all reactions are not as significant for the current process, the knowledge could still be of relevance for future development. Nickel-based superalloys contain small amounts of titanium and aluminum which makes hydrofluoric acid slightly relevant in that case as well.

Table 3: Representation of the etching solutions with the highest significance for the current etching process. The importance is represented by the colors green and red which indicate highly important and less important respectively. Combo refers to a mixture of hydrofluoric acid and nitric acid.

	HF	HCl	H_2SO_4	HNO_3	$FeCl_3$	CH_3COOH	Combo
Ti-Base	🟩	🟥	🟥	🟥	🟥	🟥	🟩
Ni-Base	🟥	🟩	🟩	🟩	🟩	🟩	🟥

4.2 Chemical reactions

To summarize the results of the study, most combinations of materials and etching solutions achieved some sort of material removal, either in the form of active dissolution or as the formation of a solid dissolution product. The red cells in Table 4 represents the etching solutions that did not show any material removal due to the high protective properties of the metal oxides and the competition between dissolution and oxide formation. An interesting note was the passivation of titanium in nitric acid. Although nitric acid is an oxidizing agent, it is fascinating that only titanium transitioned into its metal oxide while the other materials formed nitrates. Another thing that needs to be acknowledged is that chromium and chromium oxide has a high resistance in fluoride environments but corrodes in solutions containing chloride, both halides. The compilation of the results can be seen in Table 4.

Table 4: Summary of results of which etching solutions have an effect on the respective materials. The green and blue colors represent metal dissolution and formation of solid dissolution products respectively, and are the reactions that are actively occurring. The light yellow, orange and red colors represent low effect, passivation and no effect respectively.

	HF	HCl	H_2SO_4	HNO_3	$FeCl_3$	CH_3COOH
Titanium Oxide	Dissolution	Dissolution	Solid Dis. product	Passivation	No Effect	No Effect
Aluminum Oxide	Solid Dis. product	Dissolution	Dissolution	Dissolution	No Effect	No Effect
Chromium Oxide	Negligible Effect	Dissolution	Dissolution	Dissolution	No Effect	No Effect
Titanium	Dissolution	Dissolution	Solid Dis. Product	Passivation	No Effect	No Effect
Aluminum	Dissolution	Dissolution	Dissolution	Solid Dis. product	Dissolution	Dissolution
Chromium	Negligible Effect	Solid Dis. Product	Solid Dis. Product	Dissolution	Solid Dis. product	Dissolution
Nickel	Solid Dis. product	Dissolution	Solid Dis. product	Dissolution	Dissolution	Dissolution
Titanium	Combo $HF+HNO_3$					

4.2.1 Titanium and Titanium Oxide

Titanium and titanium oxide has the ability to be dissolved in all solutions with the exception of ferric chloride and acetic acid. This is due to the competition with the formation of titanium oxide during the oxidation process in aqueous solutions. Since ferric chloride and acetic acid cannot dissolve titanium oxide, the surface will eventually be completely covered. Additionally, the influence of the combination of hydrofluoric acid and nitric acid was also investigated. The proposed reactions will be presented in this section.

For these two materials, the two most important interactions are with hydrofluoric acid and the combination of hydrofluoric acid and nitric acid. The other etching solutions are less important due to their use mostly on nickel-based superalloys, where titanium and titanium oxide is a minority.

4.2.1.1 Hydrofluoric Acid

Hydrofluoric acid is known for being highly corrosive to most metals including titanium. In hydrofluoric acid, titanium metal will be oxidized by the protons present in the solution. The oxidation will initially result in trivalent titanium ions. It has however been found by Singh Rajput et al. that the trivalent titanium ions will quickly be oxidized further to the tetravalent state. Finally, the titanium ions will react with the fluoride ions to form a titanium hexafluoride according to the reaction presented in Equation 18 [33].

$$2Ti(s) + 6HF(aq) \Rightarrow [TiF_6]^{2-}(aq) + 3H_2(g) \tag{18}$$

A competing reaction is that titanium spontaneously forms a passive oxide layer which protects the metal from further oxidation. However, hydrofluoric acid can, already at very low concentrations, break down the oxide layer and reveal the unprotected metal below. The dissolution reaction is believed to consist of two major reaction steps. The two steps are first a charge transfer reaction followed by desorption of adsorbed ions or compounds. Fluoride ions in the acidic solution will form complexes with the titanium oxide through the following reaction, Equation 19 [34].

$$TiO_2(s) + 6HF(aq) \Rightarrow [TiF_6]^{2-}(aq) + 2H^+(aq) + H_2O(l) \tag{19}$$

Both reactions reach the same final product but with slightly different mechanisms and reaction paths.

4.2.1.2 Combination of Hydrofluoric Acid and Nitric Acid

For etching of titanium metal in a combination of hydrofluoric acid and nitric acid, different articles have not come to an agreement of exactly which reaction that occurs. However, all research that has been investigated has reached a final product that contains tetravalent titanium which has reacted with fluoride ions from the etchant solution [33], [34].

Li et al. has proposed two possible reactions where titanium metal is dissolved in hydrofluoric acid and nitric acid according to Equation 20 and 21.

$$Ti(s) + 6HF(aq) + 4HNO_3(aq) \Rightarrow 3H_2TiF_6(aq) + 4H_2O(l) + 4NO_2(g) \tag{20}$$

$$3Ti(s) + 12HF(aq) + 4HNO_3(aq) \Rightarrow 3TiF_4(s) + 8H_2O(l) + 4NO_2(g) \tag{21}$$

Where the nitric acid is the main oxidizing agent resulting in the tetravalent titanium which further reacts with the free fluoride ions from the solution to form the titanium fluoride compounds. It was also noted that although fluoride ions are a strong reduction agent, these did not contribute to the redox reaction. Another important aspect of using nitric acid is that the formation of hydrogen gas can be reduced [34].

Likewise, Singh Rajput et al. has proposed a similar reaction mechanism but using a slightly modified stoichiometry and final product, see Equation 22.

$$Ti(s) + 6HF(aq) + 2HNO_3(aq) \Rightarrow \\ \Rightarrow [TiF_6]^{2-}(aq) + NO_2(g) + NO(g) + HNO_2(aq) + 3H_2O(l) \qquad (22)$$

It was also found that the composition of the etchant solution has a large impact on the surface topography. This composition will however vary if alloying elements have been incorporated into the titanium. For titanium alloy containing aluminum and vanadium, such as Ti-6Al-4V, the mole fraction of hydrofluoric acid and titanium alloy should be roughly 6:1 in order to achieve the most even surface. In parallel with the mole fraction of metal and acid, it was also found that the ratio of the two acids is of great significance when considering the etching efficiency. There is a side reaction that takes place between metallic titanium and nitric acid resulting in the formation of titanium oxide which occurs if the concentration of hydrofluoric acid is too low [33].

4.2.1.3 Reactions of Lower Importance

4.2.1.3.1 Hydrochloric Acid

Titanium metal is in general very reactive in its pure form and will readily react with the environment. In aqueous solutions it will commonly react with the water and air to passivate but it is also possible for the titanium to oxidize through the production of hydrogen gas. The oxidation state of the titanium ions will then be dependent on the concentration of the oxidizing agent which in this case would be protons. It has been shown by Tolulope Loto that two reactions of titanium in hydrochloric acid are common when complete chlorination is considered. The two reactions can be expressed as Equation 23 and 24 [35].

$$Ti(s) + 2HCl(aq) \Rightarrow TiCl_2(aq) + H_2(g) \qquad (23)$$

$$Ti(s) + 4HCl(aq) \Rightarrow TiCl_4(aq) + 2H_2(g) \qquad (24)$$

But, both these products will react with water to form titanium oxide and hydrochloric acid. This can be problematic due to the protective properties of titanium oxide but since this reaction occurs further from the surface, or at least not directly on the surface, the protective properties are generally not as strong. Additionally, the chloride ions have the ability to attack titanium oxide which makes the protective properties of the oxide layer worse compared to solutions without chloride ions [35].

Vaughan et al. has performed a thorough investigation into which titanium chloride compounds that are formed depending on the oxidation state of the titanium ions. The reaction is highly dependent on the reactivity of the chloride ions but the most likely and commonly occurring are titanium di-, tri-, and tetrachloride from the trivalent titanium as well as titanium oxydichloride, titanium oxytrichloride and titanium oxytetrachloride for the tetravalent titanium [36]. Divalent titanium was however not considered.

When titanium oxide comes in contact with an aqueous solution of hydrochloric acid, two separate mechanisms occur to dissolve the oxide layer with the first being a reaction with protons which removes oxygen from the oxide. Secondly, chloride ions can adsorb on the oxide surface. It has been observed that the oxidation state of titanium is retained in both of these reaction mechanisms but it does not always become fully chlorinated [37], [38]. The reaction for fully chlorinated and partially chlorinated titanium oxide can be expressed as Equation 25 and 26.

$$TiO_2(s) + 4HCl(aq) \Rightarrow TiCl_4(aq) + 2H_2O(l) \tag{25}$$

$$TiO_2(s) + 2HCl(aq) \Rightarrow TiOCl_2(aq) + H_2O(\mathrm{l}) \tag{26}$$

4.2.1.3.2 Sulfuric Acid

In an aqueous solution, sulfuric acid will be deprotonated resulting in a solution containing sulfate groups and protons. The protons are prone to reduction while simultaneously oxidizing another species. Ban et al. has investigated the interaction between metallic titanium in sulfuric acid solutions. The results found that two reactions occur close to the metal surface. Firstly, the oxidized metal can react with sulfate groups to form titanium sulfate. Secondly, the titanium can interact with hydrogen to instead form titanium hydride. The reactions for the dissolution of metallic titanium can be written as Equation 27 and 28 [39].

$$Ti(s) + 2H_2SO_4(aq) \Rightarrow Ti(SO_4)_2(s) + H_2(g) \tag{27}$$

$$Ti(s) + H_2(g) \Rightarrow TiH_2(s) \tag{28}$$

However, there is a competition between the two reactions above with the formation of titanium oxide. The dissolution of titanium oxide in sulfuric acid propagates mainly through two reactions which take place simultaneously. The scientific research of Dubenko et al. and Ban et al. are in agreement formed products are titanium sulfate and titanium oxysulfate. The dissolution mechanism is believed to be a two-step reaction of charge transfer and then desorption. The two reactions can be expressed as Equation 29 and 30 [40], [39].

$$TiO_2(s) + 2H_2SO_4(aq) \Rightarrow Ti(SO_4)_2(s) + 2H_2O(l) \tag{29}$$

$$TiO_2(s) + H_2SO_4(aq) \Rightarrow TiOSO_4(s) + H_2O(l) \tag{30}$$

Dubenko et al. implemented reactions containing sulfuric acid hydrates due to the consideration that the water cannot be regarded as a pure phase in concentrated sulfuric acid. From thermodynamic calculations it was found that the more stable product was the titanium sulfate but that the spontaneous formation of oxysulfates from sulfates was impossible at the experimental conditions.

4.2.1.3.3 Nitric Acid

The oxidation of titanium metal in nitric acid can happen due to the oxidative properties of nitric acid. The mechanism that results in the oxidation of titanium metal can be divided into two separate components. Firstly it is possible via hydrogen evolution. The protons will partly come from the nitric acid in solution but can also be as a result of auto hydrolysis. On the other hand, the nitrogen has the ability to change oxidation state. In the reaction proposed by Jayaraj et al. the main focus was placed on the oxidation by nitrogen [41]. The reaction can be expressed as Equation 31.

$$3Ti(s) + 4HNO_3(aq) \Rightarrow 3TiO_2(s) + 4NO(g) + 2H_2O(l) \qquad (31)$$

The limitation of dissolving titanium metal using nitric acid as etchant solution is that titanium oxide is formed as a product. Titanium oxide is very stable against attack from nitric acid and will therefore almost completely stop further oxidation of the metal. This is the case already at very thin oxide layers [41].

Corrosion by nitric acid is affected greatly by the reduction reaction that can occur in oxidizing environments. The reduction process is an autocatalytic mechanism that is very complex in nature and will reduce the nitrate groups to nitrous acid among others. The formation of nitrous acid contributes to a noble shift in potential as the concentration of nitric acid increases. Therefore, when temperature and nitric acid concentration increases, the reduction rate also increases leading to lower potentials. But, the increase in reduction rate of nitric acid will simultaneously increase the formation of nitrous acid and thereby reduce the oxidizing effect, see Equation 32 [42].

$$HNO_3(aq) + H^+(aq) + e^- \Rightarrow NO_2(g) + H_2O(l) \qquad (32)$$

It is possible for nitric acid to dissolve titanium oxide to a low degree but the resulting free titanium ions will quickly react with air or water in the environment to return to a passive state. It was noted that the corrosion rate increased with temperature and acid concentration but also that the thickness of the oxide layer stayed practically constant regardless of acid concentration [43].

4.2.1.3.4 Ferric Chloride

Since titanium oxide is highly resistant towards dissolution in ferric chloride, research of how ferric chloride affects oxidation of metallic titanium is very scarce. It can however be reasoned that from the oxidative property of ferric chloride, is should definitely be able to oxidize metallic titanium. The factor that would counteract dissolution is if the solution contains oxygen which can result in the formation of titanium oxide. There would be a competition between oxygen and chloride ions to react with the titanium ions but since titanium oxide and titanium chloride are insoluble and soluble respectively, the surface would eventually be covered by titanium oxide. Persson has reported that free chloride ions are formed in aqueous solutions of ferric chloride [44]. It would be possible that the titanium oxide can be attacked and to some degree dissolve but the low chloride concentrations would make this process very slow.

4.2.1.3.5 Acetic Acid

Titanium metal will quickly be oxidized through hydrogen evolution if the surrounding solution contains protons, which is the case for aqueous solutions [45]. In a solution of acetic acid, it could be possible for the titanium ion to react with acetate groups to form titanium acetate but no articles have been found to support this.

This is however very unlikely, or practically impossible, since in order for the acetic acid to dissociate, water needs to be present and the water will passivate the titanium surface [45]. There will be a competition between the water and the acetate groups to react with titanium.

Therefore, it is most likely that the surface will quickly become passivated by the water and completely discard the effect of acetic acid. Additionally, any dissolved oxygen will also compete to react with the titanium. The only way to achieve continuous dissolution by acetic acid would be if the system consisted of dissociated acetic acid and if it was completely free from any oxygen containing compounds which in practice is extremely unlikely or impossible.

4.2.2 Chromium and Chromium Oxide

In this section, the dissolution behavior of chromium metal will be presented and discussed. Most solutions had the capability to dissolve chromium metal and chromium oxide but the mechanism differed in most cases. Examples of variations in the reaction mechanism are direct reaction with the components in the solution, and the formation of chromium hydroxide which acts almost as an intermediate, among others.

Chromium oxide is the greatest component of the oxide scale on nickel-based superalloys. Because of this, the most important interactions are with the constituent of Schantz etchant but due to the low effect of ferric chloride and acetic acid on the oxide, these two are of lower importance [46]. Likewise, the low effect of fluoride ions disqualifies hydrofluoric acid into the category of low importance [47].

4.2.2.1 Hydrochloric Acid

The reaction of chromium metal in hydrochloric acid is a traditional redox reaction where protons in the solutions are reduced by the electrons released when chromium oxidizes. The suggested reaction by Kim et al. expressed only the oxidation reaction of chromium but the aqueous chloride ions can promptly react and form chromium chloride according to Equation 33 [48].

$$Cr(s) + 3HCl(aq) \Rightarrow CrCl_3(s) + \frac{3}{2}H_2(g) \tag{33}$$

In addition to the reaction mentioned above, another reaction is also possible with another reaction mechanism. When chromium metal comes in contact with water, it is possible for chromium dihydroxide to form on the surface. Thereafter, chloride ions can adsorb onto the chromium hydroxide to finally form chromium oxychloride. The mechanism requires multiple steps but it can be simplified as Equation 34 [49].

$$Cr(s) + 2H_2O(l) \Rightarrow Cr(OH)_2(ad) + 2H^+(aq) \overset{Cl^-}{\Longrightarrow} CrOCl(ad) + H_2O(l) \tag{34}$$

For the dissolution of chromium oxide, protons will also have significant influence. This is especially the case for hydrous chromium oxide. As trivalent chromium ions are formed from the removal of oxygen as water, these can interact with the negatively charged chloride ions and create chromium chloride. Reartes et al. has described the dissolution of hydrous chromium oxide by protons and the reaction with chloride ions can be expected to follow Equation 35 [50].

$$Cr_2O_3{\bullet}nH_2O(s) + 6HCl(aq) \Rightarrow 2CrCl_3(s) + (3+n)H_2O(l) \tag{35}$$

Furthermore, the anhydrous chromium chloride can, in the presence of water, form chromium chloride hexahydrate which is significantly more soluble in water [51].

4.2.2.2 Sulfuric Acid

The interaction between metallic chromium and sulfuric acid is rather interesting since the reactants depend on for example acid concentration but the product will be the same regardless. In a solution of sulfuric acid, the oxidation can be facilitated either by water, hydrosulfate anions or undissociated acid molecules depending on the acid concentration. The products formed from the interaction between the metal and the solution are mainly chromium oxides and hydroxides. Stypula and Banaś has, in their article, expressed three different reaction mechanism for the production of passivating chromium oxyhydroxide at the interface between the metal and the solution. At acid concentrations lower than 6 M, metallic chromium will primarily react with water to achieve the reaction expressed in Equation 36.

$$Cr(s) + 2H_2O(l) \Rightarrow CrOOH(s) + 3H^+(aq) + 3e^- \tag{36}$$

At slightly higher concentration, between 6M and 8 M, there is a combination of water and hydrosulfate anions that contribute to the reaction. In the region of 8M up to 14 M, hydrosulfate anions dominate the reaction according to Equation 37.

$$\begin{gathered} Cr(s) + HSO_4^-(aq) \Rightarrow CrHSO_4(ad) + e^- \\ CrHSO_4(ad) \Rightarrow CrOOH(s) + SO_2(aq) \end{gathered} \tag{36}$$

At concentrations above 14 M, there are not enough water molecules in order for dissociation of sulfuric acid to occur in a notable amount. Therefore, the dominating reactant in this case, would be the sulfuric acid molecule. The reaction can be written as Equation 38 [52]:

$$\begin{gathered} \mathrm{Cr(s) + H_2SO_4^-(aq) \Rightarrow CrHSO_4(ad) + H^+(aq) + e^-} \\ \mathrm{CrHSO_4(ad) \Rightarrow CrOOH(s) + SO_2(aq)} \end{gathered} \tag{38}$$

Additionally, Shankar et al. have found that the passive layer formed from chromium also contains chromium oxide, although the specific reaction was not presented. The presence of chromium oxide was determined by X-ray Photoelectron Spectroscopy (XPS) measurements [53].

Chromium oxide will react with sulfuric acid to form chromium sulfate according to research performed by Geveci et al. The proposed reaction is presented as Equation 39 [54].

$$Cr_2O_3(s) + 3H_2SO_4(aq) \Rightarrow Cr_2(SO_4)(s) + 3H_2O(l) \tag{39}$$

The dissolution mechanism has been investigated by Reartes et al. and it was found that both the protons and the sulfate groups in solution can initiate the disintegration of the chromium oxide. The protons adsorb onto the metal oxide to form hydroxides which are more soluble and sulfate groups will cause complexation at the surface [50].

It is however possible for the chromium sulfate to form complexes with water and become hydrated. In that case, the solubility of the product can change significantly and instead dissolve in water [51]. It was reported by Geveci et al. that the dissolution efficiency of chromium oxide in sulfuric acid reaches a plateau where no further dissolution occurs. The efficiency at which the plateau begins is highly dependent on the environmental conditions [54]. This is likely due to the formation of anhydrous chromium sulfate, which adheres to the surface and restricts the accessibility of the sulfuric acid.

4.2.2.3 Nitric Acid

The dissolution of chromium metal in nitric acid will be very similar to that of chromium oxide with the only large difference being the way the trivalent chromium is transferred into the solution. Instead of the deterioration of chromium oxide by protons, the chromium would be oxidized directly from the metallic state into chromium ions by hydrogen evolution [55]. The chromium ions would later react with the oxygen containing constituents in the solution to form chromium oxide.

The dissolution of chromium oxide in nitric acid utilizes the same primary mechanism as hydrochloric acid and sulfuric acid where the protons liberates the chromium ions from oxygen to form water. The chromium ions are then able to form complexes with negatively charged ions in the solution. In the case of an aqueous nitric acid solution, negatively charged nitrate groups will be present. After the protons have broken down the chromium oxide into water and trivalent chromium ions, these chromium ions will react with the nitrate groups in the solution according to Equation 40 [56].

$$2Cr^{3+}(aq) + 3NO_3^-(aq) + 5H_2O(l) \Rightarrow 2HCrO_4^-(aq) + 5H^+(aq) + 3HNO_2(aq) \quad (40)$$

It was found by Badet and Poineau, using Scanning Electron Microscopy (SEM) that the deterioration of the chromium oxide was at the grain boundaries where the acid concentration is high [56].

In this reaction, the trivalent chromium will be oxidized to the hexavalent state. The hydrogen chromate is only slightly soluble in water, which can inhibit further dissolution of chromium or chromium oxide [57].

4.2.2.4 Reactions of Lower Importance

4.2.2.4.1 Ferric Chloride

The oxidative properties of ferric chloride results in the transformation of chromium metal either into divalent or trivalent chromium ions which thereafter can react with the free chloride ions in the solution. Park et al. has proposed the following two reactions, Equation 41 and 42, to describe the formation of the products. It is important to realize that the produced ferrous chloride instead can act as a reducing agent. Therefore, there is an equilibrium between the two chromium chloride products [58].

$$Cr(s) + 3FeCl_3(aq) \Rightarrow CrCl_3(s) + 3FeCl_2(aq) \quad (41)$$

$$Cr(s) + 2FeCl_3(aq) \Rightarrow CrCl_2(aq) + 2FeCl_2(aq) \qquad (42)$$

The solubility of these products are very different in an aqueous environment. The divalent chromium chloride will dissolve in water but the trivalent chromium oxide has very low solubility in pure water. However, if the solution contains divalent chromium ions, the solubility increases significantly [59].

The effect of ferric chloride on chromium oxide is not considerable but it is important to consider the effect of chloride ions on the oxide layer. In aqueous solutions, ferric chloride could dissociate into trivalent iron ions and chloride ions. It can also form complexes with water. The most commonly occurring complexes are, according to Persson, hydrated ferric monochloride and ferric dichloride. The presence of these two complexes are dependent on both the concentration of ferric chloride and also the concentration of free chloride ions in the solution [44]. Furthermore, the free chloride ions can react with water molecules to form hydrochloric acid which has been seen to have an effect on the chromium oxide dissolution. From the before mentioned aspects to the solution composition, it can be deduced that the ferric chloride itself does not influence the dissolution of chromium oxide but the addition will lead to the formation of compounds that will have an effect.

4.2.2.4.2 Acetic Acid

The weak acidic properties of acetic acid makes it less likely to dissociate, but the protons still have the ability to act as an oxidizing agent. In the etching process of chromium metal in an acetic acid solution, the protons will oxidize the chromium and form hydrogen gas and divalent chromium ions. The chromium ions will thereafter react with the acetate groups in the solution to form chromium acetate. This reaction mechanism has been described by Hibi and Mano as Equation 43 [60].

$$Cr(s) + 2CH_2COOH(aq) \Rightarrow Cr(CH_3COO)_2(aq) + H_2(g) \qquad (43)$$

The probability that this reaction is faster than that of the formation of chromium oxide is however negligible. Therefore it is highly unlikely that this reaction will impact the overall dissolution behavior since acetic acid is unable to dissolve chromium oxide.

4.2.2.4.3 Hydrofluoric Acid

In aqueous solutions containing hydrofluoric acid, chromium will quickly react with oxygen or fluoride ions in order to form chromium oxide, hydroxide or fluoride. Although, these three compounds can form on the surface, the majority appears as chromium oxide and hydroxide with only a small portion being chromium fluoride. Most commonly, the chromium metal will oxidize with reduction of water or hydrogen evolution as reduction reaction [47]. The reactions of the formation of the three products can be expressed as Equation 44-46, and happen simultaneously.

$$2Cr(s) + 3H_2O(l) \Rightarrow Cr_2O_3(s) + 6H^+(aq) \qquad (44)$$

$$Cr(s) + 3H_2O(l) \Rightarrow Cr(OH)_3(s) + 6H^+(aq) \qquad (45)$$

$$Cr(s) + 3HF(aq) \Rightarrow CrF_3(s) \tag{46}$$

Since all reaction products are solids, the surface will eventually be covered and protected from further metal oxidation. Additionally, chromium oxide is resistant against fluoride attack. Hydrofluoric acid will therefore not be a crucial reaction for the dissolution process of chromium oxide [47].

4.2.3 Aluminum and Aluminum Oxide

All investigated etching components were able to dissolve the pure metal but ferric chloride and acetic acid showed no effect on aluminum oxide. The dissolution of the metal include firstly oxidation followed by further reaction with the constituents from the etchant solutions in order to finally achieve the final dissolution product. In most cases, the oxidation was as a result of hydrogen evolution. The only exception was the ferric chloride where instead the trivalent iron acts as an oxidation agent. The dissolution mechanism for aluminum oxide was primarily charge transfer followed by desorption of adsorbed ions or compounds.

4.2.3.1 Hydrofluoric Acid

In a solution containing hydrofluoric acid, aluminum metal will be oxidized through hydrogen evolution into trivalent aluminum ions. These will rapidly interact with the aqueous fluoride ions to form an aluminum fluoride. This reaction can be written as Equation 47 [61].

$$2Al(s) + 6HF(aq) \Rightarrow 2AlF_3(aq) + 3H_2(g) \tag{47}$$

If the aluminum surface has already been oxidized, it will instead be aluminum oxide on the surface. The reaction is however quite similar but the mechanism is certainly not the same. In order to control the thickness of aluminum oxide layers on metal surfaces it is common to use fluorination reactions in order to transfer the aluminum oxide into aluminum fluoride. The reaction that takes place can be written as Equation 48 [62], [63].

$$Al_2O_3(s) + 6HF(aq) \Rightarrow 2AlF_3(s) + 3H_2O(l) \tag{48}$$

Varshney et al. has described the mechanism of how the reaction proceeds. The proposed reaction steps can be expressed as Equation 49 and 50.

$$Al_2O_3(s) + 3H_2O(l) \Rightarrow 2Al(OH)_3(aq) \tag{49}$$

$$2Al(OH)_3 + 6HF(aq) \Rightarrow 2AlF_3(s) + 6H_2O(l) \tag{50}$$

Where the aluminum oxide initially reacts with the surrounding water to form aluminum hydroxide which can react with the hydrofluoric acid to form aluminum fluoride and water. Since the water is a reactant in the first reaction step, the reaction will be self-promoting [62].

4.2.3.2 Hydrochloric Acid

The reaction of aluminum metal in hydrochloric acid was expressed in the simplest terms by Graedel as Equation 51.

$$Al(s) + 3HCl(aq) \Rightarrow AlCl_3(aq) + \frac{3}{2}H_2(g) \tag{51}$$

It was later realized that this reaction was not very representable of the actual mechanism that occurs. In actuality, the aluminum metal will firstly be oxidized through hydrogen evolution followed by a reaction with hydroxide ions to form trivalent aluminum hydroxide. Lastly, aluminum chloride will be formed after a three step chlorination reaction where the hydroxyl groups are substituted by chloride ions. In aqueous solutions, the aluminum chloride is very unstable and will quickly react with water and reappear as aluminum hydroxide or aluminum oxide [64].

The reaction between aluminum oxide and hydrochloric acid during the etching process has been investigated thoroughly in previously published articles. The consensus is that when the aluminum oxide reacts with hydrochloric acid, aluminum chloride and water is formed according to Equation 52 [38], [65], [66].

$$Al_2O_3(s) + 6HCl(aq) \Rightarrow 2AlCl_3(aq) + 3H_2O \tag{52}$$

4.2.3.3 Sulfuric Acid

In sulfuric acid, aluminum metal will be oxidized and transferred into aluminum sulfate. The oxidation reaction is enabled by the reduction of protons in the acidic solution, leading to evolution of hydrogen gas. The protons originate from the sulfuric acid that has been deprotonated when it enters the aqueous solution. The oxidized aluminum can then react with the sulfate groups. This reaction was explained by Poznyak et al. and expressed as Equation 53 [67].

$$2Al(s) + 3H_2SO_4(aq) \Rightarrow Al_2(SO_4)_3(aq) + 3H_2(g) \tag{53}$$

In the solution, it is however not only the reaction with the acid that occurs but also the formation of aluminum oxide. For the etching process of aluminum oxide in sulfuric acid, the formation of aluminum sulfate is the reaction that the scientific research mostly agree upon. There has however, been slight variations in the proposed reactions depending on the experimental conditions [65], [68]. The reaction can be expressed as Equation 54.

$$Al_2O_3(s) + 3H_2SO_4(aq) \Rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l) \tag{54}$$

It was noted by Wanta et al. that the aluminum oxide could be transferred into aluminum hydroxide in the aqueous solution. Both the aluminum oxide and aluminum hydroxide reacts readily with the sulfuric acid to form aluminum sulfate [68].

It was also found that the reaction resulted in different products at elevated temperatures. In the temperature interval of 220-320°C it was noted that gaseous SO_3 was formed as well as the previously mentioned product. This gas formation results in slight stoichiometry changes. At these conditions, the proposed reaction can instead be written as Equation 55 [65].

$$Al_2O_3(s) + 7H_2SO_4(aq) \Rightarrow Al_2(SO_4)_3(aq) + 4SO_3(g) + 7H_2O(l) \tag{55}$$

4.2.3.4 Nitric Acid

Nitric acid can act as an oxidizing agent. In the solution, the aluminum metal will undergo a redox reaction where protons are reduced to form hydrogen gas and at the same time, metallic aluminum is oxidized to trivalent aluminum ions. Thereafter, the aluminum ions can react to form compounds with the environment. Iwata et al. has shown that the oxidation of aluminum metal results in the growth of aluminum oxide on the surface. The reason for this is believed to be due to the decomposition of nitric acid into nitric oxide, nitrous oxide, water and oxygen atoms, as expressed in Equation 56 [69].

$$2HNO_3(aq) \Rightarrow NO(g) + NO_2(g) + H_2O(l) + 2O(aq) \tag{56}$$

The oxygen atoms react with the aluminum ions to form a protective oxide scale on the surface but it was noted that the dissolution resulted in cylindrical pores which continued the oxidation process. It could be seen that the thickness of the oxide layer increased with time but eventually the surface would be practically protected [69]. The reaction can in very simple terms be expressed as Equation 57.

$$2Al^{3+}(aq) + 3O(aq) \Rightarrow Al_2O_3(s) \tag{57}$$

In the surface evaluation, there was no apparent presence of aluminum nitrate but this is believed to be due to the water solubility. Instead of adhering to the surface, the aluminum nitrate dissolves into the solution but the formation is most likely very small in comparison with aluminum oxide [69].

In a nitric acid solution, aluminum oxide can react, together with water, to form hydrated aluminum nitrate. The reaction is exothermal and will occur spontaneously with regards to the thermodynamics. Singh et al. has proposed a chemical reaction between aluminum oxide, nitric acid and water to form hydrated aluminum nitrate containing twelve water molecules. This reaction is presented as Equation 58 [70].

$$Al_2O_3(s) + HNO_3(aq) + 9H_2O(l) \Rightarrow 2Al(NO_3)_3 \bullet 12H_2O(aq) \tag{58}$$

4.2.3.5 Ferric Chloride

Oxidation of aluminum in ferric chloride is a traditional redox reaction where the trivalent iron ions are reduced while oxidizing aluminum. In order for the aluminum to reach its trivalent oxidation state it is necessary that three trivalent iron ions are reduced. The iron and aluminum can thereafter react with the chloride ions in the solution to for aluminum chloride and ferrous chloride according to Equation 59 [71].

$$Al(s) + 3FeCl_3(aq) \Rightarrow AlCl_3(aq) + 3FeCl_2(aq) \tag{59}$$

If aluminum at the surface is already reacted into aluminum oxide, the iron specie in ferric chloride does not contribute in the reaction itself. It is mainly the chloride ions in the solution that contribute to the dissolution. At the interface between the metal oxide and the etching solution, the composition is commonly an aluminum oxyhydroxide, onto which the chloride ions adsorb. The adsorption can be explained by the isoelectric point, the pH where the net charge is zero, of aluminum which is roughly pH 9-9.5. At pH lower than the isoelectric point, the surface will be slightly positively charged which promotes adsorption of negatively charged chloride ions [72].

It has been proposed by Abdel-Gaber et al. that when the chloride ions adsorb to the aluminum oxyhydroxide, the hydroxide group is substituted by the chloride to form aluminum oxychloride. Later it can react with two additional chloride ions to reach the final product aluminum chloride. Experiments using radioactive labels have also been performed to inspect the depth into the oxide film at which the chloride ions can interact. The result showed that the interaction depth is restricted to the surface where the chloride ions chemisorb are form oxide-chloride complexes [73].

4.2.3.6 Acetic Acid

The corrosion mechanism of aluminum in an acetic acid solution can be described by four steps, namely diffusion of acetic acid to the metal surface, surface adsorption, surface reaction and finally desorption. In the system, there are two separate reactions that take place simultaneously. These two reactions are firstly the reaction between aluminum and acetic acid and secondly the reaction of aluminum and protons. Zhang et al. have studied the corrosion behavior of aluminum in dilute acetic acid solutions and expressed the reaction as Equation 60 and the equilibrium system as Equation 61 [74].

$$Al(s) + 3CH_3COOH(aq) \Rightarrow Al(3CH_3COO^-)_3(aq) + \frac{3}{2}H_2(g) \tag{60}$$

$$\begin{gathered} Al(s) + H_3O^+(aq) \rightleftharpoons AlH^+(ad) + H_2O(l) \\ AlH^+(ad) + e^- \rightleftharpoons AlH(aq) \\ 2AlH(aq) \rightleftharpoons H_2(g) + 2Al(s) \end{gathered} \tag{61}$$

Due to the weak acidic properties of acetic acid, it did not have the ability to dissolve aluminum oxide.

4.2.4 Nickel

Nickel has in its metallic phase a standard potential slightly lower than the standard hydrogen electrode. Therefore, in the presence of an electrolyte and an oxygen source, oxidation of nickel metal is a spontaneous mechanism. Although the components of the etchant solution are not all oxidizing agents, they contain oxidizing constituents that are released when dissolved in water. Because of this, nickel readily reacts will all of the different solutions and form dissolution products. The reactions for the dissolution of nickel metal in each etchant compound are presented in this section.

4.2.4.1 Hydrochloric Acid

The reaction mechanism where nickel metal is dissolved in hydrochloric acid is not very complex. It utilizes firstly reduction of the protons that originate from the acid to oxidize the metal. The nickel ions can thereafter readily react with the free chloride ions to form nickel chloride. The reaction of the oxidation step was presented by Kim et al. and the complete reaction can be written as Equation 62 [48].

$$Ni(s) + 2HCl(aq) \Rightarrow NiCl_2(aq) + H_2(g) \tag{62}$$

4.2.4.2 Sulfuric Acid

Due to the high activity of nickel, it will form nickel sulfate in sulfuric acid solutions at all concentrations. But, at high concentrations, the dissolution of nickel metal will be stopped due to the low water solubility of nickel sulfate and the formation of a very compact and passive film on the metal surface. The formation of nickel sulfate has been proposed by Ouarga et al. and can be written as Equation 63 [75].

$$Ni(s) + 4H_2SO_4(aq) \Rightarrow NiSO_4(s) + SO_2(aq) + 2H_3O^+(aq) + 2HSO_4^-(aq) \tag{63}$$

4.2.4.3 Nitric Acid

The reaction mechanism is similar to the previously mentioned acids since the oxidation of the metal is facilitated by the reduction of protons into hydrogen gas. The nickel ions will react with the aqueous nitrate groups to form a nickel nitrate salt according to the following reaction, Equation 64, proposed by Ans et al. [76].

$$Ni(s) + 2HNO_3(aq) \Rightarrow Ni(NO_3)_2(aq) + H_2(g) \tag{64}$$

Practical experiments have proved that gaseous nitrogen containing compounds can also be formed by the reaction. Therefore, the second reaction can be used when the production of nitrogen oxide is formed, see Equation 65.

$$3Ni(s) + 8HNO_3(aq) \Rightarrow 3Ni(NO_3)_2(aq) + 2NO(g) + 4H_2O(g) \tag{65}$$

4.2.4.4 Reactions of Lower Importance

4.2.4.4.1 Ferric Chloride

In the case of nickel metal in ferric chloride, the dissolution mechanism is different compared to the other acids. Instead of the oxidation reaction originating from hydrogen evolution, it is achieved by reduction of ferric chloride into ferrous chloride. The divalent nickel ions and the aqueous chloride ions in the solution can react into a water-soluble nickel chloride salt. The oxidation reaction was proposed by Liao and Wu and the complete reaction can be expressed as Equation 66 [77].

$$Ni(s) + FeCl_3(aq) \Rightarrow NiCl_2(aq) + FeCl_2(aq) \tag{66}$$

4.2.4.4.2 Acetic Acid

In systems containing water and acetic acid, oxidation and passivation of nickel metal are processes that promptly occur in room temperature. Badea and Badea investigated the interaction of metallic nickel in aqueous solutions of acetic acid at different concentrations ranging from 0.5-13 M [78].

The experimental results did not show any significant release of hydrogen gas and therefore, the oxidation mechanism was not explained by hydrogen evolution but instead by interaction with water. Firstly, water reacts with nickel metal on the surface to form adsorbed nickel hydroxide which then desorbs and enters into solution as a positively charged nickel hydroxide compound. Thereafter, the nickel hydroxide compound reacts with acidic protons resulting in the removal of water and a divalent nickel ion [78].

Depending on the acid concentration, and more specifically the presence of free ions, the passivation reaction utilized different reactants and different final compositions. At low concentrations, less than 3 M, the formation of passive nickel hydroxide is the most common but as acid concentrations increased, so did the abundance of free ions in the solution. At concentrations greater than 3 M, the formation of nickel hydroxide is inhibited by the presence of free ions and the lack of free water molecules. Instead, acetate groups will interact with the nickel surface, mostly the thin layer of nickel hydroxides, to generate adsorbed nickel acetate compounds [78]. It has been noted by Schütze et al. that as the concentration approaches pure acetic acid, the corrosion rate decreases [79]. This is likely due to the absence of water restricting the dissociation of acetic acid.

4.2.4.4.3 Hydrofluoric Acid

The oxidation of nickel metal in hydrofluoric acid gives rise to the production of nickel fluoride compounds. The oxidation event is caused by the reduction of protons in the solution. As the nickel is oxidized, it reacts with the fluoride ions present in the solution. This reaction can be described as Equation 67.

$$Ni(s) + 2HF(aq) \Rightarrow NiF_2(s) + H_2(g) \tag{67}$$

Since the nickel fluoride is only slightly soluble in water, a solid salt film will be formed on the surface and causing passivation [80].

4.3 Effect of Concentration

As can be seen in Table 5, the different combinations of metal or metal oxide and etching solution did in many cases show a positive relationship between etch rate and etching solution concentration. The positive effect can be attributed to the higher presence of reactants as concentration increases. This is clearly visible for the green cells in Table 5. The red cells are not considered due to the insignificant etching effect. When the focus is moved to orange cells, another trend becomes obvious. From low concentrations, there is an increase as the concentration increases, in a similar manner as for the green cells. But, as the concentration increases, a maximum will eventually be reached after which the rate begins to decrease. This behavior is believed to be connected to the dissociation of the acids in the presence of water. For dissociation to occur, water must be present and when the acids reach very high concentrations there will no longer be sufficient amounts of water for the dissociation to occur. The result where the rate reached a maximum was only visible for investigations using very wide concentration intervals. Therefore, it is likely that this behavior appears for all acids but that the measurements were taken inside an interval where the rate only increased.

It is also possible that a similar trend occurs for ferric chloride as well. When Park et al. investigated dissolution of chromium in ferric chloride at high concentrations, the rate would constantly decrease as the concentration increased [58]. Here it is possible that the maximum has already been reached and that the rate measurements only covered a region after the maximum. Other articles have however not been found to examine this at lower concentrations. A more specific explanation of the effect of concentration for each material-etching solution combination can be found in Appendix A3.

Table 5: Summary of results of effect of concentration on the etch rate. The green color represents a positive effect. The red color represents reactions where there was no effect. The orange color represents other effects. The text in the cells is a notification of how concentration effects the etch rate.

	HF	HCl	H_2SO_4	HNO_3	$FeCl_3$	CH_3COOH	Combo
Titanium Oxide	🟩	🟧 Increase & Decrease	🟧 Increase & Decrease	🟩	🟥	🟥	
Aluminum Oxide	🟩	🟩 Plateau	🟩	🟩	🟥	🟥	
Chromium Oxide	🟥	🟩	🟧 Increase & Decrease	🟩	🟥	🟥	
Titanium	🟩	🟩	🟩	🟥	🟥	🟥	🟩
Aluminum	🟩	🟩	🟩	🟩	🟩	🟩	
Chromium	🟥	🟩 Plateau	🟧 Increase & Decrease	🟩	🟧 Decrease at high Conc.	🟩	
Nickel	🟧 Passive	🟩	🟩	🟩	🟩	🟧 Increase & Decrease	

4.4 Effect of Temperature

In almost all investigated reactions, the rate was affected positively by increased temperature. This is visualized by the green cells in Table 6. There were five cases where this trend was not followed. The three yellow cells represent reactions where the effect of temperature was very low of not visible at all. The last two exceptions were chromium and chromium oxide in sulfuric acid where the rate initially increased until it reached a critical point, after which the rate remained constant. The explanation for this is that at a specific point, temperature is no longer the limiting factor. At temperatures above the critical value, diffusion is ample and the activation barrier can be overcome.

The behavior in the orange cells could possibly also be explained using the same reasoning. It is possible that the critical temperature was already reached when the measurements were taken. Therefore, all recorded dissolutions rates were collected on the plateau with no significant change. However, the accuracy of this explanation can be debated since the lowest temperature was room temperature and it is unlikely that these conditions are enough.

The red cells are, as previously mentioned, not considered due to the insignificant etching but complete results for each material and etching solution can be found in Appendix A3.

Table 6: Summary of results of effect of temperature on the etch rate. The green color represents a positive effect. The red color represents reactions where there was no effect. The orange color represents other effects. The text in the cells is a notification of how concentration effects the etch rate.

	HF	HCl	H_2SO_4	HNO_3	$FeCl_3$	CH_3COOH
Titanium Oxide	🟩	🟩	🟩	🟧 Always Low	🟥	🟥
Aluminum Oxide	🟩	🟩	🟩	🟩	🟥	🟥
Chromium Oxide	🟥	🟩	🟩 Plateau	🟩	🟥	🟥
Titanium	🟩	🟩	🟩	🟥	🟥	🟥
Aluminum	🟩	🟩	🟩	🟩	🟩	🟩
Chromium	🟥	🟧 Low Effect	🟩 Plateau	🟩	🟩	🟩
Nickel	🟩	🟧 Low Effect	🟩	🟩	🟩	🟩

5. Conclusion

To conclude this study, most of the metals and metal oxide are in some way affected by the etching solutions with the exception of titanium oxide, aluminum oxide, chromium oxide and titanium metal which were not affected by ferric chloride and acetic acid. Additionally, a few materials formed passive layers that hindered further dissolution, such as chromium and chromium oxide in hydrofluoric acid, titanium in nitric acid and nickel in hydrofluoric acid.

It was also possible to see some interesting kinetics. In most cases, the dissolution rate increased with acid concentration and temperature. However, in some cases, specifically with regards to acid concentration, the rate increased initially up until a certain critical value, where the rate instead decreased. This was the case for titanium oxide in hydrochloric acid and sulfuric acid, chromium oxide in sulfuric acid, chromium in sulfuric acid and nickel in acetic acid. The reason for this was that water is needed for the acids to dissociate, otherwise the effect is greatly inhibited. Overall, temperature had a catalyzing effect and, in some cases, such as chromium and chromium oxide, the dissolution rate reached a plateau. The reason for the improvement can be explained by the system having more energy to overcome the activation energy for the reactions and most likely enhanced diffusion rates.

Due to the usage of different units for corrosion rate in the investigated articles and sources, it is difficult to compare actual values for the corrosion rate but it is possible to understand the general behavior of the corrosion process when temperature and the concentration of the etching solution is varied.

5.1 Future Work

In this thesis, only existing literature has been used to collect information. Therefore, it has been challenging to find articles where all factors, such as temperature range and composition, completely agreed with the conditions that the etching process at GKN Aerospace utilize. Therefore, there are a number of further investigations of how the etchant solutions interact with the specific material and also to do practical measurements. It would be possible to preform composition measurements on the etchant solution by using Inductively Coupled Plasma (ICP) and on the metal surface by using Electron Dispersive X-ray Spectroscopy (EDX) or X-ray Photoelectron Spectroscopy (XPS) to determine what compounds are formed on the surface and dissolved into the solution.

Furthermore, it would be of great use to investigate and compare the actual rate for each reaction in order to easier determine which etching solution is most efficient for each material. This would be of great use in the etching process during manufacturing at GKN Aerospace.

Lastly, it would be interesting, and in the case for GKN Aerospace necessary, to investigate the interaction between etching compounds since mixtures are most commonly used in practice instead of each etching compound separately. One such example was taken into account in the study but it is highly likely that more synergisms exist. This would especially be the case for solutions containing nitric acid since it has the ability to manage hydrogen release. This can be of high importance due to the risk of hydrogen embrittlement when hydrogen diffuses into the material.

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Appendix

Appendix A1

The nominal composition, wt.%, of the nine superalloys are presented in Table 7.

Table 7: Nominal composition of the titanium-based and nickel-based materials.

	Ti-64 [14]	Ti-6242 [15]	Inconel 718 [81]	Inconel 718+ [82]	Inconel 625 [83]	Haynes 282 [84]	Haynes 230 [85]	Waspaloy [86]	René 41 [87]
Ti	90	85.9	0.65-1.15	0.5-1	0.3	2.1	0.1	3	3.1
Ni			50-55	45-57	60	Bal.	Bal.	54	52
Cr			17-21	17-21	22	20	22	19.5	19
Al	6	6	0.2-0.8	1.2-1.8	0.3	1.5	0.3	1.4	1.6
Co			1	8-10		10	5	13.5	11
V	4								
Sn		2							
Zr		4						0.06	
Mo		2	2.8-3.3	2.5-3.1	9	8.5	2	4.25	10
Si		0.1	0.35	0.35	0.25	0.15	0.4	0.75	0.5
B			0.006	0.008		0.005	0.015	0.006	0.006
C			0.08	0.06	0.05	0.06	0.1		0.12
Cu			0.3					0.5	
Fe			Bal.	8-10	4	1.5	3	2	5
Mn			0.35	0.35	0.3	0.3	0.5	1	0.1
Nb			4.75-5.5	4.75-5.8	3.5		0.5		
P			0.015	.0.2	0.01			0.03	
S			0.015	0.01	0.003			0.03	0.015
W				0.5-1.5			14		
Ta			0.05						
La							0.02		

Appendix A2

In Table 8 and 9 below, follows a representation of the search strategy. Since there were many sections that were inspected in very close proximity of time and also the search was continuous over longer time periods, the specific dates at which the search was performed is better expressed as a time interval.

Table 8: Search strategy for chapter 2 Background.

Time Interval	Keyword	Filter Limits
29/1-2024-1/3-2024	Titanium based superalloys	No filter
-	Nickel based superalloys	-
-	Additive manufacturing	-
-	Laser beam melting	-
-	Electron beam melting	-
-	Hot isostatic pressing	-
-	Linear corrosion kinetics	-
-	Parabolic corrosion kinetics	-
-	Oxidation of titanium 64	-
-	Oxidation of titanium 6242	-
-	Oxidation of Inconel 718	-
-	Oxidation of Inconel 718 plus	-
-	Oxidation of Inconel 625	-
-	Oxidation of Haynes 282	-
-	Oxidation of Haynes 230	-
-	Oxidation of Waspalloy	-
-	Oxidation of Rene 41	-
-	Chemical milling	-
29/4-2024-3/5-2024	General corrosion	-
29/4-2024-3/5-2024	Localized corrosion	-

Table 9: Search strategy for chapter 4 Results and Discussion. For the metallic components, the addition of the search word “metallic” was occasionally added.

Time Interval	Keyword	Filter Limits
1/3-2024-29/4-2024	Dissolution of titanium oxide in –	No filter
-	- hydrofluoric acid	-
-	- hydrochloric acid	-
-	- sulfuric acid	-
-	- nitric acid	-
-	- ferric chloride	-
-	- acetic acid	-
-	Dissolution of aluminum oxide in –	-
-	- hydrofluoric acid	-
-	- hydrochloric acid	-
-	- sulfuric acid	-
-	- nitric acid	-
-	- ferric chloride	-
-	- acetic acid	-
-	Dissolution of chromium oxide in –	-

-	- hydrofluoric acid	-
-	- hydrochloric acid	-
-	- sulfuric acid	-
-	- nitric acid	-
-	- ferric chloride	-
-	- acetic acid	-
-	Dissolution -OR- oxidation of titanium in –	-
-	- hydrofluoric acid	-
-	- hydrochloric acid	-
-	- sulfuric acid	-
-	- nitric acid	-
-	- ferric chloride	-
-	- acetic acid	-
-	Dissolution -OR- oxidation of aluminum in –	-
-	- hydrofluoric acid	-
-	- hydrochloric acid	-
-	- sulfuric acid	-
-	- nitric acid	-
-	- ferric chloride	-
-	- acetic acid	-
-	Dissolution -OR- oxidation of chromium in –	-
-	- hydrofluoric acid	-
-	- hydrochloric acid	-
-	- sulfuric acid	-
-	- nitric acid	-
-	- ferric chloride	-
-	- acetic acid	-
-	Dissolution -OR- oxidation of nickel in –	-
-	- hydrofluoric acid	-
-	- hydrochloric acid	-
-	- sulfuric acid	-
-	- nitric acid	-
-	- ferric chloride	-
-	- acetic acid	-

Appendix A3. Effect of Concentration and Temperature

A3.1 Titanium Oxide

A3.1.1 Hydrofluoric Acid

Low fluoride concentrations are enough to initiate dissolution of titanium oxide. Ren et al. reported that the dissolution rate of the oxide film will increase with the acid concentration. Initially, when the concentration is still low, there is a competition between the oxide dissolution and passivation [88]. It has also been found by Wang et al. that there is a concentration region where the dissolution rate and passivation rate are equal and a dynamic equilibrium is reached. In this region, the protective properties remain rather constant. But, if the concentration exceeds this region, then the passivating properties are lost and the oxide will be dissolved. It was recorded by open circuit potential measurements that the critical region for titanium oxide is roughly 1-5 mM fluoride ions [89]. Bright and Readey have documented that the dissolution rate followed a linear relation to acid concentration within the interval 0.1-1 M. It was also noted from experiments, using a combination of hydrofluoric and hydrochloric acid, that the dissolution rate had the same relationship with regards to the concentration of hydrofluoric acid when hydrochloric acid was added [90]. This gives a strong indication that hydrofluoric acid is of great importance when considering the dissolution rate of titanium oxide.

Mizuhata et al. found that the dissolution rate of titanium oxide in an aqueous solution of hydrofluoric acid is positively affected by an increase in temperature. The experiment used a temperature interval of 30°C-50°C. This was achieved using an Arrhenius plot of the logarithm of the rate constant as a function of the inverse of temperature. After plotting the experimental data using this format, a clear linear relationship between the two components could be seen [91]. Bright and Readey performed similar experiments, but at temperatures between 37.5°C-95°C. The results were also similar with a significant increase in dissolution rate as the temperature approached the highest value [90].

A3.1.2 Hydrochloric Acid

Abdullahi Baba et al. investigated the influence of acid concentration and temperature on the dissolution according to Equation 25. It was found that initially the degree of dissolution increased with acid concentration. However, as the concentration of hydrochloric acid exceeded 4 M, the dissolution efficiency decreased in the entire measurement time interval. On the other hand, the temperature dependence showed that the dissolution steadily increased as temperature increased in the temperature interval of 28-80°C [37].

The reaction according to equation was shown by Cui et al. but it was found that the formation rate of titanium oxychloride was very slow [38]. It has also been seen that titanium tetrachloride is highly corrosive but also extremely unstable in aqueous solutions and will quickly react with water to form hydrochloric acid and titanium compounds including titanium dioxide, titanium hydroxide and titanium oxychloride [92]. Due to this, it is possible that the titanium oxide scale can to some degree regenerate but since different products can be formed, the passivation properties will be slightly worsened.

A3.1.3 Sulfuric Acid

After investigating the dependence of temperature on the Gibbs free energy it could be noted that increasing temperatures leads to an increase in Gibbs free energy for titanium sulfate. This is attributed to the need of high molecular order during the formation of the sulfate crystals. The reaction proceeds with a decrease in entropy which is counteracted by the increase in temperature. For the oxysulfate however, the opposite trend could be seen. This is because the necessary structural order needed for the formation of the oxysulfate crystals is less than that of the titanium oxide. Therefore, the dependency of temperature was not as significant [40].

In an article by Prando et al. it was researched how temperature and acid concentration influence the dissolution of titanium and its oxide. It was found that temperature has a very positive impact on the dissolution rate where an increase in temperature resulted in higher dissolution rate [45]. Ban et al. saw also that this was true within the temperature interval of 25°C-90°C [39]. The relationship with acid concentration was however not as simple. Up until roughly 10 percent acid concentration, the increase in dissolution rate was linear. After 10 percent, the increase slows down up until roughly 40 percent before dropping down to a local minimum at 60 percent. At acid concentrations exceeding 60 percent, the dissolution rate increases massively [45].

A3.1.4 Nitric Acid

It has been noted that the corrosion rate increased with temperature and acid concentration but also that the thickness of the oxide layer stayed practically constant regardless of acid concentration [43].

Additionally, the dissolution rate is dependent on etching time. Initially the rate is very low but after a few days it increased and stabilized. It is however important to realize that the corrosion rate is insignificant regardless of temperature, acid concentration and exposure time. Ningshen et al. explains that the main reason for the low corrosion rate is the formation of titanium oxide but another factor could be the reduction of nitric acid into nitrous oxide gas and nitrous acid in the presence of acidic protons and electrons. The reaction can be written as Equation 32 [42].

This reaction has a large effect on the redox potential and leads to a noble shift in potential when the concentration of nitric acid increases. Therefore, an increase in acid concentration and temperature would both increase the corrosion rate due to the addition of more reactant. It would however simultaneously inhibit the corrosion rate due to the increased reduction reaction rate [42]. Due to the low corrosion rate, the significance of nitric acid on titanium oxide is in practice negligible.

A3.2 Aluminum Oxide

A3.2.1 Hydrofluoric Acid

It was investigated by Cano et al. how temperature and hydrofluoric acid concentration affected the oxide layer. It was found that as temperature increases so does the etch rate and the thickness of the newly formed aluminum fluoride layer. On the contrary, the thickness of the aluminum oxide layer decreases. The same trends could be seen regarding changes in hydrofluoric acid concentration. X-ray photoelectron spectroscopy was also performed to examine the chemical composition after the etching process. It was then found that the composition of aluminum stayed almost completely constant, while the fluorine and oxygen showed opposite trends compared to each other. The composition of fluorine and oxygen increased and deceased respectively as hydrofluoric acid concentration increased which gives a clear indication that the reaction is occurring [63].

A3.2.2 Hydrochloric Acid

Cui et al. evaluated how acid concentration and temperature affected aluminum oxide dissolution. The result was that as the acid concentration increased, the dissolution rate increased in the early parts of the etching process but it was noted that there most likely exists a threshold for how high the acid concentration can be before the added acid does not improve the performance. In the study, acid concentrations between 3 M and 7 M were used. Up until 6 M, the dissolution rate increased with increased acid concentration. But for the 7 M solution, the total dissolution reached a plateau earlier compared to the other samples and at the end of the measurement period. The total amount of dissolved aluminum oxide was less for the 7 M solution than both the 5 M and 6 M solutions [38].

It could also be seen in the study that the temperature has a significant influence on the degree of dissolution that could be achieved. The measurement was made in a 6 M acid solution with temperatures ranging from 40°C up to 106°C. Interestingly, the measurement for 40°C, 50°C and 60°C there was not a very large difference in the final amount of dissolved oxide. The same was the case for the three measurement series with the highest temperatures, 90°C, 100°C and 106°C. There was however a massive gain when the temperature was increased from 60°C to 90°C after 120 minutes dissolution time. At 60°C the final amount of dissolved oxide was roughly 20% compared to 60% at 90°C [38].

From the results presented above, it gives an indication of at which conditions the etching process should be performed at in order to the achieve most favorable result at the same time as process safety and energy consumption is kept at the best possible level.

A3.2.3 Sulfuric Acid

Franke et al. reported the kinetics of the reaction with regards to temperature and concentration of sulfuric acid. It was shown that both factors contributed to that same trend. As temperature and acid concentration increased, the dissolution rate did also increase. Yet, it could also be seen that the dissolution rate was non-linear. In the beginning, the rate was very high but with time it began to slow down. In the measurements, the time interval was not long enough to see if the rate reached a plateau but the shape of the curve showed a strong indication that this would eventually happen [93].

It was believed that the concentration of free aluminum ions could be the cause of the decrease in dissolution rate with time. Experiments where additional aluminum ions were added and where the solution was rerun after reacidification was performed, showed no significant variation from the original results. This hypothesis could therefore be discarded. It is instead believed to be related to the adsorption-desorption mechanism of hydrogen onto the metal surface [93]. Dash et al. investigated the influence of sulfate groups and found that the dissolution can be hindered when the sulfate concentration increases. This is because although aluminum sulfate can dissolve in water, it is not fast enough if the formation of aluminum sulfate becomes too large. Therefore, an increase in acid concentration can have both a positive effect due to the acid dissolution of the aluminum oxide but also a negative impact from the production of compounds that hinder further dissolution [94].

A3.2.4 Nitric Acid

It has been observed that the efficiency of which the nitric acid dissolved the aluminum oxide scale was largely dependent on the acid concentration. At low concentrations, the migration of the nitrate ions is slow. This results in that the metal surface is able to passivate itself at a higher rate than the dissolution. Therefore, nitric acid has low influence on the passivity of the aluminum metal at low acid concentrations. The corrosive behavior that could be seen was localized pitting. At high acid concentrations however, the migration of nitrate ions is no longer a limiting factor and the dissolution propagates at a higher rate than the oxide regeneration and dissolution will ensue. Likewise, the temperature did also play an important role for the dissolution kinetics. It was noted that as temperature increased, the steady state corrosion potential decreased, indicating that the stability of the oxide layer was decreasing. This would result in that the dissolution rate increases with temperature [70].

A3.2.5 Ferric Chloride

In addition to investigating the adsorption mechanism, Abdel-Gaber et al. did also delve into the kinetics of the dissolution with regards to temperature and chloride concentration. Although the experiments were based on the influence of chloride ions in a sulfuric acid solution, general trends are still applicable since the concentration of sulfuric acid was kept constant. The introduction of chloride ions to the system showed to have a noteworthy effect on the corrosion and so did the temperature. There was a clear linear trend for both chloride concentration and temperature where an increase in these two factors would increase the dissolution rate. However, it is important to recognize that the values of the corrosion rate might be misleading, if only the chloride ions are taken into account, since the solution also consisted of sulfuric acid which in section 4.2.3.3 has shown to be corrosive toward aluminum oxide [73].

A3.3 Chromium Oxide

A3.3.1 Hydrochloric Acid

Reartes et al. have investigate how acid concentration impacted the dissolution rate at 65°C. The results showed that the rate was quite low up until roughly 2 M but at concentrations exceeding 2 M, the dissolution rate increased exponentially. It was however notably lower compared to experiments preformed at the same conditions but using sulfuric and nitric acid instead of hydrochloric acid but it can clearly be seen that higher acid concentration is beneficial for the dissolution [50].

The results from the relationship of acid concentration and dissolution rate could be used to formulate equations that expressed the kinetic of the entire dissolution. In these equations, the temperature was a linear variable. Although no experiments were performed to specifically investigate the influence of temperature, the kinetics equation would indicate that temperature has a basically linear effect on the dissolution rate [50].

A3.3.2 Sulfuric Acid

It was also studied by Geveci et al. how the acid concentration and temperature influenced the dissolution behavior. It could be seen that the dissolution efficiency is non-linear and will reach a maximum and then decrease. This is believed to be due to the decreasing reactivity of sulfuric acid as the concentration increases to high levels. When the temperature was increased it was noted that the dissolution also increased initially. But the increase was not continuous. At high temperatures, a plateau was reached and the dissolution efficiency stayed almost constant [54].

A3.3.3 Nitric Acid

In addition to investigating the reaction, Badet and Poineau researched the kinetics of the reaction. The results showed clear increases in metal dissolution by increasing temperature and acid concentration. Furthermore, it could be seen that temperature accelerated the dissolution to a higher degree compared to acid concentration although the trend was very similar for both variables [56]. The influence of acid concentration was also studied by Reartes et al. for chromium oxide in nitric acid, with the same results that the rate increases with acid concentration [50].

It should be noted that the measured corrosion rates in all cases were very low and would in practice not be considered as significant for the time scales used in etching processes. The study focused on materials that utilize chromium oxide as a protective layer in storage containers but the results can be applied for etching since the effect of the nitric acid was the main factor in the corrosion mechanism.

A3.4 Titanium

A3.4.1 Hydrofluoric Acid

The roughness of the surface could be partially connected to the acid concentration. It was noted that as the hydrofluoric acid concentration increased, so did the pitting. This is believed to be due to gas formation. It was also found that at high concentrations, the reaction rate increased greatly. This causes deterioration of the surface. The etch rate followed a clear trend within the examined concentration interval of 1-4 M. The material removal increased steadily with acid concentration [33].

In the experiments performed by Mizuhata et al. the dissolution of both samples with and without an oxide scale was evaluated. The removal of the oxide scale was achieved through pickling, which is a process where the oxides are selectively removed leaving behind a clean metal surface. These samples showed the same behavior as the oxide covered samples, described in section 4.2.1.1, with regards to how the dissolution rate is affected changes in temperature. Temperature was shown to improve the dissolution within the entire measurement interval of 30°C-50°C [91].

A3.4.2 Hydrochloric Acid

It was found by Shliakhetka et al. that higher acid concentrations will improve the dissolution of titanium metal. The results were presented as a plot of dissolution rate as a function of time and at different acid concentrations ranging from 10-30 wt.%. There was a significant increase in the dissolution rate between the two end points in the concentration interval, roughly a factor of 20 difference after 528 hours. It was also possible to see that as time increased, the increase in dissolution rate started to slow down and an indication of a plateau presented itself. The explanation of this is likely the formation of titanium oxide, from the reaction of titanium chloride with water. The titanium oxide will to a certain degree protect the surface but since this reaction is not necessarily a surface reaction, the protection is likely not as strong [95].

The temperature dependence was investigated by Jaszay et al. and it was found that increased temperatures promoted dissolution of titanium. This was the case in the entire temperature interval of 15°C-100°C. The experiments were performed in deaerated hydrochloric acid but it was noted that the presence of oxygen does have some sort of impact on the mechanism although this was not studied further [96]. The reason for why oxygen can impact the dissolution could possibly be explained by affinity of chloride ions to adsorb to titanium oxide and form titanium oxychloride compounds [36].

A3.4.3 Sulfuric Acid

The dissolution of metallic titanium was shown to have a large effect on the surface roughness which would later affect the formation rate of titanium hydride on the surface. Initially, the rate of formation is higher than the rate of dissolution but the formation rate decreases with time. In due course, the two rates will reach equilibrium and the average thickness of the titanium hydride layer will stay constant. This is believed to be due to the increase in surface roughness. An interesting discovery was that in contact with the surrounding air or water medium, titanium hydride can react to form passive titanium oxide on top of the titanium hydride layer and this layer is generally thinner than that of titanium metal which has been oxidized in open air [39].

There is a clear relationship between temperature and dissolution rate. Ban et al. presented data in the form of an Arrhenius plot as well as weight loss as a function of time at different temperatures where it clearly showed that as temperature increased, so did the weight loss. The measurements were taken for temperatures between room temperature and 90°C. This is also supported by the measurements of the surface roughness at different temperatures where higher temperatures resulted in higher roughness. The plot of weight loss versus time and surface roughness versus time shared notable resemblance with regards to general shape [39].

In an article by Shliakhetka et al. it was found that similarly to temperature, the concentration of sulfuric acid is a vital factor for the dissolution rate. As the acid concentration increased, so did the rate. This was the case for both porous and wrought titanium but the porous titanium was more susceptible to the acid attack compared to the wrought. The experiments were carried out for concentrations between 40 wt.% and 80 wt.%. This is most likely due to differences in surface area. It could however be seen that with the progression of time, the dissolution rate approached an almost constant state which was represented by a plateau in the plot of dissolution rate as a function of time. This can be attributed to the low solubility of titanium sulfate which will restrict contact between the sulfuric acid and the titanium surface [95].

A3.4.4 Combination of Hydrofluoric Acid and Nitric Acid

It has been found that the composition of the etchant solution has a large impact on the surface topography. This composition will however vary if alloying elements have been incorporated into the titanium. For titanium alloy containing aluminum and vanadium, such as Ti-6Al-4V, the mole fraction of hydrofluoric acid and titanium alloy should be roughly 6:1 in order to achieve the most even surface. In parallel with the mole fraction of metal and acid, it was also found that the ratio of the two acids is of great significance when considering the etching efficiency. There is a side reaction that takes place between metallic titanium and nitric acid resulting in the formation of titanium oxide which occurs if the concentration of hydrofluoric acid is too low [33].

A3.5 Aluminum

A3.5.1 Hydrofluoric Acid

Straumanis and Wang investigated the relationship between acid concentration and dissolution rate for this reaction mechanism. It was found that at lower concentrations, the increase in rate was almost proportional to the increase in acid concentration. At higher concentrations, the dissolution rate increased very quickly with a behavior that can be described as having more of an exponential shape [61]. This behavior is similar to what Singh Rapjut et al. noted in their research of titanium metal in hydrofluoric acid [33]. The reaction in both cases are very similar with the main difference being that titanium does not react with fluoride ions in the trivalent state.

Carroll et al. saw that as temperature increases, the open circuit potentials shifted towards active corrosion (to lower potentials). It should be noted that this conclusion was drawn from only two different temperatures, room temperature and 47°C, and that it would be uncertain if the same trend continues in the same manner at even higher temperatures [97]. It is however likely that the corrosion rate, to some degree continues at higher temperatures since the heat will make it easier for the reaction to overcome the energy barrier.

A3.5.2 Hydrochloric Acid

An increase in chloride concentration and temperature was shown by Abdel-Gaber et al. to benefit the aluminum dissolution. The trend for both variables could be seen to have an almost linear relationship to the dissolution rate. Within the acid concentration and temperature intervals, within which the measurements were performed, the effect of the variables was almost identical percentage wise [73]. The trends could however be slightly misleading since both intervals were rather small. The temperature varied between 25°C and 40°C and the chloride concentration was always very low. It can also be considered that when acid concentrations approach pure acid, the dissociation will be less frequently occurring which will inhibit dissolution.

A3.5.3 Sulfuric Acid

Uma et al. has performed research regarding the kinetics of the dissolution of aluminum in sulfuric acid. The results showed that acid concentration has a positive impact on the dissolution rate. It could be seen that as concentrations exceeded 1 M, the effect of additional acid did not improve the dissolution at the same rate as at lower concentrations [98]. The same results were found by Arellanes-Lozada et al. where the dissolution rate approached a plateau as acid concentrations increased [99].

The temperature dependence of the dissolution kinetics was analyzed by Ebenso. Higher temperatures caused increased dissolution rate for all studied concentrations, in the entire temperature interval of which the measurements were executed, 30°C-60°C. The temperature showed a stronger effect at higher acid concentrations compared to lower. At low temperatures and low concentrations, the effect was not considerable but as the concentration was raised, there was a more significant increase in the dissolution [100]. Very similar results were also achieved by Patil and Sharma [101].

A3.5.4 Nitric Acid

Iwata et al. noted that dissolution of aluminum increased with acid concentration initially. As the solution approached pure nitric acid the dissolution was becoming more troublesome. Due to the lack of water, nitric acid is unable to dissociate which leads to a decrease in reactivity. As a consequence, the pores are not formed and the oxide layer becomes more uniform [69].

Patil and Sharma have evaluated the kinetics with regards to temperature changes. The dissolution of aluminum increased with temperature within the temperature interval of 25°C-40°C. The dissolution rate was plotted as weight loss as a function of time at different temperatures. The slope of the curves was in all cases positive at the end of the measurement which indicates that the same trend would continue at higher temperatures as well. It was however possible to notice that the slope of the curve gradually decreased but not massively which also gives in indication that the relationship between temperature and dissolution rate is not constant [101].

A3.5.5 Ferric Chloride

The temperature dependence of the etching rate was investigated by Catir and it was observed that the etching depth had an almost linear relationship with temperature. As the temperature increases, so does the rate at which the etchant solution dissolves the metal. It was however also found that the temperature had an effect on the roughness of the surface. The roughness of the surface would increase as the temperature increased. The etching was carried out at temperatures ranging between 20°C and 50°C. The etch rate were however quite low. When using 1.25 M ferric chloride at 50°C, the etch rate was 1.25 µm/min [71].

Mahmood et al. have performed experiments to evaluate the influence of an elevation of ferric chloride concentration on the dissolution rate. It was found that additions of ferric chloride led to higher rates. Solutions between 0.5M and 5M were used. Furthermore, it could be seen that the application method was an important parameter to take into account. If the solution was added as one singular droplet, the dissolution rates were considerably lower compared to if the solution volume was added as two smaller droplets. This is believed to be attributed to the generally higher availability of moisture which can assist to keep the corrosion products in a hydrated state. Interestingly, analysis of the corrosion products showed the presence of various iron hydroxides, oxyhydroxides and oxides which most likely are formed from the interaction of ferric chloride with water in the solution [102].

A3.5.6 Acetic Acid

It was observed by Zhang et al. that both temperature and acid concentration have a positive effect on the corrosion rate by measuring the current density as a function of temperature and at different acid concentration. It could clearly be seen that the corrosion increased with both temperature and acid concentration but it could also be noted that the effect was slightly more prominent at lower concentrations [74]. This research was conducted at quite mild conditions, up to 1 M and between 25°C and 55°C, and does not cover the corrosion behavior at higher concentrations or higher temperatures but it has been found by Vargel that carboxylic acids in general, react violently at high temperatures, high acid concentrations and low water content [103]. This is in alignment with what was presented previously and gives an indication that the trends noted by Zhang et al. can be relevant at more aggressive conditions.

A3.6 Chromium

A3.6.1 Hydrofluoric Acid

In aqueous solutions containing hydrofluoric acid, chromium will quickly react with oxygen or fluoride ions in order to form chromium oxide, hydroxide or fluoride. Although, these three compounds can form on the surface, the majority appears as chromium oxide and hydroxide with only a small portion being chromium fluoride. Since all reaction products are solids, the surface will eventually be covered and protected from further metal oxidation.

A3.6.2 Hydrochloric Acid

Kim et al. studies the kinetics and the Gibb’s free energy of the reaction. Although the calculation was performed only at 90°C and showed that the reaction was spontaneous, dissolution experiments showed that the reaction is not very temperature dependent within the interval of 50-90°C with only a slight increase in efficiency as the temperature increased [48].

The reaction was however more dependent on the acid concentration. Measurements of the dissolution efficiency at 90°C after 120 min found that the efficiency almost doubled when the acid concentration was increased from 1 M to 3 M. Above 3 M, the efficiency remained high and constant [48].

It should be noted that it is possible that the oxidized chromium instead reacts with oxygen, or oxygen containing compounds, to form a protective chromium oxide film but considering the high dissolution efficiency, it is not indicated that this proceeds fast enough to influence the dissolution rate. This does also give a strong indication that chromium chloride, although it has low solubility in water, does not passivate the surface. The explanation could be that the chromium chloride becomes hydrated in the aqueous solution. The chemical database PubChem explains that chromium chloride hexahydrate is soluble in water. Chromium chloride hexahydrate is created when anhydrous chromium chloride comes in contact with water [104].

A3.6.3 Sulfuric Acid

The formation of passivating chromium compounds on the metal surface will simultaneously be counteracted by dissolution in sulfuric acid. The metallic chromium will firstly by oxidized and reacted into the passivating compound that later will be dissolved into water soluble chromium sulfate complexes in the same way as described in section 4.2.2.2, with the same kinetics.

A3.6.4 Nitric Acid

The dissolution of chromium metal in nitric acid will be very similar to that of chromium oxide with the only large difference being the way the trivalent chromium is transferred into the solution. Instead of the deterioration of chromium oxide by protons, the chromium would be oxidized directly from the metallic state into chromium ions by hydrogen evolution [55]. The chromium ions would later react with the oxygen containing constituents in the solution to form chromium oxide. The rest of the dissolution mechanism was the same as for chromium oxide with the formation of hydrogen chromate. Therefore, the kinetics would also be equivalent to that of dissolution of chromium oxide. For an in-depth explanation, see section 4.4.3 [56].

A3.6.5 Ferric Chloride

Park et al. has found that there is a correlation between temperature and acid concentration with etching rate. Increased temperature caused an increase in rate but interestingly, an increase in ferric chloride concentration resulted in lower etch rates. Although it should be considered that all experiments used ferric chloride solution of 48 degrees of Baumé or higher. This represents concentrations significantly higher than 40 wt.%. This result is only representative for very high concentrations [58].

A3.6.6 Acetic Acid

Parhi et al. have thoroughly investigated the kinetics of chromium metal dissolution in acetic acid solutions. It was found that the acid concentration and temperature have a large impact on the dissolution rate and efficiency. It was noted that an increase in both factors lead to a great increase in chromium dissolution during the entire time interval of the experiments. There was however a notable difference between at which time during the experiment the two factors had the most effect. Early in the experiment, the improvement by increasing the temperature was a lot lower compared to an increase in acid concentration. On the other hand, at the final stages of the experiment, the temperature accounted for a more significant improvement. The investigated temperature and acid concentration intervals were 30°C-90°C and 0.25-3 M respectively. It is important to remember that although the rate and efficiency improved with temperature and acid concentration, the highest measured efficiency was only a bit less than 60% after 150 minutes [105]. Therefore, both the temperature and acid concentration should be kept as high as possible, within the capabilities of the experimental setup, in order to achieve the highest etching rates.

A3.7 Nickel

A3.7.1 Hydrofluoric Acid

A study performed by Noel and Chidambaram showed that at low acid concentrations, the dissolution of metal was evenly distributed over the entire surface. This was also the case if any nickel oxide was present on the surface. The constituents of hydrofluoric acid have the ability to both oxidize metal and dissolve metal oxides. However, when acid concentrations exceeded 5 M, it was noted that the dissolution became highly selective and localized. Therefore, at concentrations above 5 M, the passive nickel fluoride layer lost its homogeneity and would instead grow as patches but eventually covered the entirety of the surface [80].

Guo et al. have seen that the corrosion rate increases with temperature. The increase is not massive but grew steadily throughout the entire measured temperature interval of 25°C-75°C. The corrosion product was found to be both nickel fluoride but also nickel oxides and hydroxides. The formation of nickel oxides and hydroxides can be attributed to the presence of water in the solution. An interesting discovery was that the corrosion rate decreased slightly with time. This can be explained by the more protective properties of the corrosion products compared to pure nickel. It can however be seen that the corrosion is not stopped. A factor that is of much greater significance is the phase of the etching solution. In the vapor phase, the corrosion rate is much higher and does not decrease with time although some of the same corrosion products are formed [106].

A3.7.2 Hydrochloric Acid

Kim et al. investigated the effect of acid concentration and temperature on the dissolution efficiency and it was found that neither acid concentration nor temperature had any large significance. There was a slight increase in the final ratio of dissolved and non-dissolved nickel metal between 1M and 3M hydrochloric acid but at concentrations above 3M, no difference was noticeable. Likewise for the temperature, over the interval 50-90°C, no change could be seen [48].

Park et al. preformed a similar study but at lower acid concentrations while also taking factors such as stirring and particle size into consideration. The dissolution efficiency was lower compared to Kim et al. but this is most likely due to the lower temperature used for the measurement. The effect of acid concentration was clearly shown as the dissolution increased steadily with acid concentration. There was also a more visible temperature dependency due to the experiment being performed at a lower acid concentration. An increase in temperature generates a higher amount of dissolved metal [107]. It should however be remembered that when acid concentrations become very high, close to pure acids, dissociation becomes more difficult which will reduce the etch rate catastrophically.

A3.7.3 Sulfuric Acid

Agacayak and Zedef examined the kinetics of nickel dissolution in sulfuric acid. Since the pure nickel metal is easily oxidized and reactive, it is more representable that the nickel metal to some degree is oxidized at the metal surface, at least the nickel atoms at the interface. The dissolution had a positive relationship with both temperature and acid concentration where an increase in these two factors resulted in improved dissolution. As the acid concentration increased, there was a steady increase in the dissolution efficiency but the improvement reached a plateau with time. The added temperature was shown to have a stronger influence. Within the temperature interval of 40°C-96°C, large improvements in both dissolution efficiency and the time it took to reach maximum efficiency was made. In a solution containing 2 M sulfuric acid at 40°C, the efficiency was roughly 35 % after 10 hours. If this is compared to the same acid concentration but instead at 96°C, where 100 % of the nickel was dissolved after barely 5 hours [108].

A3.7.4 Nitric Acid

The kinetics of the dissolution mechanism was investigated by Ans et al. and showed that the temperature and concentration of nitric acid both had a positive relationship with the dissolution rate. Although, neither of the factors have linear relationships with the rate. Higher temperature causes an exponential increase in dissolution rate within the entire temperature interval of 20°C-180°C. On the other hand, acid concentration did also generate a large improvement in the dissolution, especially in the early stages of the measurement. It could however be seen that if the acid concentration is increased above 2 M, the effect was a lot less pronounced. At later stages of the experiment, the dissolution efficiency of all nitric acid solutions with concentrations over 2M were almost identical but significantly higher than for the 1M solution [76]. Kim et al. performed a similar experiment where the same results were found. Additionally, a comparison of etch rates for nitric acid, hydrochloric acid and sulfuric acid was carried out. This showed that nitric acid had a much higher rate than both the other acids. Furthermore, sulfuric acid had higher rate than hydrochloric acid [109].

A3.7.5 Ferric Chloride

In the article by Liao and Wu, it was found that the etch rate was highly influenced by the concentration of ferric chloride. The used concentration interval was 0.1-1 M. The explanation of this could be that since it is the iron ions that act as the oxidation agent, but do not take part in the reaction as a reactant it can return to the trivalent oxidation state. Thereby, the oxidative performance of the solution can remain high. Another interesting component of the etching system was that the addition of chloride ions did not have any significant effect on the etch rate. The main reason for this is that the chloride ions mainly attack metal oxides and not the metals themselves [77].

The influence of temperature during the etching process was found to have a positive correlation. As temperature increased, so did the etch rate. This relationship was quite constant throughout the entire temperature interval of 10°C to 50°C that was used in the measurement. At 1 M and 26°C, the etch rate was 1 mm/day which corresponds to roughly 0.7 µ/min. This is not very high but still considerable [77]. The effect of temperature was not as strong as for a change in concentration. Therefore, if high etch rates are wanted, it is more efficient to increase the concentration.

A3.7.6 Acetic Acid

The concentration dependency is explained in section 4.2.4.4.2 but Schütze et al. have seen that the corrosion rate of nickel in acetic acid has a positive relationship with temperature although the rates are generally quite low. The presence of air has a much larger influence. It has been reported that nickel in two solutions with the same acid concentration and temperature, but one of them are in a deaerated environment, then the corrosion rates will differ by roughly a factor of one hundred [79].

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