Depth Profiling of the Passive Layer on Stainless Steel using Photoelectron Spectroscopy

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Abstract

The physical properties of the protective passive films formed on the surface of stainless steels under electrochemical polarization in different electrolytes were studied. The structure of these films was analyzed as a function of depth using photoelectron spectroscopy (PES).

Depth profiling (using PES) of the surface layer was achieved by either changing the angle of incidence to achieve different analysis depths (ARXPS), by argon ion etching, or by varying the energy of the incoming x-rays by the use of synchrotron radiation. The use of hard x-rays with high resolution (HAXPES) provided novel quantified information about the nickel content underneath the passive films.

A complex environment was found in these surface layers composed of an outermost monolayer of iron on top of a layer of chromium hydroxides covering an underlayer of chromium oxides. Molybdenum was enriched in the interface between the metal and oxide. Nickel is enriched underneath the passive film and therefore nickeloxides are only present in the surface layer in low concentrations.

A comparison was performed on austenitic and duplex stainless prepared by hot isostatically pressed (HIP) or cast and forged processes. HIP stainless steel was produced using the burgeoning technique of pressing gas atomized powders together. The structure of these steels is far more homogenous with a lower porosity than that of the conventionally prepared equivalents. It was shown that hot HIP austenitic steel had better pitting corrosion resistance than its conventional counterpart.

Finally, the duplex steel was cycled in a Li-ion battery to explore its potential application as a current collector. It was shown that the passive film formed in the organic solvents is similar in composition and thickness to the films formed in aqueous solutions. However, it is doubtful if steel could be used as current collector in batteries due to its high reactivity with lithium.

Keywords: depth profile, stainless steel, passive film, XPS, HAXPES, corrosion, powder metallurgical

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Till mamma och pappa
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


Reprints were made with kind permission from the different publishers.
Papers not included in this thesis:


My contribution to the papers

Paper I. I planned and executed all the experimental work. I wrote the initial manuscript and was involved in all discussions.

Paper II. I planned and executed most of the experiments. I was involved in all discussions and wrote most of the text.

Paper III. I was involved in the planning and discussions. The experimental work was done together with the main author, where I participated in the electrochemical measurements and performed the XPS measurements. I contributed to the manuscript. The calculations and iterative processes were mostly performed by the main author.

Paper IV. I planned all the work and executed all the XPS measurements and wrote the initial manuscript and was involved in all discussions.

Paper V. I planned the project and executed all the XPS measurements. I analyzed, discussed, and wrote the text together with my supervisor.
# Contents

Introduction.......................................................................................................................... 11

Theory.................................................................................................................................. 14
- Stainless steel ..................................................................................................................... 14
- Passive films on stainless steel .......................................................................................... 16
- Corrosion of stainless steels in liquids ............................................................................... 18
- Production of stainless steels ............................................................................................ 22

Methods for studying passive films on stainless steel ....................................................... 25
- Polarization of the steels ................................................................................................... 26
- X-ray photoelectron spectroscopy ..................................................................................... 27
- Scanning Electron Microscopy (SEM) ................................................................................. 32

Introduction to the result section .......................................................................................... 33

The passive layer formed in water based systems ................................................................. 34
- Molybdenum in the passive film ......................................................................................... 34
- Manganese in the passive film ........................................................................................... 36
- Nickel, chromium, and iron in the passive film analyzed with high resolution XPS ................................................................................................................................. 39

Pitting corrosion on P/M and conventional steels in water based solutions .................... 45

The passive layer formed in a non aqueous solution ............................................................ 52
- Analysis of iron and chromium in the passive layer in a non aqueous solution ................. 52

Depth profiling of passive layers on steel ............................................................................ 58

Concluding remarks ............................................................................................................. 59

Sammanfattning på svenska .................................................................................................. 61

Acknowledgements ............................................................................................................... 64

References............................................................................................................................. 66
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARXPS</td>
<td>Angular Resolved X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>FC</td>
<td>Fuel Cell</td>
</tr>
<tr>
<td>HAXPES</td>
<td>Hard X-ray Photoelectron Spectroscopy</td>
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<tr>
<td>HIP</td>
<td>Hot Isostatic Pressing</td>
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<tr>
<td>PEMFC</td>
<td>Polymer Electrolyte Membrane Fuel Cell</td>
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<td>PES</td>
<td>Photoelectron Spectroscopy</td>
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<tr>
<td>P/M</td>
<td>Powder Metallurgy</td>
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<tr>
<td>SEI</td>
<td>Solid Electrolyte Interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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</table>
Introduction

Corrosion is a reaction between the steel and the environment which is in many cases detrimental to the material. Despite formation of protective passive films on the steel surface, there is always a risk that a specific chemical environment can destroy the film leading to corrosion. Therefore, awareness of the corrosion processes of stainless steel is important when choosing the material for a certain purpose.

The interest for stainless steels in different applications is constantly growing. In, for example, fuel cells it is possible to replace the bipolar plates that today are made of graphite. Plates of steel can be made thinner and are easier to shape. Important properties for the plates are high electric conductivity, high corrosion resistance, and low contact resistance and steel is therefore a good candidate. However, due to the low pH in the fuel cell it has been shown that steel corrodes and a suitable protective coating is most probably needed to enhance the life time of the steel plates [1, 2]. Another interesting application for stainless steels is as current collector material in lithium-ion batteries where there is a constant demand for decreasing the cost and increasing the efficiency of the battery.

Stainless steels is a wide class of materials based on iron-chromium alloys with at least 10.5 wt% Cr combined with a low carbon content [3]. The early history of stainless steels started already in the 19th century. Michael Faraday was one of the first to work on the development of steel alloys [4]. In 1836 he discovered the presence of a protecting film on the surface of iron and thought that it was responsible for the increasing corrosion resistance [5]. In 1821 Berthier studied properties of iron-chromium alloys. He showed that the dissolution resistance in certain acids increased with increasing the chromium content [4]. But at that time there were difficulties in obtaining alloys with a sufficiently low carbon content, and since this was not yet understood the improvement of the steels slowed down [6]. It was not until the late 1890s that Carnot and Goutal discovered that a high carbon content had a detrimental effect on the corrosion resistance for iron-chromium alloys [4]. This opened up a new research field and in the early 1900s low carbon steels could be manufactured. A series of articles were published on iron-chromium and iron-chromium-nickel alloys by Guillet, Portevin, and Giesen [6]. Philip Monnartz was one of the first to study the corrosion resistance of these new materials, which he showed was related to the passivation of the surface [4] The passivity was related to the protecting passive film on the
surface, since the dissolution rate of the alloy decreased due to the film. Monnartz stated the following important conclusions regarding the passivity and corrosion resistance [4]:

“The corrosion rate decreases remarkably when the chromium content is close to 12 wt%”

“Passivity is the phenomenon responsible for the increase in corrosion resistance”

“Low carbon content is important, since a high carbon content may increase the number of carbides that prevents passivity”

“Molybdenum has a favorable effect in enhanced corrosion resistance”

In 1909 three principal classes of stainless steels had been defined in terms of their atomic structure: ferritic, austenitic and martensitic. A fourth member of the classes is duplex steels, that was first discovered in 1927 by Bain and Griffiths [7]. Duplex steels consist of a mixture of austenitic and ferritic phases [3]. Stainless steels were first manufactured around 1910, but it was not until almost half a century later that they were produced on an industrial scale [6].

The chemical composition varies between the steel classes and gives them different important properties for various kinds of applications. The austenitic steels are preferred for very corrosion demanding situations, such as applications in contact with food and pharmaceuticals and also for household utensils. They are also used in transport vehicle structures and in equipments for chemical and papermaking industries [6]. The ferritic steels are, for example, used in applications for the exhaust systems within the automobile sector.

Duplex steels combine many of the beneficial properties of austenitic and ferritic steels. They have a high content of chromium, nitrogen and also molybdenum and can therefore offer a good resistance to both local and uniform corrosion. It is the duplex microstructure, which contributes to their high strength and high resistance to, for example stress corrosion cracking. Important applications are therefore in heat exchangers, pressure vessels, rotors and in the pulp and paper industry [8].

The excellent corrosion resistance of stainless steels is due to a passive film on the surface, which is mainly composed of oxides and hydroxides of iron and chromium [9, 10], but also other alloying elements such as molybdenum and manganese are part of it. Nickel is enriched underneath the passive film and only a low amount of nickel oxides are found in the surface film [9, 11, 12]. This passive film has been widely studied over the years to increase the understanding of the properties of the steels.

It was not until surface analysis was started to be used in the 1970s that a more detailed information of the chemical composition and the thickness of the passive film could be obtained. The dominating approach used is to
combine electrochemical methods with x-ray photoelectron spectroscopy (XPS) [9, 11, 13, 14] or Auger electron spectroscopy (AES). Other techniques, e.g., atomic force microscopy (AFM) [15, 16], scanning tunneling microscopy [17], ellipsometry [18, 19], etc., have also been used. All these techniques are surface sensitive but still XPS is one of the most powerful since it provides both chemical composition and thickness information on the passive film.

The scope of this thesis is to contribute with a more detailed understanding of the passive film and how the different alloying elements are affecting the formation of the film in different electrolytes. For this a deep knowledge of the distribution of different species within the passive film is necessary. Hence, one of the main goals of this thesis has been to explore several different ways to extract as detailed information as possible from both in-house and synchrotron based XPS methods.

Some different steel grades have been examined, where focus has been on austenitic 316L and two duplex grades, 2101 and 2205. The chemical complexity of the passive film was evaluated for all steels from polarization curves and XPS, PES and SEM.
Theory

Stainless steel

The main element in all stainless steels is iron and therefore it is important to recall that iron has different allotropic forms. At atmospheric pressure and low temperatures up to 910 °C pure iron has a body centered structure, bcc (Figure 1a), known as α-iron. Above 910 °C the structure transforms to γ-iron, which has a face centered cubic structure, fcc (Figure 1b). At 1400 °C the structure transforms back to bcc and in this range it is called δ-iron [20, 21].

In steels, the bcc structure is referred to as ferrite and the fcc structure as austenite.

Iron has a high solubility for carbon atoms that can find room in interstitial sites in the structure. How much carbon that can be dissolved depends on the structure of the iron allotrope. Fe-C steels with different properties can be formed. However, to make corrosion resistant steels parts of the iron has to be substituted for other metals and chromium, nickel and molybdenum are common alloying elements.

When chromium is added to iron, the chromium atoms will substitute some of the iron atoms in the crystal structure. The solid solution is known to be substitutional since chromium are found at exactly the same positions as the iron [22]. Chromium itself has a bcc structure and stabilizes therefore the ferrite phase in steels. The carbon (0.1 wt%) in the iron-chromium alloys are distributed in the gaps between the other atoms forming an interstitial solid solution. If a larger amount of carbon is added there will not be enough interstitial sites and the excess carbon will combine with chromium to form carbides. These carbides segregate at the grain boundaries [22].
Nickel promote the fcc structure and is referred to as an austenite stabilizer. Molybdenum is an important alloying element and a ferrite stabilizer and acts to support chromium and thereby the resistance to mainly pitting corrosion can be improved.

To summarize, the different alloying elements can be divided into two groups depending on their respective microstructure. The common ferrite stabilizers include, beside chromium and molybdenum, also silicon, titanium, niobium, vanadium, tungsten, aluminum and tantalum. The common austenite stabilizers are, beside nickel, also carbon, nitrogen and manganese [6].

The ferrite or austenite structures form the bases for the four main groups of stainless steels: ferritic, austenitic, duplex and martensitic.

**Ferritic steels**, bcc, have the same crystal structure as iron at room temperature and they are magnetic. The ferritic steels contain between 11 and 27 wt% chromium, no or only a minor part nickel and a maximum of 0.2 wt% carbon in the wrought condition [22]. The ferritic steels do not harden at higher temperatures [23]. The yield strength is relatively high but the ductility is low. Common ferritic grades are 16-18Cr referred to as EN 1.4016 or ASTM 430 [8], see Table 1.

<table>
<thead>
<tr>
<th>Grade</th>
<th>ASTM</th>
<th>EN Micro-structure</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>N</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>1.4016</td>
<td>Ferritic</td>
<td>16.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>304</td>
<td>1.4301</td>
<td>Austenitic</td>
<td>18.1</td>
<td>8.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>316L</td>
<td>1.4432</td>
<td>Austenitic</td>
<td>16.8</td>
<td>10.6</td>
<td>2.6</td>
<td>1.6</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>LDX2101</td>
<td>1.4162</td>
<td>Duplex</td>
<td>21.7</td>
<td>1.54</td>
<td>0.3</td>
<td>5.1</td>
<td>0.22</td>
<td>0.03</td>
</tr>
<tr>
<td>2205</td>
<td>1.4462</td>
<td>Duplex</td>
<td>23.4</td>
<td>5.5</td>
<td>3.4</td>
<td>0.8</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>410</td>
<td>1.4006</td>
<td>Martensitic</td>
<td>12.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The non-magnetic **austenitic steels** have fcc structure, which is also the high temperature structure of iron. The austenitic steels have excellent toughness due to the fcc structure [3]. Typical alloying elements are chromium and nickel. Nickel plays a special role for the stabilization of the fcc structure and it delays the formation of intermetallic phases in austenitic steels. The austenitic steels have compositions that contain sufficient amounts of chromium (at least 16%) to offer good corrosion resistance and enough of nickel (commonly 8-10%) for the fcc stabilization. The most common austenite is the steel alloy with 18 wt% chromium and 8 wt% nickel, referred to as EN 1.4301 or ASTM 304 [8, 22]. To improve the corrosion resistance, it is possible to increase both the chromium and nickel contents, but also the amount of other alloying elements, such as molybdenum. One example of a molybdenum containing steel is the austenite with a molybdenum content restricted to 7.5 wt%. This austenitic steel is called EN 1.4432 or ASTM 316L, for composition, see Table 1.
The duplex steels have a two-phase micro-structure consisting of austenite and ferrite phases. The phase balance can be between 30 – 70% ferrite for favorable properties but a ratio close to unity is most commonly used [3]. The molybdenum content is restricted to 4 wt%. A higher molybdenum content increases the probability to form intermetallic phases that can be detrimental to the material [3]. The nickel content in duplex steels is usually lower than in the austenitic steels, approx. 4-6 wt%. To compensate for the low amount of nickel, the duplex steels have a higher content of manganese and chromium than the austenitic and ferritic steels. Due to the high chromium content (maximum of around 27 wt%) the duplex steels offer good resistance to, for example, local and uniform corrosion. In duplex steels, nickel is important for increasing the toughness in the austenitic phases and for the improved corrosion resistance since it helps to reduce the rate of the propagation of corrosion on steel. Duplex steels have a good weldability but they are also harder than the austenitic [24]. Common duplex steels are EN 1.4162 also called ASTM S32101 or LDX 2101, and EN 1.4462 or ASTM S32205 or 2205; compositions are displayed in Table 1.

Martensitic steels are also magnetic and contain from 12 to 20 wt% chromium. They are formed by heat treatment above 910 °C which leads to the formation of austenitic structures. By accelerated cooling the austenite is transformed to martensitic steel. The martensitic structures generally have high hardness, but with reduced toughness and they are brittle. The martensitic steels are used in applications where high hardness and strength is needed. This is achieved due to the carbon atoms in the alloy. When the structure transforms from fcc to bcc upon cooling there will be less space for the interstitial carbon atoms. If the cooling is slow there will be enough time for the carbon atoms to move around and form carbides at the grain boundaries, but with rapid cooling the precipitated carbides are trapped in the newly formed bcc. This structure is badly distorted resulting in increased hardness and strength [22]. The corrosion resistance of the martensitic steels is worse than for the austenitic ones. An example of a martensitic steel is EN 1.4006 or ASTM 410 [8], see Table 1.

The composition and properties of stainless steels are well covered in several text books and theses, see for example refs. [5, 20-23, 25-27].

Passive films on stainless steel
The corrosion resistance of stainless steels is mainly due to a 1-3 nm thin oxide-hydroxide film on the surface [28]. The film is formed naturally during a reaction between the metal and oxygen present in the surrounding environment and its main constituent is chromium oxide with significant contributions from iron and molybdenum oxides [10, 29]. However, the composition of the oxide film varies with alloy composition in the stainless steel and a minimum chromium content of 10.5 wt%, is necessary for the formation of
a stable chromium oxide film [3]. Since the film reduces the dissolution rate of the alloy elements it is usually referred to as the passive film [28, 30]. On stainless steel this passive film is extremely important, since it is a prerequisite for the corrosion resistance. The film must completely cover the surface to reduce the reaction rate between the metal and the surrounding. A detailed knowledge of this layer is hence necessary for understanding how maximum corrosion resistance can be obtained.

The mechanism by which the oxide/hydroxide layer forms can be described by a transition from a two-dimensional adsorbed oxygen layer to a three-dimensional oxide film. This transition is gradual and islands of the adsorbed oxygen nucleate and grow laterally across the surface [31]. The passive films has for a long time been described to have a duplex character, [9-11, 13, 30-36] consisting of an inner barrier oxide film of chromium and iron oxides and an outer chromium hydroxide or salt film [9, 10, 31].

If the film is formed in air it will have a relatively high fraction of iron. However, a passive film can be influenced by changing the environment and in an acid and with an increased applied potential there is an enrichment of chromium with a concentration of up to around 70%. This is due to selective dissolution of iron leaving chromium enriched [37]. There are low amounts of nickel oxides in the passive film since nickel is not as readily oxidized as iron and chromium. In austenitic and duplex steels an enrichment level of nickel has been found in the bulk underneath the passive oxide layer [10, 12, 13, 38]. Molybdenum increases the strength of the passive film, since it decreases the ingress of anions and thereby decreases the corrosive attack. One theory about molybdenum is that molybdate absorbed in the passive film has an inhibiting effect and changes the anion selectivity [39, 40]. Molybdenum shows a complex structure with different oxidation states in the passive film. Hexa-valent molybdenum has been found at the surface while tetra-valent molybdenum has been shown to be homogeneously distributed throughout the film [9, 41]. The role of molybdenum for pitting corrosion resistance has been reviewed by Jargelius et al. [42]. It has been suggested that there will be point defects in an oxide lattice that are dominated by tri-valent species. The presence of the tetra- and hexa-valent molybdates tend to cancel these point defects [36]. For an almost defect-free film it will be more difficult for anions to penetrate. A schematic representation of a typical passive film is seen in Figure 2. One of the important reviews of passivity on metals and alloys was published by Uhlig in 1979 [43].
The composition of the passive film and the oxidation states of the elements in the film can be influenced by outer parameters, such as the oxidizing power and pH of a surrounding solution. Local pH within the film, the age of the film and the location of the metal ion relative to the external surface can also affect the passive film composition [31].

One way of influencing the film is by varying the potential between the steel and the environment; the thickness will then increase with increasing potential in the region where there is a stable passive film [44]. The pH has a main influential effect on the dissolution rate where an increased pH gives decreased rate and a thicker film with a higher iron content, since iron oxides are more stable at higher pH [10, 44].

To know how the chemical species within or directly underneath the passive layer of a stainless steel are distributed is hence of particular importance for the understanding of how the outer parameters, such as electrolyte and potential, but also production routes, influence the corrosion properties of the steel. Carefully measured depth profiles are essential and the passive film has thus been studied both in this thesis (all papers) and in a number of different publications in this respect. A detailed discussion on how to use XPS to determine depth profile information is given in the chapter with the title ‘Methods for studying passive films on stainless steel’.

Corrosion of stainless steels in liquids

Corrosion means that there is a breakdown of a material due to a physical-chemical reaction where there is a thermodynamic driving force for a transformation of the metal to a more stable compound. The reaction results in changes of the properties of the metal and thereby the function will in most cases be destroyed [45]. As already mentioned, steel is protected from corrosion due to the passive oxide surface layer that drastically reduces the corrosion rate of the material [46]. There are some different types of corrosion that may vary in nature and appearance in different media.
The corrosion cell consists of a negative electrode, an electrolyte, and a positive electrode. At the negative electrode the oxidation of the metal (or other compound) occurs, which means that electrons are released. At the positive electrode there is an uptake of electrons and reduction occurs. The two electrode reactions are called half-cell reactions. Between the two electrodes there is an electronically insulating but ionically conducting electrolyte.

Rusting of iron is a common example of corrosion, where oxides or salts of the original metal are formed on the surface where the oxidation then can be as follows in Equation (1):

\[
2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + 2\text{e}^{-} \tag{1}
\]

and a common reduction is, Equation (2):

\[
\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^{-} \rightarrow 2\text{OH}^- \tag{2}
\]

The two half-cell reactions means that two electrodes with different electrode potentials come into contact in an electrolyte where a chemical reaction uses or generates an electric current and an electromotive force (voltage). The generated current is called the corrosion current and is a measure of the corrosion rate and has therefore the unit mA/cm². More common is, however, to describe the effect of corrosion as the increase of the depth zone of the corroded area as a function of time and the unit is then, e.g., μm/year.

There are some different types of corrosion, which are briefly described in the following sections. It should be mentioned, however, that pitting corrosion is of particular interest in this thesis since this was the main focus in paper IV. Therefore the description of this type of corrosion is more extensively discussed in this section.

**Uniform corrosion**

Uniform corrosion occurs when a large part of the passive film is destroyed. Corrosion reactions occur over the whole exposed surface and cause a more or less uniform removal of metal [45, 46]. Uniform corrosion mainly occurs in acids or in hot alkaline solutions. Resistance from this kind of corrosion can, for example, be improved by increasing the chromium content [46].

**Galvanic corrosion**

This type of corrosion occurs when two different materials are in contact in an electrolyte and hence a galvanic couple is formed [46, 47]. There will be a potential difference between the two materials, which will be the driving force for the severely attacked anode. The other metal will be the cathode and protected against corrosion [46]. The corrosion resistance of the two
coupled metals might differ significantly from their behavior when uncoupled. In many environments stainless steels are nobler than other construction metals and stay passive if coupled to a less noble material [46].

**Stress corrosion cracking**

Stress corrosion cracking (SCC) is a corrosion process that occurs when the steel is subjected to a mechanical force, such as tensile stress, in a corrosive medium, usually chloride containing acids [45, 46, 48]. Important surrounding factors for SCC are often the oxygen concentration, the pH and the electrode potential [45]. The cracks might be both across or through the individual crystals of a metal (transcrystalline) and along the boundaries between crystals or grains of a metal (intercrystalline) and it often leads to brittle failures [45].

**Corrosion fatigue**

A material can fail if subjected to a cyclic load at the same time as exposed to a corrosive environment. Also this form of corrosion cause brittle failures. Cracks are often transcrystalline, straight and un-branched [46].

**Intergranular corrosion**

Intergranular corrosion means corrosion in the grain boundaries of the material, based on the fact that these grains might get different properties than the rest of the material after heat treatments from the production process [45, 49]. The most common intergranular types of corrosion are the ones caused by precipitation of chromium carbides or intermetallic phases.[45]. If austenitic steels are subjected to temperatures in the range 550-850°C chromium carbides precipitate in the grain boundaries [46]. The alloy adjacent to the grain boundaries become chromium depleted and therefore less corrosion resistant than the matrix. A material with precipitates in the grain boundaries is said to be sensitized, which can occur as a result of welding or hot forming at an inappropriate temperature. To decrease the precipitates the material can be solution annealed at 1000-1200°C, where the chromium carbides are dissolved and thereafter the material is rapidly cooled [46].

**Localized corrosion**

Pitting is a localized form of corrosion which is characterized by corroding pits that grow on a metal surface. The pits start to grow in small discrete areas that have been attacked by anions, for example halide ions [46]. The main mechanisms for pitting initiation can be summarized as follows; first anions diffuse through and weaken the passive layer by exchanging the oxy-
gen ions, secondly the passive layer ruptures and finally the anions are selectively adsorbed on the metal surface. The most critical stage of the pitting corrosion mechanism is the initiation phase. After a pit is initiated there will be a fast growing localized corrosion pit. The process is autocatalytic. Pits usually starts in defects on the surface, such as a scratch in the protective film, a dislocation or slip, or a compositional heterogeneity such as an inclusion, segregate or precipitate [50]. The mechanism of pitting corrosion is schematically shown in Figure 3.

![Figure 3. Schematic representation of the mechanism of pitting corrosion on a steel surface.](image)

Inside the pit there will be oxidation reactions forming metal ions and electrons according to Equation (1). The electrons will reach the metal surface and react with oxygen and water according to Equation (2). The metal ions in the pit will attract the negative chloride ions and increase the acidity according to Equation (3):

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2Cl^-$$  \hspace{1cm} (3)

Further corrosion will then be accelerated due to the increased acidity inside the pit, compared to outside the pit. There are usually two major corrosion products of iron, magnetite (Fe$_3$O$_4$) and rust (FeOOH).

Different materials can withstand pitting corrosion in different ways. A common way to compare different materials is by using the pitting resistant equivalent number (PREN), which is dependent on the chemical composition of the alloy. The PREN is determined by Equation (4):

$$PREN = \%Cr + 3.3 \times \%Mo + 16 \times \%N$$  \hspace{1cm} (4)

The factor for nitrogen varies between 10 and 30, but 16 is a commonly used number [24, 41]. Duplex steels, compared to the austenitic steels usually have a larger quantity of both chromium and molybdenum and have very good pitting resistance [41]. The austenitic steel grade 316 has limited use in hydrochloric acid because of the risk of uniform and localized corrosion,
whereas the duplex steels with higher chromium content have better corrosion resistance [46]. In paper IV it was shown that the pitting resistance of duplex 2205 was better than that of the austenitic 316L steel in hydrochloric acid. This will be discussed in more detail in this thesis in the part called pitting corrosion of the surface.

Crevice corrosion is another type of localized corrosion that occurs in or close to a crevice of the material [45]. This type of corrosion generally occurs because part of a metal surface is in a shielded environment and the rest of the material is exposed to a large volume of electrolyte [50]. The mechanism for crevice corrosion is similar to that of pitting corrosion and also here the risk of corrosion increases with the chloride content. The environment in the crevices easily changes in terms of pH or concentration of halide ions and therefore the corrosion rate is accelerated within the crevices [45].

Production of stainless steels

Conventional casting and forging
The conventional way of producing stainless steels is by melting the raw materials together in an electric furnace. The properties of the final alloy can be tailored by varying the amounts of the elements. The molten steel is then cast into semi-finished steels followed by forming through different operations such as hot rolling, into bars, wires, plates, strips and sheets. After the steel is formed it is important to heat treat the material to relieve internal stresses and soften the material. Most steels undergo annealing, where the steel is heated and cooled in different steps. The heat treatment methods are optimized for the different types of steel to avoid defects like carbides and intermetallic phases. After the annealing steps it is common to pickle the steels to remove scales that were built up during the processing [22].

Powder metallurgical (P/M) production route including gas atomizing and HIP
It is also possible to use other production routes for stainless steels. One of them is a powder metallurgical (P/M) route including gas atomizing and hot isostatic pressing (HIP). In gas atomizing the melting is often conducted under protective atmosphere or under vacuum. This is done to protect the elements from being oxidized. The particle size in gas atomization is controlled by the pressure of the atomizing medium and the result is a perfectly spherical powder shape with excellent reproducibility [51]. The gas atomization process starts with molten metal pouring through a nozzle. The stream is then hit by jets of neutral gas, such as argon or nitrogen, and is atomized into small droplets. The droplets cool down and solidify when falling through the nozzle, Figure 4. The size of the gas atomized particles is homogeneously distributed. Finally, the powders are collected in capsules.
By using hot isostatic pressing on the gas atomized powder it is possible to reduce the porosity of the metals. It is performed in a pressure containment vessel where the material is subjected to both elevated temperature (900-1250°C) and isostatic gas pressure (100-200 MPa). Pressure is applied to the material from all directions to provide isostatic properties and 100% densification. One of the studies in this thesis compares the corrosion properties of P/M austenitic and duplex steels with their conventional counterparts (Paper IV). The P/M steels were gas atomized and HIPed. The P/M steels from this route with gas atomizing and HIPing have a finer microstructure with smaller grains and smaller inclusions than their conventional counterparts, Figure 5.
Figure 5. Optical microscope images showing the microstructures of the different P/M and conventional steels that were analyzed in paper IV in a) P/M316L, b) conventional 316L, c) P/M2205, and d) conventional 2205 (from paper IV).

Figure 5a and 5c show the microstructure of the austenitic and duplex P/M treated steels, and it is clearly seen that they have a more homogeneous structure with finer grains than their conventional counterparts in 5b and 5d. It can also be seen that the small dark spots, the inclusions, are in some cases larger on the conventional steels than on the P/M steels. The darker areas in 5c and 5d are the ferrite phases and the lighter areas are the austenitic phases. The different phases are much smaller in the P/M steel.
Methods for studying passive films on stainless steel

It is common to use electrochemical measurements followed by surface characterization techniques to study the passive films. The build-up of this film is typically studied via polarization (where there is a change in the equilibrium potential of the steel sample). The resulting polarization curves give information on how the surface and passive film behave at different potentials; this has been one of the principle methods used in papers I-IV. The passive film then can be studied with different surface sensitive techniques. X-ray photoelectron spectroscopy (XPS) is one of the most used techniques for analysis of passive films on steel, since the escape depth of photoelectrons from the surface is a few nm and the thickness of the passive film is in the range of 2 nm [9, 11, 13, 14]. There are also other surface sensitive methods such as Auger spectroscopy, but in this thesis XPS has been the main characterization tool and the text is therefore concentrated to explain the benefits and drawbacks of this method.

XPS can be used for both determining the thickness and chemical content of the film. XPS can also be used for depth profiling and there are several different ways of doing this: ion etching, angle resolved XPS, and changing the photon energy of the incoming beam (synchrotron based photoelectron spectroscopy). The different alternatives will be more explained in the following sections.

In this thesis focus has been on using XPS for analysis of composition and thickness of passive films on different steels that have been electrochemically influenced in different ways. It should thus be kept in mind that when analyzing the passive films on steel there will be monolayer of carbon from the atmosphere. This carbon monolayer can be minimized by washing the samples properly. The washing procedure was optimized throughout the studies.

In papers I-IV analysis were made using in-house XPS with PHI Quantum 2000 and Perkin Elmer PHI 5500 (paper V). Depth profiles were performed by angle resolved XPS (ARXPS) in papers II and III, while argon ion etching was performed in paper V. In paper II we also had the opportunity to use synchrotron based hard x-ray photoelectron spectroscopy (HAXPES), which gives high resolution spectra deep through the passive layer into the bulk (at 12 keV up to ~20 nm can be reached [52-54]). New insight in the composition of the surface layer was obtained by mainly analyzing the
chromium and nickel spectra deeper into the bulk than possible with our in-house XPS. The high resolution spectra resulted in a new way of deconvoluting the spectra and a depth profile through the passive layer all the way into the bulk was created.

Another important technique is scanning electron microscopy (SEM) that was used for studying the topography of the surface, and it was mainly used in papers IV and V. Other characterization techniques have also been used in this work but to a minor extent.

Polarization of the steels

Polarization is performed to study the property of a stainless steel and its passive film. The material that is subjected to examination is usually the working electrode connected in a three-electrode setup also comprising a reference electrode and a counter electrode. These are in contact in an electrolyte. The potential of the working electrode in the electrochemical cell is measured vs. the reference electrode. An example of a reference electrode is the standard hydrogen electrode (SHE), which has been set to 0 V. Other common, and more practical, reference electrodes are the standard calomel electrode (SCE) and the silver/silver-chloride electrode (Ag/AgCl), in relation to the SHE, where the SCE is +0.244 vs. SHE and Ag/AgCl is +0.197 vs. SHE [55]. A potentiostat applies pre-determined potentials to the working electrode and a measurement of the cell current can be made [56]. In Figure 6, an example of a polarization curve is depicted. Some important parameters for the passive film evaluation are marked in the figure.

![Polarization curve for 316L in 0.5 M H₂SO₄.](image)

*Figure 6. Polarization curve for 316L in 0.5 M H₂SO₄.*

The important parameters, such as corrosion current ($i_{corr}$) and potential ($E_{corr}$), passivation current ($i_{passivation}$) and potential ($E_{passivation}$), and passive
current \( (i_{\text{passive}}) \) and potential \( (E_{\text{passive}}) \) are commonly used for describing the passive film behavior. At a low potential, under the corrosion potential in Figure 6 the metal is behaving as a cathode and the net current is negative and dominated by reduction of hydrogen:

\[
2H^+ + 2e^- \rightarrow H_2 \quad (3)
\]

A possible anode reaction in the low potential region is the oxidation of water on the auxiliary electrode:

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (4)
\]

At higher potentials metal dissolution occurs. At a certain potential the anodic current equals the cathodic and this potential is called the corrosion potential or the mixed potential [28]. Under the corrosion potential the metal is not passivated. At a further increase of the potential there is an increase in the corrosion rate which reaches a maximum at the passivation potential. Upon further increase in potential, the current density decreases drastically when the metal is passivated and the oxide film is built up. In the passive region there is a film covering the surface and the current density is rather low. The current density in the passive region comes from oxidation of the metals and the diffusion of the ions through the passive oxide layer. Finally there will be an increase in the current density again at high potentials when entering the transpassive region and the current is due to further dissolution of the metals and possibly pitting propagation [50].

With the potentiostat it is also possible to perform chronoamperometric measurements where a constant potential is applied and the current is recorded. From the polarization curve it is common to choose the potentials for the chronoamperometric measurements. Passive films formed at different potentials varies in thickness and composition [9, 10, 44]. Chronoamperometric measurements have been performed in the studies in papers I-IV.

**X-ray photoelectron spectroscopy**

X-ray photoelectron spectroscopy (XPS) is a widespread technique for characterizing surfaces. It is in many cases non-damaging to the surface and gives information on the chemical composition of the surface. It is a technique that is accomplished by irradiating a sample with x-rays with a known energy and then analyzing the energy of the emitted electrons. The latter is a consequence of the photoelectric effect, Figure 7. A photon is absorbed by an atom, which causes emission of a photoelectron if the energy of the photon is larger than the binding energy of the electron. When the material relaxes also an Auger electron can be emitted. In this process an outer electron falls into the inner orbital vacancy, and a second electron (the Auger elec-
tron) is emitted, Figure 7. This auger electron carries the excess energy [57]. For the electrons to reach the analyzer the measurements have to be performed in ultra high vacuum (UHV).

![Figure 7. Illustration of the photoelectron and auger electron process.](image)

The kinetic energy, $E_k$, of the emitted photoelectron is well defined and depends on the energy of the incoming x-ray according to

$$E_k = h \nu - E_b - \phi$$

(5)

where $h \nu$ is the energy of the photon, $E_b$ is the binding energy of the atomic orbital from which the electron originates, and $\phi$ is the work function of the spectrometer. The kinetic energy of the emitted electrons is measured and from Equation (5) the binding energy is calculated. Since the binding energy of the atomic orbital is specific for each element, identification of the surface composition is possible. The amount of photoelectrons is measured as a function of their kinetic energy and a spectrum can be obtained. Figure 8 displays a typical spectrum where the intensity of the photoelectrons varies with the amount in the examined material and as a function of the binding energy for the different photoelectrons.
Figure 8. A typical spectrum for a stainless steel sample. The intensity of the photoelectrons varies with the amount in the sample and is a function of the binding energies.

**Depth profiling by photoelectrons**

XPS is not sufficiently sensitive for characterizing the distribution of different species within passive films. However, the surface sensitivity of XPS can be enhanced to obtain a depth gradient of a surface up to the penetration depth of the beam (~5 nm for an Al Kα in-house spectrometer), either by changing the angle between the incoming x-ray beam and the sample, called angular resolved XPS (ARXPS) (paper II and III) or by argon ion etching (paper V). The simplest way of performing a depth profile is to use argon (or krypton) etching (sputtering). By bombarding the surface by argon ions, removing the outermost surface layer by layer and making an analysis between each etching step a depth profile can be obtained. The disadvantage with ion etching is that it can destroy the outer surface of the sample. With respect to stainless steels, another disadvantage is that chromium and iron are preferentially etched faster than molybdenum thus inducing an artificial gradient in the profile. For the battery study in paper V, sputtering was a necessary tool to penetrate through the thick and non-uniform layers (in the order of 5-10 nm) of the interface between the electrode and the electrolyte.

**Angular resolved x-ray photoelectron spectroscopy (ARXPS)**

A more common method for depth profiling of the passive layer on smooth and polished stainless steel is ARXPS. It is a non-destructive approach which is favorable when studying very thin layers. By tilting the sample it is possible for the incoming photons to reach to different depths. A set of different analysis angles, from perpendicular to grazing incidence can be employed. This method has for a long period been successful for studying the
distribution of different elements on materials such as aluminum-based alloys and stainless steels for a long period [9, 58-60].

The angular resolved XPS measurements in papers II and III were performed with a PHI Quantum 2000 XPS instrument equipped with a hemispherical analyzer of mean radius 297.4 mm [61]. The x-ray source was Al Ka with energy of 1486.7 eV and analysis depths of up to a few nm can be obtained [62]. The depth can be calculated by taking $3\lambda\sin\theta$, since 95% of the signal comes from that depth [63], where $\lambda$ is the mean free path and $\theta$ is the analysis angle. When analyzing the spectra from XPS measurements the background can be corrected in different ways.

The probing depth using the in-house ARXPS setup on the steel samples used for the research in this thesis varied from 1.0 nm up to 5.4 nm for angles 11° up to 90°. Quantitative information on the passive films can be obtained by using ratios of oxide to metal peak intensities. The procedure was first described by Brox et al. [13] and modified by Olsson et al. [64]. A simplified version of the formula is seen in Equation (6)

$$d_{ox} = \lambda_{i}^{ox} \sin \theta \cdot \ln \left( 1 + \frac{I_{i}^{ox} c_{i}^{ox}}{I_{i}^{met} c_{i}^{ox}} \right)$$

where $I_{i}^{ox}$ and $I_{i}^{met}$ are the intensities in the film and the metal phase for element i, respectively. $c_{i}^{ox}$ and $c_{i}^{met}$ are the concentration of element i in the oxide and metal phase, respectively, and $\lambda_{i}^{ox}$ and $\lambda_{i}^{met}$ are the inelastic mean free paths in the oxide and the metal phase, respectively. This was the main equation used for the calculations performed at one angle in all five papers. For the calculations and cation distribution in the film studied in paper III this formula was used in combination with other formulas that allow for a variable density in the passive film. An in-house program was written to construct the cation depth profiles through the films. Further assumptions had to be made, where the molybdenum signal was fixed to a best possible value. The chromium and iron signals were thereafter fixed in an iterative process. This is further explained in paper III.

**Hard X-ray Photoelectron Spectroscopy (HAXPES)**

A complementary and less commonly used way of performing a depth profile is to change the energy of the incoming photon using synchrotron based photoelectron spectroscopy (PES). A higher energy of the incoming X-rays than for a conventional in-house spectrometer results in an increased inelastic mean free path, $\lambda$, and also increased escape depth. The inelastic mean free path means the distance covered by an electron between two inelastic shocks and changes with kinetic energy. The mean free path is only of the order of a few nm [62].
In paper II the goal was both to obtain a depth gradient through the passive film of the steel and also to probe the bulk underneath the film. Hence, it was necessary to use photons with higher kinetic energy. This method is called HAXPES (hard x-ray photoelectron spectroscopy) or HIKE (high kinetic energy). One example of a hard x-ray facility with the possibility of changing the incoming beam energy is beam-line KMC-1 at the Helmholtz Zentrum BESSY II in Berlin, Germany. The measurements in paper II were performed at the HIKE experimental station at the KMC-1 bending magnet beamline. Figure 9 illustrates the end-station in BESSY II, where the beamline is equipped with a Scienta R4000 hemispherical analyzer with a 200 mm mean radius and with the analyzer connected to an experimental chamber. It can be seen that the analyzer is positioned at 90° with respect to the incoming beam. It is possible to analyze energies up to 12 keV [52-54] (compared to ~1.5 keV with in-house XPS). The samples are introduced in a load-lock chamber where some sample preparation such as sputtering with an ion gun can be performed.

Figure 9. The HIKE end-station at the KMC-1 beamline is equipped with a Scienta R4000 electron energy analyzer (from paper II).

The beamline is equipped with a high resolution double crystal monochromator which consists of different sets of crystals, Si(1 1 1), Si(3 1 1), and Si(4 2 2) [65]. The crystals can be changed very rapidly and in Figure 10 it is illustrated how the energy resolution varies with photon energy for the different crystals. When the photon energy is tuned to higher energies the resolution is progressively lowered. The beam energy can be varied between 1.7 and 12 keV to have good working conditions with high resolution and flux. When calculating the probing depth from the inelastic mean free path, \( \lambda \), it is up to 20 nm [53]. However, in this study the probing depth were calculated by 3\( \lambda \), since 95 % of the signal comes from that depth [63].
Figure 10. Experimentally determined resolution of the different sets of crystals available at the KMC-1 beamline [paper II].

The pass energy of the electron analyzer was 200 eV and samples used in our study were analyzed at 2 and 4 keV. The lower energy was monochromated with the Si(111) and the higher energy with Si(311).

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to study the topography of the surfaces. The technique uses a beam of electrons that hit the surface resulting in ejections of electrons from the surface that can be detected. The instrument requires a vacuum chamber, where the electrons can be accelerated by voltages in kV from an electron gun containing a filament (usually FEG or LaB₆). On the way towards an anode the electrons are passing some electromagnetic lenses and finally a focused electron beam enters the sample surface. Emitted electrons can be detected with, for example, backscatter detector or secondary electron detector.
Introduction to the result section

The different elements: molybdenum, manganese, chromium, nickel and iron in the passive films on austenitic and duplex stainless steels were studied in papers I-III, which will first be summarized in this section. The purpose was to study the details of film formation and degradation of specifically selected steels as a function of exposure to different electrolytes and electrochemical treatments. Common for all studies is that XPS has been the main technique to study the depth profile of the passive film.

Iron is the base material in stainless steels and is known to be oxidized in the passive film. Molybdenum as well as chromium are ferrite stabilizers and are added to stainless steels for increased corrosion resistance. The role of molybdenum and the concentration depth gradient of iron and chromium were investigated in paper III and the more detailed results, based on a novel deconvolution process, will be summarized here. Manganese is an austenite stabilizer and is added to steels in a sufficient amount to be sure to maintain the austenitic phase in cases where the nickel content is low. But for manganese, it is important to keep in mind that increasing the amount also increases the available sites for pitting initiation in the form of MnS. This is studied in paper I. Chromium was studied in all papers in this thesis.

Thereafter, the pitting corrosion properties of austenitic and duplex steels were studied and evaluated in paper IV and the most important results are discussed below. It was shown that the production route of the steel did have a major impact on the corrosion resistance of the steel, mainly due to differences in defects and porosities.

Finally, in paper V, the passive film and corrosion behavior of one duplex steel was evaluated in a non aqueous solution for possible application as current collector in Li-ion batteries. Due to the low amount of water present in the Li-ion batteries it is possible that the passive film differ from that formed in water based solutions. Not many studied have been reported of steels in non aqueous solutions, but our results showed that a passive film of chromium and iron oxides/hydroxides was formed also in the non-aqueous solution.
The passive layer formed in water based systems

Molybdenum in the passive film

Molybdenum has a strong beneficial influence on the resistance to pitting since it increases the strength of the passive film, especially in chloride containing liquids. In the PREN formula, molybdenum is often attributed a corrosion resistant effect about three times that of chromium. It has been shown that molybdenum lowers the concentration of chloride in the oxide products [66-68]. Pure molybdenum will not form a passive film in an aqueous solution at anodic potentials [13]. It is, however, possible to use thermal oxidation to create an oxide film [69, 70], as well as using anodic polarization in glacial acetic acid [71]. The latter approach was used in the study in paper III.

To better understand the role of molybdenum it is useful to understand the distribution of molybdenum within the film, which was the aim of paper III. The depth distribution of molybdenum was studied by ARXPS, where angles from grazing incidence of 12 to 85° were used. The data was then deconvoluted using Equation 6 described in the X-ray photoelectron spectroscopy section.

Molybdenum was studied in 316L (EN 1.4432) samples that were polarized in either 0.5 M H₂SO₄ or concentrated CH₃COOH containing 0.2M Na₂B₂O₇ ·10H₂O and 1M H₂O. The reason for choosing acetic acid is that the mobility and dissolution of molybdenum is much lower than for chromium and iron in this electrolyte. This implies that the fraction of molybdenum in the passive film can be enhanced and it is even possible that molybdenum replaces chromium in the matrix. Two different methods were used for building up the passive film; the samples were either ramped at 10 mV/s or stepped to the final potential for polarization, at which it stayed for 15 minutes. The final potential was either 0.7 V or 1.5 V.

The concentration of molybdenum in the passive film was determined from XPS spectra. For systems with two or fewer elements, it is possible to find a numerical solution of the depth distribution within the film. However, stainless steels are multi-phase alloys and then this is more complicated. It has recently been shown that it is possible to use a matrix-based analytical approach [72] requiring boundary conditions. In paper III an iterative ap-
proach was applied where the intensity resulting from a tentative concentration profile is calculated. Iteration is performed until a fit to the experimental data is reached. The following conditions were used:

- The largest angle relative to the surface was used for determining the passive layer thickness;
- Only intensities coming from the oxide layer were used in the angular evaluations;
- The film density is assumed to be homogeneous throughout the film;
- The concentrations are assumed to vary in discrete concentration steps;
- A five-layer concentration profile was employed where the three middle layers were treated as one layer, resulting in a thin surface layer, a thicker middle layer and a thin inner layer.

The results obtained are hence based on the mathematical description formulated in paper III.

In Table 2 it can be seen that the concentration of molybdenum cations was around 5 wt% in the passive films formed in acetic acid, while it was around 3 wt% when formed in H₂SO₄, indicating a higher fraction in the films formed in acetic acid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Angle</th>
<th>% MoOx</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄ 0.7 V ramp</td>
<td>85°</td>
<td>3.4</td>
</tr>
<tr>
<td>H₂SO₄ 1.5 V ramp</td>
<td>85°</td>
<td>1.9</td>
</tr>
<tr>
<td>H₂SO₄ 0.7 V step</td>
<td>85°</td>
<td>2.2</td>
</tr>
<tr>
<td>H₂SO₄ 1.5 V step</td>
<td>85°</td>
<td>2.0</td>
</tr>
<tr>
<td>HAc 0.7 V ramp</td>
<td>85°</td>
<td>3.7</td>
</tr>
<tr>
<td>HAc 1.5 V ramp</td>
<td>85°</td>
<td>6.2</td>
</tr>
<tr>
<td>HAc 0.7 V step</td>
<td>85°</td>
<td>4.7</td>
</tr>
<tr>
<td>HAc 1.5 V step</td>
<td>85°</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The XPS spectra for molybdenum are quite complex, since the Mo3d₃/₂ and Mo3d₅/₂ peaks are relatively close and therefore difficult to separate in the XPS deconvolution. It is also seen in Figure 11 that there are both tetra- and hexa-valent molybdenum present as oxides and hydroxides. Details on fitting the molybdenum peaks can be found in a paper by Olsson et al. [73].
Low amounts of molybdenum can be found spread throughout the passive film, which has also been shown elsewhere [9], but the majority concentration was essentially found in the inner part of the oxide film as shown in paper III. This was also indicated by Goetz et al. [74, 75]. It was shown that the enrichment of molybdenum in the film is very thin, only in the order of a monolayer. This proves that molybdenum can replace chromium in the passive film matrix. The results show that it is possible to create a different distribution of the elements in the film by varying the surrounding media and future studies could be performed to determine how this affects the corrosion properties of the steels. The method of combining XPS results with iterative calculations has been very useful and it realistically shows the cation depth distribution in the passive layer.

Manganese in the passive film

Manganese is an important alloying element in stainless steels which enhances the solubility of nitrogen in the matrix at higher temperatures, which will lead to lower probability for nitride formation during thermal treatment [76, 77]. The role of manganese in stainless steels has not been studied as much as the role of molybdenum. Studies that focus on manganese are mainly on its role in inclusions and as initiation sites for pitting corrosion [50, 78].

In some alloys the manganese content may be as high as 5 wt% and the interaction with other alloying elements is important to evaluate. Two steels with similar corrosion resistance were studied; one had high manganese content, while the other had low. The two steels were the austenitic...
grade 316L (EN 1.4432) and the duplex steel LDX 2101 (EN 1.4162) with compositions as seen in Table 1.

To examine the role of manganese in the passive layer the samples were polarized in 0.5 M H₂SO₄ at different potentials. The grown passive films were then analyzed with XPS (in this study only the analysis angle of 45° was used). However, deconvoluting the manganese spectra is not trivial due to the significant overlap between the Auger Ni-LMM Auger and the Mn 2p peaks when Al Kα X-ray is used in the XPS. Due to this overlap the metals were first evaluated on a surface where the oxide was Ar ion etched. The resulting peak shapes were defined on these sputter cleaned samples and are shown in Figure 12.

![Figure 12. Mn2p3/2 spectral region on a sputter cleaned surface, showing the metal contribution of Mn2p and Ni-LMM for 316L in a) and LDX2101 in b) [paper I].](image)

No oxides should be present on the sputter cleaned surfaces and therefore it was easier to identify the curve shapes for manganese metal peaks and Ni-LMM. The curve shapes were then fixed but the ratio between Ni-LMM and Ni2p3/2 were estimated to vary with the oxide film thickness and an exponential decay was assumed of the intensities in the film according to Equation (7):

\[
I_{\text{measured}} = I_0 \cdot e^{-c/\lambda_c \sin \theta} \cdot e^{-d/\lambda_o \sin \theta}
\]

where \(c\) is the layer of carbon contamination, \(d\) is the passive film thickness, \(\theta\) is the take-off angle (45°) and \(\lambda\) is the attenuation length in the carbon contamination layer (c) and in the passive film (o). The attenuation lengths were determined by the method described by Seah and Dench [79] to be 1.8 and 2.1 nm respectively. The ratios were then calculated from Equation (8):

\[
\frac{I_{\text{Ni-LMM}}}{I_{\text{Ni2p3/2}}} = \frac{I_{0\text{Ni-LMM}}}{I_{0\text{Ni2p3/2}}} \cdot \frac{e^{-d/2.1 \sin \theta}}{e^{-d/1.8 \sin \theta}}
\]
Once the ratios were fixed they were used to fix the Ni-LMM intensities in the Mn 2p region. The manganese spectra from the XPS measurements on the polarized samples are seen in Figure 13. The Mn 2p$_{3/2}$ metal peak was identified at a binding energy of 638.9 ± 0.5 eV. Two oxide peaks were chosen to be deconvoluted in the peak fit.

Oxidation states for manganese are usually reported to be between I and IV, but there is not any definite agreement on the binding energies. Manganese oxide has been investigated in weld oxides by Westin et al. [80]. In paper I the reported oxidation states for manganese were Mn(II) and Mn(VI). The high oxidation manganese was found at binding energy of 644.8 eV, which earlier has been reported to be at 644.2 for K$_2$MnO$_4$ [81] and at 645.8 eV [82].

![Figure 13. Curve fits for the Mn 2p region on duplex steels. The Ni-LMM peak was fixed in the ratio to the Ni 2p$_{3/2}$ metal contribution [paper I].](image)

The oxide film thickness increases with increasing potential [83] and it is known that iron and chromium are selectively dissolved at higher potentials [37]. This means that the other alloying elements will be enriched in the metal phase underneath the film. In Figure 14 it is displayed how the manganese concentration varies for the two samples polarized at the different potentials.
Manganese was found to be oxidized but the content of manganese in the oxide seems to be independent of the bulk metal concentration, Table 1. Both steel grades show similar behavior where manganese was enriched in the metal phase in the high passive region. Manganese is not only enriched under the oxide film (just as nickel) but it is at the same time also oxidized. Also in the oxide it is seen that the content is fairly similar for the two steel grades even though there are different bulk contents of manganese. These results confirm earlier studies of the dissolution characteristics of the passive film [84].

Nickel, chromium, and iron in the passive film analyzed with high resolution XPS

**Nickel**

Nickel is known to generally decrease the dissolution rates of the metals in the steel and to be enriched underneath the passive film [10, 12, 13], which has been shown from XPS studies [10, 11, 13, 14]. By the use of HAXPES the position and the nickel content could be quantified in the bulk of steel 304 [10] in a way not previously demonstrated. To confirm this, depth profiling of the more complex steel grade 316L using a combination of ARXPS with HAXPES was conducted [paper II]. The better energy resolution from the HAXPES resulted in smaller full width half maximums (FWHM) in the spectra from HAXPES compared to ARXPS. In Figure 15 the PES profiles for nickel from the two techniques are compared and it is clearly seen that the FWHM was smaller for the HAXPES measurement. With HAXPES the
passive film could be studied at a greater depth (up to 12 keV) all the way into the bulk of the steel than is possible with in-house ARXPS (~1.5 keV).

![Graph showing comparison between ARXPS and HAXPES measurements](image)

Figure 15. The nickel metal peak measured with ARXPS with a FWHM of 1.1 nm in a) and from HAXPES with a FWHM of 0.7 nm in b) [paper II].

Nickel was found to be enriched to about 25 wt% a little bit under the oxide-metal interphase (analysis depth of 7.8 nm, paper II). Also Rao et al. [38] have shown similar results using EDX analysis across the oxide/metal interface but not with the same precision in content and position of the nickel layer. The nickel spectra from the ARXPS measurements showed that the nickel intensity increases with increasing depth while those of the HAXPES measurement showed a decrease with increasing depth. This supports the indication of nickel enrichment under the oxide-metal interphase.

**Chromium**

Chromium oxides in the oxide/hydroxide film are usually referred to as Cr$_2$O$_3$ and Cr(OH)$_3$, but with the HAXPES high resolution spectra it was necessary to include a third peak in the curve fitting. The third chromium oxide peak was suggested to be CrO$_3$. Even though the CrO$_3$ was unexpected from a thermodynamic viewpoint it could be explained to be due to interacting processes from the different elements in the steels and due to a local pH increase. It has been discussed by Clayton et al. [85] and also Olsson et al.
that CrO$_3$ can co-exist with Cr$_2$O$_3$ in the inner oxide due to the similar standard free enthalpies they have. The film formation would provide an environment of H$_2$O and OH$^-$ around the Cr(VI) ions that is analogous to a the environment of the higher pH solution [85]. Figure 16 displays spectra for chromium measured both with ARXPS and HAXPES where peaks of the three different oxides/hydroxides of chromium are seen.

Figure 16. Spectra for chromium measured with ARXPS in a) and HAXPES at 0.6 V in b) [paper II].

The CrO$_3$ signal decreases with increasing depth and increases with increasing potential. The peaks in Figure 16 are normalized with respect to the chromium metal signal, but note that there is a larger scale on the y-axis for the HAXPES compared to the ARXPS measurements (the metal peak is larger for the HAXPES measurements compared to the ARXPS). According
to Pourbaix diagrams [86] CrO$_3$ gets more stable at higher potentials. The Cr(OH)$_3$ signal decreases with increasing depth meaning that the top layer of the oxide film is composed mainly of chromium hydroxide, with chromium oxide underneath.

Iron
Also for iron in Figure 17 it is clearly seen that the FWHM was smaller for the HAXPES (Figure 17a) measurements compared to the ARXPS (Figure 17b), again showing the high resolution that is achieved. Based on the refinement of the HAXPES data three different iron oxides could be identified, referring to FeO, Fe$_3$O$_4$ and Fe(III) where Fe(III) represents both Fe$_2$O$_3$ and FeOOH [12], Figure 17.
The distribution of the cations of the different elements was discussed in paper III. The results from the ARXPS measurements were used in the iterative in-house computer program to extract more detailed results from the measurements. For iron new important information could be found. This is basically a result of the grazing incidence measurements that were performed. It was shown that there is a monolayer of iron on top of the chromium rich film. This finding was only observed in this study since no other grazing incidence angle study using ARXPS was performed in this thesis. The passive film is generally considered to consist of an inner chromium oxide rich film and an outer hydroxide film [10]. This is usually explained by iron dissolving and chromium getting enriched and oxidized [37].
sible explanation to iron on top of chromium hydroxide is that when the local surface concentration of iron ions increases, iron hydroxides precipitate and form a hydroxide layer on top of the chromium hydroxide. It is also possible that when the potential is ramped to the final polarization potential iron starts oxidizing at a lower potential than molybdenum and the iron oxide or hydroxide could precipitate on the surface when the sample was in the active region. Later passivation of the pre-formed passive film could then lead to a film with an enrichment of iron on the surface.

To summarize: the main conclusions from papers I-III was that nickel is enriched in the bulk. The passive film consists of oxides of chromium, iron, molybdenum and manganese (in steels where manganese is present in sufficient amounts) and of mainly chromium hydroxides. Chromium and tetravalent molybdenum are quite evenly distributed throughout the film, while hexavalent molybdenum is closer to the surface as depicted in the schematic picture (Figure 18) for the passive film, which is also shown for molybdenum in paper III. Iron is found to be quite evenly distributed within the film, but with the grazing incidence ARXPS measurements in paper III, a monolayer of iron is found at the surface.

![Figure 18](image)

*Figure 18.* Schematic representation of the composition of the passive film and the bulk.

Due to the HAXPES technique it was possible to show a more precise description of the passive layer and of the bulk directly underneath the passive layer than earlier reported.
The corrosion properties of powder metallurgical produced stainless steel have earlier been shown to be worse than for conventional cast and forged steels. The structure for the P/M steels has been very porous, which is not suitable from a corrosion point of view. However, the production route for P/M steels have been improved over the years and the steels studied in paper IV were gas atomized and hot isostatic pressed (HIP) leaving a fine microstructure with small grains and basically no pores, see Figure 5. One aim in the paper was to examine pitting corrosion based on the passive film behaviour on P/M austenitic and duplex steels compared to conventional cast and forged steels with the same compositions. The steels studied were 316L and 2205 and as is seen in Table 3, the bulk compositions of the steels are similar, except for the slightly higher chromium content seen for the conventional 2205 sample and the somewhat higher manganese content for the conventional 316L sample compared to their P/M counterparts.

Table 3. Chemical bulk and surface composition of the steel grades

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Cr (wt%)</th>
<th>Ni (wt%)</th>
<th>Mo (wt%)</th>
<th>Mn (wt%)</th>
<th>Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/M316L Bulk</td>
<td>17.3</td>
<td>12.6</td>
<td>2.4</td>
<td>1.1</td>
<td>66.0</td>
</tr>
<tr>
<td>P/M316L Surface</td>
<td>35</td>
<td>1</td>
<td>3</td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>Conv. 316L Bulk</td>
<td>17.0</td>
<td>12.4</td>
<td>2.5</td>
<td>1.6</td>
<td>65.4</td>
</tr>
<tr>
<td>Conv. 316L Surface</td>
<td>28</td>
<td>3</td>
<td>3</td>
<td></td>
<td>65</td>
</tr>
<tr>
<td>P/M2205 Bulk</td>
<td>21.9</td>
<td>5.3</td>
<td>3.0</td>
<td>0.6</td>
<td>66.2</td>
</tr>
<tr>
<td>P/M2205 Surface</td>
<td>43</td>
<td>3</td>
<td>4</td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>Conv. 2205 Bulk</td>
<td>23.4</td>
<td>5.5</td>
<td>3.4</td>
<td>0.8</td>
<td>68.3</td>
</tr>
<tr>
<td>Conv. 2205 Surface</td>
<td>49</td>
<td>3</td>
<td>4</td>
<td></td>
<td>47</td>
</tr>
</tbody>
</table>

The surface compositions were determined with XPS on polished but non-polarized samples. For all samples the chromium surface concentration was higher than the bulk concentration, which is in good agreement with the presence of a passive layer enriched in chromium [9-11, 13, 14]. The chromium surface composition was significantly higher for the P/M316L compared to conventional 316L indicating a passive layer of better quality. It is also worth noting that the chromium content of the duplex steels is higher than in the austenitic ones. According to the PREN in equation (4) the con-
tent of molybdenum is of particular interest, but since the molybdenum content in the examined steels is relatively similar it is most truly that in this case the chromium content will play an important role in the particularly good pitting resistance shown for duplex steels in certain chloride containing media. It has also been stated that the higher chromium content is important for a higher pitting corrosion resistance [46].

The pitting resistance for P/M316L was better than for conventional 316L, when 0.5M HCl was used as electrolyte. In Figure 19 SEM micrographs of 316L are shown. Figure 19a) is for P/M316L where basically no pits are seen. For conventional 316L, (Figure 19b) the surface is much more damaged by pits.

![Figure 19. SEM image for P/M316L in a) and conventional 316L in b) after amperometric experiments at 0.2 V in 0.5 M HCl [paper IV].](image)

The micrographs in Figure 19 were taken on surface that had been polarized at the constant potential at 0.2 V and already at this relatively low potential pits appeared on the surface of conventional 316L but not on the other samples. This is not surprising considering the shape of the polarization curves shown in Figure 20, where results for conventional and P/M steels in HCl are shown. For the conventional 316L sample (black curve in Figure 20a) it can be seen that there is a fluctuating current starting above 0.1 V followed by an increase in current density. This fluctuating behavior is due to pit initiation followed by repassivation. The sharp current increase at around 0.5 V is due to pit growth. Similar results were also shown by Wegrelius et al. [66]. This behavior is not seen for the P/M316L sample (red curve in Figure 20a).
Another interesting feature in Figure 20 is that the polarization curves for the austenitic steels in Figure 20a) show three mixed potentials, while the polarization curves for the duplex steels show only one mixed potential. A mixed potential is defined where the anodic and cathodic currents are equal (i.e. where the net, or the total, current is equal to zero [28]). It can be noted that the third mixed potential for the P/M316L sample was located at a significantly higher potential. Although polarization curves exhibiting three mixed potentials have been described previously [87, 88] the electrochemical origin has not been fully explained. When discussing polarization curves it should be remembered that the measured current always is the difference between the anodic and the cathodic partial currents. The cathodic currents seen at the most negative potentials can be ascribed mainly to hydrogen evolution although there should also be a contribution from the reduction of dissolved oxygen.

The passive film formation starts at about -0.2 V for the conventional 316L sample. After the initial passive film formation the cathodic partial current exceeds the anodic partial current and the total current turns cathodic again. This cathodic current can be ascribed to oxygen reduction. A third mixed potential is consequently obtained at higher potential when the current turns anodic again. The total current for the conventional 316L sample became dominated by the pitting corrosion current at potentials larger than +0.1 V, i.e., after the third mixed potential for the black curve in Figure 20a). The total currents remained cathodic all the way up to a potential of about +0.65 V for the P/M 316L (red curve in Figure 20a) and for both duplex samples (both curves in Figure 20b). This cathodic current was due to oxygen reduction as hydrogen evolution is thermodynamically unlikely at these potentials. Therefore, it can be concluded that the third mixed potential is dependent on the balance between oxygen reduction current and the current.
in the passive region. One important conclusion of this study is that the results indicate that discussions of the shapes of polarization curves and mixed potentials should be based on the anodic and cathodic partial currents, including the reduction of oxygen.

The passive films on the four different samples were analyzed with XPS. The recorded spectra for chromium after polarization at 0.2 V and 0.75 V in 0.5 M HCl are seen in Figure 21. Two different chromium oxides were used in the curve deconvolution and correspond to Cr$_2$O$_3$ and Cr(OH)$_3$. The binding energies of the oxides agree well with databases for XPS results [89].

Figure 21. XPS spectra for chromium in 0.5 M HCl for a) P/M316L at 0.2 V, b) conventional 316L at 0.2 V, c) P/M2205 at 0.2 V, d) conventional 2205, and samples polarized at 0.75 V for e) P/M316L, f) conventional 316L, g) P/M2205, and h) conventional 2205 [paper IV].
For samples polarized at 0.2 V (Figure 21a-d) all curves have the same general shape, but when comparing conventional 316L at 0.2 V in b) and at 0.75 V in f) it is clearly seen that the chromium metal peak for 0.75 V has almost disappeared, whereas the Cr(OH)₃ has increased. This indicates that the oxide is thicker at the higher potential. The thickness was calculated for all the different samples and it was estimated to be 3.4 nm for all samples treated at 0.2 V in HCl. The same value was also found for all samples treated at 0.75 V except for conventional 316L which had an oxide thickness of about 5.1 nm. The high thickness might be due to corrosion products (FeOOH and Fe₃O₄) on the surface.

XPS spectra for iron on samples polarized in HCl are seen in Figure 22. Since all spectra for chromium were fairly similar for all samples except for conventional 316L only the iron spectra for both the 316L samples are displayed here. For iron three different oxide peaks were identified (FeO, Fe₃O₄ and Fe(III)) in addition to the iron metal peak. Once again it is clearly seen that the metal peak has almost disappeared for 0.75 V (in Figure 22d) compared to 0.2 V (shown in Figure 22b) for conventional 316L. This further states that the oxide is thicker. Another interesting feature in the spectra in Figure 22 is that the intensity for FeO has decreased at the high potential, meaning that higher oxidation state of iron oxide has increased. As was mentioned in the theory part for stainless steels this is due to formation of corrosion products (Fe₃O₄ and FeOOH) on the surface.
Figure 22. XPS spectra for iron on conventional 316L after polarization at 0.2 V in a) and b), and 0.75 V in c) and d). The results for P/M 316L are in a) and c) while the results for conventional 316L are displayed in b) and d) [paper IV].

It was obvious from both the polarization curves and the XPS measurements that there are differences in the passive film composition on conventional 316L compared to the other samples. This could be related to differ-
ences in corrosion resistance. The corrosion resistance was shown to be clearly better for P/M 316L (Figure 19) than that for the conventional counterpart. For the duplex steels no difference in passive film or pitting corrosion resistance could be observed in this study.

These studies confirm again the complexity of the passive film behavior. The different production routes clearly result in varying microstructures with different homogeneities and porosities, which gives the characteristics of the materials.
The passive layer formed in a non aqueous solution

Stainless steel could possibly replace copper and/or aluminum as current collectors in lithium-ion (Li-ion) batteries. This would reduce the cost of the battery. It is therefore important to evaluate the passive film behavior of stainless steels in the non aqueous liquids (a lithium salt in organic solvents) typically used in battery electrolytes. Due to the low amount of water molecules present in the non aqueous solution it is very likely that the passive film behavior differs from that in water based solution. In paper V the passive film behavior of one kind of duplex steel tested in a Li-ion battery with an electrolyte of LiPF$_6$ in ethylene carbonate/diethyl carbonate was tested and compared to a sample that had only been stored in the same electrolyte but not electrochemically cycled.

Analysis of iron and chromium in the passive layer in a non aqueous solution

The passive film was formed by cycling a Li-ion battery cell containing duplex LDX 2101 (EN 1.4162) as a current collector and working electrode (for chemical composition see Table 1). From cyclic voltammetry (Figure 23) it was found that during the first cycle the chromium and iron will react at potentials between 2.4-1.2 V with lithium and form Li$_2$O. Further lithiation leads to the irreversible formation of a Solid Electrolyte Interface (SEI) at ~0.5V vs. Li/Li$^+$ due to the thermodynamically instable electrolyte solvents at these low potentials. The reduction peaks for the consecutive cycles were less dominant than for the first cycle.
Figure 23. Cyclic voltammetry for a Li-ion battery with duplex LDX 2101 as current collector [paper V].

The passive film is built up due to oxidations of the metals, which is seen as the increase in current for the second and third cycles between 2-4 V. The Li$_2$O is known to split at these potentials if the particles are nano-sized. It was clearly shown also in the XPS curves (figures 24, 25 and 26) that the surface contained the SEI. The SEI is usually >50Å thick and therefore it is more suitable to use Ar ion etching than ARXPS for depth profiling. The SEI layer is known to be composed of alkyl carbonates (CH$_2$OCO$_2$Li), Li$_2$CO$_3$, oxalate, LiF and polyethylene oxide (PEO), among others [90-92]. The cycled sample was compared to a sample that had only been stored in the same electrolyte and a clear difference was seen. For the stored sample only a thin surface layer was detected, which was etched away almost completely after the first sputter cycle, while the SEI was still remaining on the cycled surface. The content in a Li-ion battery is highly reactive and sensitive to humidity and air. A disadvantage with the in-house ARXPS equipment is that the transfer to the UHV has to be performed at atmospheric pressure. It is, however, possible to avoid this by using a portable transfer vacuum chamber which could be done with the Perkin Elmer PHI 5500 instrument used in paper V. From overview XPS spectra for stored non-cycled and electrochemically cycled samples before sputtering in Figure 24a) and b), respectively, the formation of the SEI was clearly visible for the electrochemically cycled sample where there is a relatively large ratio between the
intensity of oxygen and fluorine to carbon compared to that for the stored sample. This indicates a thicker SEI on the cycled sample.

Figure 24. XPS overview spectra for the non-cycled with no sputtering in a) the non-cycled with 30 s sputtering in b) the cycled with no sputtering in c) and the cycled with 30 s sputtering in d).

For samples that were etched 30 s, the difference between cycled and stored samples is more obvious since the intensity for fluorine is higher for the cycled than for the stored samples.

The XPS spectra for chromium and iron showed clearly the formation of fluorides during cycling, see Figures 25 and 26, respectively. Already in the stored sample chromium fluoride could be detected, while iron fluoride (not shown here, but in paper V) needed the electrochemical cycling for its formation. These fluorides were formed as a reaction between the anion in the lithium salt (LiPF$_6$) used in the electrolyte. Underneath the SEI a passive oxide film was formed upon cycling. Peaks of chromium and iron oxide/hydroxides were present in the spectra, as can be seen in Figures 25 and
26. The peaks become clearer after the first Ar ion etch cycle when most of the SEI has been sputtered away.

Figure 25. Cr spectra for a cycled sample [paper V].
To summarize: during the cycling of the duplex steel in a Li-ion battery Li$_2$O is formed in the surface and on top of the surface SEI is deposited. It was also evident that fluorides of iron and chromium formed due to reactions with the lithium salt in the electrolyte. A schematic representation of the passive film and the SEI is seen in Figure 27.

*Figure 26. Fe spectra for a cycled sample [paper V].*
The schematic presentation in Figure 27 displays the observed similarities between the passive film formed in water based and non aqueous solutions. Both oxides and hydroxides of chromium and iron are present in the film. The thicknesses of the formed films in the different solutions are also in the same order of magnitude.

To use stainless steel as a current collector in Li-ion batteries could be possible at potentials between 3-4.5 V vs. Li/Li⁺, however at lower potentials the current density (Figure 23) is in the same order as that for lithium insertion in a typical anode material. This means that the steel is too reactive and there will be too many electrochemical reactions occurring in parallel to the desired battery reactions and unfortunately this steel cannot replace the inert but expensive copper current collectors.
Depth profiling of passive layers on steel

Different ways of depth profiling through the surface layer of stainless steels that have been influenced by different kinds of chemical environments is the common denominator for all studies in this thesis.

ARXPS is one of the most used depth profiling techniques for the passive layer of stainless steels. This technique is well suited for this since the escape depth of the photoelectrons is in the same range as the thickness of the passive film. However, for the heterogeneous and thick (>50Å) SEI layer formed on top of the passive oxide layer on steel used as an electrode in a Li-ion battery it is difficult to receive useful information with ARXPS. There are both organic and inorganic reaction products in the SEI layer. Therefore Ar ion etching was used for obtaining useful information and it could be shown that also in electrolytes of organic solvents and fluorinated salts a passive film is formed on the surface of the steel. Ar ion etching must be, however, used with care. It is known that there will be preferential sputtering of both the SEI-components, leading to an overestimation of the amount of Li₂CO₃ [93] present in the film, and of the different elements in the passive layer of the steel.

In papers II and III the depth profiling using ARXPS followed standard procedures in handling the XPS profiles and the scientific focus was to probe the chemical contents in the film. An attempt to reach further in extracting more detailed information from the ARXPS data was made in paper III where a cation distribution within the passive film was constructed. The ARXPS results were deconvoluted into concentration-depth profiles by an in-house written computer program and it was possible to show how the components varied throughout the passive film.

The third depth profiling tool used in this thesis was the HAXPES technique with high resolution. This technique is not yet as well established in the field of studying passive layers of steel but the results in paper II shows its high potential. The technique is based on the ability to vary the photon energy of the incoming x-rays. There is the possibility to have lower or higher photon energies than can be used with in-house XPS systems. In this thesis, higher photon energies were used which resulted in both a depth profile through the passive layer and of the chemical composition deeper in the bulk structure. These experiments have to be carried out at a synchrotron and therefore it should be seen as a valuable complement to the ARXPS that has the advantage that it could be used in-house.
Concluding remarks

The aim with this thesis was to describe the passive film formed on steel surfaces in different environments by depth profiling. Also how the process to manufacture the steel has influenced the passive film was studied.

Using XPS as a tool for monitoring the complex chemistry of the passive film composed of oxides and hydroxides of mainly chromium and iron, but also of molybdenum and manganese, on different steels, the following conclusions have been obtained:

- Nickel was shown to be enriched in the bulk underneath the passive film. The content could be quantified to 25 wt% at a depth of 7.8 nm.
- Chromium is evenly distributed throughout the film with hydroxide on top of the oxide. The presence of Cr(VI) was clearly demonstrated by the use of HAXPES and is discussed in the light of the experimental conditions.
- Iron was found throughout the film. The outermost layer consists of a monolayer of iron on top of the chromium hydroxide.
- The passive film was depth profiled after the sample was polarized in acetic acid by deconvoluting the ARXPS results into iterative calculation steps. Molybdenum could essentially be concentrated to the inner part of the passive film.

Also for the passive film formed on the steel surface in non aqueous solutions the main component is chromium in the form of oxides and hydroxides, but also iron is oxidized in the film. After cycling the steel in a battery context, the top of the passive film is covered by a solid electrolyte interphase that is formed from the electrolyte during cycling. It was also shown that fluorides from the electrolyte salt reacted with the metals in the steel.

Steels can be produced with different techniques and all have their advantages. The corrosion resistance is dependent on the resulting composition and structure of the material. It is therefore important to minimize initiation sites for corrosion, such as inclusions and precipitates. Also the porosity of the material is important. Production of steel with P/M technique including gas atomizing and HIP:ing serves as an alternative to conventional casting and forging, since the HIP:ed material has no porosity. It was shown that the P/M material had similar compounds in the passive film as the material from conventional casting and forging, but the corrosion resistance was remarkably better for the austenitic steel. For the duplex steel the corrosion resistance was similar for materials from the two production routes.
The results in this thesis are a consequence of varying the production route or by simply varying the properties of the surrounding environment for the material. The complex passive film varies in the different studies and for finding new applications for steels it is important to have knowledge of how the properties of the steels and passive film changes with the outer parameters. It has been shown that depth profiles of the passive films can be achieved by ARXPS, Ar ion etching and HAXPES. All these techniques are complementary and important in the research of passive films on stainless steel.

It would be interesting to use these different PES tools to study passive films of stainless steel that have been electrochemically treated in more reactive environments.
Stål är ett samlingsnamn för en bred klass av material som baseras på mestadels järn som blandas med andra metaller till en legering. Den vanligaste metallen är krom, men även till exempel nickel, molybdén, mangan, titan, niob, vanadin är vanligt förekommande. Olika legeringsämnen ger olika egenskaper hos materialet och med kunskap om detta och hur legeringsämnen påverkar materialet kan man styra egenskaperna hos stålet att passa den miljö de ska användas i.

Rostfria stål används från allt inom hushåll till livsmedelsindustri och oljeindustri. Att ett material är rostfritt innebär ökad korrosionsbeständighet och därmed minskad risk för skador.

Det utmärkta korrosionsmotståndet kommer av att ytan skyddas av ett tunt oxidskikt, en så kallad passivfilm. Denna film är ca 2 nm tjock (1 nm är $\frac{1}{100000000}$ eller $1 \times 10^{-9}$m), vilket är så tunt att det inte går att se med blotta ögat. Filmen bildas spontant när stål kommer i kontakt med en miljö där det finns syre, vilket kan vara i vanlig rumsatmosfär eller en vattenlösning. Filmen består av oxid och hydroxid av de olika legeringsämnena i stål. För att ett stål ska klassas som rostfritt ska det innehålla minst 10.5 vikts-% krom. Det är kromoxid som utgör det största korrosionsskyddet för materialet.

Man kan styra sammansättning och tjocklek på passivfilmen genom att variera miljö och yttre betingelser där stålet finns. Ett vanligt sätt att studera filmen är att ha stålet i en elektrolyt av t.ex. svavelsyra eller saltsyra. Om man ökar spänningen mellan materialet och omgivningen, med hjälp av ett instrument, så kan man öka tjockleken på passivfilmen. Att behandla ett prov så kan enkelt kallas för att provet polariseras.


I denna avhandling har ytan hos rostfritt stål analyserats på olika djup främst med hjälp av fotoelektronspektroskopi där vinkeln varierats men även med synkrotroner och med Ar-joner. Några olika stålsorter har använts i de olika studierna, men gemensamt för alla är att det visade sig att passivfilmen till största delen består av kromoxid/hydroxid efter att en potential lagts på ytan. I bulken har de rostfria stål som analyserats här haft mellan 60 och 70 vikts-% järn, medan det i de polariserade proverna har varit kring 70 vikts-% krom i passivfilmen, dvs. kromkonzentrationen har ökat markant i passivfilmen jämfört med bulken. Detta kommer av att mer järn löses ut i lösningen under polariseringarna och lämnar krom kvar i filmen. I de olika studierna som ledde till denna avhandling visade det sig att krom är relativt jämnt fördelat i hela filmen, men att det vid ytan är främst kromhydroxid (Cr(OH)₃) och under ligger kromoxid (Cr₂O₃). Se schematisk figur nedan.

![Figur 1. Schematisk figur över passivfilmen.](image)

I en studie där väldigt liten infallande vinkel användes gick det att bestämma att det allra ytterst finns ett tunt lager av järnoxid (FeO), men i övrigt finns järnoxid fördelat i hela filmen. Nickel bidrar inte alls till passivfilmen utan stannar istället kvar i bulken och anrikas under filmen. Detta kommer av att nickel inte reagerar och löses ut i omgivande miljö med samma hastighet som järn och krom.
Molybden är ett viktigt legeringsämne som ofta tillsätts i stål för att öka korrosionsmotståndet i vissa miljöer som innehåller aggressiva joner. Dessa joner kan förstöra passivfilmen och på så sätt blotta materialet som då utsätts för korrosionsangrepp.

En vanlig typ av korrosion i havsvatten är gropfrätning (pitting corrosion på engelska). Detta innebär att det kan bli stora gropar i materialet och det kan på sikt förstöra materialets egenskaper och hållfasthet. En typisk mekanism för gropfrätning visas schematiskt i figuren nedan.

![Figur 2. Schematisk figur som visar mekanismen för gropfrätning.](image)

Korrosionsprodukter, som främst består av olika järnoxider som FeOOH och Fe₃O₄ kan lägga sig vid öppningen till gropen. Detta kan bli som ett lock och de aggressiva joner blir instängda i gropen, vilket leder till ökad reaktionshastighet mellan joner och materialet inne i gropen.

Tillverkningsmetoden för stål påverkar egenskaperna och kan man minska på antalet defekter och fel i materialet ger detta egenskaper som drastiskt ökar korrosionsmotståndet. Porositet har visat sig vara en viktig faktor. I en studie där pulverstål pressats samman med en metod som kallas het isostatisk pressning (HIP), vilket innebär att porositeten försvinner och lämnar ett helt kompakt material, var korrosionsmotståndet bättre än för ett material med liknande sammansättning men som tillverkats på ett annat sätt.

Intresset för att använda stål ökar konstant och nya användningsområden hittas hela tiden. Ett potentiellt område är i Li-jon batterier som strömledare. I ett Li-jon batteri finns det ingen vattenlösning med syre tillgängligt, vilket kan påverka hur passivfilmen ser ut. Det kunde dock visa sig att det bildas en passivfilm även då ett stål används i ett Li-jon batteri med en organisk elektrolyt närvarande. Dock bildas det ett lager utanför passivfilmen som består av fluorider och kolföreningar som bildats av reaktion mellan den organiska lösningen och stålytan. Stål kan mycket väl användas som ledare av ström vid de högre potentialerna i ett batteri, men vid de låga potentialerna reagerar stål med elektrolyten, vilket inte är så lämpligt för stål som en möjlig ledare i batterier.
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