Corrosion and Surface Studies of Stainless Steel and Chromium Carbide Thin-Films

JONAS HöGSTRÖM
Abstract

Although the passive films that form on stainless steels have been extensively studied, the concentration depth profiles are not fully understood. Their thinness makes passive films hard to study, but angle-resolved X-ray photoelectron spectroscopy (ARXPS) is a non-destructive technique that can be used to obtain depth information. An iterative approach to deconvolute ARXPS measurements into depth profiles is discussed, and the chemistry of passive films on a molybdenum-containing 316L stainless steel is investigated. Bipolar electrochemistry, in which the sample is placed along an electric field created by two driving electrodes in an electrolyte, is investigated as a screening tool. It is shown that the method is useful to create corrosion gradients on 304 stainless steel, both under pitting and non-pitting conditions. Chromium carbide thin films were deposited by magnetron sputtering with a variety of deposition parameters on stainless steel, and subsequently analyzed. It is shown that these films present a promising material system for protective coatings to improve the corrosion resistance of stainless steels while also maintaining other useful properties, such as low interfacial contact resistance. Particular attention is given to the electrochemical evaluation of the films, whose high carbon concentrations necessitates different interpretations of the electrochemical results compared to for stainless steels.

Keywords: corrosion, electrochemistry, thin film, stainless steel, passive film, chromium carbide, carbon oxidation, surface, depth profile, XPS, SEM, EQCM, sputtering

Jonas Högström, Uppsala University, Department of Chemistry - Ångström, Box 523, SE-751 20 Uppsala, Sweden.

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Contributions to the included papers

I Major part of the planning, experimental work (electrochemistry, XPS) and data analysis. Took part in the development of the data deconvolution algorithm via discussions with C.-O. A. Olsson, who coded. Main author.

II Took part in the planning. Participated in the discussions when analyzing the results.

III Took part in the planning. Participated in the discussions when analyzing the results. Performed the corrosion experiments and analyzed the corrosion results.

IV Took large part in the planning. Performed the experimental work (electrochemistry, XPS). Major part of the analysis of the results. Main author.

V Took part in the planning. Performed the corrosion tests and analyzed the results. Recorded the SEM images. Took part in the discussions during the analysis of the results for all experiments.
Contents

1 Introduction ............................................................................. 7
  1.1 Metals and society ......................................................... 7
  1.2 Approaches to prevent corrosion of metals ...................... 8

2 Theory .................................................................................. 10
  2.1 Passivity ........................................................................... 10
    2.1.1 The formation of passive films .................................. 10
    2.1.2 Corrosion types ....................................................... 11
  2.2 Thin-film coatings made by magnetron sputtering .......... 13
  2.3 Analysis techniques ........................................................ 14
    2.3.1 Chronoamperometry ............................................... 14
    2.3.2 Voltammetry .......................................................... 14
    2.3.3 Bipolar electrochemistry ......................................... 16
    2.3.4 EQCM ................................................................... 17
    2.3.5 XPS and ARXPS ..................................................... 18
    2.3.6 SEM ..................................................................... 19

3 Background on the employed materials ..................... 21
  3.1 Stainless Steel ............................................................... 21
    3.1.1 General background on the studies of stainless steels .. 21
    3.1.2 Molybdenum ......................................................... 21
  3.2 Chromium Carbides ....................................................... 22

4 Results ............................................................................... 24
  4.1 Stainless steel ............................................................... 24
    4.1.1 Profiling of molybdenum-containing passive films .... 24
    4.1.2 Bipolar corrosion screening .................................... 33
  4.2 Chromium carbides ....................................................... 37
    4.2.1 Films prepared by magnetron sputtering ................. 37
    4.2.2 Electrochemical measurements ............................... 38
    4.2.3 Effect of deposition temperature on the corrosion resistance ............................................. 47

5 Concluding remarks .......................................................... 52
  5.1 Characterization of passive films on stainless steel .. 52
  5.2 Magnetron-sputtered chromium carbide thin-films .... 52

Sammanfattning på Svenska ......................................................... 54
1. Introduction

1.1 Metals and society

The widespread use of metals dates back several thousand years, or a few hundred generations. During this time, the state of the art has developed from the simple mechanical reshaping of naturally occurring metals, alloying and extraction methods such as smelting, to the highly automated production lines and minutely fine-tuned materials of today.

Without the use of metals, very few of the technological developments that have been achieved by today would have been possible at all. One of the most widely used metals in our society is iron, much thanks to its abundance and relatively inexpensive production. With the introduction of stainless steel about 100 years ago [1], it became possible to overcome a major problem of iron and steel as a construction material, corrosion. Even so, non-stainless steel is still widely used today due to its lower cost.

Even with the increased production costs associated with the use of stainless steel or other corrosion prevention methods, the long-term cost savings due to increased service life often renders the use of technology that prevents corrosion cost-effective in the long run. In a federally funded 2001 report [2], corrosion in the United States of America was estimated to account for costs reaching about 6 percent of the country’s USD $15 \times 10^{12}$ gross domestic product [3], or about 900 billion US dollars, implying that the potential savings from improved corrosion prevention technologies are huge.

Combating corrosion also reduces the environmental impact, perhaps the biggest drawback of our technologically developed society. Longer service life of the materials used in constructions implies that less resources need to be used over time to replace degraded parts or entire structures. The lower use of resources also results in decreased emissions and less refuse ending up in landfills.

Corrosion involves the degradation of a material in contact with its environment. A commonly known form of corrosion is the rusting of iron (see Figure 1.1), \textit{i.e.}, the oxidation of iron to iron oxihydroxide, oxide and hydroxide. In order for the oxidation to take place, there must however also be a reduction present. For atmospheric corrosion of iron, the species undergoing reduction is oxygen from the air. The oxygen receives electrons from the iron and reacts with water to form hydroxide ions. Thus, the presence of water is also necessary for this type of corrosion to take place, but the adhered layer that forms as a result of humidity in the air is often thick enough to promote corrosion.
reactions [4]. The relative humidity required for a corrosion-enabling water film to form varies greatly with the presence of contaminants such as various salts in the water film and the porosity of the surface [4]. Apart from attracting water to the surface at lower relative humidities, the presence of salts also increases the conductivity, thereby increasing the risk for corrosion [4]. With a more conductive electrolyte, coupled oxidation and reduction reactions may be located at a greater physical distance, thus increasing the risk of formation of electrochemical cells between parts of the material where conditions are more oxidizing and more reducing, respectively. Some ions, such as chloride ions present in both sea water and de-icing salt, also facilitate corrosion by breaking down the passive film formed on stainless steels [4].

1.2 Approaches to prevent corrosion of metals
Since the corrosion of metals and the possibilities to prevent it are of such great importance to our society, several methods to achieve more corrosion-resistant metals are in use. New routes as well as the refinement of existing techniques continue to be explored to this day.

Some metals possess the ability to form a passivating oxide layer that stays on the surface, thus preventing further corrosion. Important examples include
aluminium, titanium and chromium [4]. The first two are important construction materials on their own, while chromium has found extensive use as the main passive-film-forming agent in stainless steel [4, 5].

Another possibility to protect metals is to coat them with a barrier to the environment. Simply painting the metal may be sufficient for some applications [6], while more advanced coatings are required for more demanding applications. Paint not only loses its ability to prevent corrosion when scratched, but may also increase the rate of corrosion by forming crevices [4] with oxygen gradients that run along the surface of the metal.

For closed systems containing an electrolyte, e.g., cooling systems, corrosion inhibitors in the electrolyte are often used [4]. The inhibitors work by impeding one or both of the oxidation and reduction reactions. Mechanisms, by which such inhibitors work, include adhering to the surface and sterically hindering the electron transfer between the metal and the electrolyte, scavenging oxygen from the system or promoting passivation of the metal surface [4].

To prevent a construction metal from corroding, a sacrificial anode of another metal that oxidizes more easily may be used. The sacrificial anode must be electrically connected to the construction metal, and they must also be ionically (electrolytically) connected, so that a closed electric circuit is formed. The more negative corrosion potential (as measured for the pure metals) of the sacrificial anode will lead to common potential of the two metals that is lower than the native corrosion potential of the construction metal. The lowered corrosion potential leads to very low corrosion rates for the construction metal as long as the sacrificial anode is not used up. Periodic replacements of the sacrificial anode makes it possible to use the method even in environments where the anode is used up at a significant rate. A drawback with this method is that the metal of the sacrificial anode cannot be recycled, since it is dissolved and washed away. Sacrificial anodes are commonly used to protect ship hulls and water heaters [6]. If a sacrificial anode is used to protect a water heater from internal corrosion, it must be in contact with both the metal of the water heater and the water inside of the heater (the water is the electrolyte). Since the outside of the water heater has no ionic connection to the sacrificial anode (the outside surface is not in contact with the water inside of the heater) there is no added protections against external corrosion of the heater. Likewise, an external sacrificial anode on a ship will not protect inside of the hull. Instead of a sacrificial anode, a battery or other direct current power supply may be used to keep the construction metal at a safe potential [4].
2. Theory

2.1 Passivity

2.1.1 The formation of passive films

A passivating metal forms an oxidized layer (an oxide for metals that passivate in air), called a passive film, which prevents further reactions of the metal [4, 5], making the passivated surface more inert although the metal itself may be very reactive. In fact, the high reactivity of the metal is beneficial to its ability to become passive [4, 5], since it speeds up the formation of the passive film. Under dry conditions, many metals, including for example iron, form a passive film that inhibits further oxidation [4]. Under wet conditions, the situation changes due to the possibility of ions dissolving in the electrolyte. Instead of forming a passive film on the surface, many metals, including iron, oxidize to cations that dissolve in the electrolyte [4]. As mentioned in the previous chapter, the adhered water layer that forms from the water present in air is often enough to work as an electrolyte.

Stainless steels owe their corrosion resistance to the formation of a 1–3 nm thick passive film, which is composed of oxides of some of the metals that comprise the steel [5, 8]. Chromium is heavily enriched during the formation of the passive film, particularly in acidic media, where iron dissolves readily [4, 9]. Nickel does not oxidize as easily as iron and chromium [5], and thus a very thin metallic layer that is heavily enriched in nickel forms under the oxide layer [7]. Figure 2.1 shows a schematic drawing of the metal, nickel enrichment layer and passive film, with the thickness of the enrichment layer [7] and oxide film [5] approximately to scale. The passive-film formation process can be described as the oxidation of elemental metals to metal ions (see Reaction R2.1), together with the reduction of oxygen resulting in the formation of hydroxide ions (see Reaction R2.2).

\[
M \rightarrow M^{n+}(aq) + n e^- \quad \text{(R2.1)}
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(R2.2)}
\]

As the concentration of metal hydroxides rise, the hydroxides will start to precipitate according to Reaction R2.3 below.

\[
M^{n+} + n OH^- \rightarrow M(OH)_n \quad \text{(R2.3)}
\]
The hydroxide may then undergo dehydration, yielding an oxide film as described in Reaction R2.4 below.

\[
\text{M(OH)}_n \rightarrow \text{MO}_{n/2} + \frac{n}{2} \text{H}_2\text{O} \quad \text{(R2.4)}
\]

For a stainless steel, the different solubilities of the metal hydroxides lead to different precipitation rates (see Reaction R2.3). Chromium(III) hydroxide precipitates to a much greater degree than iron(II) hydroxide, resulting in chromium-enrichment in the hydroxide compared to the levels of chromium and iron in the metal. Upon dehydration (see Reaction R2.4), part of the formed hydroxide is transformed to oxide, with the remaining hydroxide being most prominent in the outer part of the passive film.

The process of passive-film formation on stainless steels is very quick [5], in the order of seconds, and stainless steels hence quickly repassivate when subjected to surface damage. This self-repairing property of the passive film is essential for it to be effective in protecting the underlying steel from corrosion in most practical applications, where surface damage will occur.

### 2.1.2 Corrosion types

There are several different types of corrosion [6]. On even surfaces that are not passivated (e.g., non-stainless steel), with no apparent variation in geometry, environment or composition of the metal, general corrosion [4] may take place, causing the entire surface to corrode at an even rate. Compared to localized forms of corrosion, such as pitting and crevice corrosion, general corrosion is much less destructive, since it affects the surface evenly. Pitting and crevice corrosion [4] represent two aggressive forms of local corrosion,
Figure 2.2. Pitting corrosion is an aggressive form of corrosion involving passive-film breakthrough. The pit forms a self-sustaining acidic and oxygen-depleted environment that facilitates further growth of the pit.

in which local variations in electrochemical potential as well as composition of the electrolyte create a significantly stronger driving force for the corrosion processes. The limiting step in many corrosion processes is the reduction of oxygen [4], either due to its slow kinetics or its diffusion to the surface. Large parts of the metal that are not attacked by local corrosion may serve as cathodes where oxygen reduction takes place, thereby increasing the rate of metal oxidation (corrosion) at the comparatively smaller anode site (the pit or crevice). As mentioned, there must be an electrolytical connection between the parts where oxygen reduction takes place and the site of local corrosion.

Pitting corrosion (see Figure 2.2) occurs as a result of passive-film breakthrough [4] on a passivating alloy by aggressive anions, such as chloride and sulfide ions. After initiation of a pit by for example chloride ions, the pit works as a container that physically impedes the diffusion away from the pit of the metal ions that form during the corrosion processes. The production of cations within the pit creates a driving force for anions to migrate into the pit (the cations will of course also migrate out of the pit), leading to increased concentrations of the anions that initially led to passive-film breakthrough [4]. Any oxygen present in the pit is quickly consumed, leading to oxygen depletion in the pit. The metal ions undergo hydrolysis, thereby lowering the pH within the pit. Since the metal surface in the pit is both electrically and ionically connected to the surface of the metal outside of the pit, the pit acts as the anode in the corrosion process where metal is oxidized, whereas the surface acts as the cathode where oxygen reduction takes place. As a result of the much larger cathode (where the often rate-limiting oxygen reduction reaction takes place) compared to the anode, the corrosion processes in the pit can proceed at a significant rate, resulting in rapid pit growth. Since pits both create an environment that facilitates corrosion and restrict the corrosion process to
a confined space, pitting corrosion can lead to quick failure [6] by corroding through parts such as pipes.

Crevice corrosion [4, 6] occurs in crevices. Although the term crevice corrosion is sometimes limited to only include corrosion in a crevice in a single piece of passivating metal [4], a more general definition [6], that includes crevices formed by mechanical constructions, e.g., parts that are clamped together or sheet metal that is folded, will be used in this text. The crevice limits the electrolyte exchange [4] and gives rise to a differential aeration cell [4]. This accelerates the corrosion processes in a way similar to that for pitting corrosion. While pitting corrosion affects metals that have passive films, crevice corrosion is possible both on passivating and non-passivating metals [4]. Other conditions that facilitate the formation of differential aeration cells, and hence corrosion modes very similar to crevice corrosion, include partial coverage of the metal by dirt, rust scales that covers part of the metal and holes in protective paint coatings [4, 6].

2.2 Thin-film coatings made by magnetron sputtering

Magnetron sputtering [10] is a technique that often is used to deposit thin-films. A magnetron sputter consists of a sample holder (often rotating) and one or more magnetrons (see Figure 2.3). A magnetron consists of magnets, a target comprised of the materials to be deposited and a counter electrode. The deposition chamber is evacuated, and a small amount of noble gas (often argon) is introduced. A magnetic field traps ions of the noble gas, which are
accelerated by a bias voltage towards the target to ballistically knock out target atoms. A potential is applied between the target and the counter electrode of the magnetron, and by tuning of the resultant target current, the rate at which atoms are knocked out of the target can be controlled. By individually regulating the current of each target in a multi-target system, the composition of the deposited film can be controlled. The function of the magnets is to trap the ions in a magnetic field close to the target, thus increasing the local ion concentration and sputter rate. Since the knocked out atoms are not charged, they are not affected by the magnetic or electric fields, and travel freely to the sample as long as they do not interact with the argon. A negative bias is often employed on the sample holder to attract argon ions [10], and a heating element makes it possible to adjust the temperature at which the substrate is coated. The heating increases the possibility for the atoms to diffuse on the surface to find a more energetically favorable position, as does the increased bombardment of argon ions that results from the negative bias.

2.3 Analysis techniques
2.3.1 Chronoamperometry
In a chronoamperometric experiment, the potential is controlled to a fixed value, whereas the current is recorded as a function of time [11]. The method is useful for evaluating both the initial and steady-state corrosion currents at different potentials, and since the potential does not vary during the entire experiment, subsequent surface analysis of samples polarized to different potentials can be used to extract information on, e.g., how the corrosion rate depends on the potential. A drawback of the method is that a large number of experiments must be performed if the sample material needs to be studied at many different potentials.

2.3.2 Voltammetry
To get a quick overview of the dependence of the current on the potential, voltammetry presents a much quicker path than chronoamperometry. In a voltammetric experiment, the potential is controlled and varied according to a predefined potential profile, while the current is recorded [11]. A common potential profile is a linear ramp [11], which is used in the recording of polarization curves [11]. In a polarization curve, the logarithm of the absolute value of the current is plotted against the potential, sometimes with the potential as the y axis. Since the potential is scanned, the shape of a polarization curve will depend on the scan rate. It is also not possible to examine the effect of different potentials on the surface of the sample after the voltammetric experiment, since the entire surface has been subjected to the full potential profile. Therefore, polarization curves are often used as a quick way to get an overview of a
Figure 2.4. A three-electrode setup used for electrochemical analyses, such as chronoamperometry and voltammetry. The left photograph shows a jacketed beaker for temperature-controlled experiments, containing (from left to right) an Ag/AgCl reference electrode, a platinum counter electrode, a thermometer and a sample holder. The sample holder is shown in more detail in the photograph on the right.
2.3.3 Bipolar electrochemistry

Bipolar electrochemistry is a relatively young technique that has several promising applications [13–28], including both the use of microscopic bipolar particles [13, 13–17, 19, 21] and larger electrodes [18, 20, 24–31].

In a bipolar electrochemistry experiment with a large bipolar electrode (see Figure 2.5), the sample is placed in an electrolyte while an electric field is imposed between two auxiliary (driving) electrodes, one on each side of the sample [20, 23, 25, 29–31]. If the sample is a much better conductor than the electrolyte (as is the case for most combinations of metallic samples and electrolytes), the surface of the sample can be considered to be an equipotential surface [20, 23, 25, 29–31]. The electric field (potential gradient) in the electrolyte stems from the current flowing between the two driving electrodes through the resistance of the electrolyte [20,23,25,29–31]. Since the sample is an equipotential surface, the potential gradient in the electrolyte gives rise to a gradient in the relative potential of the surface compared to the electrolyte,
such that the relative potential of the sample will be more positive near the negative driving electrode and *vice versa* [20, 23, 25, 29–31]. As the surface of the sample then will host a continuum of potentials from cathodic to anodic, a single experiment is sufficient to generate a surface that can be subsequently examined by other techniques to extract information on the influence of all potentials. It should be mentioned that although the potential gradient in the electrolyte induces a relative potential gradient along the surface of the bipolar electrode, the system is not static. It is therefore possible that the current-density profile along the surface is less dynamic than the potential profile or that both the current density and potential profiles vary greatly over time. It is hence not certain that a particular bipolar experiment will be possible to correlate to a series of either potentiostatic or galvanostatic experiments.

The potential at any given point can be measured by using a fine-tipped reference electrode that is held close to the surface and electrically connected to the sample [25], and measuring the potentials at several different parts of the sample simultaneously could be achieved by the use of an array of fine-tipped reference electrodes. This can, however, be hard to accurately implement in practice because of the increasingly strong vertical component of the electric field towards the edges of the sample [29–31]. The vertical component of the electric field results in a potential difference between the tip of the reference electrode and the surface directly underneath the reference electrode, and hence introduces an error in the measurement. Even if the potential could be measured without errors, the current density at different parts of the surface would remain unmeasurable. It can, however, be modeled [25, 29–31].

Another approach is to combine bipolar electrochemistry with chronoamperometric experiments at a few potentials, or galvanostatic experiments at a few current densities, followed by mapping of the potentials or current densities of the reference experiments along the bipolar electrode. Such a mapping could be done by, *e.g.*, comparing scanning electron microscope (SEM) micrographs of the reference and bipolar surfaces.

### 2.3.4 EQCM

Electrochemical quartz crystal microbalance (EQCM) experiments combine an electrochemical technique, such as chronoamperometry or voltammetry, with the ability to detect mass changes of the working electrode (sample) [11]. This technique can be useful to determine, *e.g.*, whether an anodic current produces a protective oxide film that stays on the surface or metal ions ending up in the electrolyte [9, 32]. The mass change is determined by depositing the sample (often in the form of a thin-film) on a quartz crystal and oscillating the crystal at its resonance frequency. A mass increase will lead to a decrease in the resonance frequency and *vice versa*, and changes in mass can thus be detected.
Figure 2.6. The principle of XPS. The X-ray radiation interacts with a core electron, which is excited. The kinetic energy \( KE_{\text{true}} \) of the excited electron is equal to the energy of the X-rays \( (h\nu) \) minus the binding energy relative to vacuum \( E_B^{\text{vac}} \) of that electron.

2.3.5 XPS and ARXPS

XPS (X-ray photoelectron spectroscopy, sometimes also referred to as ESCA—electron spectroscopy for chemical analysis) is a surface analysis technique that can be used to extract information about the chemical environments of the elements in a sample [33, 34]. The technique makes it possible to determine the chemical bonding of the investigated elements. In an XPS analysis (see Figure 2.6), the sample is irradiated with X-rays of a specific wavelength (with energy quantum \( h\nu \)). The X-rays interact with the core electrons of the atoms in the sample, which then are excited and form photoelectrons. If the kinetic energy of a photoelectron is high enough, the photoelectron will escape from the surface. The kinetic energy of a knocked-out electron \( KE_{\text{true}} \) is equal to the energy of the X-ray quantum that excited it out minus the binding energy relative to vacuum \( E_B^{\text{vac}} \) of the electron (see Equation 2.1).

\[
KE_{\text{true}} = h\nu - E_B^{\text{vac}}
\]  

(2.1)

Since the energy of the X-ray quantum is known and can be controlled, the binding energy of the electron can be calculated. Different oxidation states and bound groups induce small shifts in the binding energy, which can be used to derive information about the binding states from an XPS spectrum [33].

In an actual instrument, it is not possible to measure the true kinetic energy \( KE_{\text{true}} \) of the ejected electrons [35], because it is not practically possible to align the energy levels of the sample and the detector so that the vacuum energy of an electron is equal to zero relative to both the sample and the detector at the same time. For conducting samples, the detector is connected electrically to the sample, thereby aligning the Fermi levels of the detector and the sample. The measured kinetic energy \( KE \) will then be equal to the X-ray quantum \( h\nu \) minus the binding energy relative to the Fermi level \( E_B^F \) minus the work function of the detector \( \phi_{sp} \) (see Equation 2.2). The work function of the spectrometer \( \phi_{sp} \) represents the energy required to lift an electron from the Fermi
level to vacuum (see Equation 2.3), and while the work function of the sample $\phi_w$ is related to the Fermi level of the sample in the same way, it does not affect the measurement.

$$KE = h\nu - E_F^B - \phi_{sp}$$  \hspace{1cm} (2.2)

$$\phi_{sp} = E_{vac}^B - E_F^B$$  \hspace{1cm} (2.3)

The detection depth is limited by the emitted electrons’ ability to escape from the sample, which decreases exponentially with increasing depth. The detection depth is usually less than 10 nm [33]. By changing the angle of the detector, the detection depth can be tuned, which is used in angle-resolved X-ray photoelectron spectroscopy (ARXPS) [33] to extract information about the changes in composition with depth [36–39]. Several algorithms to deconvolute ARXPS signals have been developed, including both numerical [40,41] and more recently matrix-based [42,43] methods. Even so, they do not present a ready-to-use solution for the deconvolution of depth profiles in arbitrary systems. ARXPS is suitable to examine thin films (such as passive films) since it is a relatively non-destructive technique compared to, e.g., sputtering.

2.3.6 SEM

Scanning electron microscopy (SEM) is used to get a visual representation of topological features that are too small to be resolved by optical microscopy. Although not equivalent to a photograph or an optical microscopy image per se, an electron microscopy micrograph looks reminiscent to a black and white photograph, and may often be interpreted analogously. In an SEM instrument (see Figure 2.7), the sample is bombarded by a very fine beam of electrons. The beam is scanned over the surface of the sample in subsequent lines, forming a rectangle, in the same way that an electron beam is scanned to form an image in an old-fashioned cathode ray tube television set or computer monitor. Some of the electrons are back-scattered by elastic interactions with the atoms of the sample. Heavier elements cause more back scattering, and will hence yield a stronger signal. Other electrons interact via inelastic scattering with $k$ electrons of the sample atoms. The $k$ electrons are subsequently knocked out of their orbitals, and give rise to the signal that is the basis of the SEM micrograph. Since such electrons have fairly low energies, only those that originate from locations very close to the surface of the sample escape, which makes it possible to achieve very high resolutions. To form the two-dimensional micrograph from the secondary electrons, the one-dimensional signal from the detector is time-resolved and synchronized with the scanning of the electron beam over the sample surface. It could be described as being the opposite to how an optical microscope works—instead of evenly illuminating the sample and spatially resolving the reflected light, the “illumination” (electron beam) is spatially (and temporally) resolved, while the detector yields only the time...
Figure 2.7. Schematic drawing of a scanning electron microscope. Electrons are accelerated towards the sample and focused by a system of lenses. Backscattered and secondary electrons that are ejected from the sample are detected by the respective detectors.

(not location) at which an electron was detected. By temporally resolving the detector signal and synchronizing it with the scanning of the electron beam, a two-dimensional micrograph can be formed.
3. Background on the employed materials

3.1 Stainless Steel

3.1.1 General background on the studies of stainless steels
The 1–3 nm thick passive film that is responsible for the corrosion resistance of stainless steels [5, 8] has been studied extensively [44–49], including studies of depth gradients obtained with transmission electron microscopy (TEM) measurements [50] and temporally resolved studies of growing films [51–54]. The main alloying element that is added to iron during the manufacturing of a stainless steel is chromium [4, 5], with an alloying concentration of about 10.5 percent usually considered as a minimum [5]. The chromium is heavily enriched [5] in the passive film. Another important alloying element in stainless steel is nickel, which mainly is used as an austenite former to increase the strength and toughness of the steel. Nickel forms a metallic enrichment layer right under the oxide [7], thus forming an additional barrier between the passive film and the underlaying bulk metal.

One of the strengths of passive films on stainless steels is their ability to dynamically adapt to different environments [5], for example by accumulating chromium(III) under conditions where iron(II) is dissolved while instead accumulating iron(III) when chromium(VI) is dissolved at more anodic potentials. The dynamic behavior of a passive film, and hence its corrosion resistance under various conditions, can be tuned by altering the composition of the steel [5]. Molybdenum, tungsten and nitrogen may be added for increased resistance to pitting corrosion [5], while the addition of manganese improves the solubility of molybdenum and nitrogen [5].

3.1.2 Molybdenum
One element that has been shown [55] to exhibit prominent depth profiles in passive films on stainless steel by the use of ARXPS is molybdenum. Sputtering would not be a good way to assess molybdenum depth gradients in passive films, since molybdenum is sputtered at a slower rate compared to iron and chromium [56–59]. The low abundance of molybdenum in stainless steel as well as its complicated chemistry [55, 60–62] make molybdenum somewhat trickier to assess compared to iron and chromium. There are several oxidation states and species to consider when deconvoluting the XPS peaks of molybdenum [55, 62].
3.2 Chromium Carbides

Chromium carbide thin-films combine good corrosion resistance with several other useful properties, such as low interfacial contact resistance (ICR), high hardness and wear resistance [63–79], making them interesting candidates to enhance the properties of stainless steel surfaces. While amorphous films have been shown to combine high hardness with low friction [63, 64], nanocrystalline/amorphous films have exhibited high mechanical wear resistance in combination with good corrosion resistance [65–70]. For some applications, it is desirable to combine good corrosion resistance with low ICR. Since the passive film that forms natively on a stainless steel has insulating properties, stainless steel does not excel in this respect [80]. Cemented chromium carbides, however, combine both good corrosion resistance and low ICR values [71, 72].

Related material systems, such as glassy chromium boride [81–83], chromium phosphide [77, 83], zirconium and titanium glasses with chromium and other metal ions [81], have also shown promising properties [84–86]. Amorphous metal alloys are often superior to crystalline materials from a corrosion perspective, especially when the crystalline material is a combination of several phases [81, 84]. The latter can be explained by the possibility to have different corrosion potentials for the separate phases, since the entire surface can facilitate oxygen reduction, while all of the corresponding oxidation (corrosion) takes place on the phase with the lowest corrosion potential. Thermodynamically stable single-phase crystalline materials may, on the other hand, exhibit lower dissolution rates than their amorphous counterparts [81]. The addition of boron has been claimed to hinder chromium from becoming active in sulfuric acid [82], while the addition of phosphorous prevents continuous dissolution of chromium [77, 83, 86]. The latter works by phosphorous enrichment during an initial chromium-dissolution period [77, 83, 86], similar to how iron is initially dissolved to enrich chromium during the formation of the passive film on stainless steel [5]. The resultant phosphide film acts as a barrier that prevents chloride-ion penetration and is stable and self-repairing [77]. Amorphous materials often repassivate quicker than their crystalline counterparts [84, 85].

The effect of different deposition parameters on the morphology of chromium carbide films fabricated by magnetron sputtering has been studied [87], as well as the effect of the grain size on the corrosion resistance of the film under both activating and passivating conditions [88, 89]. While larger grain sizes proved beneficial under activating conditions, the opposite was found to be true for passivating conditions [88, 89]. Chromium carbide films have been shown to passivate by the formation of a chromium(III) oxide layer at elevated temperatures in air [73, 90, 91] as well as in supercritical water [74]. While the corrosion resistance is poor in alkaline aqueous solutions [92], it
has been shown to be good in non-alkaline aqueous solutions [93] as well as in aggressive, acidic, non-aqueous [75] electrolytes.
4. Results

4.1 Stainless steel

4.1.1 Profiling of molybdenum-containing passive films

Electrochemical film growth
In Paper I, passive films on 316L stainless steel samples were studied with ARXPS. In addition to native passive films, passive films formed at different potentials during polarization in either 0.5 M sulfuric or acetic acid containing 0.02 M Na$_2$B$_4$O$_7$·10H$_2$O and 1 M H$_2$O were studied. The samples were either kept at open circuit or polarized at −1.5, +0.7 or +1.5 V vs. Ag/AgCl (sat.) in the sulfuric and acetic acid solutions, respectively (see Figures 4.1 and 4.2). Before each polarization experiment at +0.7 or +1.5 V, the sample was first pre-polarized in sulfuric acid at −1.5 V to reduce the native passive film. The potential was then either ramped or stepped to the final polarization potential.

The purpose of using the acetic acid solution was to investigate if it had any effect on the way molybdenum was incorporated in the passive film. Whereas pure molybdenum does not form a passive film under aqueous conditions [56], it has been shown that it is possible to form an oxide film on molybdenum by thermal oxidation [60, 61] or electrochemically in acetic acid containing 0.02 M Na$_2$B$_4$O$_7$·10H$_2$O and 1 M H$_2$O [94].

Electrochemical results
Looking at the polarization curves recorded between −1.5 and +0.7 or +1.5 V vs. Ag/AgCl (sat.) (see Figures 4.1e and 4.2e), it is clear that the electrochemical behavior of the steel was very different in the acetic acid solution compared to in the sulfuric acid solution. While the samples polarized in sulfuric acid displayed a clear passive region, this was not the case for the acetic acid solution. The currents were also much higher and the sample surfaces got visibly more etched in the acetic acid solution.

Thickness measurements
The thickness of the passive film on a stainless steel can be calculated by an iterative method based on an XPS measurement at one angle by relating the intensity of the signal from the metal to the intensity of the signal from the oxide [56,95]. In essence, the first step is to assume values for the densities of the oxide and metal ($D^{ox}$ and $D^{met}$) and use these together with the intensities for element $i$ in the oxide and metal, respectively ($I_i^{ox}$ and $I_i^{met}$), to calculate the
Figure 4.1. The applied potential programs (a and b), current-density time transients (c and d) and polarisation curves (e) derived from the data in (c) for 316L stainless steel samples studied in 0.5 M H₂SO₄. The dotted vertical lines in (c) and (d) denote the times at which the current density changed from cathodic (left side) to anodic (right side).
Figure 4.2. The applied potential programs (a and b), current-density time transients (c and d) and polarisation curves (e) derived from the data in (c) for 316L stainless steel samples studied in acetic acid containing 0.02 M Na₂B₄O₇·10H₂O and 1 M H₂O. The dash-dotted vertical lines in (c) and (d) denote the times at which the electrolyte was changed from 0.5 M H₂SO₄ (left side) to the acetic acid solution (right side), whereas the dotted vertical lines in (c) and (d) denote the times at which the current density changed from cathodic (left side) to anodic (right side).
thickness \( d^{ox} \) of the oxide layer. In the equations below, \( \alpha \) is a spectrometer constant, \( \lambda \) denotes the attenuation length whereas \( \sigma \) represents the photoionization cross section. \( \theta \) is the detection angle.

\[
d^{ox} = \lambda_i^{ox} \sin \theta \times \ln \left[ 1 + \frac{I_i^{ox} \lambda_i^{met} \sigma_i^{met}}{I_i^{met} \lambda_i^{ox} \sigma_i^{ox}} \right]
\]  

(4.1)

Based on the calculated thickness of the oxide layer, concentrations of the constituent cations in the oxide as well as atoms in the underlaying steel can be calculated. Below, \( T(E_{kin}^i) \) denotes the transmission function of the kinetic energy for element \( i \) and \( \theta \) is the photoelectron take-off angle relative to the sample surface.

\[
C_i^{ox} = \frac{\lambda_i^{ox} \sigma_i^{ox} T(E_{kin}^i) \left( 1 - e^{-d^{ox}/\lambda_i^{ox} \sin \theta} \right)}{\sum_{j=1}^{N} \lambda_j^{ox} \sigma_j^{ox} T(E_{kin}^j) \left( 1 - e^{-d^{ox}/\lambda_j^{ox} \sin \theta} \right)}
\]  

(4.2)

\[
C_i^{met} = \frac{\lambda_i^{met} \sigma_i^{met} T(E_{kin}^i) e^{-d^{ox}/\lambda_i^{ox} \sin \theta}}{\sum_{j=1}^{N} \lambda_j^{met} \sigma_j^{met} T(E_{kin}^j) e^{-d^{ox}/\lambda_j^{ox} \sin \theta}}
\]  

(4.3)

Since the calculated thickness is based on assumed densities of the oxide layer and metal, it is most likely inaccurate. However, based on the calculated concentrations, it is possible to calculate new densities for the oxide and metal, which can be done by summing up the fractions of the respective elements multiplied by the respective densities in their pure form. In the following equations, \( D_j \) denotes the density of the pure oxide or metal of element \( j \) whereas \( C_j \) denotes the previously calculated concentration of element \( j \) in the oxide or metal.

\[
D^{ox} = \frac{1}{\sum_{j=1}^{N} C_j^{ox} D_j^{ox}}
\]  

(4.4)

\[
D^{met} = \frac{1}{\sum_{j=1}^{N} C_j^{met} D_j^{met}}
\]  

(4.5)

Using the new densities, a new thickness can be calculated with Equation 4.1, and then the iteration loop is continued until the thickness, concentration, and density values stabilize.

Figure 4.3 shows the calculated thicknesses of all the films studied in Paper I, divided into oxide and hydroxide layers for each thickness. The surface concentrations of cations are also showed for each film. It is apparent that
Figure 4.3. Thicknesses of the oxide and hydroxide layers (red, left bar in each pair), as well as the total concentrations of the metal cations (blue, right bar in each pair) for oxide films on 316L stainless steel formed under different conditions in 0.5 M H₂SO₄, acetic acid containing 0.02 M Na₂B₄O₇·10H₂O and 1 M H₂O, and deionized water. Note that the −1.5 V samples, as well as all other samples, were subjected to air and deionized water during their transfer to the XPS instrument. The numbers within parentheses above some bars indicate the number of analyzed samples when more than one sample was used. The relative standard deviation for the total film thickness was 12 %, whilst those for the oxide and hydroxide layers were 14 % and 15 %, respectively. The corresponding values for the iron, chromium and molybdenum concentrations were 18 %, 7 % and 26 %, respectively. The relative standard deviations were pooled values (assuming equal variances of the sample sets) based on three sets of repeated samples.
the thicknesses of films were similar in both electrolytes. Increased levels of molybdenum can also be discerned for some of the films that were polarized in the acetic acid solution, and this will be examined further below in the evaluation of the angularly resolved data.

**Deconvolution of ARXPS data**

The evaluation of cation concentration gradients that are present in the passive film requires measurements at several angles and a more involved approach to deconvolute the acquired data, compared to the comparatively straightforward iterative calculation of the thickness described above. Although only angularly resolved data is treated here, the same method should be applicable, with some minor adaptations, to excitation-energy-resolved data as well.

While both angularly resolved [96,97] and excitation-energetically resolved [96] XPS measurements often are used without deconvolution, precise quantitative conclusions about the actual concentrations at different depths cannot be drawn from such evaluations. Although the intensity is more biased towards the signal from the deeper parts of the sample for angles close to perpendicular to the surface and more biased towards signal from the surface for angles close to gracing, signals from all depths are present for all measurement angles. For simple binary systems, such as SiO$_2$ or TiO$_2$, the ARXPS data can be analytically deconvoluted into depth profiles, and it is also possible to deconvolute more complex systems by assuming that the depth profiles can be represented by some well-defined function, e.g., a monotonic function or a single maximum [40, 41].

To deconvolute an ARXPS measurement on an oxide film on stainless steel into cation depth profiles without any assumption on monotonicity or number of maxima, it is possible to use an iterative approach, in which an initial depth profile is assumed, whereafter the corresponding ARXPS signals are calculated and compared to the actual ARXPS data. Adjustments are then made to the assumed depth profiles to improve the agreement between the calculated and actual ARXPS signals, until a good fit is achieved. This process can be performed manually or automatically by some optimization algorithm or even brute force. The depth profiles discussed in Paper I were derived by a combination of an implementation of the Lewenberg-Marquardt algorithm from the ALGLIB project [98] and manual profile optimization.

The first step in the deconvolution process discussed here is to determine the thickness of the oxide layer, as described above. This thickness is then considered constant in the subsequent calculations, and only the cation intensity signals originating from the oxide are analyzed. After determining the thickness of the oxide layer, the latter was divided into a finite number of tiers. Figure 4.4 shows two models, one with 3 and one with 100 tiers, together with experimental data. Each tier may have an individual concentration of each of the three different cations, i.e., iron, chromium and molybdenum. In the manual, iterative optimization process, these concentrations were ad-
Figure 4.4. Molybdenum, chromium and iron ion concentration depth profiles based on the presence of thin outer and inner tiers (⅕ of the total thickness each) and a thick middle tier (⅓ of the total thickness) for a 316L stainless steel sample kept at the OCP in deionised water (a), and the corresponding calculated ARXPS response shown together with experimental data points (depicted by the dots) (b). The error bars in a represent one standard deviation and were calculated based on results from five different experiments. The corresponding concentration depth profiles based on a 100-tier model (c) and the corresponding calculated ARXPS response showed together with experimental data points (depicted by the unfilled square, triangular and circular markers) (d).
Table 4.1. The compositions of the outer, middle and inner parts of the passive film for the different experimental conditions used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface (at. %)</th>
<th>Middle (at. %)</th>
<th>Inner (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Cr</td>
<td>Mo</td>
</tr>
<tr>
<td>H₂SO₄ OCP (+0.1 V)</td>
<td>55</td>
<td>45</td>
<td>—</td>
</tr>
<tr>
<td>H₂SO₄ −1.5 V</td>
<td>63</td>
<td>37</td>
<td>—</td>
</tr>
<tr>
<td>H₂SO₄ 0.7 V ramp</td>
<td>85</td>
<td>15</td>
<td>—</td>
</tr>
<tr>
<td>H₂SO₄ 0.7 V step</td>
<td>57</td>
<td>43</td>
<td>—</td>
</tr>
<tr>
<td>H₂SO₄ 1.5 V ramp</td>
<td>78</td>
<td>22</td>
<td>—</td>
</tr>
<tr>
<td>H₂SO₄ 1.5 V step</td>
<td>91</td>
<td>9</td>
<td>—</td>
</tr>
<tr>
<td>HAcBor OCP (−0.3 V)</td>
<td>65</td>
<td>35</td>
<td>—</td>
</tr>
<tr>
<td>HAcBor −1.5 V</td>
<td>100</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HAcBor 0.7 V ramp</td>
<td>1</td>
<td>99</td>
<td>—</td>
</tr>
<tr>
<td>HAcBor 0.7 V step</td>
<td>24</td>
<td>76</td>
<td>—</td>
</tr>
<tr>
<td>HAcBor 1.5 V ramp</td>
<td>28</td>
<td>72</td>
<td>—</td>
</tr>
<tr>
<td>HAcBor 1.5 V step</td>
<td>61</td>
<td>39</td>
<td>—</td>
</tr>
<tr>
<td>H₂O OCP (+0.3 V)</td>
<td>40</td>
<td>60</td>
<td>—</td>
</tr>
</tbody>
</table>

justed for each tier. To keep the process manageable, it was initially chosen to work with a five-tier model. After trying the model on a few oxide films, it was found that the middle three tiers were usually very similar, with the surface and inner tiers differing. To increase the speed, and also the robustness of the method, the three middle tiers were therefore combined into one tier, resulting in a three-tier model with 20 percent of the thickness in each of the surface and inner tier, and the remaining 60 percent in the middle tier (see Figure 4.4a). The general results for the 100-tier model (see Figure 4.4c) were similar to those for the three-tier model (see Figure 4.4a), indicating that the much simple three-tier model was a good compromise between versatility and simplicity. Although the fit to the experimental data was slightly better with the 100-tier model (see Figure 4.4d) the three-tier model also provided fairly good fits (see Figure 4.4b). To test the repeatability of the film formation and ARXPS measurements combined with the three-tier model, five 316L samples were prepared and analyzed in the same way. The standard deviations of the resultant atomic concentrations are represented by the error bars in Figure 4.4a. It should be noted that the profiles depicted in Figure 4.4a were derived from the measurements on one of the five samples. The presence of variations both in the concentrations and the thickness made the construction of an average profile somewhat complicated, and it was deemed better to show one representative profile.

The surface tier
Table 4.1 summarizes the deconvolution of the ARXPS signals for all samples. Some common trends could be seen for all experimental conditions. In gen-
eral, the surface contained only iron and chromium ions and no molybdenum. Mesquita et al. [55] on the other hand, who recently investigated molybdenum in the passive films formed in air or in chloride solutions of pH 7 or 10 with ARXPS at 30 and 90°, concluded that molybdenum was present in the outer part of the film. Looking at the ARXPS data in Paper I, it is, however, seen that the drop in intensity for the molybdenum signal becomes significant only at angles below 30°. Consequently, it is advisable to include such angles in any ARXPS analysis of passive films. Although both the samples and especially the polarization conditions differed in Paper I compared to those of Mesquita et al., the raw data in the latter study actually suggest the possibility of a similar passive-film depth profile, without molybdenum at the surface, in agreement with the results in Paper I.

In general, surfaces polarized in sulfuric acid exhibited a preference for iron ions in the surface layer, whereas chromium ions were more prevalent for surfaces polarized in the acetic-acid-based electrolyte. This can be explained by the solubilities of the salts of the metal ions in the different solutions. It was also found that the highest potential, i.e., +1.5 V, favored iron ions, as did steps compared to ramps. This finding is explained by the lower solubility of the iron(III) that is formed at +1.5 V compared to the iron(II) that is formed at +0.7 V, as well as the higher solubility of the chromium(VI) that forms at +1.5 V compared to the chromium(III) that forms at +0.7 V [99]. When the potential was ramped, there was also more time for iron to dissolve and chromium to enrich before reaching the final potential.

The middle tier

The middle tier was found to be comprised mainly of chromium oxide for all films, although films formed at higher potentials, especially after a step or in acetic acid at any potential, also contained around 20 percent iron. This could be explained by the different solubilities of the different oxidation states of iron and chromium ions in the different solutions.

The inner tier

The inner tier showed various degrees of molybdenum enrichment for the different films, with iron making up for the balance, since chromium was found to be absent. In general, polarization in the acetic acid solution yielded higher molybdenum enrichments in the inner tier, especially at higher potentials. This effect is explained by the high degree of iron and chromium dissolution at those potentials. Interestingly, in sulfuric acid, the lowest polarization potential (−1.5 V vs. Ag/AgCl (sat.)) yielded the highest molybdenum enrichment, whereas the same potential produced the lowest molybdenum enrichment in the acetic acid solution.

The generally observed structure of the passive film, with iron enriched at the surface (compared to the generally chromium-enriched passive film) and molybdenum enriched close to the metal is in good agreement with previ-
ous findings [5] and may be explained on the basis of the polarization curves of iron, chromium and molybdenum [4, 100]. Chromium is oxidized at the least anodic potential, iron at a potential very close to that of chromium and molybdenum at a more anodic potential than the other two. In an anodic scan, chromium and iron should hence start to oxidize first and molybdenum last. The same order should be observed in a galvanostatic experiment [11], as well as when the passive film is formed natively in contact with oxygen. Since the passive-film growth takes place at the metal-oxide interface, the last element to oxidize, i.e., molybdenum, should end up deepest within the oxide film.

Given the higher oxidation potential of molybdenum compared to chromium and iron, the higher molybdenum enrichments at higher potentials are not surprising, although it is important to remember that solubilities also play an important role in determining which elements that get enriched.

4.1.2 Bipolar corrosion screening

Surface gradient and image analysis

While ARXPS is a very useful tool to extract detailed information about thin films such as the passive films evaluated in Paper I, it is time-consuming and only gives information about the behavior of the samples at a limited set of potentials. It is often more practical to be able to quickly screen for the response of a number of potentials simultaneously. In Paper II, type 304 stainless steel samples were investigated by bipolar electrochemistry in 1 M sulfuric acid or 100 mM hydrochloric acid. Two approaches were used to create the electric field in the electrolyte: either by keeping the potential difference constant at 5 to 6 V, or by keeping the current constant between 100 and 300 mA.

In a completely static system, controlling the current would lead to a certain potential, and controlling the potential would lead to a certain current. In a real system, there are however several dynamic factors affecting the behavior of the system in time. One of the most important effects is that the surface of the sample will change during the experiment. When the surface is oxidized, metals that oxidize more easily than others might become depleted, thus decreasing the total speed of oxidation at that point of the surface. Passivation of the surface is another factor that reduces the oxidation reaction rate, while surface roughening as a result of the dissolution of ions increases the rate of the reaction. Other effects include changes in the conductivity of the solution due to the dissolution of ionic species from the sample. Since the potential drop in the bulk solution between the two driving electrodes follows Ohm’s law and is equal to the current multiplied by the total resistance, an increased conductivity would lead to an increased current if the potential was kept constant, whereas if the current was kept constant, the potential would decrease with time.
In Paper II, a corrosion gradient was successfully obtained in sulfuric acid by using a constant-potential setup. An approximately 1.5 millimeter long portion of the sample was analyzed in detail by SEM (see Figure 4.5), and a clear corrosion gradient towards the anodic side of the sample was seen in the form of increasingly large cracks between the grains of the metal. By the use of energy-dispersive X-ray spectroscopy, it was found that some of the ions that dissolved at the anodic side of the sample re-deposited at the cathodic side. This phenomenon complicates the evaluation of the electrochemical behavior of the sample at the cathodic potentials. By the use of a flow cell, with the electrolyte flowing perpendicular to the electric field to continuously replace the electrolyte, it should be possible to avoid redeposition of dissolved ions in bipolar experiments.
An important type of corrosion is pitting corrosion (see Figure 2.2), which can occur when the passive film breaks down locally. Anions like \( \text{Cl}^- \) and \( \text{S}^{2-} \) can penetrate the oxide film, causing pitting corrosion \([101]\), and hydrochloric acid is hence a suitable test electrolyte for pitting-corrosion investigations. In Paper II, type 304 stainless steel was tested for pitting corrosion in hydrochloric acid, employing a constant current between the two driving electrodes. Over a length of almost one centimeter, a pit-size gradient was clearly discernible (see Figure 4.6), with the severity of the attacks (size of the pits) increasing towards the anodic side of the sample. The number of pits per unit area was fairly constant, in line with the common view \([4]\) that the initiation of pits takes place at defect sites, such as inclusions. Since the area concentration of inclusions should be constant, the same number of pits for a given area developed as long as the starting potential reached values above the critical pitting potential. In the constant-current experiments employed in the pitting experiments in Paper II, the potential in the areas of pit formation decreased with time as the pits grew, since pits facilitate active dissolution, which requires lower potentials to sustain the same current density. As a result of the zero net current to the sample, the potential of the sample would continuously assume the dynamic value for which the anodic and cathodic partial currents were equal.

**Correlating distance to potential or current density experimentally**

Once a gradient has been investigated (e.g., by measuring the size of the pits as a function of distance along the sample), it needs to be correlated to a potential or current-density profile along the surface. Since a bipolar experiment is dynamic (i.e., it changes over time, as discussed above), any given point on the surface may experience changes in both current density and potential over time, but as will be discussed below, the bipolar experiments in Paper II included conditions that were comparable and could hence be correlated to galvanostatic experiments.

For the constant-potential experiment in Paper II (see Figure 4.5), neither potentiostatic nor galvanostatic experiments yielded surfaces that were similar to the different regions on the bipolar electrode, indicating that the different regions of the bipolar electrode experienced significant variations with time both in the current densities and the potentials. In the case of the constant-current bipolar experiment (see Figure 4.6), comparing galvanostatic experiments to the different regions on the bipolar electrode gave a reasonable fit between different current densities in the galvanostatic experiments and different regions on the bipolar electrode, i.e., the distance along the surface could be correlated to the current density. Based on a closer examination of the conditions during the bipolar experiments, this is not surprising. In a galvanostatic experiment where the pitting-corrosion potential is reached or surpassed, the potential is expected to decrease as the pits grow, since the corrosion processes in the pits would be able to uphold the constant current at a lower potential due to the
larger active surface area compared to an intact film. In the bipolar case, once
the pits formed and started to grow, the potential of the sample would decrease
to keep the net current to the sample to zero, as discussed above. The lower
potential of the sample would be able to uphold the increased cathodic current
that would be necessary to balance the anodic current (caused by the pits).
Since the presence of the pits would also increase the fraction of the current
flowing through the sample, the amount of current flowing through the elec-
trolyte parallel to the sample would decrease, decreasing the iR drop and thus
decreasing both the anodic and cathodic overpotentials on the bipolar sample.
The net effect of these effects at any given point in the pitting region would
be that the relative potential of the sample to the solution decreased as the
experiment went along, which would be similar to the situation in a galvanos-
tatic experiment. An additional effect is that the reduced anodic overpotential
would lower the current increase as the pits grew, thus making the current den-
sities in the bipolar experiment less variable with time and hence more similar
to the current densities under galvanostatic conditions.

**Correlating distance to potential or current density theoretically**

A different approach to determine the potential along the length of the surface
involves calculations or simulations. Duval *et al.* [29–31] have extensively
calculated the potential and current-density profiles along the surface by mod-
eling parameters such as reaction kinetics and diffusion of the electroactive
species, while Ulrich *et al.* [25] implemented a simpler model based on con-
agreement between their simulated and measured data, but neither of their
methods could (easily) be adopted for an arbitrary system. For the methods
described by Duval *et al.* [29–31], it is imperative to understand the system,
including all the reactions taking place, well. When this is achievable, this
method allows for very nice and detailed simulations, but the method can thus
only handle systems that are well understood.

The simplistic approach taken by Ulrich *et al.* [25], on the other hand, does
not model the faradaic reactions that take place on the bipolar electrode, but
instead introduces an artificially high resistance in the sample. The increased
resistance of the bipolar electrode in the model limits the amount of current
flowing through the electrode. Instead of modeling the surface as an equipo-
tential surface and the current density as a function of the relative potential
of the surface to the solution (based on calculations of all partial reactions in
the case of Duval *et al.* [29–31]), the bipolar electrode surface assumes its
own potential gradient in the model as a result of the current flowing through
the internal resistance of the sample. The sample and solution are then simply
considered as two conductive media in contact with each other. With such a
model, faradaic reactions cannot be directly accounted for. An example of an
effect that could not be modeled with this approach is the large difference in
current density between the passive and transpassive area [4] for a passivating metal.

A different approach, that could be useful for complicated systems where not all partial reactions can be accurately modeled, or simple differences in conductance cannot sufficiently model the system, is to use the data from a polarization curve to account for the faradaic reactions on the bipolar electrode, without having to know the details about each partial reaction. Since the flow of current to the bipolar electrode both depends on and affects the potential profile in the solution, an iterative approach to calculate the potential profile and equipotential (and thus also current flow to the bipolar electrode) would be appropriate. The calculations could be done in one, two or three dimensions, by estimating the potential profile in the solution using a function in the one-dimensional case and by solving the Laplace equation for the two- and three-dimensional cases.

Such an approach would be useful for modeling a bipolar experiment without fully understanding all reactions, but with one important prerequisite: that the current densities in the polarization curve were representative of the bipolar sample. For some cases, this assumption should hold, but for other cases, such as when pitting corrosion takes place, the conditions in the bipolar case might differ significantly from those during the recording of a polarization curve. While a series of galvanostatic measurements at different potentials could prove useful for cases when a polarization curve could not be used, the practical usefulness of this is questionable, since the bipolar experiment then would lose one of its main advantages as a quick screening test.

4.2 Chromium carbides

4.2.1 Films prepared by magnetron sputtering

In Papers III, IV and V, chromium carbide thin-films were studied as coatings to further increase the corrosion resistance of stainless steel. In Paper III, a series of chromium carbide films with various compositions were deposited at 300 °C by magnetron sputtering. The sputtering setup comprised two elemental targets, carbon and chromium (see Figure 2.3), and the composition of the films was adjusted by tuning the chromium target current. Both examinations by X-ray diffraction and TEM indicated that the films were amorphous, although the TEM analysis indicated the presence of two phases: an amorphous chromium carbide phase, and an amorphous carbon phase. Other studies have shown a tendency for non-reactively sputtered magnetron films to be amorphous [63, 102–105], while reactively sputtered films often are crystalline [106–112]. The structure of the deposited films was found to change from a columnar structure for the most chromium-rich film to one that appeared to be denser as the carbon content increased, in line with results for other binary carbide systems, such as titanium carbide and niobium carbide.
XPS analyses of the films in Paper III clearly showed that the carbon was bound mostly to chromium for the most chromium-rich film, and mostly to carbon for the most carbon-rich film. Annealing at 500 °C did not change the amorphousity of the films, but a sample that was annealed at 800 °C (the most chromium-rich sample) showed clear carbide peaks in the X-ray diffractograms. Both the hardness and elasticity of the films increased with the chromium content, as did the conductivity.

The films showed promising results in initial corrosion tests at room temperature in Paper III, with generally lower currents in the passive region of the polarization curves compared to for the 316L stainless steel reference sample. The electrochemical properties were examined in more detail in Paper IV.

4.2.2 Electrochemical measurements

The polarization curves for the chromium carbide films investigated in Papers III and IV (see Figure 4.7) show that the most chromium-rich film exhibited lower current densities in both the cathodic and passive regions compared to the three more carbon-rich films at 22 °C. The 316L stainless steel sample yielded the highest current densities of all samples in the passive region. At 80 °C (see Figure 4.8), there was no significant difference in the passive region, although the most chromium-rich film displayed the lowest current density in the cathodic region also at the higher temperature. The current densities at potentials below the transpassive region for the three more carbon-rich films were indistinguishable from each other both at 22 and 80 °C, respectively (see Figures 4.7 and 4.8). As was found in Paper III, an important difference between the most chromium-rich and the other three films was that the former contained mainly chromium carbide, while the latter three contained significant amounts of amorphous carbon in addition to the chromium carbide. The finding that the chromium carbide films with significant amounts of amorphous carbon exhibited very similar current densities indicates that the amorphous carbon must also have been oxidized in the passive region.

In the transpassive region, higher chromium content correlated to higher current densities both at 22 and 80 °C, indicating that transpassive dissolution of chromium was the major contributor to the much larger current densities at these potentials, although the current densities did not scale perfectly with the chromium content. The chromium carbide films did hence not benefit from a second passivation at higher potentials in the same way as the 316L stainless steel did thanks to its high iron content [4].

EQCM measurements on a film (deposited on a gold-coated quartz crystal) with a similar composition as that of the most chromium-rich film while scanning the potential anodically did not reveal any significant mass change in the passive region (see Figure 4.9a). This indicates that very little chromium(0) was available to be oxidized to chromium(III), suggesting that a film
Figure 4.7. Polarization curves and the corresponding voltammograms for magnetron-sputtered chromium carbide films and 316L stainless steel at 22 °C.
Figure 4.8. Polarization curves and the corresponding voltammograms for magnetron-sputtered chromium carbide films and 316L stainless steel at 80 °C.
Figure 4.9. EQCM measurements on a Cr$_{0.75}$C$_{0.25}$ film that was very similar to the most chromium-rich film tested in Paper IV. The passive region is shown in a, while b shows the transition into the transpassive region.
of chromium(III) oxide was already present. In this context, it is worth mentioning that several reactions could take place when oxidizing carbide-bound chromium, since the chromium atoms can either form oxide and stay on the surface or dissolve as chromium(III) ions, while the carbon either can form free carbon that stays on the surface or detaches, or is oxidized to, e.g., carbon dioxide. The following reaction can be assumed if chromium(0) is oxidized to chromium(III) ions:

\[
\text{CrC}_x \rightarrow \text{Cr}^{3+} + x\text{C} + 3\text{e}^- \quad (R4.1)
\]

For the case where chromium(0) is oxidized to chromium(III) oxide, the following reaction can be assumed:

\[
2\text{CrC}_x + 3\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 2x\text{C} + 6\text{H}^+ + 6\text{e}^- \quad (R4.2)
\]

Likewise, if both chromium(0) and carbon are oxidized, yielding chromium(III) ions and carbon dioxide, the following reaction is obtained:

\[
\text{CrC}_x + 2x\text{H}_2\text{O} \rightarrow \text{Cr}^{3+} + x\text{CO}_2 + 4x\text{H}^+ + (3 + 4x)\text{e}^- \quad (R4.3)
\]

The reaction in which chromium(0) is oxidized to chromium(III) oxide and carbon to carbon dioxide can analogously be written as:

\[
2\text{CrC}_x + (3 + 4x)\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 2x\text{CO}_2 + (6 + 8x)\text{H}^+ + (6 + 8x)\text{e}^- \quad (R4.4)
\]

For the investigated $\text{Cr}_{0.75}\text{C}_{0.25}$ film, $x = \frac{1}{3}$ in Reactions R4.1 to R4.4. Given the reaction paths proposed in Reactions R4.1 to R4.4, it is possible to have growth of a chromium(III) oxide film with both mass decrease and increase, depending on the amount of chromium loss due to the formation of chromium(III) ions. Hence, the absence of any mass change in the EQCM experiments does not exclude the possibility of film growth, although it should be pointed out that it is highly unlikely that film growth and loss of material to the solution precisely balanced each other during the entire passive region of the scan, particularly as the films most likely had a native oxide film already before the EQCM experiments. The starting potential in the scan was $-0.5$ V vs. Ag/AgCl (sat.), which most likely was not cathodic enough to reduce any pre-existing passive film.

There were no significant differences between the charges obtained during the 1-hour chronoamperometric experiments at 80 °C, and the subsequent inductively coupled plasma - optical emission spectroscopy analysis of the used electrolytes did not indicate the presence of any increased concentrations of metal ions in the electrolytes.

The three most carbon-rich films were also indistinguishable in SEM micrographs (see Figure 4.10b and d), all exhibiting a cauliflower-like appearance
Figure 4.10. SEM micrographs of the most chromium-rich film (left) and the most carbon-rich film (right). The micrographs shown in c and d show parts of the depicted areas in a and b at a larger magnification. The micrographs show the films after 1-hour chronoamperometric tests in 1 mM sulfuric acid. The scale bars in the upper micrographs denotes 10 µm, while those in the lower represent 1 µm.
with small grains, while the most chromium-rich film had large grains that formed a turtle-like pattern (see Figure 4.10a and c). Within the large grains of the most chromium-rich film, very faint, fine grains could be distinguished. The more columnar and thus less dense structure of the most chromium-rich film explains the lower current densities observed for that film in the passive region of the polarization curves at 22 °C. While it might seem counter-intuitive that a less dense structure would yield lower currents at first, the less dense structure would allow the chromium carbide to be oxidized to chromium(III) oxide to a greater extent prior to the polarization scans or early on in the cathodic region.

The surfaces of films were analyzed by XPS both before and after the chronoaerometric oxidation step at 80 °C (see Figure 4.11 and 4.12), and the C1s peak (see Figure 4.11c) revealed that the most chromium-rich film had very little oxidized carbon before the oxidation step, whereas the three more carbon-rich films had increasing levels of oxidized carbon incorporated in the films. The amount of oxidized carbon was similar for all four films after the oxidation steps (see Figure 4.12c). While the fraction of oxidized carbon increased during the oxidation step for the most chromium-rich film, it was unchanged for the second most chromium-rich film and decreased for the two most carbon-rich films. These results indicate that carbon oxidation contributed to the significantly larger current in the passive region for the most chromium-rich film at 80 °C.

An examination of the O1s peak (see Figure 4.11b) in the XPS spectra revealed that the film with the highest content of chromium displayed a much stronger presence of chromium oxide than the other three films (see Figure 4.12b). The much more prominent presence of chromium(III) oxide before the oxidation step for the most chromium-rich film is in line with the interpretation that the less dense structure of that film (see Figure 4.10) allowed a greater extent of the chromium carbide to be oxidized to chromium(III) oxide. Given that all films exhibited low current densities in the potentiostatic tests, and that there were no detectable amounts of chromium in the used electrolytes for any of the films, the more carbon-rich films seemed to be able to provide very good corrosion resistance even without a dense and fully covering chromium(III) oxide film on the surface. This could prove beneficial for applications where a low ICR is desirable, as the ICR was found to decrease with increasing carbon content, see Paper III.

Looking at the difference between the C1s peak (see Figure 4.11c) before and after the 1-hour chronoaerometric experiments, the amount of free carbon compared to carbon that was bound to chromium increased for the three more carbon-rich films (see Figure 4.12c), in line with the interpretation that carbidic chromium was oxidized, thereby releasing free carbon (see Reactions R4.1 and R4.2), although this does not exclude the possibility that some of the carbon also was oxidized. The most chromium-rich film showed a slight decrease in the relative amount of carbon- or hydrogen-bound carbon, in line
Figure 4.11. XPS spectra, showing the curve fits used to analyze the surface of the low- to high-carbon films in Paper IV.
Figure 4.12. For each element, fractions bound to different elements or groups derived from the surface measurements of the low- to high-carbon films in Paper IV presented in Figure 4.11. The C–O areas of the bars from the C1s spectrum are divided into two parts. The upper part denotes the C=O double bonds, while the lower part represents the C–O single bonds.
with the interpretation that carbon oxidation was significant for this film at 80 °C, while the chromium(III) oxide layer remained largely unaffected. The mixed potentials were similar for the three more carbon-rich films, while the mixed potential was much more cathodic for the most chromium-rich film at 22 °C (see Figure 4.7). Increasing the temperature to 80 °C (see Figure 4.8) led to an anodic shift in the mixed potential for all films, although much more pronounced for the most chromium-rich film. This yielded similar mixed potentials for all films at 80 °C. The 316L steel, on the other hand, had a mixed potential in between those for the more carbon-rich films and the most chromium-rich film at the 22 °C, and was shifted cathodically to yield the most cathodic mixed potential at 80 °C.

The cathodic mixed potential at 22 °C and considerably more anodic mixed potential at 80 °C for the most chromium-rich film could be explained by early passivation at 80 °C, in the cathodic region where the anodic partial current would be smaller than the cathodic partial current [115]. After passivation, the anodic partial current remained low, allowing the cathodic partial current to dominate to a higher potential. In the case of the three more carbon-rich films, the presence of significant amounts of amorphous carbon already before the oxidation step adds the possibility of carbonaceous surface reactions, which includes both cathodic and anodic reactions, with a gradient of standard reductions potentials for different surface groups [116]. The presence of cathodic surface group reactions in combination with the smaller anodic partial current from chromium oxidation can explain the significantly higher cathodic current densities for these films, and thus also the more anodic mixed potentials at 22 °C. Since oxygen reduction should be mass-transport-controlled in the potential region at or below the mixed potentials of the films, its contribution to the anodic partial current should be equal for all of the films.

4.2.3 Effect of deposition temperature on the corrosion resistance

The chromium carbide material system was further investigated in Paper V, where a low- and a high-carbon film were fabricated using a range of deposition temperatures. Here, it is important to note that both the low- (Cr_{0.6}C_{0.4}) and high-carbon (Cr_{0.3}C_{0.7}) films had compositions within the range of the three more carbon-rich films analyzed in Papers III and IV. The two compositions used in Paper V will subsequently be referred to as the low- and high-carbon films. While films of both compositions were deposited at temperatures of 20, 300, 500 and 700 °C, the films deposited at the highest temperature were found to exhibit poor adhesion and peeled off from the surface, and consequently only the films deposited at temperatures of 500 °C and lower were evaluated electrochemically.

Polarization curves recorded at 80 °C in 1 mM H_2SO_4 for the low- and high-carbon films after deposition at 20, 300 and 500 °C looked very similar
to those obtained for the three more carbon-rich films in Paper IV, with the exception of the low-carbon film deposited at 20 °C, which displayed lower currents in the cathodic region compared to the other films. The low-carbon films gave rise to slightly higher currents compared to the high-carbon films in the transpassive region, in line with the results in Papers III and IV.

Based on the chronoamperometric tests of the low- and high-carbon films (performed as in Paper IV), two trends could be discerned. The oxidation charge increased with decreasing deposition temperature, and the low-carbon films yielded higher charges than the corresponding high-carbon films. If the charge corresponded directly to the amount of chromium in the film, it should have been about twice as large for the low-carbon films as for the high-carbon films. The difference was, however, generally smaller, indicating that carbon was also oxidized in addition to chromium, in line with the results in Paper IV. The ratio between the charges for the low- and high-carbon films decreased with increased deposition temperature, reaching a value of about unity for films deposited at 500 °C.

Figure 4.13 depicts cross-sectional SEM micrographs of the low- and high-carbon films. It is seen that the films exhibited columnar structures after deposition at 20 and 300 °C (see Figure 4.13a–d) and that this structure was absent after deposition at 500 °C. SEM micrographs of the surfaces of the native films revealed that all films had similar cauliflower-like morphologies to that obtained for the three more carbon-rich films in Paper IV, although the low-carbon film that was deposited at 500 °C looked coarser than the others. SEM micrographs of the surfaces (see Figure 4.14) after the chronoamperometric experiments did not reveal changes in the appearance for any of the films. The micrographs of the samples that had been scanned up to +1.5 V were however duller and less sharp in appearance, which would be expected after dissolution of chromium, leaving amorphous carbon on the surface. The more coarse-looking low-carbon film that was deposited at 500 °C developed a perforated appearance after having been scanned to +1.5 V, indicating that the chromium was more localized to crystallites in this film.

XPS analyses of Cr2p peaks for the films gave rise to similar results as for the films in Paper IV, i.e., increased amounts of oxidized species after the chronoamperometric tests and the presence of less chromium(III) oxide on the high-carbon films. It was further found that the amount of oxidized chromium compared to non-oxidized chromium on the as-deposited films decreased with increasing deposition temperature. This result is well in line with the tighter appearance of those films in the SEM micrographs, indicating that the maximum depth at which oxidations could take place was less for the films deposited at higher temperatures.

Looking at the C1s peak, it was found that the amount of oxidized carbon increased by about 100 percent during the electrochemical oxidation step for all films, independent of their carbon content and deposition temperature. This result is compatible with carbon surface group oxidation, as suggested also
Figure 4.13. Cross-sectional SEM micrographs of chromium carbide films fabricated 20 °C (a and b), 300 °C (c and d) and 500 °C (e and f), with the left micrograph depicting the low-carbon film and the right micrograph the high-carbon film for each temperature. The scale bar in each micrograph represents 200 nm.
<table>
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*Figure 4.14.* SEM micrographs of the low- and high-carbon chromium carbide films deposited at different temperatures, before and after both chronoamperometric polarization for 1 hour at +0.643 V vs. Ag/AgCl (sat.) and linear scans up to +1.5 V vs. Ag/AgCl (sat.). The scale bar in each micrograph represents 500 nm.
by the results in Papers III and IV. The chromium to carbon ratio did not change significantly during the chronoamperometric experiments, indicating that carbon was not oxidized to species that detached from the surface. Hence, the previously proposed Reactions R4.1 and R4.2 in combination with the oxidation of carbon are likely to describe the oxidation reactions.
5. Concluding remarks

5.1 Characterization of passive films on stainless steel

Paper I focused on the detailed analysis of the intrinsic details of passive films on stainless steels, and a method for semi-automatic deconvolution of ARXPS data into depth-concentration profiles was presented. This method should, with minor adjustments, be applicable to other convoluted data as well, such as for example energy-resolved XPS results. Being able to better understand passive films on the nanometer level opens up for better understanding of the passivation mechanisms of stainless steel, which would enable more informed design decisions when fine-tuning the properties of future materials for specific applications. The technique may prove useful also in completely different fields that likewise require the ability to (relatively) non-destructively obtain depth-profiles, such as the analysis of the solid electrolyte interphase on the anodes of lithium-ion batteries—a key area to improve the performance of such batteries.

Taking on a different corrosion study approach in Paper II, the aim was to obtain a method for rapid scanning of the corrosion properties of stainless steels by the use of bipolar electrochemistry. While the technique is able to quickly provide a sample with a gradient of corrosion potentials or current densities for further analysis with an appropriate imaging (or other) system, such as SEM, it also introduces the problem of linking the various areas of the sample to different potentials or current densities. It was shown that correlating the surface area to current densities by comparative SEM analysis of galvanostatic experiments may constitute a better solution than the corresponding potential mapping for the case when pitting corrosion is examined. The prospect of using an iterative method based on polarization curves to calculate the potential profile along the bipolar electrode was also discussed. The development of such a method may present a quick way to obtain estimates for the potential profiles when screening samples using bipolar electrochemistry, although only for experiments where the potential profile on the bipolar electrode can be kept reasonably static.

5.2 Magnetron-sputtered chromium carbide thin-films

In Papers III, IV and V, magnetron-sputtered chromium carbide thin-films on stainless steel were studied to gain a better understanding of their properties,
particularly their resistance to corrosion. It was found that chromium carbides showed very promising results with good corrosion resistances, and also that it was possible to tune the properties of the films by altering their composition and the deposition temperature. The interpretation of the electrochemical tests were discussed in some detail, and it was found that an in-depth understanding of the polarization curves and currents in the chronoamperometric tests is imperative in order to draw useful conclusions from such tests. In particular, the much higher carbon content of chromium carbide materials compared to stainless steels implies that the interpretations of the electrochemical data are not analogous to those for stainless steel samples. A better understanding of the promising corrosion properties of amorphous chromium carbide films opens up possibilities for new functional coatings, and thus new applications for stainless steels.
Sammanfattning på Svenska

I avhandlingen undersöks passivfiler på rostfria stål, dvs den tunna oxidfilm som gör att rostfria stål inte korroderar eller rostar. Även möjligheterna att ytterligare förbättra stålets egenskaper genom att belägga det med en tunnfilm av materialet kromkarbid utvärderas. Avhandlingen har stort fokus på metoderna som används i utvärderingen. Dels diskuteras en ny metod för att mäta vilka ämnen som finns på olika djup i passivfilmen på ett rostfritt stål, och dels diskuteras hur korrosionsegenskaperna för kromkarbider ska utvärderas.


Det finns flera olika metoder för att förhindra korrosion. Ibland räcker det med att lackera materialet, men skadas lacken kan korrosionsproblem uppstå. I början av 1900-talet upptäckte man att stål inte rostar om man tillsätter minst 10.5 procent krom. Detta blev startskottet på utvecklingen av rostfria stål. På grund av nackdelarna med korrosion kan man fråga sig varför stål som kan rosta används i så stor utsträckning när det finns rostfria stål. Svaret är enkelt:
det är dyrare att tillverka rostfria stål. För små föremål är den högre materi-
alkostnaden ofta ett mindre problem än för stora föremål, och följaktligen är
rostfria skruvar och bestick betydligt vanligare än rostfria bilar.

Rostfritt är dock ett relativt begrepp. Ett stål som är rostfritt om det exem-
pelvis används för att tillverka bestick kan mycket väl angripas av korrosion
i aggressivare miljöer, till exempel om det läggs i en syra. Därför finns det
många olika sorters rostfria stål, och nya utvecklas fortfarande. För att kunna
ta fram bättre rostfria stål är det viktigt att kunna förstå hur de fungerar, och
hur man kan påverka stålets egenskaper.

Gemensamt för alla rostfria stål är att de bildar en passivfilm. Denna består
huvudsakligen av kromoxid—precis som järn tappar kromet elektroner och
förenar sig med hydroxidjoner, men till skillnad från järnet så bildas det ett tätt
lager av kromoxid i stället för rost. Kromoxdien fungerar precis som en lack,
och isolerar den underliggande metallen från både syrgas och vatten. Krom-
oxidlagret är dessutom självreparerande, och återbildas sekundsnabbt om en
skada i oxidlagret skulle uppstå. Att förstå hur denna film är uppbyggd och
hur den påverkas av olika grundämnen som tillsätts när stålet produceras är
mycket viktigt för att kunna utveckla nya och bättre rostfria stål.

Studier av passivfiler kompliceras av att de är så tunna. Normalt håller
sig tjockleken för passivfiler i intervallet 1 till 3 nanometer, vilket innebär
att det skulle krävas ungefär 30 000 lager passivfilm för att uppnå tjockleken
för ett mänskligt hårstrå. I den här avhandlingen har passivfiler studerats
med en teknik där provet kan undersökas med hjälp av röntgenstrålning. Det
rör sig inte om röntgenbilder, utan röntgenstrålningen slår ut elektroner från
provet. Dessa elektroner ger sedan information om vilka atomer som finns i
passivfilmen, och vilka andra atomer de binder till. Utifrån dessa mätdata har
djupprofiler skapats. I djupprofilerna kan man se på vilket djup olika atomer
sitter, och därmed få en bättre bild av hur passivfilmen är uppbyggda. För att
ta fram djupprofilerna har det dödvändigt att analysera mätdata på ett nytt sätt,
ta och denna process beskrivs i avhandlingen.

Det är även viktigt att kunna undersöka hur bra ett stål klarar sig under olika
omständigheter. Ett vanligt sätt att göra det på är att utsätta provet för olika
elektriska potentialer i en elektrolyt. Eftersom man vill veta vad som händer
vid flera olika potentialer kan detta vara tidsödande, då många experiment behöver utföras. I avhandlingen diskuteras en ny teknik (bipolär elektrokemi)
där ett prov (en stålbit) läggs på botten av en bägare, som fylls med elektrolyt.
Sedan används två elektroder för att driva en ström genom elektrolyten, men
elektroderna står inte i kontakt med provet. Den elektriska strömmen genom
elektrolyten (som bärs av att elektrolytens joner rör sig) ger upphov till en gra-
dient av olika potentialer i elektrolyten. Provet placeras så att det ligger längs
med denna gradient, och på så vis kan man i ett enda experiment undersöka vad
som händer med provet vid många olika potentialer. Det är också tänkbart
att testa många prov i ett enda experiment, även om analysen i avhandlingen
fokuserar på hur man kan analysera ett prov.
I vissa fall räcker inte ett rostfritt stål till. Om ett stål skulle användas till en elektrisk kontakt skulle passivfilmen göra att kontakten blev dålig, och ytan skulle inte glida så bra (den skulle ha hög friktion). För applikationer där även sådana egenskaper är viktiga kan en lösning vara att belägga stålet med en tunnfilm av ett annat material. I avhandlingen studeras filmer av kromkarbid som var ungefär hundra gånger så tjocka som en passivfilm och korrosionsskyddet som kromkarbidfilmerna erbjöd jämfördes med det för obelagt rostfritt stål.

I avhandlingen diskuteras hur olika tillverkningsparametrar påverkar kromkarbidernas egenskaper. Tillverkningstemperaturens betydelse liksom inverkan av förhållandet mellan krom och kol i filmen undersöks. Kromkarbidfilmerna visade sig erbjuda ett gott korrosionsskydd, och det var möjligt att påverka egenskaper såsom hårdhet, kontaktresistans och elasticitet genom att ändra förhållandena som används när filmen tillverkades. Möjligheten att ändra egenskaperna för rostfria stål genom att använda en ytbeläggning utökar möjligheterna att hitta nya användningsområden för rostfria stål.

Såväl tekniker för att kunna karaktärisera passivfilmerna på rostfria stål och deras korrosionsstabilitet under olika förhållanden liksom möjligheten att ändra egenskaperna genom att belägga ytan med en tunnfilm av ett annat material är viktiga för att rostfria stål ska kunna utvecklas, presteras bättre och användas i nya tillämpningar i framtiden. Den nya metoden för att ta fram djupprofiler för passivfilmer leder till en ökad förståelse för passivfilmernas uppbyggnad, vilket ger nya möjligheter att förbättra stålen. De nya kromkarbiderna uppvisade goda egenskaper, och har potential att i framtiden kunna användas för att förbättra egenskaperna för rostfria stål under förhållanden där den vanliga passivfilmen inte räcker till. Den ökade förståelsen för hur korrosionssegenskaperna för kromkarbider ska utvärderas leder till att vi bättre kan analysera nya material framöver.
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