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Lifetime Model For FSS Interconnects Based On Chromium Content



Thesis for the degree of Master of Science, Materials Chemistry

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Chalmers University of Technology
The High Temperature Corrosion Center
Department of Chemistry and Chemical Engineering



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Cover:

Sample of AISI409 alloy exposed at 850°C for 1008 hours.

Abstract

The world is currently experiencing an unprecedented demand for energy. The high demand for energy is a result of the growth of human civilization and our consumption behavior. Electricity that is made from sources that are both green and renewable usually have a significant obstacle. The obstacle is that the energy production doesn't always match the times for when energy is needed and therefore is reliant on energy storage. Solid oxide fuel cells (SOFC) are a potential solution to the problem as they can be used for power generation, long term energy storage, and reversible operations for grid support. Cost and lifetime are however currently two of the things holding SOFC back. A vital part of a SOFC is its interconnects, which are what electrically connect the individual cells of a fuel cell stack. Interconnects are also one of the main contributors to the cost of a SOFC and its lifetime. Today ferritic stainless steels (FSS) alloys are used for interconnects. FSS interconnects are cost-effective compared to precious used ceramics, but degrade under the harsh operation temperatures in a SOFC. Coating the FSS have proven to be effective in reducing the corrosion phenomena that causes the degradation, such as the formation of chromium vapor and oxide scale growth.

The thesis acts as a continuation of research that has been done to make SOFCs more commercially viable. More specifically it focuses on the concerns surrounding the lifetime of the interconnects. The research showed similar net mass gain for different FSS alloys in the same environment when they have been coated with a Ce/Co coating. Therefore different Ce/Co coatings have been examined. The aspects that have been investigated regarding the coating are primarily: (i) How does the coating effect lifetime of different FSS alloys; (ii) can the lifetime of coated FSS alloys be predicted; and (iii) how does cerium lead to improved lifetime. By investigating the corrosion behavior a lifetime model was constructed and a better understanding of how cerium contributes to protecting the alloys was gained.

Keywords: Solid Oxide Fuel Cell; High-temperature Corrosion; Lifetime model; Interconnect; Reactive Elements Effects

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Nomenclature

- **ICE:** Internal Combustion Engine
- **PEM/PEMFC:** Proton Exchange Membrane Fuel Cell
- **SOFC:** Solid Oxide Fuel Cell
- **SOEC:** Solid Oxide Electrolyzer Cell
- **FSS:** Ferritic Stainless Steel
- **SHE:** Standard Hydrogen Electrode
- **AFC:** Alkaline Fuel Cell
- **PAFC:** Phosphoric Acid Fuel Cell
- **MCFC:** Molten Carbonate Fuel Cell
- **TEC:** Thermal Expansion Coefficient
- **YSZ:** Yttria-Stabilized Zirconia
- **CGO:** Gadolina-Doped Ceria
- **MIEC:** Mixed Ionic-Electronic Conductor
- **H-MIEC:** heterogeneous MIEC
- **TPB:** Triple-Phase-Boundary
- **LSM:** LaMnO_3
- **HTC:** High-Temperature Corrosion
- **PBR:** Pilling-Bedworth Ratio
- **ASS:** Austenetic Stainless Steels
- **FCC:** Face-Centered Cubic
- **BCC:** Body-Centered Cubic
- **RE:** Reactive Elements
- **REE:** Reactive Elements Effect
- **MCO:** $(\text{Mn,Co})_3\text{O}_4$
- **PVD:** Proprietary Physical Vapor Deposition
- **STF:** Single Tube Furnace
- **4TF:** Four Tube Furnace
- **BIB:** Broad Ion Beam
- **SEM:** Scanning Electron Microscope
- **EDX:** Energy Dispersive X-rays spectroscopy
- **SE:** Secondary Electrons
- **BSE:** Backscattered Electrons

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1 | Introduction

1.1 Motivation

The world is currently experiencing an unprecedented demand for electricity. The high demand for electricity is a result of the growth of human civilization and our consumption behavior. To meet the demand, electricity can be produced by burning non-renewable fossil fuels. Since these fuels aren't renewable they cannot be replenished, and per definition therefore are not sustainable. On top of not being sustainable the combustion releases greenhouse gasses, that have a negative effect on the climate and environment. Depletion of known reservoirs combined with higher demand for electricity means that price will eventually increase which at some point will lead to economic and socio-economic disturbance across the globe [1].

Solutions to the high electricity demand do exist. The solutions range from suggestions for the consumer to for example buy more energy efficient products, to larger things like the energy sector moving towards green and renewable resources. While it may be relatively easy for consumers to buy more energy efficient products, this only reduces the problem if fossil fuels continue to be used. The move to green and renewable resources offers a solution which in theory could eliminate both the supply problem and a large amount of the greenhouse gasses [1].

Electricity that is made from sources that are both green and renewable usually have a significant obstacle. The obstacle is that the energy production doesn't always match the times for when energy is needed and therefore is reliant on energy storage. Research by both industry and academia is being done to find the best possible solution to this problem [1]. One promising technology is fuel cells. Fuel cells are electrochemical devices that can convert the energy locked up in chemical bonds to electrical energy at high efficiencies. The high efficiency is achieved by converting a fuels chemical energy to electrical energy in a single step. Conventional internal combustion engines (ICE) rely on multiple steps for converting a fuels chemical energy to mechanical or electrical energy. ICEs are therefore inherently inefficient as energy is lost during each step. A fuel cells efficiency is scalable and offers higher efficiencies at both full and partial operational loads. The CO₂ emissions of a fuel cell when run on carbon-based fuels, like methane, is due to higher efficiency lower. The emissions are also free from additional pollutants like nitrogen oxides and completely emission free when operating on hydrogen [2].

The most widespread fuel cell technology is the proton exchange membrane fuel cell abbreviated as PEMFC or just PEM [3]. The PEMFC has a relatively low operation temperature and has a short start up time [4]. The fuel used is hydrogen, but due to the low operation temperatures an expensive catalyst is required. The catalysts durability against impurities in both air and fuel is low due to potential surface poisoning. The application of PEMFC is therefore limited to use with relatively pure hydrogen and air [5]. Another more versatile type of fuel cell is the solid oxide fuel cell (SOFC). The operation principles are the same as for PEMFC, but since SOFCs operation temperature

is higher a catalyst is not required. The high operation temperatures means that SOFCs have a longer startup time, but also that the fuel flexibility is higher. SOFCs can operate on hydrocarbon and hydrogen fuels [6]. The SOFC can therefore be used with the current hydrocarbon fuel infrastructure and then later with hydrogen for emissionless power generation.

SOFCs are interesting because they as mentioned can be used for efficient power generation. They are however also interesting because they can be used for long term energy storage, and reversible operations for grid support. For power generation the SOFC runs in fuel cell mode where a fuel is used to generate electricity. For long term storage applications, a SOFC can be operated reversely as a solid oxide electrolysis cell (SOEC), where electricity is consumed to produce a fuel like hydrogen from water. The fuel can then be stored and used at a later time in fuel cell mode. This ability to operate reversible makes the technology a prime candidate for helping the move towards renewables. Operating reversible allows for energy storage when demand is low and energy production when demand is high, independent on weather or time of the day [7].

The commercialization potential of SOFC technology is, due to the before mentioned, significant but cost and lifetime are currently two of the things holding it back. A vital part of a SOFC is interconnects which are what electrically connects the individual cells of a fuel cell stack. These interconnects are also one of the main contributors to the cost of a SOFC and their degradation [8],[9]. Historically ceramic materials have been used for the interconnects, but today ferritic stainless steels (FSS) are used. The FSS interconnects are more cost-effective than the ceramics, but degrade under the harsh operation temperatures in an SOFC. As the FSS degrade certain corrosion phenomena have been observed to occur, like chromium evaporation and continuous oxide scale growth. These phenomena negatively affect the performance of the SOFC as the chromium vapor poisons the cathode and the oxide scale increases the electrical resistance of the FSS. Coatings of the FSS have proven to be effective in suppressing the formation of chromium vapor and the oxide scale growth. Coating FSS alloys have proven so good at suppressing the vaporization and growth that cheaper low FSS alloys display the same mass gain as more expensive high alloys [7], [10].

1.2 Aim of The Thesis

The thesis acts as a continuation of research that has been done to make SOFCs more commercially viable. More specifically it will focus on the concerns surrounding the lifetime of the interconnects that electrically connects the individual cells in series to form fuel cell stacks. The thesis will be based on findings that show similar net mass gain for different FSS alloys in the same environment at 800°C when they have been coated with Ce/Co, see Figure 1.1a and Figure 1.1b. The thesis intends to further explore these findings at different temperatures and make a model that can assist with predicting the lifetime of FSS interconnects. Moreover the thesis aims to improve the understanding of the beneficial effect, of cerium, in the Ce/Co coating, which reduces the oxide scale growth.

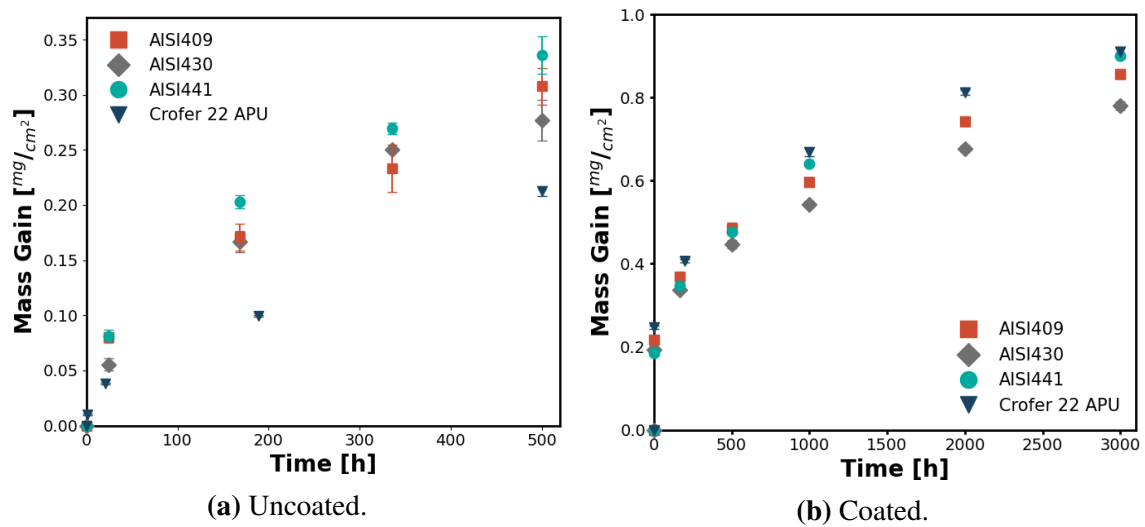


Figure 1.1: (a) Findings from previous research showing different uncoated alloys having different mass gain profiles. (b) Findings from previous research showing different coated alloys having similar mass gain profiles. Applied coating consisted of 10 nanometers of cerium and 600 nanometers of cobalt [10].

1.2.1 Research Questions

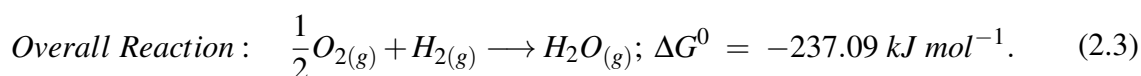
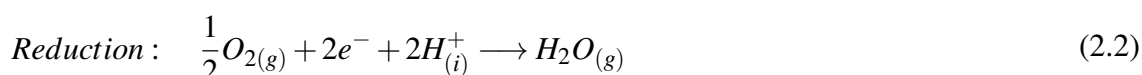
The goal of the project is to gain an improved understanding of coated FSS oxidation mechanisms by exposing different FSS to SOFC operating conditions. The findings will be used to make a predictive lifetime model. The following research questions will be reviewed to conclude the goal:

- In what temperature range is it possible to predict lifetime?
- Will FSS show similar oxidation mechanisms at 900°C as at 800°C?
- Is it possible to establish the direct correlation between lifetime and chromium content?
- What benefits, if any, does a thick Ce/Co coating provide over a thinner one?
- What is the cause of the beneficial effect gained from Ce in the Ce/Co coating?

2 | Background

2.1 Fuel Cells

The information presented in this section is primarily based on books by Paul Breeze [11], and James Larminie and Andrew Dicks [12]. Fuel cells are electrochemical devices. Comparisons can be made to batteries in that they both use energy from a chemical reaction to generate electricity, thereby the word electrochemical. In contrast to batteries fuel cells have the chemicals needed for the generation of electricity supplied externally. While this might make fuel cells sound complex the operation principle is simple. The operation principle can be explained by visualizing a fuel cell as a construction made of three parts; an electrolyte and two electrodes. The electrolyte separates the two electrodes and is a semipermeable membrane that allows ions through but not electrons. High ion conductivity and low electron conductivity are the two main requirements for the electrolyte. To understand why these properties are needed an understanding of what goes on at the electrodes is required. The two electrodes are not identical, one is a cathode and the other is an anode. At the cathode reduction takes place and at the anode oxidation takes place. Equation 2.1 and 2.2 show the individual reactions taking place at the anode and cathode for a standard hydrogen fuel cell. By looking at Equation 2.1 and 2.2 it is apparent that electrons have to migrate from the anode to the cathode and that hydrogen ions need to move from the cathode to the anode for Equation 2.3 to be true. Since the electrolyte that separates the electrodes allows ions to pass through hydrogen ions can freely pass through to the other side. Electrons are not as lucky as the low electron conductivity of the electrolyte forces the electrons to move through an external circuit. It is this forced flow of electrons that makes it possible to harness the chemical potential as an electrical current [11], [12].



The overall reaction seen in Equation 2.3 can be described by ΔG^0 , which is the Gibbs free energy under standard conditions (298 K, 1 atm) for 1 mol of H_2O , but also by the standard cell potential E_{cell}^0 . The standard cell potential describes the reaction's maximum electrical potential while ΔG^0 describes "the energy available to do external work while neglecting any work done by changes in pressure and/or volume" [11], [12]. The two quantities are related accordingly (Equation 2.4):

$$\Delta G^0 = -nFE_{cell}^0, \quad (2.4)$$

where n is the number of electrons involved in the overall reaction and F is the Faraday constant. The standard cell potential is the total cell potential of Equation 2.3 and is therefore defined by the standard so-called half-cell potentials of Equation 2.1 and 2.2:

$$E_{cell}^0 = E_{ox}^0 + E_{red}^0. \quad (2.5)$$

The potentials are measure by measuring the difference in potential between the working electrode and a reference electrode. A common reference electrode is the standard hydrogen electrode (SHE). The potentials for the reactions in Equation 2.1 and 2.2 are $E_{ox}^0 = 0V$ vs SHE and $E_{red}^0 = 1.23V$ vs SHE giving a standard cell potential of $E_{cell}^0 = 1.23V$ [13]. At conditions different from standard conditions, cell potential can be calculated using the Nernst equation [14]:

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln Q, \quad (2.6)$$

where T is the temperature, R the gas constant, and Q a coefficient for the activity of the reactants and products of the reaction defined as:

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}. \quad (2.7)$$

Equation 2.7 is based on the basic chemical equation: $aA + bB \longrightarrow cC + dD$. The cell potential of 1.23V vs SHE is the theoretical value but in reality, the useful potential of Equation 2.3 is around 0.7V vs SHE [12]. This voltage drop is due to four major irreversible processes: Activation losses, Fuel crossover and internal currents, Ohmic losses, and Mass transport or concentration losses [12]. Activation losses are a result of the energy required to drive the chemical reaction that transfers electrons to or from the electrode. Fuel crossover and internal currents refer to the energy lost due to the diffusion of fuel through the electrolyte and potential electron conduction of the electrolyte. The Ohmic losses are simply due to the combined electrical resistance of the electrodes and interconnect. Mass transport or concentration losses are voltage losses caused by the change in reactant concentration at the electrodes as fuel is consumed [12]. As illustrated in Equation 2.6 the cell potential is affected by the effective concentration of reactants. The low voltage of a single fuel cell means that individual fuel cells need to be connected to get a useful voltage. A system of multiple connected cells is called a stack. In a stack, the fuel cells are connected by interconnects as seen in Figure 2.1. The requirements for the interconnects vary for different types of fuel cells but common is that the interconnect needs to be good conductors since even a small voltage drop is important with a cell voltage of 0.7V [11], [12].

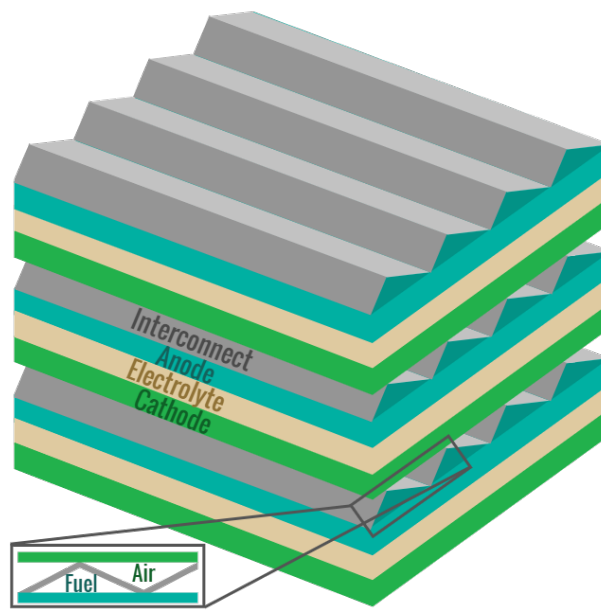


Figure 2.1: Fuel Cell Stack [12].

2.1.1 Fuel Cell Families

In their books P. Breeze [11], J. Larminie and A. Dicks [12] explain the basics of a fuel cell, but also the problems and the different types of fuel cells. They explain that fuel cells as a technology have some inherent problems. The main problem with fuel cells is that while energy is being released at the anode the reaction doesn't proceed at an unlimited rate. The reaction has an activation energy barrier that needs to be overcome for the reaction to proceed. The probability of a molecule in a fuel cell having enough energy to overcome the barrier is low, which means that the reaction will proceed slowly. A slow reaction rate leads to a low current. The main strategies for dealing with the slow reaction rate are to use a catalyst, raise the temperature, and increase the surface area of the electrodes. The catalyst will help by lowering the energy barrier and an increase in temperature will result in an increase of collisions among the reactants and an increase in the number of reactant molecules with sufficient energy to overcome the activation energy barrier. Increasing the electrodes surface area increases the area of reaction. The oxidation and reduction take place on the electrodes as electrons either need to be removed or added to the reaction as seen in Equation 2.1 and 2.2. Another problem is that hydrogen currently is not a readily available fuel.

To mitigate these problems different fuel cells designs have been proposed and five of the more popular ideas are alkaline fuel cell (AFC); polymer electrolyte membrane fuel cell (PEMFC); phosphoric acid fuel cell (PAFC); molten carbonate fuel cell (MCFC); solid-oxide fuel cell (SOFC). The differences, in regards to temperature and chemicals, can be seen in Figure 2.2. These fuel cells mainly differ in their electrolyte which then influences the operation temperature, fuel flexibility, and cost [11], [12]. The low-temperature fuel cells (AFC, PEMFC, and PAFC) operate at temperatures so low that they can't achieve practical reaction rates at the cathode and anode without a noble metal electrocatalyst like platinum. The high-temperature fuel cell (MCFC and SOFC) do not have the same need

and the higher temperature allows for the use of different kinds of fuels [15].

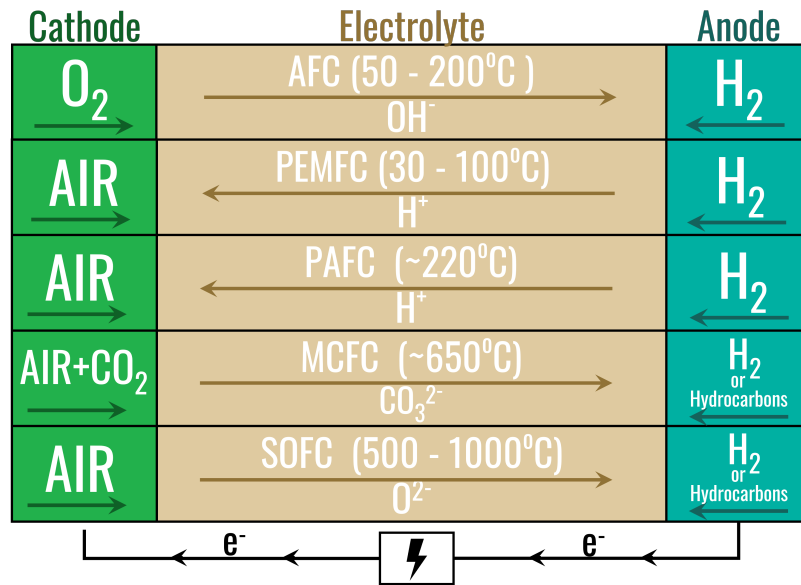


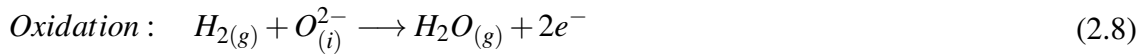
Figure 2.2: Different fuel cell families [12].

As of 2019 the two most widespread fuel cell technologies are PEMFC and SOFC [3]. While they are the most widespread technologies they do not share many similarities. The electrolyte in the PEMFC is a polymer electrolyte membrane, also known as a proton exchange membrane, and it enables the permeation of hydrogen ions. The operation temperature of a PEMFC is $<100^\circ\text{C}$ which allows for fast start-up, but also means that an expensive platinum catalyst is needed for operation [12]. The PEM electrolyte also demands a pure H_2 fuel free of CO contaminants. The SOFC has a solid oxide electrolyte that enables the permeation of oxide ions. To achieve satisfactory ion conductivity with this electrolyte the operation temperature needs to be high and is usually in the 500°C to 1000°C range [12]. This high temperature negates the need for an expensive catalyst for the reactions to occur at a satisfactory rate. The solid oxide electrolyte is more flexible in what type of fuel can be used as not only a contaminated H_2 fuel can be used but also hydrocarbon fuels like ethanol, methanol, and diesel reformat [16]. The fuel flexibility is a great benefit for the SOFC since the infrastructure for these fuels is well developed and widespread [17]. Using hydrocarbon-based fuels does however result in the formation of CO_2 . While not ideal a SOFC release less CO_2 than a conventional internal combustion engine, due to not being limited thermodynamically by the Carnot cycle [12]. Not being limited gives SOFC a higher electrical efficiency than those of combustion engines. The electrical efficiency is also higher than that of other fuel cells with reported efficiencies of up to 60% [18], while they for PEMFC has been reported to be 50% [19]. A SOFC plant can furthermore achieve an overall fuel efficiency of up to 90%, or more, by harnessing the waste energy through for example feeding it into central heating systems [16]. The high temperature does not only offer benefits. The high temperatures cause issues with material degradation and slow start-up times. The slow start-up time limits the applications of the technology, and it is most viable for stationary applications, range-extenders, or auxiliary power units in trucks or similar. The bigger problem that arises from operat-

ing at high temperatures are those related to material degradation. Material degradation is undesirable since it leads to fuel cell failure [11], [12].

2.2 Solid Oxide Fuel Cell

The SOFC has a solid oxide electrolyte that conducts oxide ions. The electrolyte remains solid even in the higher operating temperature range. As both the electrodes are solid as well, the SOFC device is a relatively simple systems as only gas and solid phases are required to describe it. That the electrolyte conducts oxide ions means that the anode and cathode reactions are different from Equation 2.1 and 2.2. When hydrogen is used as fuel Equation 2.8 and 2.9 are the SOFC anode and cathode reaction, the overall reaction is the same as Equation 2.3 [20].



The operation principle of the SOFC can be seen in Figure 2.3, where the movement of the reactants and products from Equation 2.8 and 2.9 is illustrated. Since the overall reaction is the same as in Equation 2.3 the standard cell potential is therefore also the same. This means that SOFC, using hydrogen as fuel, also produces a voltage less than 1V per cell. SOFC cells are therefore also stacked as seen in Figure 2.1 to produce a useful voltage [20].

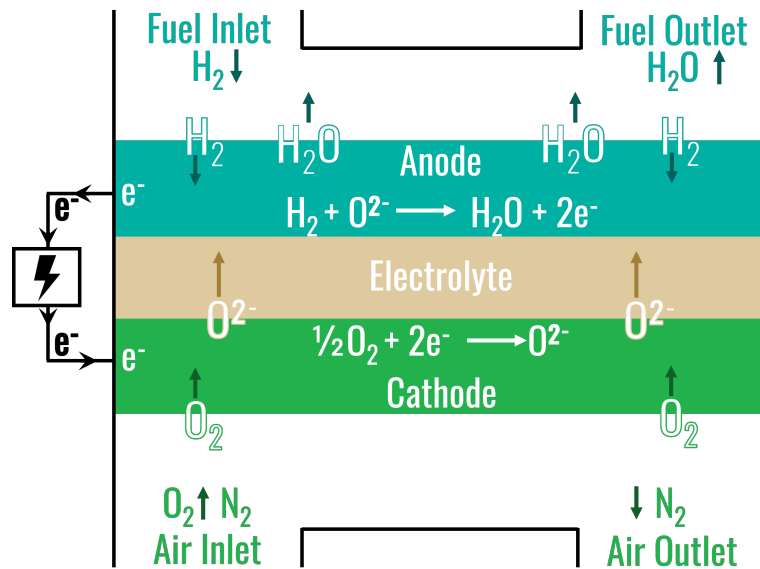


Figure 2.3: Solid Oxide Fuel Cell Operation Principle [20]

As illustrated in both Figure 2.1 and 2.3 the anode, cathode, electrolyte and interconnect are in contact with each other. The proximity of the parts and the environment they are put in during operation require them to fulfill certain requirements. Each part has unique

requirements they must fulfill to enable desirable operation, but a common requirement for the anode, cathode, electrolyte, and interconnect is that they must have a similar thermal expansion coefficient (TEC). Differences in TEC can result in a build-up in thermal stresses during the heating cycles and ultimately reduce the lifetime of the cell. Other more specific requirements will be discussed in the following [12], [20].

Electrolyte: As mentioned in Section 2.1 the two most important properties of a fuel cell electrolyte are high ion conductivity and low electron conductivity, to divert the electrons into an external circuit. This is also the case for the solid oxide electrolyte used in a SOFC. In addition to this, the electrolyte needs to be stable at high temperatures and in an environment with the anode atmosphere on one side and the cathode atmosphere on the other. The electrolyte also needs to be dense and non-porous as to not allow the different atmospheres to mix. The electrolyte needs to be inert to the molecules in the different atmospheres, but also inert to the anode and cathode materials. Many oxide formulations have been investigated to find a suitable material. The most commonly used materials that fulfill the requirements are oxides which crystallize in fluorite- or perovskite structure. Materials that have been investigated are among others Ba_2O_3 , CeO_2 , Ta_2O_5 , LaGaO_3 , yttria-stabilized zirconia (YSZ), and gadolima-doped ceria (CGO). YSZ is one of the best electrolyte materials due to its good stability, low electron conductivity, and acceptable oxide ion conductivity above 800°C . SOFC development is currently exploring the possibility to go to lower operating temperatures due to complications associated with high temperatures. The lower temperature limit for use of YSZ electrolytes is based on conductivity and mechanical properties 700°C . At temperatures below this Scandia-doped zirconia offers a higher ion conductivity and at temperatures in the 550°C range, CGO is preferred [12], [21].

Anode: The anode is the surface upon which fuel oxidation occurs according to Equation 2.8. The anode material therefore first of all needs to be catalytically active towards Equation 2.8 and provide sufficient active sites for the before mentioned oxidation during operation. The anode also needs to be made of a material that is stable at high operating temperatures and in a wide range of oxygen partial pressure. The oxygen partial pressure varies from fuel inlet to outlet due to increased levels of H_2O towards the outlet (Figure 2.3). In Equation 2.8 three phases are present: gas phase, an intermediate phase for transport of the oxide ions, and a phase to carry the electrons to the external circuit. Based on the phases present the requirements of the anode material can be understood. To transport the hydrogen gas to an active site the material needs to be porous and to move the oxide ions as well as electrons the materials need to have ion and electron conductivity. Porosity allows for good transport of reactants and products through the anode and also has the benefit of providing a larger surface area which results in more active sites. To solve the need for high ion- and electron conductivity, composites made of a material with high ion conductivity and a material with high electron conductivity have been investigated. The materials that make up the composite are commonly a good electron conductor mixed with the material of the electrolyte, which is a good ion conductor. These composite materials are called mixed ionic-electronic conductors (MIECs). Using the same material as that of the electrolyte also ensures that the TEC is relatively similar. Using a composite made of two materials that serve different purposes requires

the design of the micro-structure to provide a large triple-phase-boundary (TPB) area so that the area on which the reaction can occur is as large as possible. A commonly used composite is Ni-YSZ cermet which is a so-called heterogeneous MIEC (H-MIEC) [12], [22], [23].

Cathode: The cathode is the surface upon which the oxygen dissociation reaction seen in Equation 2.9 occur. The cathode material needs to fulfill similar requirements to the anode with one exception which is that the cathode mainly has to be stable in an atmosphere with a high oxygen partial pressure. Like the anode, the cathode needs to be catalytically active, but towards the reduction of oxygen seen in Equation 2.9 and be stable at the high operating temperatures. In Equation 2.9 the same three phases discussed in the anode section are present meaning that the cathode also needs to be porous and have high ion- and electron conductivity. The cathode also needs to be inert towards the air and compatible with the other cell components. The requirement of high ion conductivity is not always fulfilled. Strontium-doped LaMnO₃ (LSM) is a commonly used cathode material and is sufficient for most SOFCs, but has a low ion conductivity in the range of $5.3 \times 10^{-4} \frac{S}{cm}$ to $6.3 \times 10^{-4} \frac{S}{cm}$ at 800°C. Compare that to YSZ which, depending on oxygen partial pressure and density, has an ion conductivity between $10^{-1} \frac{S}{cm}$ to $10^{-0} \frac{S}{cm}$ at 800°C [22] [24]. The low ionic conductivity limits the active area to the interface between the cathode and the electrolyte and therefore the electrolyte material, often YSZ is used to create a LSM/YSZ composite that increases the TPB. LSM has another problem which is that it is severely affected by CrO₂(OH)₂ vapor, which can form when chromia from a metallic interconnects reacts with oxygen and water. CrO₂(OH)₂ vapors affect LSM severely because LSM has a limited TPB area and this is the preferential site for CrO₂(OH)₂ to deposit. The before mentioned problems with LSM and relatively high activation energy for oxygen reduction on LSM have led to efforts into developing MIEC materials to solve the problems. Materials that receive attention are primarily p-type conducting perovskite structures, which also have improved performance at lower temperatures, but some compatibility issues [12], [25].

Interconnect: The interconnect is as mentioned earlier what electrically connects individual cells to form a stack, see Figure 2.1. The requirements of the interconnect material are similar to that of the electrolyte in that it needs to be able to withstand high temperatures and the different atmospheres present on the cathode and anode side while having a similar TEC to the rest of the components [12]. Interconnects differentiates from the electrolyte in that it needs to have a high electron conductivity and a low ion conductivity [12]. The interconnect also needs to be non-permeable to the gaseous molecules in the two atmospheres. Good thermal conductivity and high chemical stability towards the anode and cathode materials are also important properties [12]. The primary function of the interconnect is to provide the external circuit, but as exemplified in Figure 2.1 the interconnect also distributes the gasses throughout the cell. The distribution of the gasses is the secondary function, but an important function that is easiest fulfilled if the interconnect material is shapeable. The distribution channels can be designed in a multitude of ways to minimize pressure drops, temperature gradients, and gas composition throughout the cell [12], [26].

The interconnect material selection is important as more than 70% of the electrical losses

in a SOFC system are due to interconnect design [27]. Traditionally ceramic materials, especially perovskites on the basis of LaCrO_3 doped with either calcium or strontium, have been used for interconnects [28]. The conductivity of LaCrO_3 is dominated by electron and positive hole contributions to an extent that gives it comparable conductivity to that of metals [28]. A high cost of raw material and manufacturing, problems with obtaining high density LaCrO_3 , brittleness (making shaping difficult), and a trend within the SOFC community of lower operating temperatures due to advances in electrolyte and electrode materials, have reduced the viability of LaCrO_3 [27]. The advancements of electrolyte and electrode materials have resulted in operation temperatures in the range of 700°C to 850°C to be more common and have enabled the use of metallic materials for interconnects [27]. Metallic materials have the potential of providing higher electrical- and thermal conductivity, easier fabrication, and cheaper manufacturing [26]. The most promising metallic materials are stainless steels or more specifically FSS, due to TEC limitations [29]. The problem associated with using FSS is however that it degrades under the aggressive conditions present during operation. Temperatures above 600°C are high for steels and combined with both high and low partial oxygen pressures corrosion is inevitable. While corrosion can not be avoided it can be limited by designing the FSS to form a slow-growing protective oxide on top of the material. The protective oxide should form on the top of the material as a barrier towards the atmosphere, while ideally not affecting any of the FSS properties. Al_2O_3 and Cr_2O_3 (Chromia) are both protective oxides, but while they have comparable thermal conductivity, Al_2O_3 is an electrical insulator while chromia is a semiconductor. Therefore chromia is better suited for FSS interconnects. While the steel is protected from heavy corrosion by the chromia scale, evaporation and deposition of Cr(VI) species from the oxide scale leads to rapid degradation of the cell performance. The performance loss is mainly due to chromium poisoning of the cathode and the cathode/electrolyte interface. Common features of considered interconnect FSS alloys are a high concentration of chromium, that ensures a sufficient chromium reservoir for chromia formation, addition of manganese to promote formation of a MnCr_2O_4 spinel oxide scale that reduce chromium evaporation, and addition of a reactive element to improve oxide scale adhesion. The chromium evaporation can other than by adding manganese be reduced by coating the alloy, see Section 2.7 [12], [27], [29].

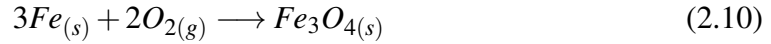
2.3 Oxidation Theory

An important phenomenon that occurs at high-temperature is oxidation. When alloys and pure metals are exposed to high temperatures in an oxidizing environment they oxidize. When discussing high-temperature corrosion (HTC), high temperature as a term is defined as a temperature where water if present will exist as vapor rather than liquid [27]. Relative to room temperature corrosion HTC is characterized by the high rates at which the corrosion products are formed and strong material degradation [27]. Corrosion at low temperatures primarily occurs when an oxidizing agent, an electrolyte, and a metal are present, but at high temperatures, corrosion may occur even without an electrolyte. The phenomenon is sometimes referred to as "dry corrosion". Gases that classify as oxidizing include O_2 , SO_2 , H_2S , H_2O , and CO_2 with O_2 being the most common oxidant. High-

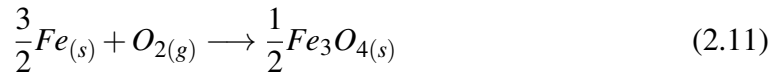
temperature oxidation usually occurs in the range of a few hundred degrees Celsius and above. The operating temperatures of SOFCs fall within this interval meaning that the FSS interconnects will corrode even in the absence of an electrolyte [30].

2.3.1 Thermodynamics of High-Temperature Oxidation

Oxidation of a metal with O_2 as the oxidizer proceeds by a chemical reaction similar to Equation 2.10 showing the oxidation of iron to Fe_3O_4 [30]:



The ΔG° of Equation 2.10 is given by the standard free energy of formation, ΔG_f° of Fe_3O_4 . The reason for this is that the reactant elements form one mole of Fe_3O_4 . The ΔG_f° can be calculated using tabulated values for the entropy- and enthalpy of formation for the products and reactions. At 800°C the ΔG_f° of Fe_3O_4 is -745.76 kJ/mol . A negative value means that at 800°C the oxidation reaction, Equation 2.10, will occur spontaneously. The free energy change can also be calculated per mole of O_2 , so Equation 2.10 becomes 2.11, which make comparing different oxides' thermodynamic behavior simpler[30]:



The change in Gibbs free energy for Equation 2.11 at 800°C is -372 kJ/mol . A tool used to illustrate different oxides' free energy change per mole of O_2 is the Ellingham diagram. The Ellingham diagram is a diagram that shows the free energy change of oxides versus temperature, Figure 2.4 [30].

Each point in Figure 2.4 can be calculated using equation 2.12 with tabulated thermochemical data. The oxidation reactions leading to the oxides shown in the diagram are spontaneous at all temperatures where the corresponding y-value is negative. The slope of each line, gives the standard change in entropy from 2.12, as so $\Delta G^\circ/dT = -\Delta S^\circ$ [30].

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.12)$$

The standard change in entropy is therefore negative for all the oxidation reactions forming the oxides shown in Figure 2.4. The formation of a solid oxide from metal and oxygen leads to a system with higher order than the reactant system, which explains why the formation of the oxides becomes less spontaneous as temperature increases [30].

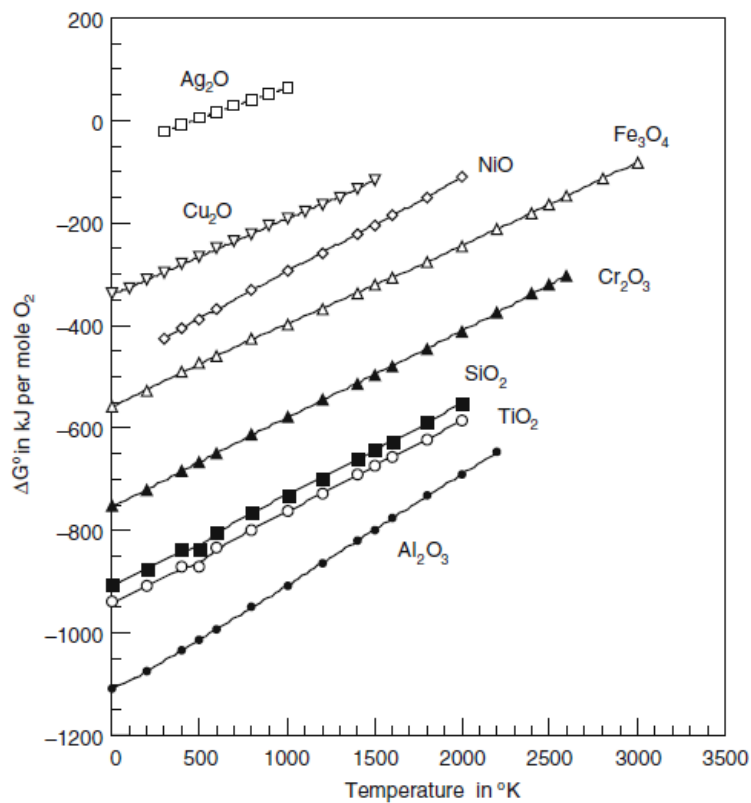


Figure 2.4: Ellingham diagram showing the free energy change of various oxides (per mole O_2) against temperature [30].

2.3.2 The Ellingham Diagram

The data presented in the Ellingham diagram is as mentioned calculated based on one mole of O_2 . Of the oxides seen in Figure 2.4 Al_2O_3 is the most stable, because the oxidation reaction has the largest decrease in free energy. The Ag_2O oxide is the least stable since it has the lowest decrease in free energy and as the Gibbs free energy becomes positive at temperatures above $\approx 180^\circ C$ ($450K$) oxidation is not spontaneous at those temperatures. Ellingham diagrams, Figure 2.4, have limitations to their use since they contain information about the tendencies of the reactions to occur but do not account for the kinetics of the reactions [30]. The tendencies that Figure 2.4 show are however useful, despite their limitations, as they can provide information about the behavior of an alloy based on its composition. Iron and nickel are major components of engineering alloys and Figure 2.4 illustrates that their corresponding oxides are less stable than the oxides formed of chromium, aluminium, and silicon. Chromium, aluminium, and silicon are alloying elements that therefore can be added to provide increased protection against oxidation of the alloy at high temperatures.

2.3.3 Equilibrium Pressure of Oxygen

Oxygen is the most common oxidant so in the majority of cases, oxygen needs to be present for metals to oxidize at a certain temperature [30]. The oxygen does not only need to be present, but also be present in a certain quantity. The amount of oxygen

needed is usually given as the equilibrium pressure of oxygen required for a certain metal to oxidize at different temperatures. The pressure of oxygen in equilibrium with the metal can be calculated with 2.13 [30],

$$\Delta G^\circ = -RT \ln(K). \quad (2.13)$$

The expression for the equilibrium constant K is the same as the expression for Q in Equation 2.7. The difference between them is that the reaction coefficient Q is calculated at non-equilibrium conditions. K will for Equation 2.11 for example be,

$$K = \frac{a_{Fe_3O_4}^{\frac{1}{2}}}{a_{Fe}^{\frac{3}{2}} p_{O_2}} = \frac{1}{p_{O_2}}. \quad (2.14)$$

The density of pure solids and liquids can be regarded as constant at a certain temperature and will only change at a significant temperature or pressure change, assuming that no phase changes occur. This means that the activity of pure solids and liquids normally are unity (the number 1) [30]. The simplification of K gives the simplified version of Equation 2.13,

$$\Delta G^\circ = RT \ln(p_{O_2}). \quad (2.15)$$

Using the $\Delta G_f^\circ = -372$ kJ/mol value for Fe_3O_4 at $800^\circ C$ gives $p_{O_2} = 7.8 \times 10^{-19}$ atm, which is the oxygen partial pressure where the metal and the oxide is in equilibrium known as the dissociation pressure. At pressures above the dissociation pressure the metal will oxidize, but at pressures below the metal is stable, and formed oxide will be reduced. From Equation 2.15 it is apparent that the dissociation pressure is a function of temperature and will increase with temperature. The dissociation pressure argument for oxidation only contains information about the tendency for the occurrence of oxidation and not the kinetics of the oxidation [30].

2.3.4 Oxidation

The Ellingham diagram and the oxygen partial pressure can be used to describe scenarios where the oxidized form of a metal is the thermodynamically stable form. The oxide being the most thermodynamically stable form does however not mean that it will be the prevalent one due to the kinetics of oxidation reactions like Equation 2.11. The kinetics determine how fast the oxide scale will grow and therefore can be used to estimate the time for material failure or time till other issues associated with oxide scale growth. Since the kinetics can provide information about the state of a metal, it is an important concept to understand [30], [31]. Oxidation reactions like Equation 2.11 occur through three steps. The steps are illustrated in Figur 2.5 and are the same for oxidation of all pure metals.

The first step is oxygen adsorption where oxygen from the environment adsorbs onto the metal surface, and the second step is metal-oxide nucleation. The rates of steps one and two are highly dependent on the metal surface so can vary depending on surface preparation, surface defects, and impurities in the metal or the gas. Step two leads to the formation of a continuous oxide scale on the metal, which when formed leads to

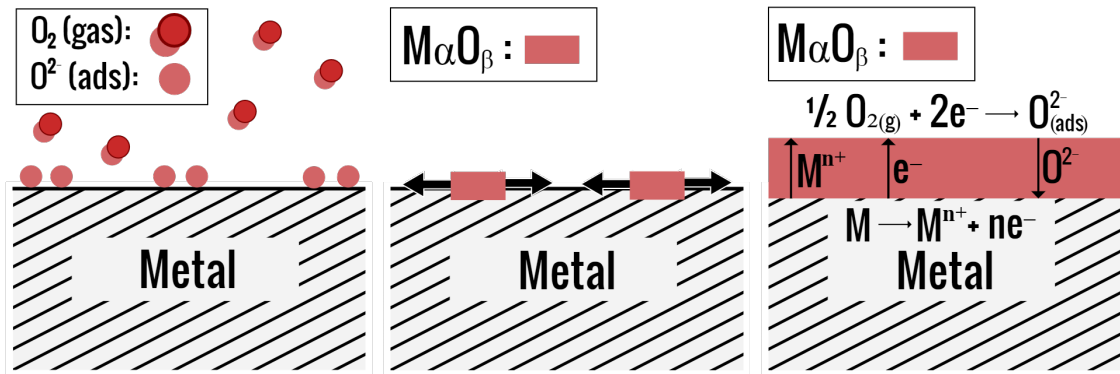


Figure 2.5: The three steps (Left - Step 1) Oxygen Adsorption, (Middle - Step 2) Oxide Nucleation, (Right - Step 3) Continuous oxide scale growth. M=Metal; O=Oxygen; α & β = Number of their respective elements in the molecule [32].

step three, scale growth. The rate at which the scale growth occurs is dependent on the solid-state diffusion of ions and electrons through the oxide scale, as illustrated in Figure 2.5. This means that the oxide must be ionic and electronic conductive to grow. The electron conductivity is usually higher than that of the ions making the ion diffusivity the rate-limiting for step three [30]. For common base metals Fe, Cu, Cr, Ni, and Co the rate-limiting step is outward cation diffusion, while it for refractory metals Nb, Ta, Hf, Ti, and Zr is inward anion diffusion of O^{2-} [30]. Steps one and two typically occur swiftly at high temperatures making the third step the most common rate-determining step. When the third step is the rate-determining and the rate of scale growth is low the scales act as a protective layer separating the metal and the oxygen. The characteristics of a protective oxide are high density, high stoichiometry, low porosity, and low diffusivity of the metal and oxygen ions. In certain environments some metals can form porous oxide scales that do not act as a solid-state diffusion barrier, making either step one or two the rate-determining step [30], [31].

2.3.5 Rate Laws

The study of high-temperature oxidation kinetics is usually done by exposing metal to high temperatures in a furnace, while periodically weighing the sample to determine the weight gained per area as the oxide is formed. The gain in weight is proportional to the thickness of the formed oxide scale. Unless certain conditions, resulting in evaporation phenomena or formation of different oxide scales, means other factors need to be evaluated as to not get a falsified mass gain [30], [31]. The kinetics of high-temperature oxidation is described mathematically using one of three main rate laws, illustrated in Figure 2.6. The rate laws are, linear, parabolic, and logarithmic. The growth behavior of oxide scales does not follow one perfectly and is in reality more a mix of the three rate equations [30], [31].

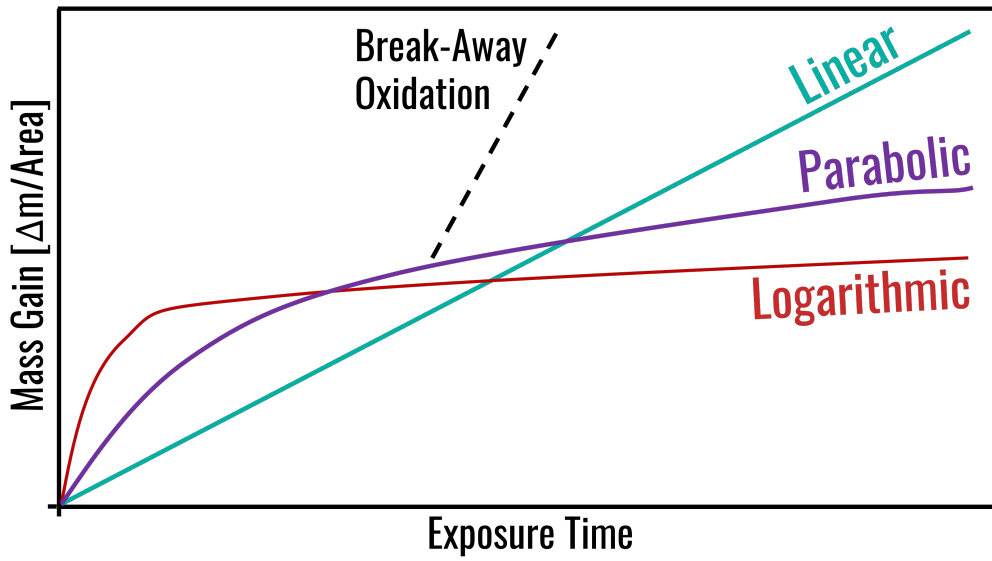


Figure 2.6: The three basic rate laws used to describe the typical behavior of an oxide scale growth [31].

The Linear Rate Law: The rate of oxidation is constant in the linear rate law:

$$\frac{dy}{dt} = k, \quad (2.16)$$

where t is the exposure time, y the thickness of the oxide scale, and k the rate of oxidation. The thickness of the oxide scale can be replaced with mass gain per area when the mass gain is proportional to the thickness, the same is the case for the other rate laws. The linear rate law is applicable when the reaction rate at the metal/oxide interface is constant. The oxide scales which growth follow the linear rate law are either highly porous or very thin to allow oxygen to reach the surface [30], [31]. Equation 2.16 can be rewritten and integrated to give the more familiar Equation 2.17:

$$y = kt + C, \quad (2.17)$$

where C is the integration constant, which value is the initial oxide scale thickness prior to exposure. The linear growth behavior illustrated in Figure 2.6 shows the mass gain increase continuously over time and materials following the linear rate law does therefore not form a protective oxide. The rate-determining step for scale growths following the linear rate law is either step one, step two (Figure 2.6), or determined by a phase boundary process [30], [31].

The Logarithmic Rate Laws: Oxide scale growth that follows the logarithmic rate law usually occurs at lower temperature, 300°C to 400°, and for oxide scales that have a thickness of 1000Å or less [30], [31]. Logarithmic scale growth can be described by two different equations, the direct logarithmic (Equation 2.18) and the inverse logarithmic rate law (Equation 2.19):

$$y = k_{\log} \log(At + 1), \quad (2.18)$$

$$\frac{1}{y} = B - k_{il} \log(t), \quad (2.19)$$

where t is the exposure time, k_{log} and k_{il} the respective logarithmic and inverse logarithmic rate of oxidation, y is the oxide scales thickness or the metals mass gain, and A and B are integration constants. The curve depicted in Figure 2.6 follows the direct logarithmic rate law. The rate determining step and the mechanisms behind the reduction in growth rate for oxides scales following the logarithmic rate laws, have not been agreed upon yet. Metals like Fe, Cu, Zn, Ni and others follow the logarithmic rate law during initial oxidation [30], [31].

The Parabolic Rate Law: The rate-determining step of oxide scales that follows the parabolic rate law is step three from Figure 2.5. Here the rate at which the oxidation happens is inversely proportional to the thickness of the oxide scale or the mass gain:

$$\frac{dy}{dt} = \frac{k'}{y}, \quad (2.20)$$

which if rewritten and integrated gives:

$$y^2 = k_p t + C, \quad (2.21)$$

where y is the oxide thickness or mass gain, t the exposure time, k_p the rate constant, and C the integration constant. The rate-determining step for scale growth that follow the parabolic rate law is solid-state diffusion through the oxide scale (Equation 2.5 [Right]). Growth following the parabolic rate law is often considered ideal in the formation of protective oxide scales. The reason for this is that in theory the ever increasing oxide scale thickness results in longer and longer diffusion times thus low growth rates at long exposures. A limitation of the parabolic rate law is that it does not describe the early stages of oxide scale growth well [30], [31].

Summation of Rate Laws: The oxidation rate of a certain scale does not only follow one of the laws as they have been found to frequently follow a combination. The reason for this can for an example be a change in the rate determining step. A commonly observed combination is that of the logarithmic rate law during initial oxidation and the parabolic rate law when a scale has formed. The three mentioned rate laws are shown in Table 2.1. In Table 2.1 a test for fit is listed which can be used to determine which rate law the oxidation follows [30], [31].

Table 2.1: Comparison of the three main rate laws for high-temperature oxidation [30].

Rate Law	Equation	Test for fit
Linear	$y = k \times t + C$	y vs. t is linear
Parabolic	$y^2 = k_p \times t + C$	y^2 vs. t is linear
Logarithmic	$y = k_{log} \log(At + 1)$	y vs. $\log t$ is linear ($\log t \geq 1$)
	$\frac{1}{y} = B - k_{il} \times \log(t)$	y vs. $\frac{1}{\log(t)}$ is linear ($\frac{1}{\log(t)} \leq 1$)

2.3.6 Temperatures effect on the oxidation rate

According to the Arrhenius equation (Equation 2.22) oxidation rates increase with temperature:

$$k = Ae^{-\frac{E_a}{RT}}, \quad (2.22)$$

where k is the rate constant, A a constant, R the gas constant, and T the temperature in degrees Kelvin. The activation energy E_a is the oxidation's energy barrier which needs to be overcome for the oxidation to occur. The Arrhenius equation can be rewritten as Equation 2.23 which allows for the determination of the activation energy E_a by plotting $\ln(k)$ against $\frac{1}{T}$ [30].

$$\ln k_p = -\frac{E_a}{RT} + \ln A \quad (2.23)$$

Another form to express Equation 2.23 is that of Equation 2.24 which enables easy calculations of unknown rate constants [30]:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2.24)$$

2.4 Oxide Properties

Oxides that follow the parabolic rate law are as mentioned limited by the third step shown in Figure 2.5, scale growth, which primarily is limited by the diffusion of ions through the existing scale. The growth can be caused by oxygen anions diffusing inwards, leading to an inward growing oxide scale, or metal cations diffusing outwards, which leads to an outwards growing oxide scale. The growth direction and the mechanism behind the growth are determined by the oxides defects [27].

2.4.1 Oxide Defects

No crystals are ideally built up and at any temperature, a certain crystal will contain different structural defects. Even Al_2O_3 and Cr_2O_3 which are highly stoichiometric have defects because the presence of defects at a certain concentration decreases the free energy of the crystal. This is because that while the formation of a defect requires energy there is a gain in entropy when forming one. The free energy in regards to the number of defects will therefore look similar to what is shown in Figure 2.7. The extent of non-stoichiometry and concentration of defects will depend on temperature, oxygen partial pressure and chemical components [27] [33].

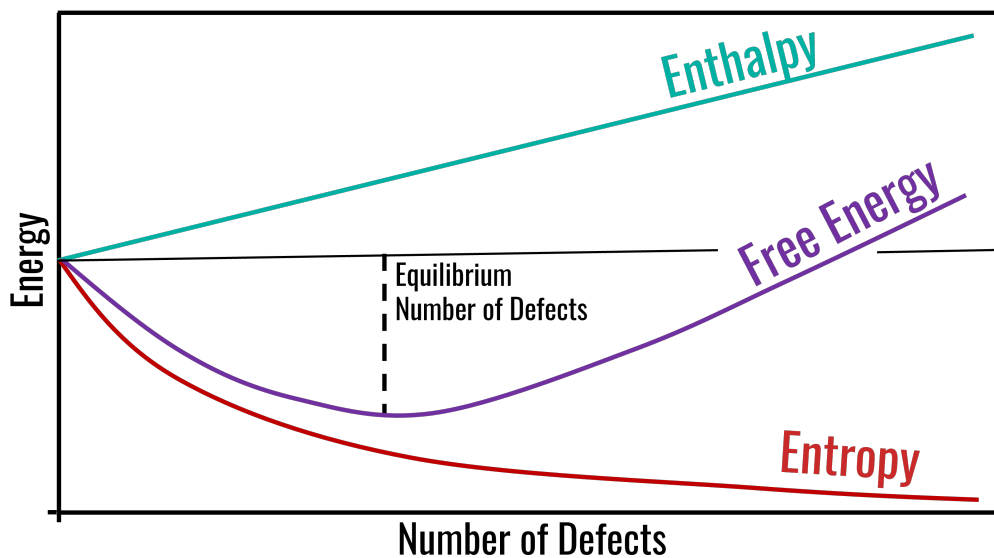


Figure 2.7: The energy of a crystal as a function of the amount of defects [33]

The types of structural defects can be divided into three main groups: Point defects; Line defects; and Plane defects. A crystal imperfection is termed a point defect if the defect is limited to one structural or lattice site and its immediate vicinity. Simple point defects are: empty sites or vacancies where constituent atoms should be but are missing; and interstitial atoms placed between the regular sites. Vacancies and interstitial atoms are commonly known as native point defects. Foreign atoms in a crystal structure, caused by e.g. doping are most often also considered point defects and called non-stoichiometric or extrinsic defects. The existence of one vacancy and one interstitial together, a so-called vacancy-interstitial pair, is called a Frenkel defect. A vacancy pair is known as a Schottky defect. Frenkel and Schottky defects are the two most common forms of so-called stoichiometric or intrinsic defects observed in oxides and are illustrated in Figure 2.8 [27] [33].

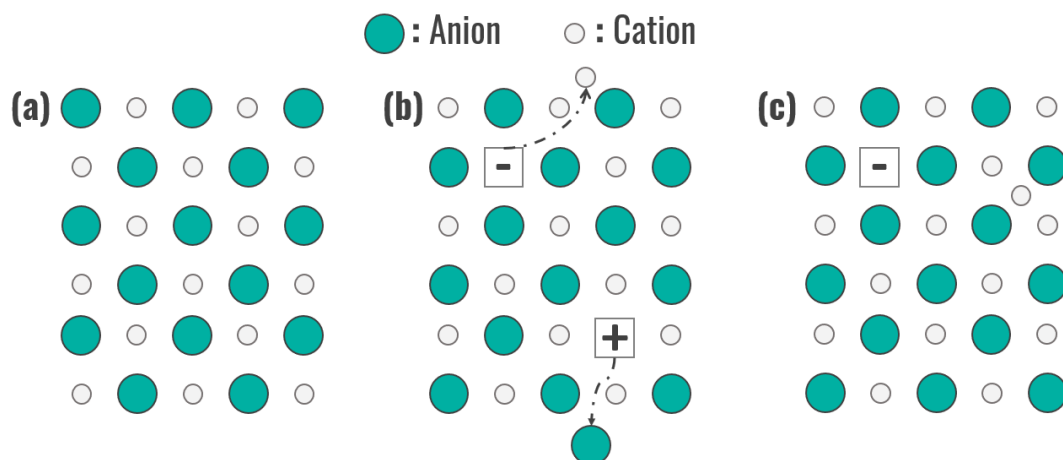


Figure 2.8: A two dimensional representation of (a) a perfect structure (b) a Schottky defect and (c) a Frenkel defect [33].

Line defects are characterised by displacements in the crystal periodic order in certain directions and are also known as dislocations. Plane defects are the imperfections in the crystal arising from: stacking faults; internal surfaces like grain boundaries; and external surfaces [27]. Each type of defect is responsible for a type of diffusion in the material. Point defects are responsible for lattice diffusion, line defects for short-circuit diffusion, while grain boundary and surface diffusion is the result of plane defects. In addition to the structural defects a crystal also has electronic imperfections. The electronic imperfections are electrons and electron holes that can move relatively free in the crystal. The electronic imperfections are what determines properties like electrical conductivity, thermoelectric power, electro-optical properties, and similar [27].

The diffusion rates of the different types of defect diffusion vary with type of defect and temperature. Lattice diffusion is the slowest form with the highest activation energy. Relative to lattice diffusion diffusion along the grain boundaries has a low activation energy and occurs much faster. The difference in activation energies make it so that grain boundary diffusion is dominant at lower temperatures while lattice diffusion dominates at higher temperatures. The dominance of lattice diffusion at higher temperatures is magnified by coarsening of grain boundaries at high temperatures [34]. The defects that form as an oxide scale grows can influence the growth direction. Figure 2.9 illustrates how the predominant defect determines whether the oxide is inward or outward growing. Depending on the predominant defect of the oxide, the oxide can be classified similarly to semiconductors into n- and p-type oxides as seen in Figure 2.9. The n-type oxides conduct electrons along the conduction band while p-type oxide conducts electron holes along the valence bands [7] [27]. The defect statements brought forward and the accompanying diffusion arguments are all valid for FSS alloys.

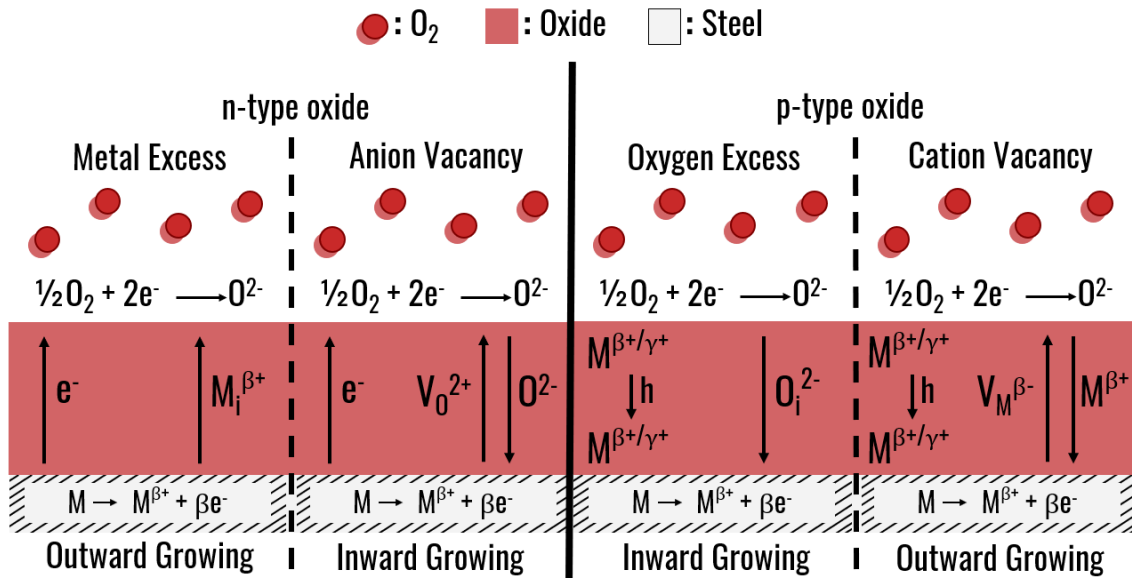


Figure 2.9: Illustration of the relationship between oxide defects and oxide growth direction. In the figure the following is the case $\gamma=\beta+1$, i=interstitial, V_x =vacancy at x lattice site, M=the oxidizing metal element, h=electron holes [7].

2.4.2 Pilling-Bedworth Ratio

The requirements and characteristics of a protective oxide scale was discussed in Section 2.3.4. An outdated but still commonly used equation used to asses whether a formed oxide is protective is the one formulated by N.B. Pilling and R.E. Bedworth, Equation 2.25. The equation relates the protectiveness of an oxide to the build-up growth stresses it can accumulate. The growth stresses are formed during oxidation and the equation describes stress level from the volume change associated with the transition from the metal lattice to the cation lattice of the oxide when only the oxygen anions are diffusing. The Pilling-Bedworth ratio (PBR) is therefore a ratio between the volume a metal ion takes up in the oxide (V_{Oxide}) over the volume the atom takes up in the metal (V_{Metal}) multiplied with the fraction of oxide formed on the scale surface (a) [27].

$$PBR = \frac{V_{Oxide}}{V_{Metal} \times a} \quad (2.25)$$

The limitations and the reason for why it is outdated is that it assumes that the growth direction of the oxide is inwards and that oxygen inward diffusion is the predominant diffusion mechanism. As shown in Figure 2.9 an oxide can grow in different ways than that. Where the PBR ratio is still useful is when it comes to the assessment of geometrically induced growth stresses. If the PBR ratio is less than one then the dominating growth stresses will be tensile causing pore formation or cracking of the scale. Is the PBR however larger than 1 compressive stresses dominates. Compressive stresses inhibits crack and pore formation and therefore oxides just above one should form protective oxide scales. Ratios much larger than one is expected to result in buckling of the oxide potentially causing spallation and exposure of the steel. PBR values for some metal-oxygen systems relevant for FSS are shown in Table 2.2 [27].

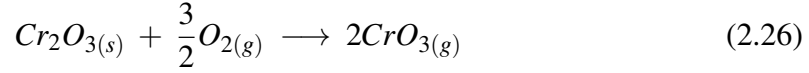
Table 2.2: PBR values for metal-oxygen systems. Iron oxide values are when on α -Fe. Values from [7] and [27]

Oxide	FeO	CoO	CeO ₂	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	Fe ₃ O ₄	Co ₃ O ₄
PBR	1.68	1.86	0.90	1.28	2.07	2.14	2.10	1.98

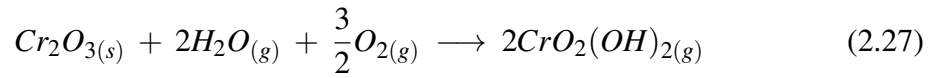
2.4.3 Volatility of Oxides

At very high temperatures some metal oxides exhibit high vapor pressure. When the vapor pressure of an oxide scale is high it becomes less protective. Wolfram, vanadium, platinum, rhodium, silicon, molybdenum and chromium are all metals which at high temperatures can form volatile species. Since the majority of the mentioned metals are not present in most FSS they will not be discussed in the following. Chromium is of major importance when it comes to making long lasting interconnects, but under certain exposure conditions complications arise with relying on it for protection. In principle the oxidation of pure chromium is a simple process to form the protective chromia scale. The complications arise after chromia has been formed and the two most important are scale

thinning and scale buckling. Chromia is considered stable in a dry atmosphere and at low oxygen partial pressure. At temperatures above 1000°C and $p(\text{O}_2) \geq 1$ the vaporization process of CrO_3 (see Equation 2.26) becomes a relevant factor for the life time of an alloy relying on the protective properties of chromia [7], [27].



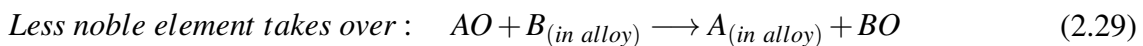
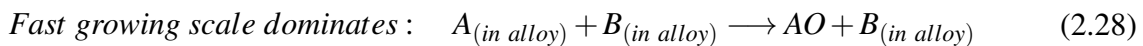
This process results in continuous consumption of the chromia scale and formation of a Cr(VI)-specie which are known to be carcinogenic. The consumption will lead to faster chromium depletion of the alloy and the evaporated species can poison the cathode in an SOFC. For SOFC operation with FSS interconnects operation temperatures of 1000°C are not reached and therefore the formation of CrO_3 is not that big of a concern. What however is more problematic is that under humid conditions another Cr(VI)-specie, $\text{CrO}_2(\text{OH})_2$ forms according to Equation 2.27 [7], [27].



The activation energy for the formation of $\text{CrO}_2(\text{OH})_2$ is lower than that of CrO_3 which means it can form at much lower temperatures. The lower temperatures means that chromium evaporation is a real concern and something that needs to be planned for when using chromia forming alloys [7], [27].

2.5 Oxidation of Alloys

An alloy can be defined as a metal made by combining metallic elements to achieve enhanced material properties such as greater strength or higher resistance to corrosion. Due to the possibilities for enhanced material properties few pure metals are used commercially today. Steels are a type of low carbon, iron based alloys that with the addition of other alloying elements can be made to posses varying properties. Stainless steels are one group of steels which get protective properties from a chromium content of at least 10wt%, see Table 3.1 for more detailed examples of stainless steel compositions [14]. When alloys oxidize the corresponding oxide will most of the time not have the same composition as the alloy and can have varying structure and composition during the oxidation. The directional growth of the oxide can also vary [34]. In a binary alloy made of element A and element B, both elements can form an transient oxide on the surface of the alloy as long as the components have a negative free energy change for their formation in the atmosphere. The formation of two oxides should in theory only happen in the initial stage of oxidation, as the faster growing oxide should overgrow the slower growing oxide with time. In practice however a displacement reaction can occur if element A's oxide is faster growing, Equation 2.28, but element B is less noble, Equation 2.29. The displacement reaction will take place at the oxide/metal interface and result in concentration gradients in both the oxide and metal [14].



If the concentration of component B in the alloy reaches a point at which it is no longer sufficient to support the oxide growth the fast growing oxide of element A will start to occur again. The change to oxidation of the more noble element A can occur even if the bulk concentration of B is sufficient if there is an depletion zone below the oxide scale. The depletion zone can form if the consumption of B to form the oxide exceeds the rate at which B is resupplied to the interface by diffusion through the alloy. It is therefore not possible to predict the dominant oxide forming element without also knowing about the solid state diffusion of the elements. Another important factor for oxidation of alloys is the solubility of oxygen in the alloy. If oxygen is soluble in the oxide then it can enter the alloy and cause internal oxidation. Internal oxidation is favored if Equation 2.30 is not fulfilled, where B is the least noble element, O oxygen, and N respectively D are mole fraction and diffusivity [14], [34].

$$N_B D_B \gg N_O D_O \quad (2.30)$$

Based on the parameters of Equation 2.30 two criteria have been derived, by Carl Wagner. The first criterion describes the necessary concentration for the formation of an external oxide scale in the initial stages. The second criterion describes the latter stages and relates to what concentration is needed to secure a sufficient supply of the oxidizing element. Since chromium is a main element for protecting stainless steels at high temperature it will be used to further explain the criteria. In the following chromium can therefore be thought of as being the previously mentioned B element that is relatively slow forming but less noble and iron as element A the fast growing more noble element [34].

For chromium to form an external Cr_2O_3 oxide scale and prevent internal oxidation from happening Equation 2.31 needs to be true.

$$\text{Criterion 1 : } N_{Cr}^{cri1} > \left[\frac{\pi g^*}{2v} \frac{V_M}{V_{M_xO_y}} \frac{N_O^{(s)} D_O}{\tilde{D}_{Cr}} \right]^{\frac{1}{2}} \quad (2.31)$$

In Equation 2.31 V_M and $V_{M_xO_y}$ are the molar volumes of the alloy and the oxide respectively. For an Fe-Cr alloy with a Cr_2O_3 oxide $V_M = 7 \text{ cm}^3 \text{ mol}^{-1}$ and $V_{M_xO_y} = 15 \text{ cm}^3 \text{ mol}^{-1}$ [35]. $\tilde{D}_{Cr}$ is chromium's chemical diffusivity, D_O oxygens diffusivity in the alloy, $N_O^{(s)}$ the solubility of oxygen in the alloy and lastly g^* is a factor defined as 0.3 according to [35]. Worth noting is that Equation 2.31 only is valid in situations where no other oxide scale has formed on the surface [34].

How sustainable the formed external Cr_2O_3 scale will be is what can be estimated using the second criterion, Equation 2.32.

$$\text{Criterion 2 : } (N_{Cr}^{(o)} - N_{Cr,i}) = N_{Cr}^{cri2} > \frac{V_M}{V_{M_xO_y}} \left(\frac{\pi k_p}{2\tilde{D}_{Cr}} \right)^{\frac{1}{2}}, \quad (2.32)$$

where V_M , $V_{M_xO_y}$ and $\tilde{D}_{Cr}$ are the same as in Equation 2.31, and k_p the parabolic rate constant. $N_{Cr}^{(o)}$ is the minimal level of chromium necessary to sustain external scale growth. $N_{Cr,i}$ is the interfacial chromium concentration and as Wagner himself pointed out, then the maximum flux of chromium available should have been reached when $N_{Cr,i} \approx 0$.

Therefore in theory N_{Cr}^{cri2} is equal to $N_{Cr}^{(o)}$ when maximum flux is reached. When Equation 2.32 is true the supply is sufficient to ensure that the oxide forms and protects the Fe-Cr alloy, but below the critical chromium concentration iron will start to oxidize instead. As previously mentioned the reason the alloy can go from being above the critical concentration to below is due to either a bulk or local depletion of chromium. A change from forming a protective slow growing oxide to forming a fast growing one as is the case here if not both criteria are met results in breakaway oxidation [34].

2.5.1 Breakaway Oxidation

Breakaway oxidation is shown in Figure 2.6 and is defined as a sudden increase of the oxidation rate. The increase in oxidation rate is the result of going from forming a protective oxide scale to forming a poorly or non-protective oxide scale. Breakaway oxidation does not occur at random, but is mainly the result of intrinsic chemical failure or mechanically induced chemical failure. Intrinsic chemical failure is primarily caused by the local or global depletion of the alloying element responsible for forming the protective oxide scale as discussed earlier in Section 2.5. Intrinsic chemical failure for an Fe-Cr alloys therefore occurs when the chromium content falls below the value of N_{Cr}^{cri2} . Mechanically induced chemical failure happens when a critical oxide thickness is reached. When the critical oxide thickness is reached the oxide scale is prone to cracking, rupturing or even detaching from the metal surface. Failure is then the result of the oxide scale not acting as a barrier anymore, as the metal and the environment can come in contact. Breakaway oxidation will however be avoided if the exposed metal region has a chromium content exceeding that of N_{Cr}^{cri1} since a new oxide scale will be able to form [32], [34]. The environment the metal is in can effect the probability of breakaway oxidation. If the environment a Cr_2O_3 forming alloys is in has a high $p(O_2)$ humid atmosphere the probability of breakaway oxidation increases due to chromium evaporation [14], [32].

2.6 Ferritic Stainless Steel Interconnects

Interconnects have previously been discussed in Section 2.2. The function and requirements were made clear as it was pointed out that FSS could be the interconnect material of the future. The coming section will elaborate on why FSS is suitable in terms of corrosion resistance, electrical conductivity and cost. Factors like alloying elements and coatings will also be discussed.

2.6.1 Material Selection

Steel is a broad term used for low carbon, iron based alloys. Common for steels used for high temperature applications is that they rely on the formation of a slow growing protective scale to limit the extend of material deterioration caused by oxidation. The process where an element of the steel alloy oxidizes preferentially to the main element iron and forms a continuous oxide layer at the steel/atmosphere interface is referred to as selective oxidation [27]. Elements that consistently form protective oxide scales are chromium, aluminium and silicon. Silicon forms SiO_2 (silica) that while protective is not stable at low pressures and decomposes to gaseous species. At high temperatures silica

also reacts with water vapor and forms Si(OH)_4 . Aluminum forms alumina which has the lowest k_p -value, meaning it is the slowest growing oxide, of the three, but is an electrical insulator and therefore undesirable for interconnects. Chromium forms chromia which is a semiconductor and therefore the best option despite chromium evaporation discussed in Section 2.4 [27]. A group of chromia forming steel alloys are stainless steels which contain at least $\approx 11\text{wt\%}$ chromium [30]. Within the stainless steel group there are different types of steels which are classified according to their crystalline structure. Austenetic and ferritic stainless steels are the two most common types. Austenetic stainless steels (ASS) have the face-centered cubic (FCC) crystal structure, while FSS have the body-centered cubic (BCC) crystal structure. Chromia forming FSS have previously seen use at maximum temperatures of 650°C . The reasoning behind the temperature limit is based on the creep properties of FSS and not the oxidation rates. ASS have been the preferable choice for higher temperatures as ASS have higher creep strength than FSS [14]. However, due to their TEC which for FSS is in the range of $11.5 \times 10^{-6} \text{ K}^{-1}$ to $14 \times 10^{-6} \text{ K}^{-1}$ and for ASS in the range of $18 \times 10^{-6} \text{ K}^{-1}$ to $20 \times 10^{-6} \text{ K}^{-1}$, FSS is favorable because its average TEC matches that of the majority of all the investigated ceramic electrolytes for SOFC [26].

Summarized the properties that make FSS desirable as a material for interconnects are the materials ease of formability, its TEC, high electrical and thermal conductivity, and relative to ceramic alternatives low cost. While all these properties make for a good interconnect material FSS would be useless if it would not be able to survive for long at high temperatures. Issues that impact the lifetime of FSS interconnects, and in extension the fuel cell itself, are primarily chromium evaporation and scale thickness. Chromium evaporation was discussed in Section 2.4 and while the resulting depletion of chromium is a problem a more problematic effect is caused by the formation of the gaseous Cr(VI) species. The gaseous species can block the cathode TPB and in doing so poisoning the cathode which leads to fuel cell degradation [26], [36]. Chromium evaporation alone has been suggested to be responsible directly or indirectly for roughly a third of the entire degradation of a fuel cell [36]. The issue associated with scale thickness is that a thicker chromia scale has an increasing electrical resistance and therefore will limit the overall fuel cell efficiency if it grows to thick. Other than chromium depletion and scale thickness, other forms of cell degradation exist, but those two are the most common ones. An example of another degradation mechanism is the effect of the dual atmosphere the interconnect is exposed to during operation. The dual atmosphere effect is however outside the scope of this thesis.

The growth rate of the chromia scale as well as the chromium evaporation can be limited by designing the composition of the FSS alloy. Adding or omitting certain elements from an alloy makes it possible to achieve good chromium retention, slow oxidation rates and good stability. The major problem with designing an alloy for a single use case is that it will have a high price relative to already commercially available materials [37]. Crofer 22 APU is an FSS alloy specifically designed for making interconnects, with a chromium content above $22\text{wt\%}$. Alloys with chromium contents higher than $20\text{-}25\text{wt\%}$ cannot be made without other alloying elements. This is because sigma phases would otherwise form making the alloy brittle. A manufacturing cost analysis made for SOFC systems

based on AISI 441 as the interconnect material have found that interconnects cost can make up between $\approx 6\text{--}10\%$ for a 30kW stack and $\approx 46\%$ for a 5kW stack [8], [9]. The values here are not what should be emphasized but instead the fact that interconnects make up a significant part of the overall stack price. AISI 441 is a more common alloy than Crofer 22 APU and, based on data from 2015, ten times cheaper [38]. Selecting a common steel over a speciality steel like Crofer 22 APU also enables sourcing from more manufacturers and reduces the risk of committing to a steel with a unknown future.

2.6.2 Common Alloying Elements & The Reactive Elements Effect

2.6.2.1 Common Alloying elements

Silicon is an alloying element present in all steels. Silicon is used as a de-oxidant during steel manufacturing and therefore exist in steels as a manufacturing byproduct. At high temperatures silicon oxidizes to SiO_2 and if the silicon content is high enough will result in a continuous SiO_2 scale. A continuous SiO_2 scale brings with it two problems. The first problem is that SiO_2 is an electrical insulator and therefore will reduce the electrical conductivity of the interconnect. The second problem is that it has been suggested that the difference in TEC of SiO_2 and FSS can cause spallation during thermal cyclings. Two methods are primarily used to reduce the negative effects of silica. The first method is mainly used for more expensive FSS where vacuum inductive melting is employed. Vacuum induced melting reduces the need for an de-oxidant but is a costly process. The second methods utilizes alloying elements that can bind silicon so it doesnt have to be removed to avoid SiO_2 . Niobium, Molybdenum and Wolfram are all examples of elements that can be added to the alloy to bind silicon. They work by forming laves phases with silicon in the steel that has the additional benefit of increasing creep strength and the hardness of the steel [27]. A higher silicon tolerance in the FSS results in lower manufacturing costs [37].

To increase the protective behavior of the chromia scales that form on FSS manganese can be added to the alloy. Manganese forms a spinel $(\text{Cr,Mn})_3\text{O}_4$ on top of the continuously growing chromia scale. The manganese spinel causes a reduction in the chromium evaporation rate by a factor of up to 2 to 3 [37]. The spinel forms at manganese concentrations as low as 0.3 to 0.5wt% [37]. Manganese does not reduce the chromium evaporation enough to eliminate chromium poisoning of the cathode.

Titanium can also be added to the alloy matrix in small quantities to form fine internal TiO_2 precipitates during oxidation. The TiO_2 precipitates are believed to strengthen the near surface region of the alloy, thereby improving the resistance to cracking [27]. Titanium along with other elements like molybdenum are also ferrite stabilizers that can inhibit the formation of austenite on heating [39].

Carbon is the alloying elements that gives steel its hardness [40]. Carbon does however also result in steels becoming more brittle and less ductile [41]. FSS have low carbon levels which results in above average ductility that allows for extensive shaping without encountering problems such as necking or cracking [41].

2.6.2.2 The Reactive Elements Effect

Formerly known as the "rare earth effect" the reactive element effect (REE) is a term which describes the multitude of benefits that can be obtained in term of oxidation behavior of alumina and chromia forming alloys, by introducing certain elements. Elements that classify as reactive elements (RE) are elements that are more oxygen active than scale forming elements in the alloy [42]. In FSS the main oxidating element is as mentioned chromium, which forms the protective chromia scale. The REE for chromia forming alloys results in enhanced selective oxidation of chromium, reduced growth rate of the chromia scale, a change in scale growth from being predominantly cation outward to oxygen inwards transport, and better adhesion of the scale especially under thermal cycling conditions. Reactive elements that are known to induce the benefits are elements such as La, Ce, Pr, Y [42], [43]. The influence of the RE have been observed to increase in the following order at 1000°C: Y, Pr, Ce, La. This indicates a correlation between influence increasing with ion radius [43].

RE addition to an alloy is primarily done by one of the following techniques: Alloy addition of the RE, fine dispersion of the RE, ion implantation of the RE, or surface applied RE oxides [44]. Surface RE oxide coatings has an advantage over the others in that it does not adversely affect the mechanical properties of the alloy and it can be easily applied to any steel offering flexibility [43]. Addition of RE using any of the four techniques have been shown to reduce the growth rate of chromia by roughly an order of magnitude at temperatures above 900 °C [42]. It is assumed that the reduction in chromia scale growth is related to the transport through the chromia scale. Fontana et al.[45] reported that the presence of RE on the chromia scale results in the formation of a MeCrO_3 perovskite ($\text{Me} = \text{RE}$) within the grain boundaries of chromia [45]. The MeCrO_3 in the grain boundaries then blocks the outward diffusion of chromium while allowing slow inward diffusion of oxygen across the grain boundaries. Thus, the chromia scale growth changes from primarily outward cation transport to predominant inward growing in the presence of reactive elements [45]. However in another study by Sattari et al.[46] investigating the REE of cerium deposited on Fe-22Cr steel they did not observe cerium in the chromia scale. Upon exposure, the Fe-22Cr steels formed a duplex $(\text{Cr,Mn})_3\text{O}_4$ spinel oxide scale on top of the chromia scale. The 10 nm Ce deposited on the steel was observed to be in this $(\text{Cr,Mn})_3\text{O}_4$ scale after 3000 hours and not in the chromia scale. This study instead suggest the possibility of cerium blocking diffusion paths for oxygen and chromium in the $(\text{Cr,Mn})_3\text{O}_4$ rather than in the chromia scale [46].

Selective Oxidation: The benefit of having selective oxidation is that the necessary amount of chromium needed for the development of the chromia scale is reduced. The formation time is also reduced which limits the formation of base metal oxide (Iron oxides). The increased selectivity is a result of an increased flux of chromium to the surface. The increased flux is not a result of the RE increasing diffusion of chromium, but rather a result of the REs promoting decreased grain sizes and an increased number of dislocation and sub-grain boundaries. The increase in dislocation and sub-grain boundaries in turn increase diffusion of chromium to the surface. The selective oxidation is more effectively achieved when the RE are dispersed since surface applied RE have not been

found to provide the same degree of selectivity [42].

Improved scale adhesion: RE have been shown to improve the spallation resistance of chromia scales during cooling. The addition of RE therefore results in an increased lifetime expectancy for an alloy that experiences cyclic heating and cooling. The spallation resistance gained is accompanied by micro-structural changes at the scale/alloy interface. The mechanism behind the improved adhesion is assumed to be due to a reduction of sulfur at the scale/alloy interface. The mechanism is based on the hypothesis that the interface interactions between the scale and the alloy are strong, but that sulfur present in the alloy goes to the interface during oxidation. At the interface the sulfur then weakens the interaction between the scale and alloy making the scale less adherent. RE have strong sulfide forming ability and are therefore believed to be able to eliminate or reduce the amount of sulfur at the interface [42].

Quantity: While the benefits obtained from adding RE might make it appear like more is better the reality is that RE should be added in amount in the range of a few hundred ppm. If the amount of RE is too high the oxidation rate can actually increase and scale adhesion will become worse. Over doping with RE can also cause the formation of a secondary oxide phase within the alloy. The formed secondary oxide phase can result in faster oxygen transport resulting in increased scale thickness. Internal oxidation may also increase which can lead to crack formation and reduced scale adhesion [42].

2.7 Protective Coatings

Cheap long lasting interconnects would increase the commercial viability of SOFC. In Section 2.6.2 it was explained how certain alloying elements can affect the properties of a FSS. Designing a FSS specifically for use as a SOFC interconnect will however always be more expensive than using a widely used FSS alloy. This realization has led to research into protective coatings.

The rate of chromia scale growth and chromium evaporation could as explained, in Section 2.6, be limited by either adding or omitting elements from the alloys. Another way to achieve similar effects is to use coatings. The obvious benefits of coating a material over designing a certain composition is that the coating can be applied to all materials without changing the manufacturing process. Coatings can therefore be applied equally to cheap and expensive FSS. The desire to make interconnects as cheap as possible have therefore also made coatings an indispensable part of modern FSS interconnects. For a coating to be beneficial to a FSS interconnect it needs to fulfill certain requirements. The main requirements are good adhesion, high electrical conductivity, compatibility with the other fuel cell parts, and then it needs to mitigate chromium evaporation while also reducing the chromia growth rate.

Materials that work well for coatings are the RE discussed in Section 2.6.2.2, due to their ability to increase scale adhesion and reduce oxidation rates. As discussed in Section 2.6.2.2 RE should not be added to the alloy in large quantities and the same is the

case for coating with RE. An applied RE oxide thickness should be less than $1\mu\text{m}$ [47]. Coatings made with RE are therefore thin and they are also porous which makes for ineffective suppression of chromium diffusion to the surface which in turn fails to limit chromium evaporation [47].

Composite spinel oxides and rare earth perovskite oxides are two widely studied coating materials for FSS interconnects [47]. Both oxides have good electrical conductivity and compatibility. The ABO_3 perovskite oxides are however ionically conductive and serve as ineffective barriers to diffusion of both volatile chromium species and oxygen [47]. The AB_2O_4 spinels on the other hand have attracted increased attention due to their ability to suppress volatile chromium species and keeping them from reaching the surface. Thereby reducing the risks of both chromium depletion and chromium poisoning [47]. The $(\text{Mn},\text{Co})_3\text{O}_4$ or MCO spinel has shown especially promising as it provides good suppression of chromium while also having sufficient electrical conductivity. MCO can be applied directly or through a conversion route where the steel is coated with cobalt which then oxidises to Co_3O_4 before outward diffusion of manganese from the steel leads to manganese enrichment of the Co_3O_4 [48], [49]. Table 2.3 shows a comparison of the discussed coating materials empathizing why the composite spinel coating is considered the most promising [47].

Table 2.3: Comparison of RE oxides, Rare earth perovskite and composite spinel oxides in terms of electronic conductivity, inhibition of chromium migration, ability to reduce oxidation rates and the simplicity of applying the coating. [47].

Coating Material	Electronic Conductivity	Inhibition of Cr Migration	Reduction of Oxidation Rates	Simplicity of Deposition
Reactive Element Oxide	Fair	Poor	Good	Good
Rare Earth Perovskite	Good	Fair	Poor	Fair
Composite Spinel Oxide	Good	Good	Fair	Good

The state-of-the-art coating used for FSS interconnects is currently a 600nm cobalt coating on top of a 10nm cerium coating. The cobalt coating forms the MCO spinel through the previously mentioned conversion route. The coating combines the chromium suppression of the spinel with the improvements to scale adhesion and reduced oxidation rates from RE [50]. The reason for coating with the specific thicknesses is that it has been observed that increasing the cobalt thickness beyond around 600nm is unlikely to significantly reduce the chromium evaporation rate further [38]. Likewise it has been shown that increasing the thickness of cerium from 10 nm to 20nm and 50nm with 600nm of cobalt does not result in any significant effect [10]. Whether a thinner than 10nm cerium coating has the same effect as 10 nm is unknown, but 10nm cerium is already a thin coating that is not expected to have any significant effect in physically separating the re-

actants. The cerium coating can theoretically be made thinner, but in practise it would be difficult to achieve satisfactory and reproducible coatings.

2.7.1 Coating Performance

The performance of the 10 nm cerium and 600 nm cobalt coating have already been proven [10]. The performance benefit gained can be seen in Figure 2.10.

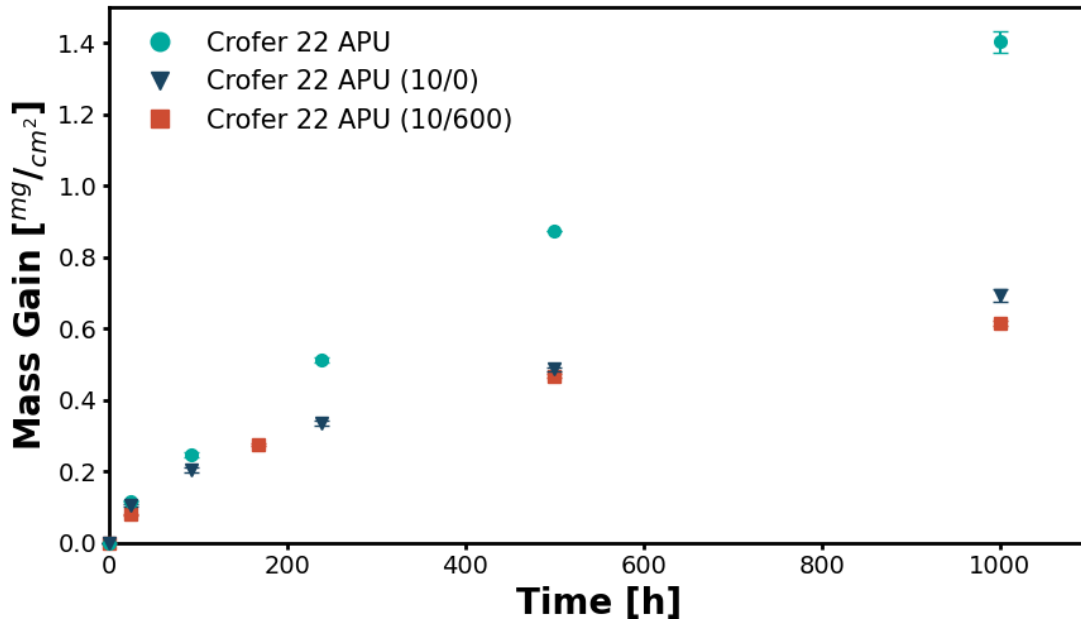


Figure 2.10: Recorded mass gain at 850°C of three different Crofer 22 APU samples. The values written in the parentheses are the coating thicknesses in nm (Ce/Co). The initial mass gain after 0.5 hours have been subtracted from Crofer 22 APU (10/600) mass gain. The mass gain of the (0/0) and (10/0) Crofer 22 APU is its mass gain plus the amount of chromium evaporated [10].

2.7.2 Self-healing Capabilities of Coatings

A cost-effective method of coating FSS interconnects is large scale roll-to-roll coating. When doing roll-to-roll coating the forming has to be done after the coating has been applied. Figure 2.11(b) illustrates the problem with pre-coating a material which is that cracks can be introduced to the coating during forming. Thankfully studies have found that despite crack formations, within limitations, coating performance remains unchanged at both 850°C, 750°C and 650°C [50], [51]. The studies suggest that a (Cr,Mn)₃O₄ spinel forms inside the cracks early on but then as time goes (168h at 850°C) cobalt diffuses from the surrounding regions to form a uniform (Co,Mn)₃O₄ scale.

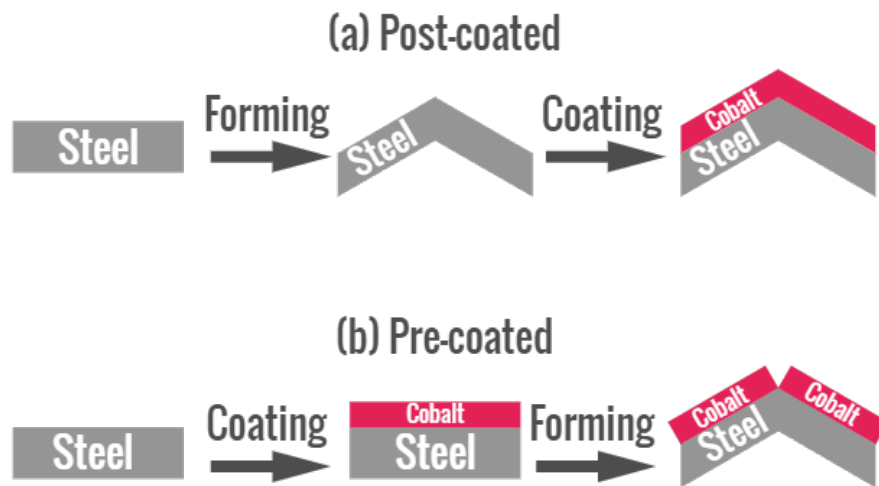


Figure 2.11: Comparison of coatings on a (a) post-coated and (b) pre-coated steel [51].

3 | Materials & Method

3.1 Materials

Four different FSS alloys were investigated for this thesis. The alloys and their composition can be seen in Table 3.1.

Table 3.1: Composition of investigated ferritic stainless steel alloys. Numbers are the elements occurrence in wt%.

Alloy	EN	Fe	Cr	C	Mn	Si	Ti	Nb	La
AISI 409	1.4512	Bal.	11.4	0.012	0.39	0.51	0.17		
AISI 430	1.4016	Bal.	16.2	0.040	0.49	0.34			
AISI 441	1.4509	Bal.	17.56	0.014	0.35	0.59	0.17	0.39	
Crofer 22 APU	1.4760	Bal.	22.92	0.004	0.38	0.01	0.06		0.07

3.1.1 Coatings

All the FSS alloys were coated prior to exposure. The coatings were applied using a proprietary physical vapor deposition (PVD) technique and were done by Sandvik Materials Technology AB. The alloys were coated as pre-cut sheets, see Figure 3.1, ensuring a sample coating coverage of 99.8%. Not all samples had the same coating, but the majority were coated with 10 nm metallic cerium followed by 600 nm metallic cobalt. The metallic elements starts to oxidize when exposed to atmospheric air, but will not completely oxidize. However Froitzheim et al. [48] reported that the metallic cobalt completely oxidizes in 30 seconds at 850°C. Coatings, alloy, sample geometry, exposure conditions and sample name can be found in Table 3.2. The exposures will be elaborated on in Section 3.2.

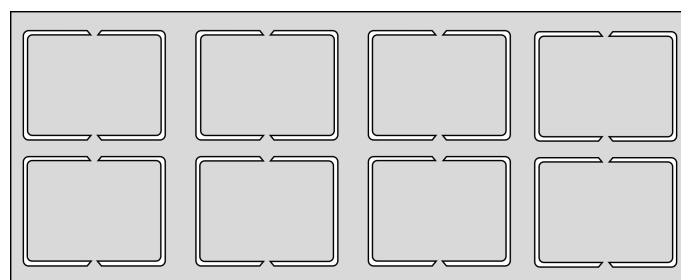


Figure 3.1: Illustration of how the alloy sheets were pre-cut to ensure high coating coverage.

3.1.2 Sample preparation

No material was modified beyond coating, but before exposure all samples were cleaned. The samples were cleaned ultrasonically for 10 minutes at 80kHz in a two step process.

The first step was cleaning in acetone and the second cleaning in ethanol after which the samples were dried in atmospheric air on a highly absorbent low-lint tissue before being weighed and placed in a clean zip-lock sample plastic bag.

3.2 Exposure

All exposures were conducted in atmospheric air containing 3% H₂O with a flow-rate of 6000 mL min⁻¹. The temperatures and alloy combination used for each experiment can be seen in Table 3.2. The furnaces used for the exposures were all tube furnaces, but some were single tube furnaces (STF) while others were 4-tube furnaces (4TF). The two furnace types can be seen in Figure 3.2. There should not be any difference between exposures done in a STF and a 4TF as all exposure conditions can be mirrored. It will therefore not be mentioned when either was used in the results. The only difference is the ease of setting the exposure temperature, where it could be more difficult to adjust the 4TFs to the desired temperature. The furnaces were set to the desired exposure temperature before the samples were inserted. The samples did therefore experience a high and non-standardized heating rate. The removal of the samples were done over the course of 25 minutes and therefore they experienced a lower, but still undefined cooling-rate. After completed exposure, the samples were placed back in zip-lock plastic sample bags.

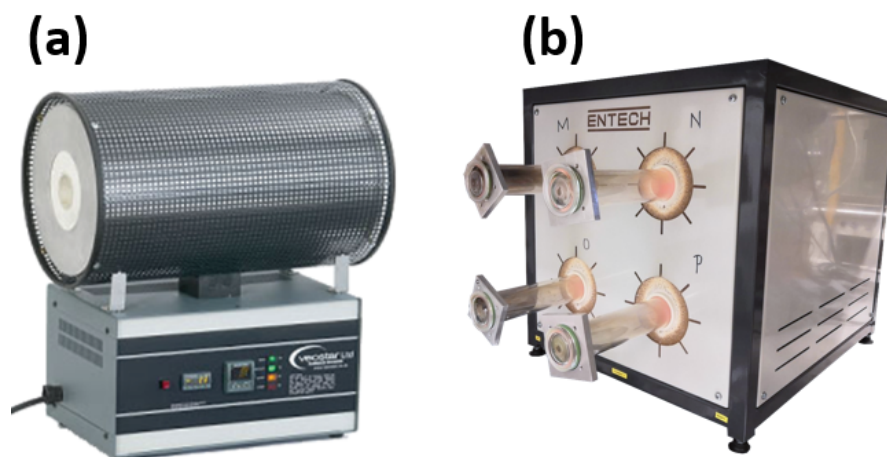


Figure 3.2: The Furnaces used to expose the samples to high-temperatures. (a) single tube furnace. (b) 4-tube furnace with four tubes.

Table 3.2: Summation of all experiments done for this thesis. All exposures were done in a tube furnace using athomspheric air with a flowrate of 6000 mL min⁻¹ and a humidity of 3% H₂O.

Material Experiment	Name	Inner	Coating Middle	Outer	Geometry [mm]	Exposure temp. [°C]
AISI 409 Lifetime Model	RJ	10nm Ce	-	600nm Co	H: 17 W: 15 T: 0.38	650/750/ 800/850/ 865/880/900
AISI 430 Lifetime Model	RI	10nm Ce	-	600nm Co	H: 17 W: 15 T: 0.38	650/750/ 800/865/ 880/900
AISI 441 Lifetime Model	SC	10nm Ce	-	600nm Co	H: 17 W: 15 T: 0.30	650/750/ 800/850 /865/880/900
AISI 441 Cerium Effect	SR	PreFe ⁽¹⁾	-	600nm Co	H: 17	850
	SS	PreFe ⁽¹⁾	10nm Ce	600nm Co	W: 15	
	SU	10nm Ce	PreFe ⁽¹⁾	600nm Co	T: 0.30	
	SW	10nm Ce	PreFeCe ⁽²⁾	600nm Co		
Crofer 22 APU Lifetime Model	SH	10nm Ce	-	600nm Co	H: 17 W: 15 T: 0.30	650/750/ 850/865/ 880/900
Crofer 22 APU Coating Thickness SI	SH	10nm Ce	-	600nm Co	H: 17	850
		50nm Ce		1200nm Co	W: 15 T: 0.30	
Crofer 22 APU Cerium Effect	SL	PreCo ⁽³⁾	-	10nm Ce	H: 17	850
	SM	PreCo ⁽³⁾	200nm Co	10nm Ce	W: 15	
	SN	PreCo ⁽³⁾	10nm Ce	200nm Co	T: 0.30	
	SO	PreCo ⁽³⁾	-	200nm Co		

(1) PreFe: 640nm co-deposited FeCr pre-oxidized at 900°C for 3min.

(2) PreFeCe: 10nm Ce then 600nm co-deposited FeCr pre-oxidized at 900°C for 3min.

(3) PreCo: 400nm Co pre-oxidized at 850°C for 30min.

3.2.1 Mass Gain

Before every exposure every sample was weighed using a Mettler Toledo XP6 microbalance. The weight of the samples were measured at different times during the exposure to follow the oxidation kinetics of the samples. When the samples were removed from the furnace they were left for an hour to cool down to room temperature. The change in mass was used to calculate the mass gain per unit area which then were used to determine the oxidation rate constant. The observed mass gain was also used to estimate or determine what mass gain leads to failure.

3.3 Analytical Techniques

Other than measuring the weight to analyse the oxidation behavior different analytical tools have been used to get a more detailed understanding of the results. The different analytical tools used were: broad ion beam milling (BIB), scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDX).

3.3.1 Broad Ion Beam Milling

Ion beam milling is a great tool for preparing cross sections that then can be analyzed using e.g. SEM/EDX. The working principle is that heavy ions hits the sample surface to sputter of the samples surface atoms layer by layer until a smooth surface is achieved, see Figure 3.3 [52]. The Leica TIC3X used for this thesis uses Ar^+ ions.

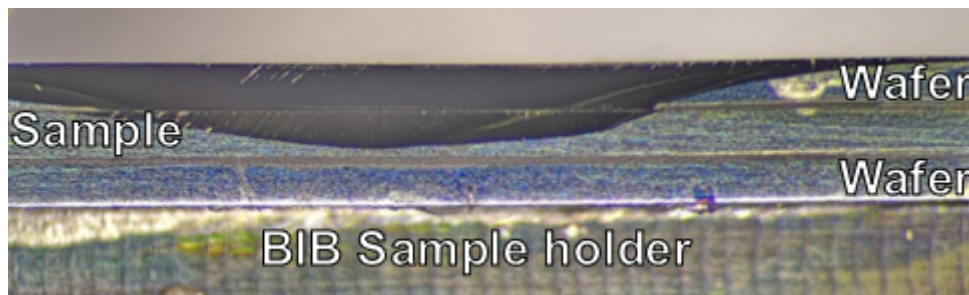


Figure 3.3: Photo of a cross-section after broad ion beam milling. The darker area is the area which have been BIB'ed.

The samples presented in this thesis needed sample preparation to enable high-quality cross-sections. First the samples were cut in half. Then a silicon wafer was glued to one or both sides (as in Figure 3.3). The purpose of the silicon wafer was to minimize damage to the thermally grown oxide during the next step, polishing. Silica carbide polishing paper was used to smoothen out the cross-section. The polishing started at 800 followed by 1200 and 2400 before lastly using grade 4000 carbide paper. The polished sample was then mounted to a Leica BIB sample holder using silver paint, for conductive reasons, before being loaded into the instrument. The milling was done at 8kV and 3mA for varying periods of time usually in the range of four to eight hours. A step-by-step description of the process can be found in Appendix A.

3.3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a powerful tool for imagining and micro-structural analysis. Combined with an energy dispersive X-Ray detector it can also be used to gain compositional data. SEM is good for investigating thermally grown oxide because it is a technique with a high resolution so it allows for clear imaging at high magnifications. The JEOL 7800F Prime used allows for imaging with a spatial resolution down to 0.5nm. As the name indicate a SEM is an electron microscope. The images are produced by detecting the interaction between electrons shot at the sample in a focused beam and the surface and near-surface atoms. The interactions between electrons and atoms result in

emission of different signals based on the type of interaction. The emitted signals are detected with different sensors that convert the signal to useful information. Three commonly analyzed emissions are those of secondary electrons (SE), backscattered electrons (BSE), and x-rays radiation. The generation process and their interaction volume vary [53]. Figure 3.4 shows how each of the different signals are generated and the interaction volume. All three types have been used for this thesis.

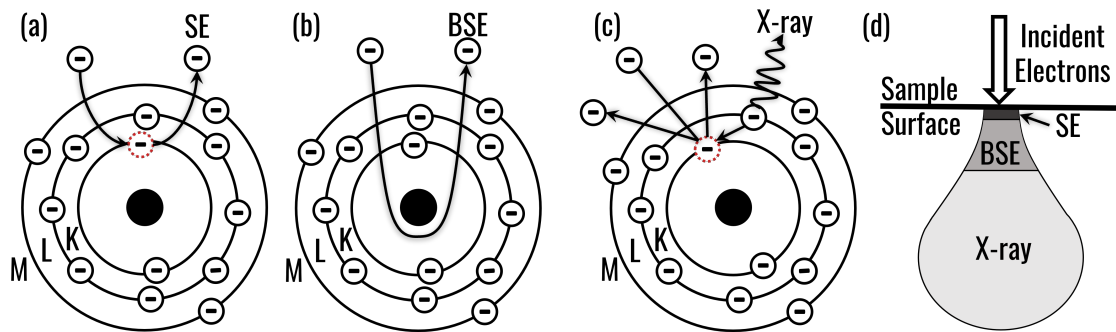


Figure 3.4: The generation of different SEM signals (a-c) and their respective interaction volume (d). SE: Secondary Electrons. BSE: Backscattered Electrons. X-ray: X-ray radiation. [53]

3.3.2.1 Secondary Electrons

Secondary electrons (SE) are weakly bound electrons that as seen in Figure 3.4a are ejected from the shell by inelastic scattering. The common energy range of SE is from 1 to 20eV but the energy can be up towards 50eV. The SE energy range is relative to the other signals low. The low energy makes it difficult for SE to escape the material and it is only those generated at or close to the surface which escape (Figure 3.4d). No bulk information is therefore gained by looking at SEs but in return SEs are highly surface sensitive. The high surface sensitivity results in high-resolution images providing information about the samples surface topography [53].

3.3.2.2 Backscattered Electrons

The backscattered electrons (BSE) are as seen in Figure 3.4b electrons that come from the electron beam but are elastically scattered at the atomic nuclei. Compositional information can be derived from the BSE signal as the nucleus of heavy atoms is greater than those for lighter ones making them able to deflect more electrons. A heavy element will therefore appear brighter than a lighter one in the resulting image. The energy of BSEs is in the range of zero to the energy of the incident beam. The majority of BSEs retain more or at least half of the incident beam energy [53].

The detection of BSEs can be done by using a detectors made of a semiconductor placed directly above the sample. Most often silicon is used and as the BSEs hit the material they excite the silicon electrons and creates an electron-hole pair. By separating the electron and hole, before recombination, using an electric circuit a current can be measured which provides the information needed to generate the image [53].

3.3.2.3 Energy Dispersive X-Ray Spectroscopy

So far SE can give information about a samples topography, and BSE information about the difference in atomic number. When an energy dispersive X-Ray (EDX) detector is used with a SEM X-Rays can be used to gain chemical information. EDX analysis works as seen in Figures 3.4(c) where the generation of X-Rays is shown. In the figure the electrons hit the inner shell of an atom to knock of an electron. Removal of the electron creates a positively charged hole that then gets filled by an electron from an outer shell. There is an energy difference between the outer (higher) and inner (lower) shell. When the electron moves from outer to inner shell, the energy is released in the form of an X-Ray. The energy released will be unique for a certain chemical element and can therefore be used to determine the element. The x-ray detection is done by a silicon drift detector and the signal is processed using software. EDX can be used to perform qualitative and quantitative analysis [53]. X-Rays can penetrate the material deeper than electrons, which means that the EDX analysis has a large interaction volume, Figure 3.4(d). The large interaction volume does however lead to a low resolution and is therefore not suitable for surface analysis [53].

4 | Results & Discussion

4.1 Lifetime Model

4.1.1 Influence of Coating Thickness

The coating primarily used in this thesis is consistent of 10 nm cerium with 600 nm cobalt, see Table 2.3. The 600 nm cobalt has been found to be optimal for decreasing the chromium evaporation. The 10 nm cerium has likewise been found to be optimal for reducing oxide scale growth. A thicker cerium coating with similar 600 nm cobalt does not provide any significant benefits and a thinner coating complicates the coating procedure. Whether a combination of an increase in cerium and cobalt thickness would result in significant improvements is not known. As seen in Section 2.7.1, the coating is very important for the lifetime. It is therefore important to understand if a thicker coating can improve the the coating performance.

To investigate whether a thicker cerium coating would provide improved protection when accompanied by a thicker cobalt coating Crofer 22 APU and AISI409 samples were coated and exposed at 850°C. Six Crofer 22 APU and six AISI409 samples were coated with 10 nm cerium and 600 nm cobalt while six additional Crofer 22 APU were coated with 50 nm cerium and 1200 nm cobalt. The AISI409 was used as a reference in the exposure to ensure that the oxidation behavior of the Crofer 22 APU sample was due to the coating.

The results of the exposure are shown in Figure 4.1. Figure 4.1a show that Crofer 22 APU and AISI409 with the same coating have similar mass gains. A rapid increase in the mass is observed during the first 0.5 hours in the exposure. This is due to the oxidation of the metallic cobalt coating to Co_3O_4 . The thicker coating is expected to show higher mass gain, since it contains a larger amount of metallic elements which needs to be oxidized. In Figure 4.1b, the initial mass gains of the samples have been subtracted. It has been subtracted to enable comparison of the oxidation kinetics of the steels with different coating thicknesses. After 3000 hours, the thicker coating is observed to have higher mass gain than the thinner coating. The observed continuous mass increase relative to the thinner coating is likely the result of the manganese enrichment of Co_3O_4 to form the $(\text{Mn},\text{Co})_3\text{O}_4$ spinel. As the thicker coating contains more Co_3O_4 to enrich it only makes sense that it increases more in weight than the thinner coating. The thicker coating does not seem to be providing any additional protection. This is in agreement with the previous studies on cobalt and cerium coatings. It therefore appears like using more than 10 nm cerium and 600 nm cobalt is a waste of material, since it will just result in a thicker and probably less conductive interconnect, that will have its manganese reservoir depleted faster. The electrical resistance over the interconnect does however need to be measured before anything definitive can be said about the conductivity. The experiment was repeated, but only run for 500 hours and the results were the same. As will be shown later coated Crofer 22 APU has a life expectancy of much more than 3000 hours. Therefore at much longer exposure times e.g. 50.000 hours the thicker coating might

have offered extra protection.

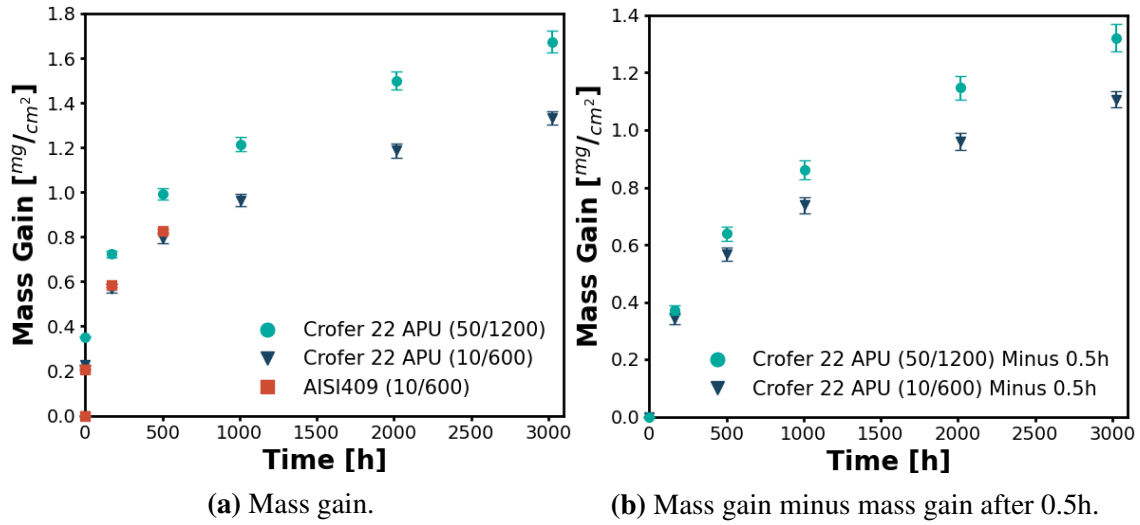


Figure 4.1: Recorded mass gain at 850°C of Crofer 22 APU with different coating thickness and AISI409. The values written in the parentheses are the coating thicknesses in nm (Ce/Co). The initial mass gain after 0.5 hours have been subtracted from the mass gain in (b).

4.1.2 Ferritic Stainless Steel Temperature Extremes

The benefits of coating with 10 nm cerium and 600 nm cobalt have already be proven, see Figure 2.10. A problem with how well the coating protects the alloys is however that determining when the alloys fail will take a long time. As oxidation kinetics are temperature dependent, meaning that oxidation increases with temperature, exposures were done at 900°C. The objective of this was firstly to get an idea about the lifetime at this temperature and secondly to get a better understanding of the temperature limits of the alloys. The results of the exposures can be seen in Figure 4.2 and Figure 4.3.

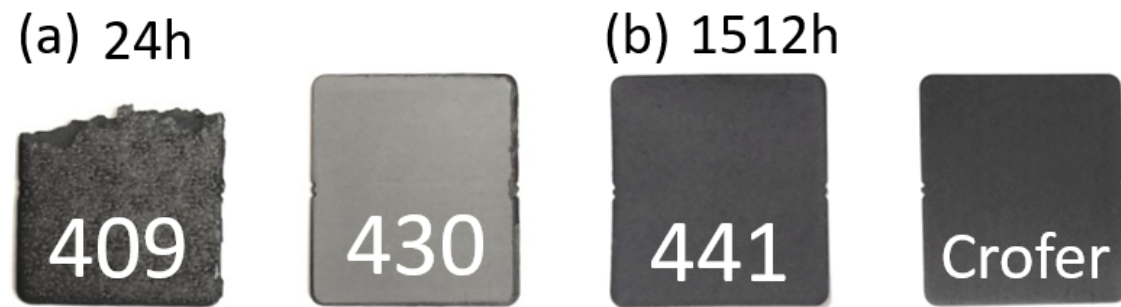


Figure 4.2: (a) AISI409 and AISI430 after 24 hours at 900°C. (b) AISI441 and Crofer 22 APU after 1512 hours at 900°C. All samples coated with 10 nm cerium and 600 nm cobalt.

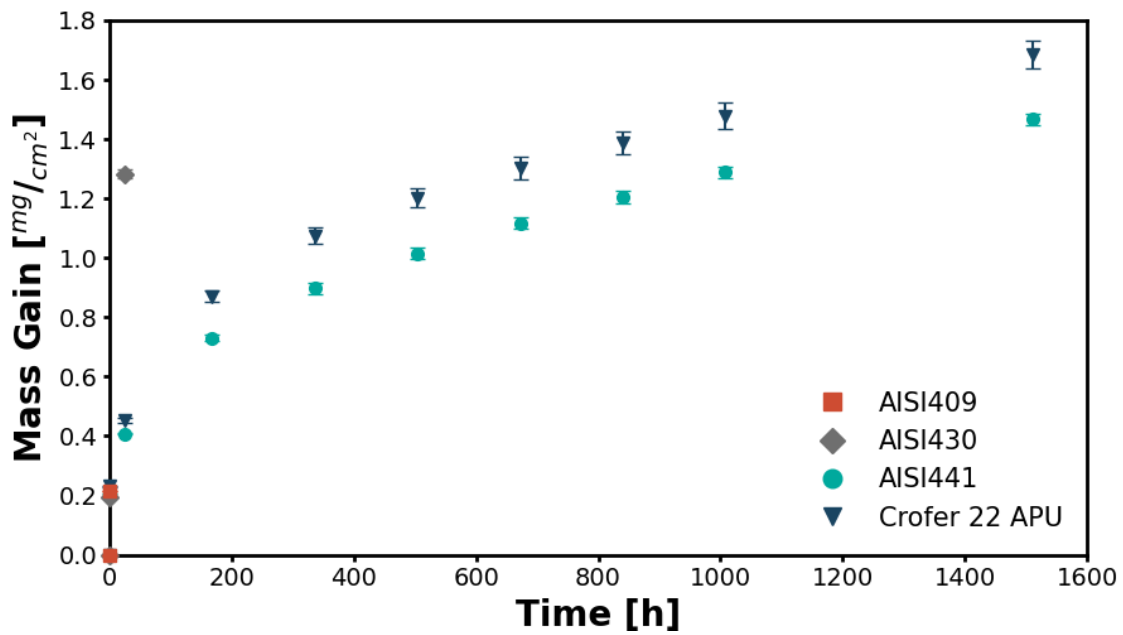


Figure 4.3: Recorded mass gain of AISI409, AISI430, AISI441 and Crofer 22 APU at 900°C. All samples were coated with 10 nm cerium and 600 nm cobalt.

The results show that AISI409 and AISI430 fail before 24 hours while AISI441 and Crofer 22 APU do not show any signs of failure even after 1500 hours. AISI409 becomes fully oxidized after the 24 hours while AISI430 only shows relatively minor corrosion at the edges. This hints that lifetime probably is not only dependent on whether the samples are coated or not. As part of the investigation of feasible exposure temperatures an exposure was done at 650°C where AISI409 also failed (Figure 4.4) before 168 hours. This defined the temperature range of interest for the lifetime model and only temperatures between 650°C and 900°C have been investigated.

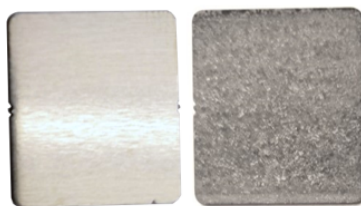


Figure 4.4: (Left) Normal coated but unexposed AISI409. (Right) Coated AISI409 that failed at 650°C.

4.1.3 Correlation Between Chromium Content & Lifetime

As highlighted in Section 4.1.2, lifetime is not only a function of an alloy being coated or not. The main difference between the investigated alloys is their chromium content. As chromium is what forms the protective chromia scale it seems likely that the chromium content is what will determine the order of when the alloys will fail. To test this all four alloys were exposed at 865°C. The results can be seen in figure 4.5.

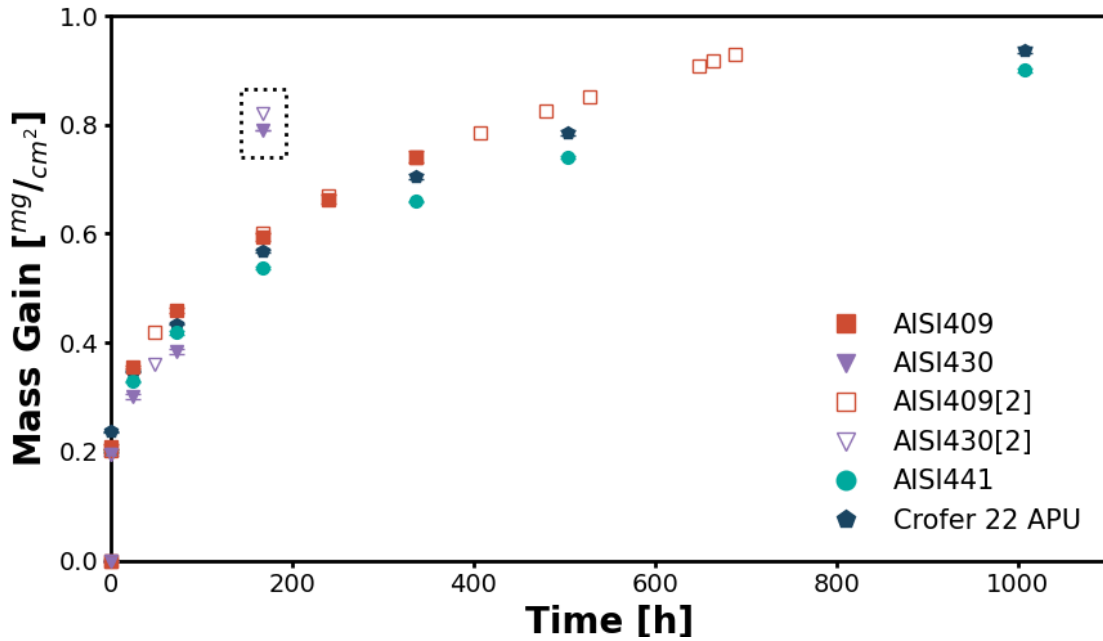


Figure 4.5: Recorded mass gain of AISI409, AISI430, AISI441 and Crofer 22 APU at 865°C. All samples were coated with 10 nm cerium and 600 nm cobalt. The [2] indicates data from a second exposure.

The results shows that AISI430 breaks before AISI409 at 865°C, as highlighted by the dashed box. This indicates that the chromium content likely is not the only element affecting FSS lifetime. Looking at the alloy composition in Table 3.1 carbon and titanium content is what separates AISI430 from the rest. Titanium strengthens the alloy-oxide interface and is a ferrite stabilizer so having no titanium makes it more prone to cracking and transitioning to austenite. The carbon content of AISI430 is oppositely relatively high. Increasing carbon levels are known to stabilize the austenetic phase, but chromium is known to stabilize the ferritic phase. It is therefore difficult to say whether the higher carbon content causes any phase transition without a ternary Fe-C-Cr phase diagram at 865°C. An internal investigation at Chalmers HTC Center of AISI430 analysing the Ferrite/Austenite ratio at different temperatures did however show that at 865°C AISI430 is $\approx 40\%$ austenite, see Appendix E. The failure of the AISI430 therefore could be due to the stresses induced by the differences between the TEC of ferrite and austenite.

Between AISI409, AISI441 and Crofer 22 APU the idea that chromium being the determining factor could still hold true. The result might still be biased towards AISI409 breaking faster than it should relative to AISI441 and Crofer 22 APU since the later two have more beneficial alloying elements. To gain an idea about when AISI441 and Crofer 22 APU should break based on chromium content an AISI409 was exposed till failure and the fatal mass gain was noted. The fatal mass gain was found to be 0.91 mg cm^{-2} after subtraction of the initial oxidation of the coating. The mass gain is equivalent to the mass of oxygen used to form oxides in the alloy system. Since the main oxide formed is chromia, when the initial mass gain is subtracted, the calculation will be made based on the assumption that chromia is the only oxide forming. Based on the mass gain the moles of oxygen can be calculated as follows:

$$n_O = \frac{\Delta m}{M_O} = 5.69 \times 10^{-5} \frac{\text{mol}}{\text{cm}^2}, \quad (4.1)$$

and since two moles of chromium is used for every 3 moles of oxygen to form chromia (Cr_2O_3) the amount of chromium oxidized in moles can be calculated:

$$n_{Cr_used} = \frac{2}{3} \times n_O = 3.79 \times 10^{-5} \frac{\text{mol}}{\text{cm}^2}. \quad (4.2)$$

To determine the amount of Cr consumed the initial chromium amount in moles needs to be known. The initial chromium concentration in weight percentage is known, Table 3.1, so the mass is what initially needs to be calculated. In Equation 4.3 the mass of the available chromium reservoir per cm^2 is calculated:

$$m_{Cr_Res} = \frac{1\text{cm} \times 1\text{cm} \times \frac{0.038\text{cm}}{2} \times \rho_{FSS}}{\text{cm}^2} = 0.149 \frac{\text{g}}{\text{cm}^2}. \quad (4.3)$$

From here the mass of chromium can be determined using the known initial chromium concentration which then can be converted to moles using the molar mass of chromium:

$$m_{0_Cr} = m_{Cr_res.} \times Cr \text{ wt}\% = 0.017 \frac{\text{g}}{\text{cm}^2}, \quad (4.4)$$

$$n_{0_Cr} = \frac{m_{0_Cr}}{M_{Cr}} = 3.28 \times 10^{-4} \frac{\text{mol}}{\text{cm}^2}. \quad (4.5)$$

Then it is just a matter of calculating how big a percentage of the total chromium content has been consumed and use that to calculate the resulting alloy concentration:

$$\%n_{Cr} = \frac{n_{Cr_used}}{n_{0_Cr}} \times 100 = 11.566\%, \quad (4.6)$$

$$Cr \text{ wt}\%_{Critical} = Cr \text{ wt}\% - (Cr \text{ wt}\% \times \frac{\%n_{Cr}}{100}) = 10.081\text{wt}\% \quad (4.7)$$

The full calculations can be seen in Appendix B. The critical chromium concentration of 10.1wt% appears to be where the sample drops below the N_{Cr}^{crit2} value from Carl Wagners second criteria, Equation 2.32. As discussed AISI409s composition is different from that of AISI441 and Crofer 22 APU, but in the following it will be assumed that they share the same critical chromium concentration. Based on the alloying elements AISI441 and Crofer 22 APU contain that AISI409 does not the calculated lifetime should in theory be an underestimation. The critical chromium concentration does not enable direct lifetime calculation and therefore the rate constant for the alloys need to be determined first.

4.1.4 Oxidation Rate Constants

The oxidation rate constants were determined using the parabolic rate laws test for fit, seen in Table 2.1, as the resulting slope equates to the rate constant. Figure 4.6a shows linearized data for AISI441 at different temperatures. Figure 4.6b shows the resulting Arrhenius plot based on the rate constants acquired from Figure 4.6a. The Arrhenius plot enables the acquisition of the activation energy and the constant A that in turn enables

the calculation of the oxidation constant at any temperature for AISI441, according to Equation 2.24.

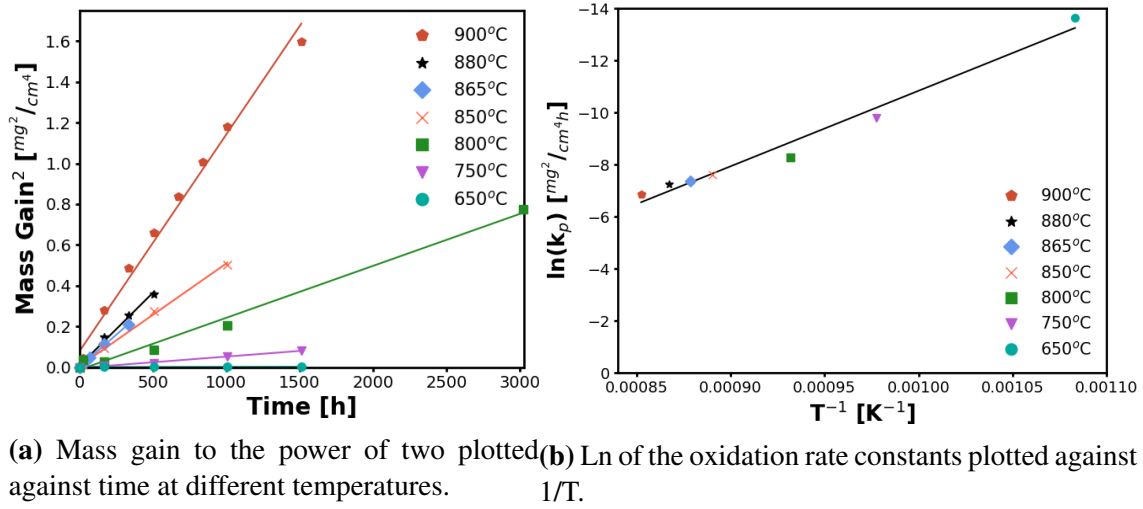


Figure 4.6: Graphical representation of the process of going from exposure data to k_p 's and to Arrhenius values that enable calculations of other k_p 's.

Plots like the ones in Figure 4.6 were constructed for all the investigated alloys. Figure 4.7 is a compiled Arrhenius plot of data for AISI409, AISI430, AISI441 and Crofer 22 APU. What is interesting here is that all the data points follow the same trend line. What is more is that 70% of the data points lay within the relatively narrow dark grey area. That they follow the same line indicates that opposite to when they are uncoated, as seen in Figure 1.1a, the alloys oxidation behavior is dictated by the coating in the entirety of the investigated temperature interval. This could be due to the beneficial effects gained from cerium.

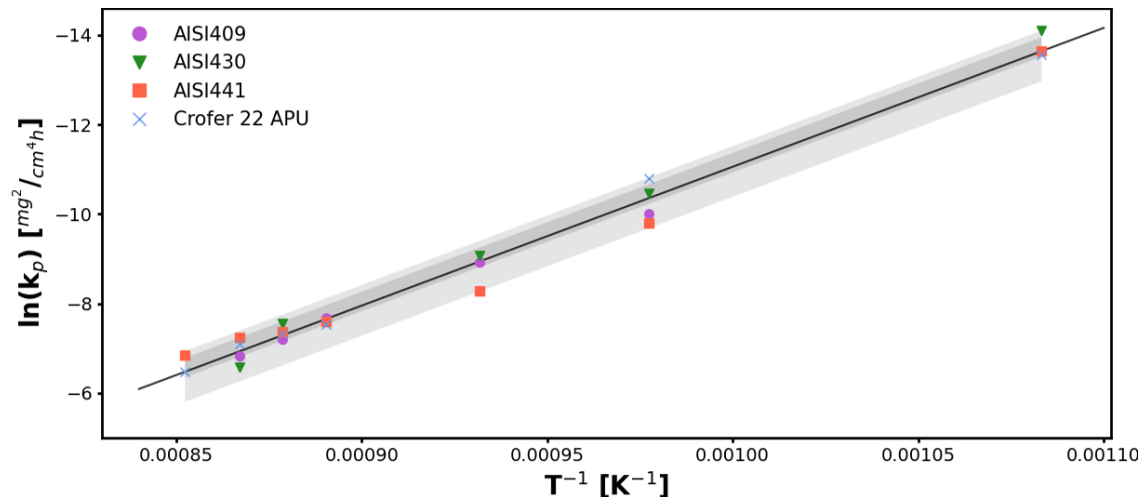


Figure 4.7: Arrhenius plot with all the oxidation rate constants for AISI409, AISI430, AISI441, and Crofer 22 APU.

4.1.5 Time till failure

Now that the rate constant and the critical chromium content is known the calculation of theoretical time to failure is enabled. Step one is determining the fatal mass gain for each sample. To do this first the moles of chromium per cm^2 of each alloy is calculated, as done in Equation 4.5 for AISI409. Then the theoretical end amount of chromium is calculated using the critical concentration of 10.1wt%, following the same method used to calculate the initial amount. The difference between the start and end value is then multiplied with 1.5, which is the ratio of oxygen per chromium in chromia (Cr_2O_3), and with the molar mass of oxygen, Equation 4.8.

$$\Delta m_{\text{Alloy}} = 1.5 \times \Delta n_{\text{Cr}} \times M_{\text{O}} \quad (4.8)$$

The fatal mass gains for the alloys are listed in Table 4.1. All the calculations can be seen in Appendix C. It is worth noting that the reason for why the fatal mass gain of AISI430 is higher than that of AISI441, despite AISI441 having a higher chromium content, is that the AISI430 samples used are thicker, Table 3.2.

Table 4.1: The theoretical mass gain leading to alloy failure. Based on a critical chromium concentration of 10.1wt%.

Alloy	Thickness [mm]	Fatal Mass Gain [mg cm^{-2}]
AISI 409	0.38	0.90
AISI 430	0.38	4.21
AISI 441	0.30	4.06
Crofer 22 APU	0.30	6.99

Then to calculate the time till failure the mass gain to the power of two has to be divided with the rate constant. Table 4.2 shows time to failure for the alloys at 850°C .

Table 4.2: Time till failure for AISI409, AISI430 and Crofer 22 APU. Values for a uncoated Crofer 22 APU is also listed for comparison reasons.

Alloy	Thickness [mm]	k_p 850°C [$\text{mg}^2 \text{cm}^{-4} \text{h}^{-1}$]	Time to failure [h]
Uncoated Cro- fer 22 APU	0.30	1.51×10^{-4}	17425
AISI 409	0.38	3.93×10^{-4}	2046
AISI 441	0.30	5.03×10^{-4}	32828
Crofer 22 APU	0.30	5.35×10^{-4}	91194

The values from Table 4.2 tells a relatively clear story. The chromium content is important as Crofer 22 APUs lifetime is larger than the rest. The values also show how coatings can be used to enable cheaper alloys in place of more expensive alloys as AISI441 shows a lifetime almost twice as high as that for uncoated Crofer 22 APU.

4.1.6 Temperature Dependence of Critical Chromium Concentration

In the previous discussion about critical chromium concentration and time till failure everything was based on data collected at 850°C. It is therefore not known whether the same data can be used to determine lifetime at other temperatures. So before assuming that the critical chromium content is constant at any temperature this will be investigated using Wagner second criteria, Equation 2.32. First the oxidation rate constants need to be converted from mass gain per area (m) to film thickness (w). This is done by dividing the rate constants with the density of chromia to the power of 2, Equation 4.9.

$$k_{\Delta w} = \frac{k_{\Delta m}}{\rho_{chromia}^2} \quad (4.9)$$

Then using Equation 2.32 with one over the PBR of chromia, Table 2.2, in place of the molarvolumes and diffusion values taken from [54] N_{Cr}^{cri2} can be calculated. As seen in Equation 2.32 N_{Cr}^{cri2} is equal to $N_{Cr}^{(o)}$ subtracted by $N_{Cr,i}$. Wagner suggested that the critical alloy concentration was reached when the interfacial concentration was $N_{Cr,i} \approx 0$. While the argument for $N_{Cr,i} \approx 0$ might make sense in that an alloy will break when there is no more chromium available, it does not make sense at the investigated temperatures. Diffusion at the investigated temperatures is so high that the supply from the bulk to the surface should be sufficient to assure that at the interface does not get depleted before the bulk. Therefore it is more likely that $N_{Cr,i}$ is the same as the experimentally determined critical value of $\approx 10\text{wt}\%$ from Section 4.1.3. This means that the true $N_{Cr}^{(o)}$ is equal to the sum of N_{Cr}^{cri2} and $N_{Cr,i}$. Table 4.3 shows the calculated N_{Cr}^{cri2} and the corrected $N_{Cr}^{(o)}$.

Table 4.3: The critical chromium concentration at different temperatures. All the values are in wt%, but calculations were done in atomic weight.

Temp.	AISI409		AISI441		Crofer 22 APU	
	N_{Cr}^{cri2}	$N_{Cr}^{(o)}$	N_{Cr}^{cri2}	$N_{Cr}^{(o)}$	N_{Cr}^{cri2}	$N_{Cr}^{(o)}$
650°C	3.40	13.40	3.96	13.96	4.37	14.37
750°C	1.91	11.91	2.28	12.28	1.48	11.48
800°C	1.25	11.25	1.84	11.84	1.46	11.46
850°C	1.08	11.08	1.32	11.32	1.45	11.45
865°C	1.22	11.22	1.31	11.31	1.32	11.32
880°C	1.31	11.31	1.14	11.14	1.34	11.34
900°C	-	-	1.05	11.05	1.34	11.34

The values in Table 4.3 can be seen to increase as temperature decreases. The reason for this trend is that the diffusion rate decreases with temperature and the interfacial values therefore need to be higher for there to be a sufficient amount of chromium to form chromia. AISI409 has a chromium content of 11.4wt% but can form chromia at 750°C. $N_{Cr,i}$ or the used diffusion values might therefore be wrong. $N_{Cr,i}$ being less than 10wt% does not seem unbelievable as it is based on a calculated average critical chromium concentration on a relatively small sample size. Were $N_{Cr,i}$ for an example 9wt% the $N_{Cr}^{(o)}$ 850°C

value would be inline with the experimentally observed value and the $N_{Cr}^{(o)}$ at 750°C and 650°C would also match what was observed in Section 4.1.2 for AISI409. The values presented in Table 4.3 should therefore be used for more of a guide when designing or selecting an alloy. In regards to lifetime calculations at other temperatures the values indicate that the calculations should be made on the basis of critical chromium concentration different from that of 10wt% from Section 4.1.3. The complete calculations can be found in Appendix D

4.2 Reactive Elements Effect - Cerium

The mechanisms behind the improved performance of the alloys in the presence of RE are highly debated. Improved understanding of the REE will enable development of better high temperature alloys. An improved understanding will also help transition from the current trial and error approach to a more focused approach to RE additions. Thus, it has the potential to make better alloys resulting in higher efficiencies, longer lifetimes, and potential cost reductions.

Formulating a full description of the beneficial effect gained from RE is beyond the scope of this thesis. In the following a more narrow investigation will be presented. The investigation focuses on the theory that RE causes the formation of $MeCrO_3$ perovskites (Me = reactive element) within the chromia grain boundaries. As mentioned in Section 2.6.2 the formation of $MeCrO_3$ at the grain boundaries, should block outward diffusion of chromium while allowing slow inward diffusion of oxygen across the grain boundaries. Therefore the theory argues that the chromia scale growth mechanism changes from primarily outward cation to predominant inward growing and that this is the cause of the beneficial effect.

To test the validity of the above hypothesis for Ce/Co coatings, Crofer 22 APU was coated according to Figure 4.8. In Figure 4.8a Crofer 22 APU was pre-oxidized at 900°C for 3 mins to form a thin chromia layer on the surface. The pre-oxidation was performed to inhibit the inner diffusion of cobalt and iron at the metal-coating interface during the exposure. The pre-oxidized Crofer 22 APU was further coated with 400 nm of cobalt using the PVD process mentioned in Section 3.1.1. The cobalt coated Crofer 22 APU was exposed to 850°C for 30 mins to oxidize the metallic cobalt to Co_2O_4 . The purpose of this exposure is to create an oxide barrier between the chromia scale formed on the steel and further coatings. Futheron, four different coating combinations were deposited on the exposed cobalt coated Crofer 22 APU, as seen in Figure 4.8b. The coatings and more information can be seen in Table 3.2.

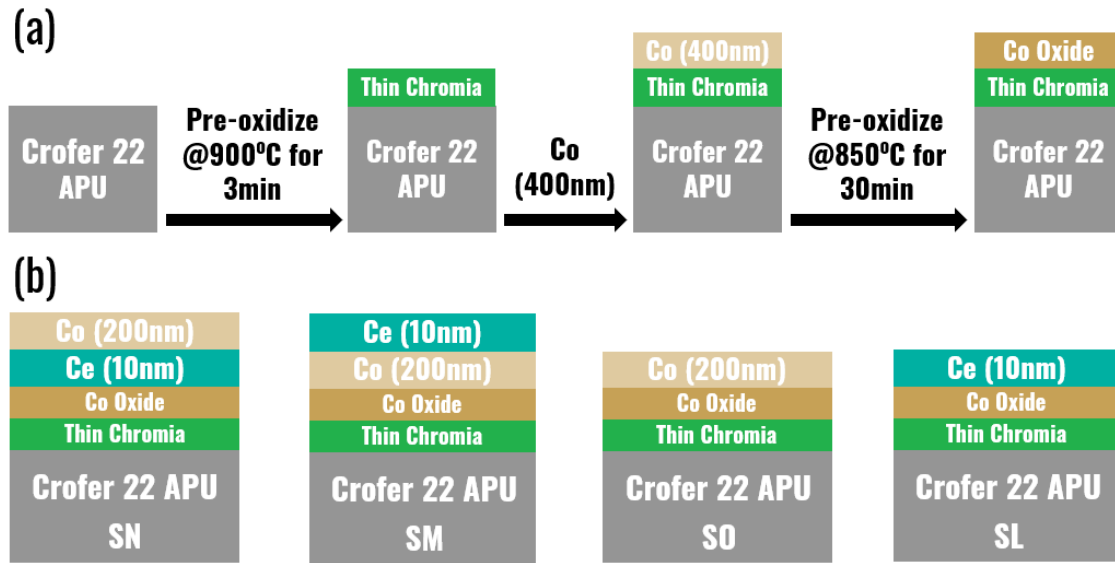


Figure 4.8: Illustrations of the coating steps used to get the desired coatings. (a) Preparation of the base sample. (b) Different applied coatings with their respective names SN, SM, SO and SL.

The samples were first exposed at 850°C for 1512 hours. The mass gain behaviour of the coated steels can be seen in Figure 4.9. The coupons marked as SN, SM, SO in Figure 4.9a showed a rapid mass gain in the first ≈ 0.5 hours of the exposure. This is due to the oxidation of the 200 nm metallic cobalt in the coating to Co_3O_4 . Such a rapid mass gain is not observed on SL due of the lack of metallic cobalt. To compare the behaviour of the coated steels, the mass gain due to the oxidation of the cobalt coating is subtracted in the plot shown in Figure 4.9b.

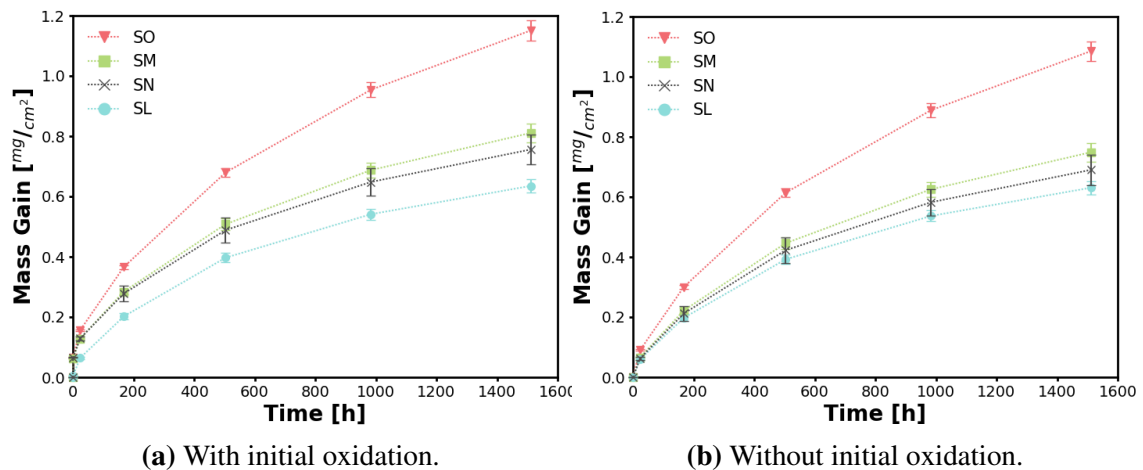


Figure 4.9: The mass gains of SN, SM, SO and SL against time to better understand the effect of cerium in the coating. (a) Is the mass gains as they were observed and (b) is the mass gains with the mass gain after 0.5 hours subtracted. The exposure temperature was 850°.

The coating with no cerium, SO, showed the highest mass gain after 1512 hours. The

other three coatings with cerium (SM, SN, SL) showed similar mass gains up to 1500 hours. Already after 168 hours, a beneficial effect of cerium was observed with a clear difference between the mass gain of the coating without cerium (SO) and the coatings with cerium (SM, SN, SL).

In a different set of exposures, the coated steels with cerium (SM, SN, SL) were exposed for varying durations. A set of coupons was removed after 0.5, 24, 168, 336, and 504 hours. The cross-section of the coupons removed at different times were prepared using BIB. The microstructure of the cross-section was further analyzed using back-scattered electrons. Since the cerium is the heaviest element in the coating, it appears bright in a back-scattered electron analysis compared to the other elements. Figure 4.10 shows SEM micrographs of the cerium coated steels (SM, SN, SL) cross-sections at the various times. The images in the figure are labelled with the codes of the coatings show in the Table 3.2 and Figure 4.8.

After 0.5 hours exposure, the cerium in SN appeared to be continuous, as seen for sample SN9 in Figure 4.10. The SM7 cerium particles are not in the form of a continuous layer. The coating appears to be porous after 0.5 hours for both SN9 and SM7. After 24 hours, the micrographs in Figure 4.10 SL7, SM7, SN7 show the cerium in the coating. In SN 7, the cerium is sandwiched in the coating while the cerium is observed at the coating-air interface in SM7 and SL7. The locations of the cerium particles in Figure 4.10 SL7, SM7, SN7 is similar to those deposited in the coating shown in Figure 4.8. Chromia scale is observed at the metal-oxide interface. After 168 hours, the SL13, SM13, SN13 micrographs in Figure 4.10 show the cerium in the coating no longer is continuous. The cerium appears to be brighter and agglomerated. Nevertheless, the locations of the cerium particles in Figure 4.10 SL13, SM13, SN13 is still similar to those deposited in the coating shown in Figure 4.8. The chromia scale appears to be thicker after 168 hour compared to 24 hours which relates well with the observed mass gains in Figure 4.9.

From the micrographs of SL13, SM13, SN13 in Figure 4.10 it can be seen that the cerium particles are separated from the chromia scale by MCO. Thus, the formation of MeCrO_3 perovskites ($\text{Me} = \text{Re}$) within the grain boundaries of chromia seems highly unlikely at 168 hours. Nevertheless, a clear difference in the mass gain is observed between the coating with no cerium (SO) and the coatings with cerium (SN, SM, SL), Figure 4.9b. A positive effect can therefore be observed before cerium has interacted with the chromia scale. This indicates that the mechanism behind the beneficial effect of cerium is due to more than blocking the chromium ions outward diffusion through the chromia scale. This points towards the findings of Sattari et al. suggesting that cerium decorates the grain boundaries in the $(\text{Cr,Mn})_3\text{O}_4$ spinel.

After 1500 hours cerium does however appear to be in the chromia scale as seen in the SL4, SM4, SN4 micrographs in Figure 4.10. This is contrary to general understanding that RE moves to the oxide-air interface during the exposure. To ensure that the cerium observed in the chromia scale had not been moved by the argon beam, samples with wafers on both sides were BIB'ed all the way through. On the double wafer samples cerium was found in the chromia scale on both sides indicating that the argon beam did not affect the cerium observed in the SEM images. From the micrographs in Figure 4.10 it is difficult to tell if cerium is moving down towards the alloy or if the cerium is being over grown.

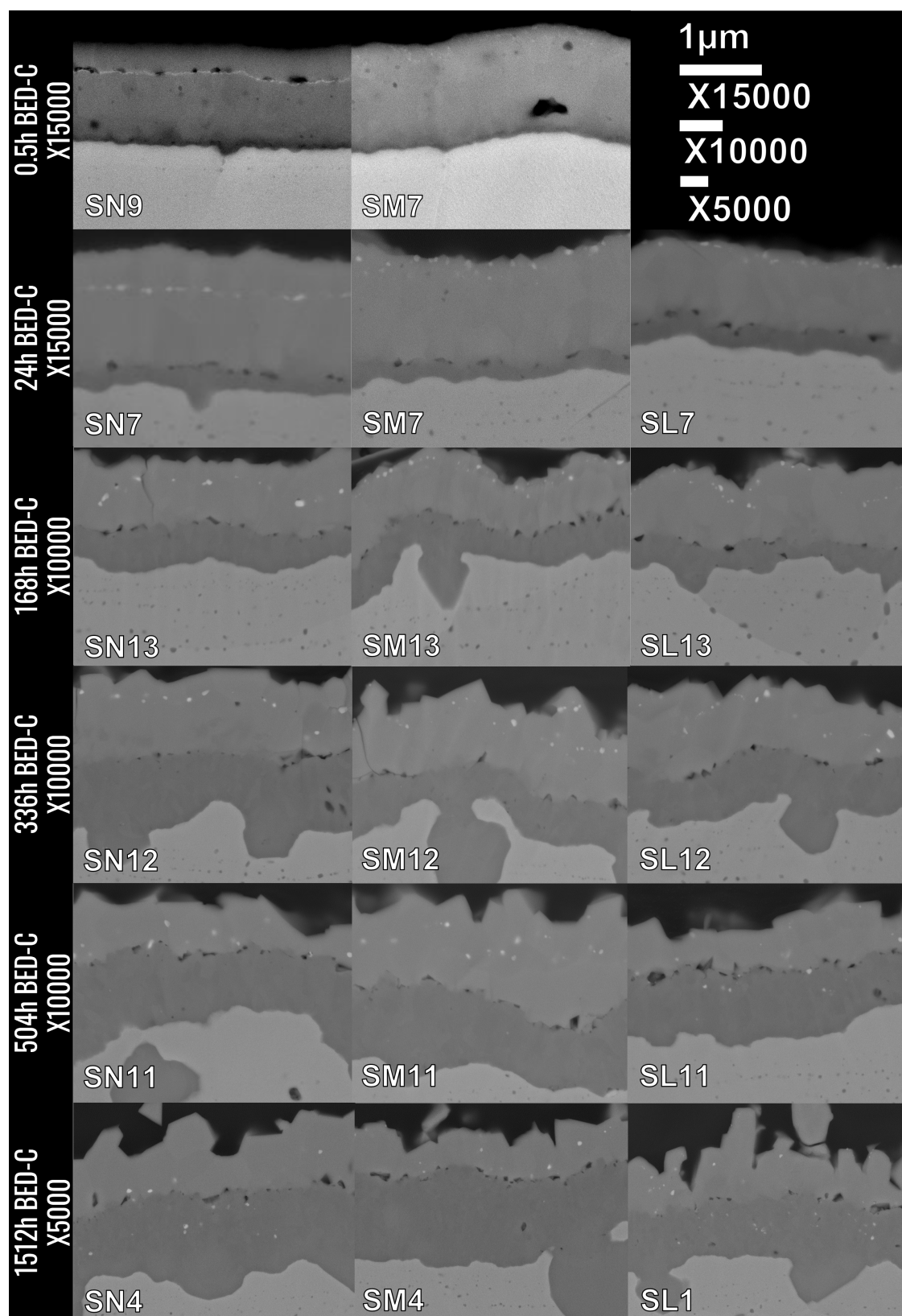


Figure 4.10: SEM images of SN, SM, and SL at different exposure times. The exposure temperature was 850°. The white spots seen in the oxide is cerium particles.

5 | Conclusion

The findings of this thesis are the result of an attempt to gain an improved understanding of coated FSS oxidation mechanisms. An improved understanding of the oxidation mechanisms has the potential to enable development of cheap and long lasting metallic interconnects for SOFCs. Four types of FSS alloys coated primarily with 10Ce600Co have been exposed at different temperatures. The alloys varied primarily in chromium content and price. Different variations of the 10Ce600Co coating were used on Crofer 22 APU for exposures at 850°C in an effort to improve the understanding of the reactive element effect of Ce in the coating.

The data showed that, contrary to how the alloys behaved when exposed uncoated, they when coated with Ce/Co had similar oxidation kinetics, strengthening previous findings. The oxidation behavior went from being dictated by the alloys elemental composition to being dictated by the coating in the entirety of the investigated temperature interval (650 - 900 °C).

Based on the observations made at different temperatures, it however became clear that the time till failure for the coated alloys still is alloy dependent. Especially chromium content in the alloy plays a critical role in the oxidation behaviour of the alloys, and in extension the time to breakaway corrosion. Since all the Ce/Co coated alloys displayed similar oxidation kinetics, a correlation between chromium content in the steel and lifetime at a specific temperature could be made. The correlation showed that, as expected, coated Crofer 22 APU (22.4 wt% Cr) has the longest theoretical lifetime of all, and almost three times greater than coated AISI441 (17.5 wt% Cr). The results however also highlighted the benefits of the coating as coated AISI441 theoretically should last twice as long as uncoated Crofer 22 APU at 850 °C. Data collected at 900°C showed AISI409 (11.4 wt% Cr) and AISI430 (16.2 wt% Cr) reach breakaway corrosion within 24 hours, while AISI441 and Crofer 22 APU showed parabolic oxidation kinetics during the exposure up to 1512 hours. Lifetime studies of alloys of different qualities are therefore difficult as they require long exposures at lower temperatures or comparison of data acquired at different temperatures. Moreover, coated AISI430 reached breakaway corrosion before coated AISI409 at 865°C. AISI430 and AISI441 have comparable chromium content but coated AISI430 reached breakaway corrosion much earlier than AISI441. This observation is however understandable as AISI430 lacks ferrite stabilizers and is $\approx 40\%$ Austenite at 865°C. The result indicates that alloying elements, other than chromium, in the steel play an important role in the oxidation behaviour.

Temperature further complicates lifetime modelling and comparison of alloys. Temperature complicates things since the critical chromium concentration was found to be a function of temperature with increasing chromium content needed with lower temperatures to ensure the formation of a protective oxide scale.

In regards to the 10Ce/600Co coating it was already known that changing the quantities of either element would not be beneficial. Increasing both the quantity of reactive

elements in the coating, and the thickness of the cobalt was likewise observed to not improve the oxidation kinetics of the coated FSS. This was evident as the coating combination of 10Ce600Co was found to be superior compared to 50Ce1200Co for exposures up to 3000 hours at 850°C.

The results of the exposures on the 10Ce600Co coating variations on Crofer 22 APU showed improved oxidation kinetics due to the presence of cerium. The beneficial effect of having cerium in the Ce/Co coating did not appear to solely be the result of inhibited outward diffusion of Cr^{3+} within the grain boundaries of chromia. The results indicated this as the beneficial effect of cerium in the coating was observed before cerium appeared to be near the chromia scale.

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Appendices

A | Appendix: Procedure used when preparing for and BIB'ing samples

Sample preparation

1. Cut a piece of a tissue and wrap it around the lower part of the sample.
2. Place the wrapped sample in the sample holder so that the holder is tightened on the paper part.
3. Mount the sample holder on the saw.
4. Start the saw and set the speed to 200 to 250 rpm.
5. Grab the part of the sample that will fall off with a tweezer right before the saw cuts through the sample so it doesn't fall down
6. Use locktite glue to glue a small piece of silicon wafer to the sample. Place the wafer parallel and slightly above the cut-face of the sample.
7. Polish/grind the sample with 800, 1200, 2400 and lastly 4000 grade sandpaper.
8. Glue the sample to the holder needed for BIB and SEM using silver paint. Use the special holder designed for making the wafer align correctly.
9. Load the sample into the BIB

BIB'ing

1. Attach the sample holder to the block used to set the correct sample distance. Then attach the sample so that it has the right distance.
2. Load the sample holder into the BIB and make sure that it makes a click sound which signifies that it has been properly inserted.
3. Look through the microscope and move the mask close to the sample.
4. Flip the sample holder and extend the sample out past the mask.
5. The focus on the wafer and make it disappear under the mask. Note where it disappears and move it 3mm back out using the scale seen.
6. Flip the sample back and forth at low magnification to ensure that a part of the wafer will be BIBed.
7. Close the BIB and press pump.
8. Purge the BIB five times at 10^{-5} before pressing start.
9. The operation values should be: 8kV, 3mA, and 6 hours.

B | Appendix: Calculation of The Critical Chromium Concentration

Mass gain to Cr consumed 409

$$\Delta m := 0.91 \frac{\text{mg}}{\text{cm}^2} ;$$

$$M_{Cr} := 51996 \frac{\text{mg}}{\text{mol}} ;$$

$$M_O := 15999 \frac{\text{mg}}{\text{mol}} ;$$

$$M_{chromia} := 151990 \frac{\text{mg}}{\text{mol}} ;$$

$$n_{O_Area} := \frac{\Delta m}{M_O} = 5.69 \times 10^{-5} \frac{\text{mol}}{\text{cm}^2}$$

$$A_{real} := 1 \text{ cm}^2 ;$$

$$n_O := n_{O_Area} \cdot A_{real} = 5.69 \times 10^{-5} \text{ mol}$$

$$n_{Cr_used} := n_{O_Area} \cdot \frac{2}{3} = 3.79 \times 10^{-5} \frac{\text{mol}}{\text{cm}^2}$$

$$V_{sample} := 1 \text{ cm} \cdot 1 \text{ cm} \cdot \frac{0.038 \text{ cm}}{2} = 0.01900000000 \text{ cm}^3$$

$$\rho_{steel} := 7.87 \frac{\text{g}}{\text{cm}^3} ;$$

$$m_{sample} := V_{sample} \cdot \rho_{steel} = 0.1495300000 \text{ g}$$

$$m_{Cr_start} := m_{sample} \cdot \frac{11.4}{100} = 0.01704642000 \text{ g}$$

$$n_{Cr_start} := \frac{m_{Cr_start}}{M_{Cr}} = 3.28 \times 10^{-4} \text{ mol}$$

$$Cr\%_{consumed} := \frac{n_{Cr_used}}{n_{Cr_start}} \cdot 100 = 11.56628915$$

$$11.4 \text{ wt}\%: n_{Cr_start} = 3.28 \times 10^{-4} \text{ mol}$$

$$x \text{ wt}\%: n_{Cr_used} = 3.79 \times 10^{-5} \text{ mol}$$

$$x \text{ wt}\% \Rightarrow l := \frac{11.4}{100} \cdot Cr\%_{consumed} = 1.318556963$$

$$x_{wt\%} := 11.4 - l = 10.08144304$$

Figure B.1: Calculation of the critical chromium concentration.

C | Appendix: Failure Calculations

$$\begin{aligned}
 Cr_{crit} &:= 10.1 : \\
 Cr_{wt_409} &:= 11.4 : \\
 Cr_{wt_430} &:= 16.2 : \\
 Cr_{wt_441} &:= 17.56 : \\
 Cr_{wt_Crofer} &:= 22.92 : \\
 \rho_{steel} &:= 7.87 \frac{\text{g}}{\text{cm}^3} : \\
 M_{\text{O}} &:= 15.999 \frac{\text{g}}{\text{mol}} : \\
 M_{\text{Cr}} &:= 51.996 \frac{\text{g}}{\text{mol}} :
 \end{aligned}$$

Mass Calculated for one square cm sample for ease of mass gain calculation:

$$\begin{aligned}
 m_{area_409} &:= 1 \text{ cm} \cdot 1 \text{ cm} \cdot \frac{0.038 \text{ cm}}{2} \cdot \rho_{steel} = 0.1495300000 \text{ g} \\
 m_{area_430} &:= 1 \text{ cm} \cdot 1 \text{ cm} \cdot \frac{0.038 \text{ cm}}{2} \cdot \rho_{steel} = 0.1495300000 \text{ g} \\
 m_{area_441} &:= 1 \text{ cm} \cdot 1 \text{ cm} \cdot \frac{0.03 \text{ cm}}{2} \cdot \rho_{steel} = 0.1180500000 \text{ g} \\
 m_{area_Crofer} &:= 1 \text{ cm} \cdot 1 \text{ cm} \cdot \frac{0.03 \text{ cm}}{2} \cdot \rho_{steel} = 0.1180500000 \text{ g} \\
 m_{area_Crofer_thin} &:= 1 \text{ cm} \cdot 1 \text{ cm} \cdot \frac{0.02 \text{ cm}}{2} \cdot \rho_{steel} = 0.0787000000 \text{ g}
 \end{aligned}$$

Start Values:

$$\begin{aligned}
 m_{Cr_start_409} &:= m_{area_409} \cdot \frac{Cr_{wt_409}}{100} = 0.01704642000 \text{ g} \\
 m_{Cr_start_430} &:= m_{area_430} \cdot \frac{Cr_{wt_430}}{100} = 0.02422386000 \text{ g} \\
 m_{Cr_start_441} &:= m_{area_441} \cdot \frac{Cr_{wt_441}}{100} = 0.02072958000 \text{ g} \\
 m_{Cr_start_Crofer} &:= m_{area_Crofer} \cdot \frac{Cr_{wt_Crofer}}{100} = 0.02705706000 \text{ g} \\
 m_{Cr_start_Crofer_thin} &:= m_{area_Crofer_thin} \cdot \frac{Cr_{wt_Crofer}}{100} = 0.01803804000 \text{ g} \\
 n_{Cr_start_409} &:= \frac{m_{Cr_start_409}}{M_{Cr}} = 0.0003278409877 \text{ mol} \\
 n_{Cr_start_430} &:= \frac{m_{Cr_start_430}}{M_{Cr}} = 0.0004658792983 \text{ mol} \\
 n_{Cr_start_441} &:= \frac{m_{Cr_start_441}}{M_{Cr}} = 0.0003986764366 \text{ mol} \\
 n_{Cr_start_Crofer} &:= \frac{m_{Cr_start_Crofer}}{M_{Cr}} = 0.0005203681051 \text{ mol} \\
 n_{Cr_start_Crofer_thin} &:= \frac{m_{Cr_start_Crofer_thin}}{M_{Cr}} = 0.0003469120701 \text{ mol}
 \end{aligned}$$

Figure C.1: Calculation of the critical chromium concentration.

Theoretical end values:

$$m_{Cr_end_409} := m_{area_409} \cdot \frac{Cr_{Crit}}{100} = 0.01510253000 \text{ g}$$

$$m_{Cr_end_430} := m_{area_430} \cdot \frac{Cr_{Crit}}{100} = 0.01510253000 \text{ g}$$

$$m_{Cr_end_441} := m_{area_441} \cdot \frac{Cr_{Crit}}{100} = 0.01192305000 \text{ g}$$

$$m_{Cr_end_Crofer} := m_{area_Crofer} \cdot \frac{Cr_{Crit}}{100} = 0.01192305000 \text{ g}$$

$$m_{Cr_end_Crofer_thin} := m_{area_Crofer_thin} \cdot \frac{Cr_{Crit}}{100} = 0.007948700000 \text{ g}$$

$$n_{Cr_end_409} := \frac{m_{Cr_end_409}}{M_{Cr}} = 0.0002904556119 \text{ mol}$$

$$n_{Cr_end_430} := \frac{m_{Cr_end_430}}{M_{Cr}} = 0.0002904556119 \text{ mol}$$

$$n_{Cr_end_441} := \frac{m_{Cr_end_441}}{M_{Cr}} = 0.0002293070620 \text{ mol}$$

$$n_{Cr_end_Crofer} := \frac{m_{Cr_end_Crofer}}{M_{Cr}} = 0.0002293070620 \text{ mol}$$

$$n_{Cr_end_Crofer_thin} := \frac{m_{Cr_end_Crofer_thin}}{M_{Cr}} = 0.0001528713747 \text{ mol}$$

Difference - Start to End:

$$n_{Cr_Consumed_409} := n_{Cr_start_409} - n_{Cr_end_409} = 0.0000373853758 \text{ mol}$$

$$n_{Cr_Consumed_430} := n_{Cr_start_430} - n_{Cr_end_430} = 0.0001754236864 \text{ mol}$$

$$n_{Cr_Consumed_441} := n_{Cr_start_441} - n_{Cr_end_441} = 0.0001693693746 \text{ mol}$$

$$n_{Cr_Consumed_Crofer} := n_{Cr_start_Crofer} - n_{Cr_end_Crofer} = 0.0002910610431 \text{ mol}$$

$$n_{Cr_Consumed_Crofer_thin} := n_{Cr_start_Crofer_thin} - n_{Cr_end_Crofer_thin} = 0.0001940406954 \text{ mol}$$

Moles of Oxygen:

$$n_{O_gained_409} := 1.5 \cdot n_{Cr_Consumed_409} = 0.00005607806370 \text{ mol}$$

$$n_{O_gained_430} := 1.5 \cdot n_{Cr_Consumed_430} = 0.0002631355296 \text{ mol}$$

$$n_{O_gained_441} := 1.5 \cdot n_{Cr_Consumed_441} = 0.0002540540619 \text{ mol}$$

$$n_{O_gained_Crofer} := 1.5 \cdot n_{Cr_Consumed_Crofer} = 0.0004365915646 \text{ mol}$$

$$n_{O_gained_Crofer_thin} := 1.5 \cdot n_{Cr_Consumed_Crofer_thin} = 0.0002910610431 \text{ mol}$$

Mass Gained:

$$m_{O_gained_409} := n_{O_gained_409} \cdot M_O = 0.0008971929411 \text{ g}$$

$$m_{O_gained_430} := n_{O_gained_430} \cdot M_O = 0.004209905338 \text{ g}$$

$$m_{O_gained_441} := n_{O_gained_441} \cdot M_O = 4.064610936 \text{ mg}$$

$$m_{O_gained_Crofer} := n_{O_gained_Crofer} \cdot M_O = 0.006985028442 \text{ g}$$

$$m_{O_gained_Crofer_thin} := n_{O_gained_Crofer_thin} \cdot M_O = 0.004656685629 \text{ g}$$

Figure C.2: Calculation of the critical chromium concentration.

Theoretical Fatal Mass Gain:

$$\Delta m_{409} := \frac{m_{O_gained_409}}{1 \text{ cm}^2} = 0.8971929411 \frac{\text{mg}}{\text{cm}^2}$$

$$\Delta m_{430} := \frac{m_{O_gained_430}}{1 \text{ cm}^2} = 4.209905338 \frac{\text{mg}}{\text{cm}^2}$$

$$\Delta m_{441} := \frac{m_{O_gained_441}}{1 \text{ cm}^2} = 4.064610936 \frac{\text{mg}}{\text{cm}^2}$$

$$\Delta m_{Crofer} := \frac{m_{O_gained_Crofer}}{1 \text{ cm}^2} = 6.985028442 \frac{\text{mg}}{\text{cm}^2}$$

$$\Delta m_{Crofer_thin} := \frac{m_{O_gained_Crofer_thin}}{1 \text{ cm}^2} = 4.656685629 \frac{\text{mg}}{\text{cm}^2}$$

$$\Delta m_{409}^2 = 0.8049551736 \frac{\text{mg}^2}{\text{cm}^4}$$

$$\Delta m_{430}^2 = 17.72330295 \frac{\text{mg}^2}{\text{cm}^4}$$

$$\Delta m_{441}^2 = 16.52106206 \frac{\text{mg}^2}{\text{cm}^4}$$

$$\Delta m_{Crofer}^2 = 48.79062234 \frac{\text{mg}^2}{\text{cm}^4}$$

Time to failure at 850C:

$$k_{p_409_850} := 0.000393488 \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}}$$

$$k_{p_430_850} := 1 \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}}$$

$$k_{p_441_850} := 0.000503265 \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}}$$

$$k_{p_Crofer_850} := 0.00053502 \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}}$$

$$k_{p_Crofer_850_uncoated} := 0.0028 \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}}$$

$$t_{409_850} := \frac{\Delta m_{409}^2}{k_{p_409_850}} = 2045.69 \text{ h}$$

$$t_{430_850} := \frac{\Delta m_{430}^2}{k_{p_430_850}} = 1.77 \times 10^1 \text{ h}$$

$$t_{441_850} := \frac{\Delta m_{441}^2}{k_{p_441_850}} = 32827.76 \text{ h}$$

$$t_{Crofer_850} := \frac{\Delta m_{Crofer}^2}{k_{p_Crofer_850}} = 91194.02 \text{ h}$$

$$t_{Crofer_850_uncoated} := \frac{\Delta m_{Crofer}^2}{k_{p_Crofer_850_uncoated}} = 17425.22227 \text{ h}$$

Figure C.3: Calculation of the critical chromium concentration.

D | Appendix: Temperature Dependence of Critical Chromium Concentration

409 kp values

$$k_{p_409_650_Theoretical} := 1.01484 \cdot 10^{-6} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_409_750} := 4.53587 \cdot 10^{-5} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_409_800} := 1.34091 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_409_850} := 3.93488 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_409_865} := 7.51657 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_409_880} := 1.086317 \cdot 10^{-3} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

441 kp values

$$k_{p_441_650} := 1.19683 \cdot 10^{-6} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_441_750} := 5.56698 \cdot 10^{-5} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_441_800} := 2.54754 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_441_850} := 5.03265 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_441_865} := 6.27254 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_441_880} := 7.14819 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_441_900} := 1.062892 \cdot 10^{-3} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

Crofer kp values

$$k_{p_Crofer_650} := 1.28709 \cdot 10^{-6} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_Crofer_750} := 2.03968 \cdot 10^{-5} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_Crofer_800} := 1.40162 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_Crofer_850} := 5.3502 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_Crofer_865} := 6.63254 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_Crofer_880} := 8.18473 \cdot 10^{-4} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

$$k_{p_Crofer_900} := 1.529111 \cdot 10^{-3} \frac{\text{mg}^2}{\text{cm}^4 \cdot \text{h}} ;$$

Figure D.1: Failure Calculations 1.

$N_{Cr}^{(2)}$ based on Iijima data

$$\begin{aligned}
 D_{Iijima_{Fe_Cr_612}} &:= 3.72 \cdot 10^{-16} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_621}} := 8.68 \cdot 10^{-16} \frac{\text{cm}^2}{\text{s}} : \\
 D_{Iijima_{Fe_Cr_654}} &:= 3.47 \cdot 10^{-15} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_671}} := 1.2 \cdot 10^{-14} \frac{\text{cm}^2}{\text{s}} : \\
 D_{Iijima_{Fe_Cr_701}} &:= 3.35 \cdot 10^{-14} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_753}} := 5.05 \\
 &\cdot 10^{-13} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_801}} := 3.56 \cdot 10^{-12} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_852}} := \\
 &1.39 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_868}} := 2.08 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : \\
 D_{Iijima_{Fe_Cr_879}} &:= 2.61 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_901}} := 4.67 \\
 &\cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} :
 \end{aligned}$$

$$N_{Cr}^{(2)} = \left(\frac{\pi \cdot k_c}{2 \cdot D} \right)^{\frac{1}{2}}$$

$$N_{Cr_409_650_Theoretical_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_409_650_Theoretical_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_654}}} \right)^{\frac{1}{2}} =$$

0.03305154596

$$N_{Cr_409_750_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_409_750_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_753}}} \right)^{\frac{1}{2}} = 0.01831649357$$

$$N_{Cr_409_800_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_409_800_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_801}}} \right)^{\frac{1}{2}} = 0.01186130690$$

$$N_{Cr_409_850_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_409_850_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_852}}} \right)^{\frac{1}{2}} = 0.01028291091$$

$$N_{Cr_409_865_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_409_865_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_868}}} \right)^{\frac{1}{2}} = 0.01161812147$$

$$N_{Cr_409_880_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_409_880_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_879}}} \right)^{\frac{1}{2}} = 0.01246854456$$

Figure D.2: Failure Calculations 2.

$N_{Cr}^{(2)}$ based on Iijima data

$$\begin{aligned}
D_{Iijima_{Fe_Cr_612}} &:= 3.72 \cdot 10^{-16} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_621}} := 8.68 \cdot 10^{-16} \frac{\text{cm}^2}{\text{s}} : \\
D_{Iijima_{Fe_Cr_654}} &:= 3.47 \cdot 10^{-15} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_671}} := 1.2 \cdot 10^{-14} \frac{\text{cm}^2}{\text{s}} : \\
D_{Iijima_{Fe_Cr_701}} &:= 3.35 \cdot 10^{-14} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_753}} := 5.05 \\
&\cdot 10^{-13} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_801}} := 3.56 \cdot 10^{-12} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_852}} := \\
&1.39 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_868}} := 2.08 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : \\
D_{Iijima_{Fe_Cr_879}} &:= 2.61 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_901}} := 4.67 \\
&\cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} :
\end{aligned}$$

$$\begin{aligned}
N_{Cr}^{(2)} &= \left(\frac{\pi \cdot k_c}{2 \cdot D} \right)^{\frac{1}{2}} \left(N_{Ni}^{(o)} - N_{Ni,i} \right) = \frac{V_{AB}}{V_{NiO}} \left(\frac{\pi k_p}{2D} \right)^{1/2} \\
N_{Cr_441_650_Iijima}^{(2)} &:= \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_441_650_Dw}}{2 \cdot D_{Iijima_{Fe_Cr_654}}} \right)^{\frac{1}{2}} = 0.03589295572 \\
N_{Cr_441_750_Iijima}^{(2)} &:= \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_441_750_Dw}}{2 \cdot D_{Iijima_{Fe_Cr_753}}} \right)^{\frac{1}{2}} = 0.02029186053 \\
N_{Cr_441_800_Iijima}^{(2)} &:= \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_441_800_Dw}}{2 \cdot D_{Iijima_{Fe_Cr_801}}} \right)^{\frac{1}{2}} = 0.01634907681 \\
N_{Cr_441_850_Iijima}^{(2)} &:= \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_441_850_Dw}}{2 \cdot D_{Iijima_{Fe_Cr_852}}} \right)^{\frac{1}{2}} = 0.01162916925 \\
N_{Cr_441_865_Iijima}^{(2)} &:= \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_441_865_Dw}}{2 \cdot D_{Iijima_{Fe_Cr_868}}} \right)^{\frac{1}{2}} = 0.01061323497 \\
N_{Cr_441_880_Iijima}^{(2)} &:= \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_441_880_Dw}}{2 \cdot D_{Iijima_{Fe_Cr_879}}} \right)^{\frac{1}{2}} = 0.01011429269 \\
N_{Cr_441_900_Iijima}^{(2)} &:= \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_441_900_Dw}}{2 \cdot D_{Iijima_{Fe_Cr_901}}} \right)^{\frac{1}{2}} = 0.009220274618
\end{aligned}$$

Figure D.3: Failure Calculations 3.

$N_{Cr}^{(2)}$ **based on Iijima data**

$$\begin{aligned}
 D_{Iijima_{Fe_Cr_612}} &:= 3.72 \cdot 10^{-16} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_621}} := 8.68 \cdot 10^{-16} \frac{\text{cm}^2}{\text{s}} : \\
 D_{Iijima_{Fe_Cr_654}} &:= 3.47 \cdot 10^{-15} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_671}} := 1.2 \cdot 10^{-14} \frac{\text{cm}^2}{\text{s}} : \\
 D_{Iijima_{Fe_Cr_701}} &:= 3.35 \cdot 10^{-14} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_753}} := 5.05 \\
 &\cdot 10^{-13} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_801}} := 3.56 \cdot 10^{-12} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_852}} := \\
 &1.39 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_868}} := 2.08 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : \\
 D_{Iijima_{Fe_Cr_879}} &:= 2.61 \cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} : D_{Iijima_{Fe_Cr_901}} := 4.67 \\
 &\cdot 10^{-11} \frac{\text{cm}^2}{\text{s}} :
 \end{aligned}$$

$$N_{Cr}^{(2)} = \left(\frac{\pi \cdot k_c}{2 \cdot D} \right)^{\frac{1}{2}} \left(N_{Ni}^{(o)} - N_{Ni,i} \right) = \frac{V_{AB}}{V_{NiO}} \left(\frac{\pi k_p}{2D} \right)^{1/2}$$

$$N_{Cr_Crofer_650_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_Crofer_650_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_654}}} \right)^{\frac{1}{2}} = 0.03722180657$$

$$N_{Cr_Crofer_750_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_Crofer_750_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_753}}} \right)^{\frac{1}{2}} = 0.01228267773$$

$$N_{Cr_Crofer_800_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_Crofer_800_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_801}}} \right)^{\frac{1}{2}} = 0.01212684625$$

$$N_{Cr_Crofer_850_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_Crofer_850_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_852}}} \right)^{\frac{1}{2}} = 0.01199044595$$

$$N_{Cr_Crofer_865_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_Crofer_865_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_868}}} \right)^{\frac{1}{2}} = 0.01091354890$$

$$N_{Cr_Crofer_880_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_Crofer_880_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_879}}} \right)^{\frac{1}{2}} = 0.01082280048$$

$$N_{Cr_Crofer_900_Iijima}^{(2)} := \frac{1}{PBR} \left(\frac{3.14 \cdot k_{p_Crofer_900_Dv}}{2 \cdot D_{Iijima_{Fe_Cr_901}}} \right)^{\frac{1}{2}} = 0.01105907474$$

Figure D.4: Failure Calculations 4.

Molecular mass of elements: Molecular mass of elements:

$$M_{Cr} := 51.996 \frac{\text{g}}{\text{mol}} ;$$

$$M_C := 12.011 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Mn} := 54.938 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Si} := 28.085 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Ti} := 47.867 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Fe} := 55.845 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Cr} := 51.996 \frac{\text{g}}{\text{mol}} ;$$

$$M_C := 12.011 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Mn} := 54.938 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Si} := 28.085 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Ti} := 47.867 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Nb} := 144.24 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Fe} := 55.845 \frac{\text{g}}{\text{mol}} ;$$

Molecular mass of elements:

$$M_{Cr} := 51.996 \frac{\text{g}}{\text{mol}} ;$$

$$M_C := 12.011 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Mn} := 54.938 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Si} := 28.085 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Ti} := 47.867 \frac{\text{g}}{\text{mol}} ;$$

$$M_{La} := 138.90547 \frac{\text{g}}{\text{mol}} ;$$

$$M_{Fe} := 55.845 \frac{\text{g}}{\text{mol}} ;$$

Composition of AISI409:

$$Cr409_{wt} := 11.4 ;$$

$$C409_{wt} := 0.012 ;$$

$$Mn409_{wt} := 0.39 ;$$

$$Si409_{wt} := 0.51 ;$$

$$Ti409_{wt} := 0.17 ;$$

$$Fe409_{wt} := 100 - (Cr409_{wt} + C409_{wt} + Mn409_{wt} + Si409_{wt} + Ti409_{wt}) \quad 87.518$$

Composition of AISI441:

$$Cr441_{wt} := 17.5 ;$$

$$C441_{wt} := 0.014 ;$$

$$Mn441_{wt} := 0.35 ;$$

$$Si441_{wt} := 0.59 ;$$

$$Ti441_{wt} := 0.17 ;$$

$$Nb441_{wt} := 0.39 ;$$

$$Fe441_{wt} := 100 - (Cr441_{wt} + C441_{wt} + Mn441_{wt} + Si441_{wt} + Ti441_{wt} + Nb441_{wt})$$

$$80.986$$

Composition of Crofer 22 APU:

$$CrCrofer_{wt} := 22.92 ;$$

$$CCrofer_{wt} := 0.004 ;$$

$$MnCrofer_{wt} := 0.38 ;$$

$$SiCrofer_{wt} := 0.01 ;$$

$$TiCrofer_{wt} := 0.06 ;$$

$$LaCrofer_{wt} := 0.07 ;$$

$$FeCrofer_{wt} := 100 - (CrCrofer_{wt} + CCrofer_{wt} + MnCrofer_{wt} + SiCrofer_{wt} + TiCrofer_{wt} + LaCrofer_{wt})$$

$$76.556$$

Figure D.5: Failure Calculations 5.

Atomic Weight percentage of 409 elements:

$Cr409_{At} :=$

$$\frac{\frac{Cr409_{wt}}{M_{Cr}}}{\frac{Cr409_{wt}}{M_{Cr}} + \frac{C409_{wt}}{M_C} + \frac{Mn409_{wt}}{M_{Mn}} + \frac{Si409_{wt}}{M_{Si}} + \frac{Ti409_{wt}}{M_{Ti}} + \frac{Fe409_{wt}}{M_{Fe}}} \cdot 100$$

$= 12.07167578$

$C409_{At} :=$

$$\frac{\frac{C409_{wt}}{M_C}}{\frac{Cr409_{wt}}{M_{Cr}} + \frac{C409_{wt}}{M_C} + \frac{Mn409_{wt}}{M_{Mn}} + \frac{Si409_{wt}}{M_{Si}} + \frac{Ti409_{wt}}{M_{Ti}} + \frac{Fe409_{wt}}{M_{Fe}}} \cdot 100$$

$= 0.05500912358$

$Mn409_{At} :=$

$$\frac{\frac{Mn409_{wt}}{M_{Mn}}}{\frac{Cr409_{wt}}{M_{Cr}} + \frac{C409_{wt}}{M_C} + \frac{Mn409_{wt}}{M_{Mn}} + \frac{Si409_{wt}}{M_{Si}} + \frac{Ti409_{wt}}{M_{Ti}} + \frac{Fe409_{wt}}{M_{Fe}}} \cdot 100$$

$= 0.3908628628$

$Si409_{At} :=$

$$\frac{\frac{Si409_{wt}}{M_{Si}}}{\frac{Cr409_{wt}}{M_{Cr}} + \frac{C409_{wt}}{M_C} + \frac{Mn409_{wt}}{M_{Mn}} + \frac{Si409_{wt}}{M_{Si}} + \frac{Ti409_{wt}}{M_{Ti}} + \frac{Fe409_{wt}}{M_{Fe}}} \cdot 100$$

$= 0.9998351357$

$Ti409_{At} :=$

$$\frac{\frac{Ti409_{wt}}{M_{Ti}}}{\frac{Cr409_{wt}}{M_{Cr}} + \frac{C409_{wt}}{M_C} + \frac{Mn409_{wt}}{M_{Mn}} + \frac{Si409_{wt}}{M_{Si}} + \frac{Ti409_{wt}}{M_{Ti}} + \frac{Fe409_{wt}}{M_{Fe}}} \cdot 100$$

$= 0.1955443889$

$Fe409_{At} :=$

$$\frac{\frac{Fe409_{wt}}{M_{Fe}}}{\frac{Cr409_{wt}}{M_{Cr}} + \frac{C409_{wt}}{M_C} + \frac{Mn409_{wt}}{M_{Mn}} + \frac{Si409_{wt}}{M_{Si}} + \frac{Ti409_{wt}}{M_{Ti}} + \frac{Fe409_{wt}}{M_{Fe}}} \cdot 100$$

$= 86.28707270$

$$Cr409_{At} + C409_{At} + Mn409_{At} + Si409_{At} + Ti409_{At} + Fe409_{At} = 99.99999999$$

Figure D.6: Failure Calculations 6.

Atomic Weight percentage of 441 elements:

$$Cr44l_{At} := \frac{Cr44l_{wt}}{M_{Cr}} \left/ \left(\frac{Cr44l_{wt}}{M_{Cr}} + \frac{C44l_{wt}}{M_C} + \frac{Mn44l_{wt}}{M_{Mn}} + \frac{Si44l_{wt}}{M_{Si}} + \frac{Ti44l_{wt}}{M_{Ti}} + \frac{Nb44l_{wt}}{M_{Nb}} + \frac{Fe44l_{wt}}{M_{Fe}} \right) \right. \cdot 100$$

$$= 18.47674757$$

$$C44l_{At} := \frac{C44l_{wt}}{M_C} \left/ \left(\frac{Cr44l_{wt}}{M_{Cr}} + \frac{C44l_{wt}}{M_C} + \frac{Mn44l_{wt}}{M_{Mn}} + \frac{Si44l_{wt}}{M_{Si}} + \frac{Ti44l_{wt}}{M_{Ti}} + \frac{Nb44l_{wt}}{M_{Nb}} + \frac{Fe44l_{wt}}{M_{Fe}} \right) \right. \cdot 100$$

$$= 0.06398914112$$

$$Mn44l_{At} := \frac{Mn44l_{wt}}{M_{Mn}} \left/ \left(\frac{Cr44l_{wt}}{M_{Cr}} + \frac{C44l_{wt}}{M_C} + \frac{Mn44l_{wt}}{M_{Mn}} + \frac{Si44l_{wt}}{M_{Si}} + \frac{Ti44l_{wt}}{M_{Ti}} + \frac{Nb44l_{wt}}{M_{Nb}} + \frac{Fe44l_{wt}}{M_{Fe}} \right) \right. \cdot 100$$

$$= 0.3497458834$$

$$Si44l_{At} := \frac{Si44l_{wt}}{M_{Si}} \left/ \left(\frac{Cr44l_{wt}}{M_{Cr}} + \frac{C44l_{wt}}{M_C} + \frac{Mn44l_{wt}}{M_{Mn}} + \frac{Si44l_{wt}}{M_{Si}} + \frac{Ti44l_{wt}}{M_{Ti}} + \frac{Nb44l_{wt}}{M_{Nb}} + \frac{Fe44l_{wt}}{M_{Fe}} \right) \right. \cdot 100$$

$$= 1.153280624$$

$$Ti44l_{At} := \frac{Ti44l_{wt}}{M_{Ti}} \left/ \left(\frac{Cr44l_{wt}}{M_{Cr}} + \frac{C44l_{wt}}{M_C} + \frac{Mn44l_{wt}}{M_{Mn}} + \frac{Si44l_{wt}}{M_{Si}} + \frac{Ti44l_{wt}}{M_{Ti}} + \frac{Nb44l_{wt}}{M_{Nb}} + \frac{Fe44l_{wt}}{M_{Fe}} \right) \right. \cdot 100$$

$$= 0.1949710470$$

$$Nb44l_{At} := \frac{Nb44l_{wt}}{M_{Nb}} \left/ \left(\frac{Cr44l_{wt}}{M_{Cr}} + \frac{C44l_{wt}}{M_C} + \frac{Mn44l_{wt}}{M_{Mn}} + \frac{Si44l_{wt}}{M_{Si}} + \frac{Ti44l_{wt}}{M_{Ti}} + \frac{Nb44l_{wt}}{M_{Nb}} + \frac{Fe44l_{wt}}{M_{Fe}} \right) \right. \cdot 100$$

$$= 0.1484349961$$

$$Fe44l_{At} := \frac{Fe44l_{wt}}{M_{Fe}} \left/ \left(\frac{Cr44l_{wt}}{M_{Cr}} + \frac{C44l_{wt}}{M_C} + \frac{Mn44l_{wt}}{M_{Mn}} + \frac{Si44l_{wt}}{M_{Si}} + \frac{Ti44l_{wt}}{M_{Ti}} + \frac{Nb44l_{wt}}{M_{Nb}} + \frac{Fe44l_{wt}}{M_{Fe}} \right) \right. \cdot 100$$

$$= 79.61283072$$

$$Cr44l_{At} + C44l_{At} + Mn44l_{At} + Si44l_{At} + Ti44l_{At} + Nb44l_{At} + Fe44l_{At} = 99.99999998$$

Figure D.7: Failure Calculations 7.

Atomic Weight percentage of 441 elements:

$$\begin{aligned} CrCrofer_{At} &:= \frac{CrCrofer_{wt}}{M_{Cr}} \left/ \left(\frac{CrCrofer_{wt}}{M_{Cr}} + \frac{CCrofer_{wt}}{M_C} + \frac{MnCrofer_{wt}}{M_{Mn}} \right. \right. \\ &\quad \left. \left. + \frac{SiCrofer_{wt}}{M_{Si}} + \frac{TiCrofer_{wt}}{M_{Ti}} + \frac{LaCrofer_{wt}}{M_{La}} + \frac{FeCrofer_{wt}}{M_{Fe}} \right) \right. \cdot 100 \\ &= 24.20622270 \end{aligned}$$

$$\begin{aligned} CCrofer_{At} &:= \frac{CCrofer_{wt}}{M_C} \left/ \left(\frac{CrCrofer_{wt}}{M_{Cr}} + \frac{CCrofer_{wt}}{M_C} + \frac{MnCrofer_{wt}}{M_{Mn}} \right. \right. \\ &\quad \left. \left. + \frac{SiCrofer_{wt}}{M_{Si}} + \frac{TiCrofer_{wt}}{M_{Ti}} + \frac{LaCrofer_{wt}}{M_{La}} + \frac{FeCrofer_{wt}}{M_{Fe}} \right) \right. \cdot 100 \\ &= 0.01828787189 \end{aligned}$$

$$\begin{aligned} MnCrofer_{At} &:= \frac{MnCrofer_{wt}}{M_{Mn}} \left/ \left(\frac{CrCrofer_{wt}}{M_{Cr}} + \frac{CCrofer_{wt}}{M_C} + \frac{MnCrofer_{wt}}{M_{Mn}} \right. \right. \\ &\quad \left. \left. + \frac{SiCrofer_{wt}}{M_{Si}} + \frac{TiCrofer_{wt}}{M_{Ti}} + \frac{LaCrofer_{wt}}{M_{La}} + \frac{FeCrofer_{wt}}{M_{Fe}} \right) \right. \cdot 100 \\ &= 0.3798333536 \end{aligned}$$

$$\begin{aligned} SiCrofer_{At} &:= \frac{SiCrofer_{wt}}{M_{Si}} \left/ \left(\frac{CrCrofer_{wt}}{M_{Cr}} + \frac{CCrofer_{wt}}{M_C} + \frac{MnCrofer_{wt}}{M_{Mn}} \right. \right. \\ &\quad \left. \left. + \frac{SiCrofer_{wt}}{M_{Si}} + \frac{TiCrofer_{wt}}{M_{Ti}} + \frac{LaCrofer_{wt}}{M_{La}} + \frac{FeCrofer_{wt}}{M_{Fe}} \right) \right. \cdot 100 \\ &= 0.01955275319 \end{aligned}$$

$$\begin{aligned} TiCrofer_{At} &:= \frac{TiCrofer_{wt}}{M_{Ti}} \left/ \left(\frac{CrCrofer_{wt}}{M_{Cr}} + \frac{CCrofer_{wt}}{M_C} + \frac{MnCrofer_{wt}}{M_{Mn}} \right. \right. \\ &\quad \left. \left. + \frac{SiCrofer_{wt}}{M_{Si}} + \frac{TiCrofer_{wt}}{M_{Ti}} + \frac{LaCrofer_{wt}}{M_{La}} + \frac{FeCrofer_{wt}}{M_{Fe}} \right) \right. \cdot 100 \\ &= 0.06883310921 \end{aligned}$$

$$\begin{aligned} LaCrofer_{At} &:= \frac{LaCrofer_{wt}}{M_{La}} \left/ \left(\frac{CrCrofer_{wt}}{M_{Cr}} + \frac{CCrofer_{wt}}{M_C} + \frac{MnCrofer_{wt}}{M_{Mn}} \right. \right. \\ &\quad \left. \left. + \frac{SiCrofer_{wt}}{M_{Si}} + \frac{TiCrofer_{wt}}{M_{Ti}} + \frac{LaCrofer_{wt}}{M_{La}} + \frac{FeCrofer_{wt}}{M_{Fe}} \right) \right. \cdot 100 \\ &= 0.02767330554 \end{aligned}$$

$$\begin{aligned} FeCrofer_{At} &:= \frac{FeCrofer_{wt}}{M_{Fe}} \left/ \left(\frac{CrCrofer_{wt}}{M_{Cr}} + \frac{CCrofer_{wt}}{M_C} + \frac{MnCrofer_{wt}}{M_{Mn}} \right. \right. \\ &\quad \left. \left. + \frac{SiCrofer_{wt}}{M_{Si}} + \frac{TiCrofer_{wt}}{M_{Ti}} + \frac{LaCrofer_{wt}}{M_{La}} + \frac{FeCrofer_{wt}}{M_{Fe}} \right) \right. \cdot 100 \\ &= 75.27959689 \end{aligned}$$

$$\begin{aligned} &CrCrofer_{At} + CCrofer_{At} + MnCrofer_{At} + SiCrofer_{At} + TiCrofer_{At} + LaCrofer_{At} \\ &\quad + FeCrofer_{At} \\ &= 99.99999998 \end{aligned}$$

Figure D.8: Failure Calculations 8.

Weight percentage of Cr at temps:

$$\begin{aligned} & \left(Cr_{409_{At}} \cdot M_{Cr} \right) / \left(Cr_{409_{At}} \cdot M_{Cr} + C_{409_{At}} \cdot M_C + Mn_{409_{At}} \cdot M_{Mn} + Si_{409_{At}} \cdot M_{Si} \right. \\ & \quad \left. + Ti_{409_{At}} \cdot M_{Ti} + Fe_{409_{At}} \cdot M_{Fe} \right) \cdot 100 \\ & = 11.39999999 \end{aligned}$$

$$\begin{aligned} Cr_{409_{wt_650_Theoretical}} &:= \left(\left(N_{Cr_409_650_Theoretical_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} \right) / \left(\left(N_{Cr_409_650_Theoretical_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} + C_{409_{At}} \cdot M_C + Mn_{409_{At}} \cdot M_{Mn} \right. \\ & \quad \left. + Si_{409_{At}} \cdot M_{Si} + Ti_{409_{At}} \cdot M_{Ti} + Fe_{409_{At}} \cdot M_{Fe} \right) \cdot 100 \\ & = 3.402977553 \end{aligned}$$

$$\begin{aligned} Cr_{409_{wt_750}} &:= \left(\left(N_{Cr_409_750_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} \right) / \left(\left(N_{Cr_409_750_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} + C_{409_{At}} \cdot M_C + Mn_{409_{At}} \cdot M_{Mn} + Si_{409_{At}} \cdot M_{Si} + Ti_{409_{At}} \cdot M_{Ti} \right. \\ & \quad \left. + Fe_{409_{At}} \cdot M_{Fe} \right) \cdot 100 \\ & = 1.914912302 \end{aligned}$$

$$\begin{aligned} Cr_{409_{wt_800}} &:= \left(\left(N_{Cr_409_800_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} \right) / \left(\left(N_{Cr_409_800_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} + C_{409_{At}} \cdot M_C + Mn_{409_{At}} \cdot M_{Mn} + Si_{409_{At}} \cdot M_{Si} + Ti_{409_{At}} \cdot M_{Ti} \right. \\ & \quad \left. + Fe_{409_{At}} \cdot M_{Fe} \right) \cdot 100 \\ & = 1.248475200 \end{aligned}$$

$$\begin{aligned} Cr_{409_{wt_850}} &:= \left(\left(N_{Cr_409_850_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} \right) / \left(\left(N_{Cr_409_850_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} + C_{409_{At}} \cdot M_C + Mn_{409_{At}} \cdot M_{Mn} + Si_{409_{At}} \cdot M_{Si} + Ti_{409_{At}} \cdot M_{Ti} \right. \\ & \quad \left. + Fe_{409_{At}} \cdot M_{Fe} \right) \cdot 100 \\ & = 1.084140501 \end{aligned}$$

$$\begin{aligned} Cr_{409_{wt_865}} &:= \left(\left(N_{Cr_409_865_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} \right) / \left(\left(N_{Cr_409_865_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} + C_{409_{At}} \cdot M_C + Mn_{409_{At}} \cdot M_{Mn} + Si_{409_{At}} \cdot M_{Si} + Ti_{409_{At}} \cdot M_{Ti} \right. \\ & \quad \left. + Fe_{409_{At}} \cdot M_{Fe} \right) \cdot 100 \\ & = 1.223191541 \end{aligned}$$

$$\begin{aligned} Cr_{409_{wt_880}} &:= \left(\left(N_{Cr_409_880_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} \right) / \left(\left(N_{Cr_409_880_Iijima}^{(2)} \cdot 100 \right) \cdot M_{Cr} + C_{409_{At}} \cdot M_C + Mn_{409_{At}} \cdot M_{Mn} + Si_{409_{At}} \cdot M_{Si} + Ti_{409_{At}} \cdot M_{Ti} \right. \\ & \quad \left. + Fe_{409_{At}} \cdot M_{Fe} \right) \cdot 100 \\ & = 1.311552398 \end{aligned}$$

$$\begin{aligned} Cr_{409_{wt_800_meier}} &:= \left(\left(N_{Cr_409_800_meier}^{(2)} \cdot 100 \right) \cdot M_{Cr} \right) / \left(\left(N_{Cr_409_800_meier}^{(2)} \cdot 100 \right) \cdot M_{Cr} + C_{409_{At}} \cdot M_C + Mn_{409_{At}} \cdot M_{Mn} + Si_{409_{At}} \cdot M_{Si} + Ti_{409_{At}} \cdot M_{Ti} \right. \\ & \quad \left. + Fe_{409_{At}} \cdot M_{Fe} \right) \cdot 100 \\ & = 1.850918754 \end{aligned}$$

Figure D.9: Failure Calculations 9.

Weight percentage of Cr at temps:

$$\begin{aligned} & (Cr44l_{Af} \cdot M_{Cr}) / (Cr44l_{Af} \cdot M_{Cr} + C44l_{Af} \cdot M_C + Mn44l_{Af} \cdot M_{Mn} + Si44l_{Af} \cdot M_{Si} \\ & + Ti44l_{Af} \cdot M_{Ti} + Nb44l_{Af} \cdot M_{Nb} + Fe44l_{Af} \cdot M_{Fe}) \cdot 100 \\ & = 17.49999999 \end{aligned}$$

$$\begin{aligned} Cr44l_{wt_650} &:= ((N_{Cr_44l_650_Iijima}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_44l_650_Iijima}^{(2)} \cdot 100) \\ & \cdot M_{Cr} + C44l_{Af} \cdot M_C + Mn44l_{Af} \cdot M_{Mn} + Si44l_{Af} \cdot M_{Si} + Ti44l_{Af} \cdot M_{Ti} \\ & + Nb44l_{Af} \cdot M_{Nb} + Fe44l_{Af} \cdot M_{Fe}) \cdot 100 \\ & = 3.957590411 \end{aligned}$$

$$\begin{aligned} Cr44l_{wt_750} &:= ((N_{Cr_44l_750_Iijima}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_44l_750_Iijima}^{(2)} \cdot 100) \\ & \cdot M_{Cr} + C44l_{Af} \cdot M_C + Mn44l_{Af} \cdot M_{Mn} + Si44l_{Af} \cdot M_{Si} + Ti44l_{Af} \cdot M_{Ti} \\ & + Nb44l_{Af} \cdot M_{Nb} + Fe44l_{Af} \cdot M_{Fe}) \cdot 100 \\ & = 2.276560453 \end{aligned}$$

$$\begin{aligned} Cr44l_{wt_800} &:= ((N_{Cr_44l_800_Iijima}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_44l_800_Iijima}^{(2)} \cdot 100) \\ & \cdot M_{Cr} + C44l_{Af} \cdot M_C + Mn44l_{Af} \cdot M_{Mn} + Si44l_{Af} \cdot M_{Si} + Ti44l_{Af} \cdot M_{Ti} \\ & + Nb44l_{Af} \cdot M_{Nb} + Fe44l_{Af} \cdot M_{Fe}) \cdot 100 \\ & = 1.842365916 \end{aligned}$$

$$\begin{aligned} Cr44l_{wt_850} &:= ((N_{Cr_44l_850_Iijima}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_44l_850_Iijima}^{(2)} \cdot 100) \\ & \cdot M_{Cr} + C44l_{Af} \cdot M_C + Mn44l_{Af} \cdot M_{Mn} + Si44l_{Af} \cdot M_{Si} + Ti44l_{Af} \cdot M_{Ti} \\ & + Nb44l_{Af} \cdot M_{Nb} + Fe44l_{Af} \cdot M_{Fe}) \cdot 100 \\ & = 1.317490375 \end{aligned}$$

$$\begin{aligned} Cr44l_{wt_865} &:= ((N_{Cr_44l_865_Iijima}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_44l_865_Iijima}^{(2)} \cdot 100) \\ & \cdot M_{Cr} + C44l_{Af} \cdot M_C + Mn44l_{Af} \cdot M_{Mn} + Si44l_{Af} \cdot M_{Si} + Ti44l_{Af} \cdot M_{Ti} \\ & + Nb44l_{Af} \cdot M_{Nb} + Fe44l_{Af} \cdot M_{Fe}) \cdot 100 \\ & = 1.203778791 \end{aligned}$$

$$\begin{aligned} Cr44l_{wt_880} &:= ((N_{Cr_44l_880_Iijima}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_44l_880_Iijima}^{(2)} \cdot 100) \\ & \cdot M_{Cr} + C44l_{Af} \cdot M_C + Mn44l_{Af} \cdot M_{Mn} + Si44l_{Af} \cdot M_{Si} + Ti44l_{Af} \cdot M_{Ti} \\ & + Nb44l_{Af} \cdot M_{Nb} + Fe44l_{Af} \cdot M_{Fe}) \cdot 100 \\ & = 1.147837126 \end{aligned}$$

$$\begin{aligned} Cr44l_{wt_900} &:= ((N_{Cr_44l_900_Iijima}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_44l_900_Iijima}^{(2)} \cdot 100) \\ & \cdot M_{Cr} + C44l_{Af} \cdot M_C + Mn44l_{Af} \cdot M_{Mn} + Si44l_{Af} \cdot M_{Si} + Ti44l_{Af} \cdot M_{Ti} \\ & + Nb44l_{Af} \cdot M_{Nb} + Fe44l_{Af} \cdot M_{Fe}) \cdot 100 \\ & = 1.047440740 \end{aligned}$$

Figure D.10: Failure Calculations 10.

Weight percentage of Cr at temps:

$$\begin{aligned} & (Cr44l_{At} \cdot M_{Cr}) / (Cr44l_{At} \cdot M_{Cr} + C44l_{At} \cdot M_C + Mn44l_{At} \cdot M_{Mn} + Si44l_{At} \cdot M_{Si} \\ & + Ti44l_{At} \cdot M_{Ti} + Nb44l_{At} \cdot M_{Nb} + Fe44l_{At} \cdot M_{Fe}) \cdot 100 \\ & = 17.49999999 \end{aligned}$$

$$\begin{aligned} CrCrofer_{wt_650} &:= ((N_{Cr_Crofer_650_Iijama}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_Crofer_650_Iijama}^{(2)} \\ & \cdot 100) \cdot M_{Cr} + CCrofer_{At} \cdot M_C + MnCrofer_{At} \cdot M_{Mn} + SiCrofer_{At} \cdot M_{Si} \\ & + TiCrofer_{At} \cdot M_{Ti} + LaCrofer_{At} \cdot M_{Nb} + FeCrofer_{At} \cdot M_{Fe}) \cdot 100 \\ & = 4.372318694 \end{aligned}$$

$$\begin{aligned} CrCrofer_{wt_750} &:= ((N_{Cr_Crofer_750_Iijama}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_Crofer_750_Iijama}^{(2)} \\ & \cdot 100) \cdot M_{Cr} + CCrofer_{At} \cdot M_C + MnCrofer_{At} \cdot M_{Mn} + SiCrofer_{At} \cdot M_{Si} \\ & + TiCrofer_{At} \cdot M_{Ti} + LaCrofer_{At} \cdot M_{Nb} + FeCrofer_{At} \cdot M_{Fe}) \cdot 100 \\ & = 1.486347020 \end{aligned}$$

$$\begin{aligned} CrCrofer_{wt_800} &:= ((N_{Cr_Crofer_800_Iijama}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_Crofer_800_Iijama}^{(2)} \\ & \cdot 100) \cdot M_{Cr} + CCrofer_{At} \cdot M_C + MnCrofer_{At} \cdot M_{Mn} + SiCrofer_{At} \cdot M_{Si} \\ & + TiCrofer_{At} \cdot M_{Ti} + LaCrofer_{At} \cdot M_{Nb} + FeCrofer_{At} \cdot M_{Fe}) \cdot 100 \\ & = 1.467766380 \end{aligned}$$

$$\begin{aligned} CrCrofer_{wt_850} &:= ((N_{Cr_Crofer_850_Iijama}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_Crofer_850_Iijama}^{(2)} \\ & \cdot 100) \cdot M_{Cr} + CCrofer_{At} \cdot M_C + MnCrofer_{At} \cdot M_{Mn} + SiCrofer_{At} \cdot M_{Si} \\ & + TiCrofer_{At} \cdot M_{Ti} + LaCrofer_{At} \cdot M_{Nb} + FeCrofer_{At} \cdot M_{Fe}) \cdot 100 \\ & = 1.451496872 \end{aligned}$$

$$\begin{aligned} CrCrofer_{wt_865} &:= ((N_{Cr_Crofer_865_Iijama}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_Crofer_865_Iijama}^{(2)} \\ & \cdot 100) \cdot M_{Cr} + CCrofer_{At} \cdot M_C + MnCrofer_{At} \cdot M_{Mn} + SiCrofer_{At} \cdot M_{Si} \\ & + TiCrofer_{At} \cdot M_{Ti} + LaCrofer_{At} \cdot M_{Nb} + FeCrofer_{At} \cdot M_{Fe}) \cdot 100 \\ & = 1.322858209 \end{aligned}$$

$$\begin{aligned} CrCrofer_{wt_880} &:= ((N_{Cr_Crofer_880_Iijama}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_Crofer_880_Iijama}^{(2)} \\ & \cdot 100) \cdot M_{Cr} + CCrofer_{At} \cdot M_C + MnCrofer_{At} \cdot M_{Mn} + SiCrofer_{At} \cdot M_{Si} \\ & + TiCrofer_{At} \cdot M_{Ti} + LaCrofer_{At} \cdot M_{Nb} + FeCrofer_{At} \cdot M_{Fe}) \cdot 100 \\ & = 1.312002687 \end{aligned}$$

$$\begin{aligned} CrCrofer_{wt_900} &:= ((N_{Cr_Crofer_900_Iijama}^{(2)} \cdot 100) \cdot M_{Cr}) / ((N_{Cr_Crofer_900_Iijama}^{(2)} \\ & \cdot 100) \cdot M_{Cr} + CCrofer_{At} \cdot M_C + MnCrofer_{At} \cdot M_{Mn} + SiCrofer_{At} \cdot M_{Si} \\ & + TiCrofer_{At} \cdot M_{Ti} + LaCrofer_{At} \cdot M_{Nb} + FeCrofer_{At} \cdot M_{Fe}) \cdot 100 \\ & = 1.340261339 \end{aligned}$$

Figure D.11: Failure Calculations 11.

Critical alloy levels

$$N_{Cr,i} := 10 :$$

$$N_{Cr_409_650_Theoretical_wt}^{(o)} := N_{Cr,i} + Cr409_{wt_650_Theoretical} = 13.40297755$$

$$N_{Cr_409_750_wt}^{(o)} := N_{Cr,i} + Cr409_{wt_750} = 11.91491230$$

$$N_{Cr_409_800_wt}^{(o)} := N_{Cr,i} + Cr409_{wt_800} = 11.24847520$$

$$N_{Cr_409_850_wt}^{(o)} := N_{Cr,i} + Cr409_{wt_850} = 11.08414050$$

$$N_{Cr_409_865_wt}^{(o)} := N_{Cr,i} + Cr409_{wt_865} = 11.22319154$$

$$N_{Cr_409_880_wt}^{(o)} := N_{Cr,i} + Cr409_{wt_880} = 11.31155240$$

Critical alloy levels

$$N_{Cr,i} = 10$$

$$N_{Cr_441_650_wt}^{(o)} := N_{Cr,i} + Cr441_{wt_650} = 13.95759041$$

$$N_{Cr_441_750_wt}^{(o)} := N_{Cr,i} + Cr441_{wt_750} = 12.27656045$$

$$N_{Cr_441_800_wt}^{(o)} := N_{Cr,i} + Cr441_{wt_800} = 11.84236592$$

$$N_{Cr_441_850_wt}^{(o)} := N_{Cr,i} + Cr441_{wt_850} = 11.31749038$$

$$N_{Cr_441_865_wt}^{(o)} := N_{Cr,i} + Cr441_{wt_865} = 11.20377879$$

$$N_{Cr_441_880_wt}^{(o)} := N_{Cr,i} + Cr441_{wt_880} = 11.14783713$$

$$N_{Cr_441_900_wt}^{(o)} := N_{Cr,i} + Cr441_{wt_900} = 11.04744074$$

Critical alloy levels

$$N_{Cr,i} = 10$$

$$N_{Cr_Crofer_650_wt}^{(o)} := N_{Cr,i} + CrCrofer_{wt_650} = 14.37231869$$

$$N_{Cr_Crofer_750_wt}^{(o)} := N_{Cr,i} + CrCrofer_{wt_750} = 11.48634702$$

$$N_{Cr_Crofer_800_wt}^{(o)} := N_{Cr,i} + CrCrofer_{wt_800} = 11.46776638$$

$$N_{Cr_Crofer_850_wt}^{(o)} := N_{Cr,i} + CrCrofer_{wt_850} = 11.45149687$$

$$N_{Cr_Crofer_865_wt}^{(o)} := N_{Cr,i} + CrCrofer_{wt_865} = 11.32285821$$

$$N_{Cr_Crofer_880_wt}^{(o)} := N_{Cr,i} + CrCrofer_{wt_880} = 11.31200269$$

$$N_{Cr_Crofer_900_wt}^{(o)} := N_{Cr,i} + CrCrofer_{wt_900} = 11.34026134$$

Figure D.12: Failure Calculations 12.

AISI409:

$$N_{Cr_409_650_Theoretical_wt}^{(o)} = 13.40297755$$

$$N_{Cr_409_750_wt}^{(o)} = 11.91491230$$

$$N_{Cr_409_800_wt}^{(o)} = 11.24847520$$

$$N_{Cr_409_850_wt}^{(o)} = 11.08414050$$

$$N_{Cr_409_865_wt}^{(o)} = 11.22319154$$

$$N_{Cr_409_880_wt}^{(o)} = 11.31155240$$

AISI441:

$$N_{Cr_441_650_wt}^{(o)} = 13.95759041$$

$$N_{Cr_441_750_wt}^{(o)} = 12.27656045$$

$$N_{Cr_441_800_wt}^{(o)} = 11.84236592$$

$$N_{Cr_441_850_wt}^{(o)} = 11.31749038$$

$$N_{Cr_441_865_wt}^{(o)} = 11.20377879$$

$$N_{Cr_441_880_wt}^{(o)} = 11.14783713$$

$$N_{Cr_441_900_wt}^{(o)} = 11.04744074$$

Crofer 22 APU:

$$N_{Cr_Crofer_650_wt}^{(o)} = 14.37231869$$

$$N_{Cr_Crofer_750_wt}^{(o)} = 11.48634702$$

$$N_{Cr_Crofer_800_wt}^{(o)} = 11.46776638$$

$$N_{Cr_Crofer_850_wt}^{(o)} = 11.45149687$$

$$N_{Cr_Crofer_865_wt}^{(o)} = 11.32285821$$

$$N_{Cr_Crofer_880_wt}^{(o)} = 11.31200269$$

$$N_{Cr_Crofer_900_wt}^{(o)} = 11.34026134$$

Figure D.13: Failure Calculations 13.

E | Appendix: The Ferrite/Austenite ratio in AISI430

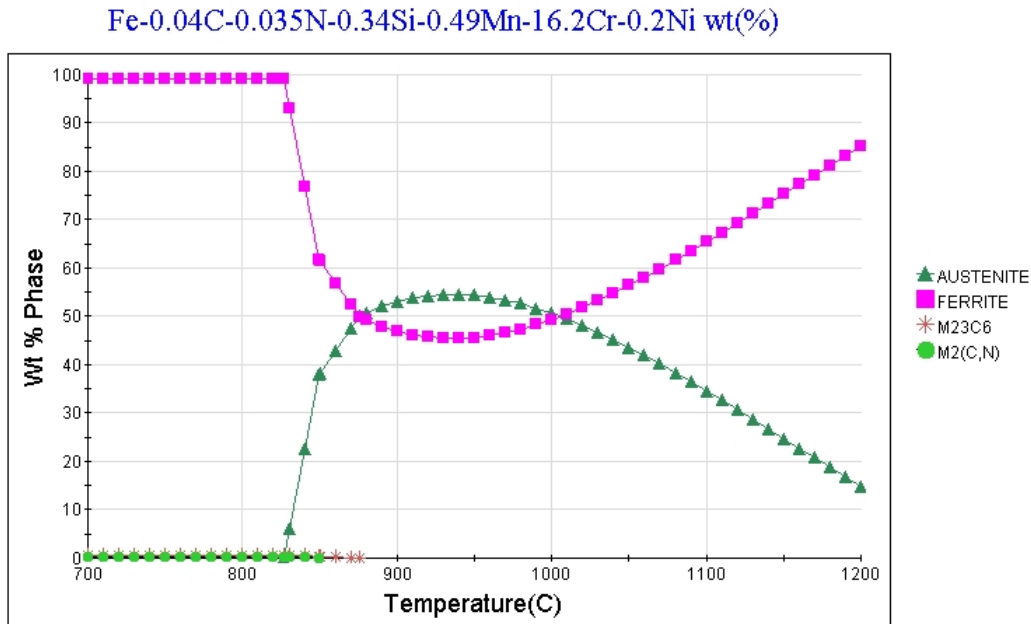


Figure E.1: The Ferrite/Austenite ratio at different temperatures for AISI430.

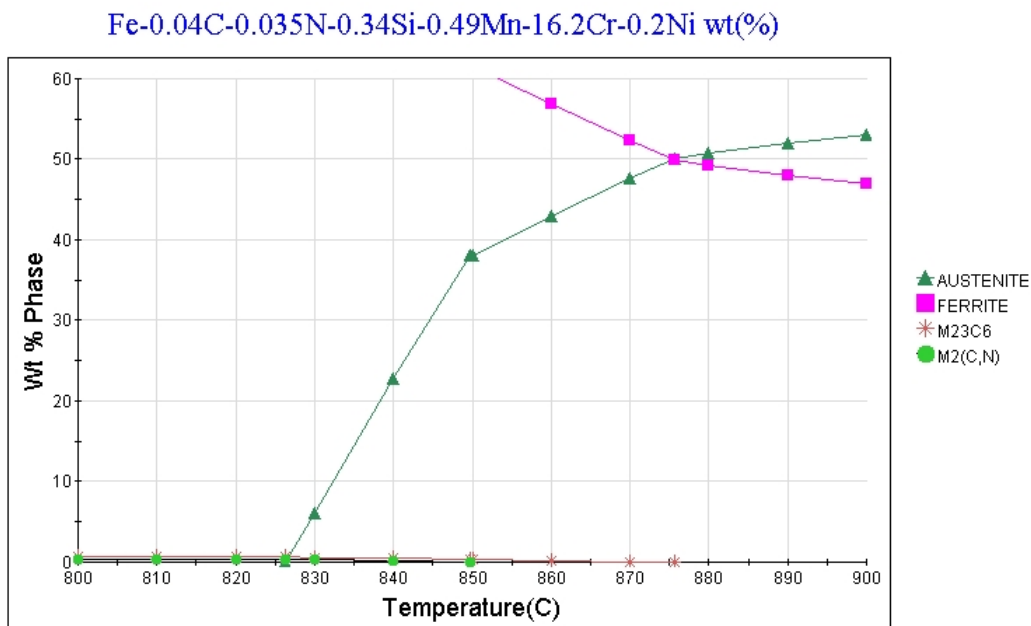


Figure E.2: The Ferrite/Austenite ratio at different temperatures for AISI430. Here focused on the area of interest.