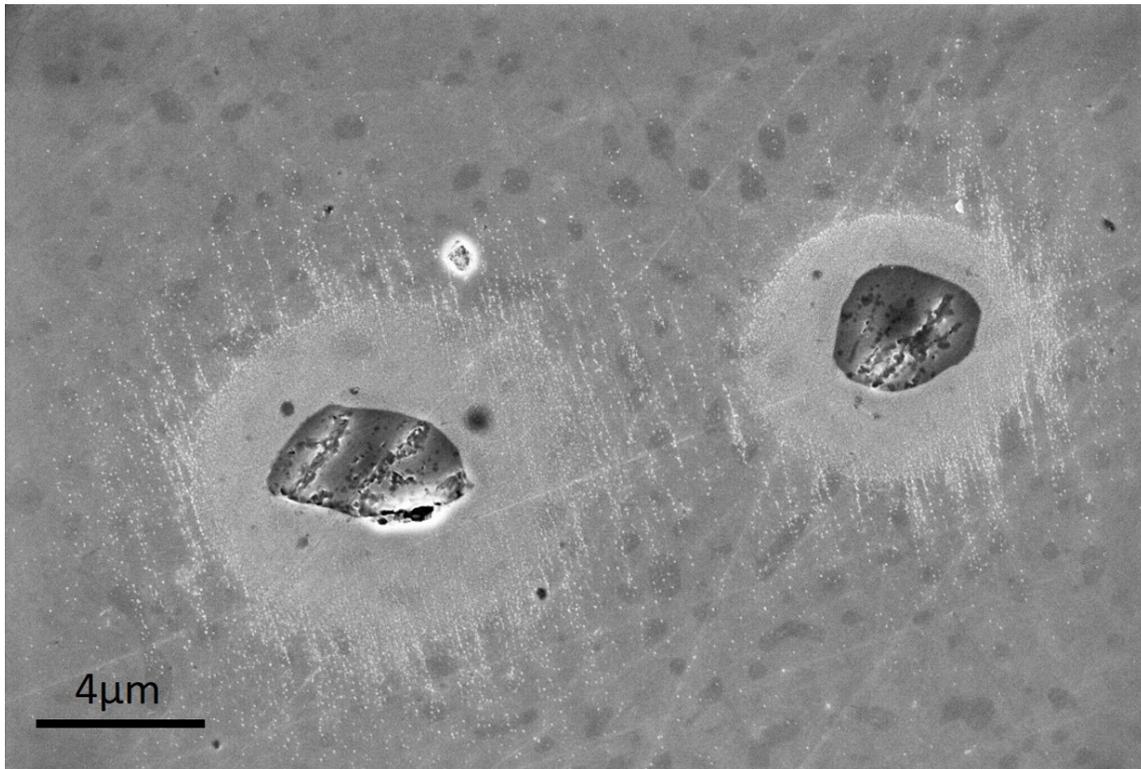




CHALMERS



Initiation of localised corrosion on bearing steel

Diploma work in the Master programme Materials Chemistry and Nanotechnology

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Initiation of localised corrosion on bearing steel

by

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Diploma work No. 168/2015

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Cover: MnS inclusions exposed to deionised water for 5 minutes, studied in SEM with secondary electrons

Chalmers Reproservice
Gothenburg, Sweden 2015

Initiation of localised corrosion on bearing steel
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Abstract

In some applications roller bearings fail prior to their expected life time. The processes of these failures are not fully understood and there are many different factors which affect the lifetime. One phenomenon which could affect the life time is the corrosion mechanisms of the steel. On defects and inclusions corrosion might be initiated even though the material does not corrode in the matrix. The aim of this project is to study the initial corrosion on martensitic AISI 52100 steel. No similar studies have been published on this kind of steel but some studies on general carbon steel were performed during the 1970s. These studies suggested that manganese sulphur inclusions play a critical roll in the initial corrosion. The present study samples were emerged in deionised water for one to ten minutes. The samples were then studied with XPS, SEM, EDX and FIB-SEM to investigate if and where the corrosion occurred. The XPS analysis showed that similar iron oxides, a few nm thick, mostly covered the samples after 5 min. exposure as well as after handling in air. Using imaging methods no clear signs of preferential corrosion was observed on samples exposed for one or two minutes, but on samples exposed for five and ten minutes. No clear signs of preferential corrosion was observed on samples exposed for one or two minutes, but samples exposed for five and ten minutes did. The analysis of the five minute exposure showed manganese sulphur inclusions which were partially decomposed. The ten minute exposure showed inclusions with thicker oxide films around them, cracks and flaking of the surface could be observed close to several inclusions. It is hypothesized that these phenomena origin from some kind of micro galvanic corrosion and/or sulphur infection of the steel matrix

Keywords: initial corrosion, inclusions, MnS, SEM, EDX, FIB-SEM

Acknowledgements

I would like to thank my supervisors Mats Norell and Leif Viskari for all their help throughout the project. I would also like to thank SKF for the financing of the project.

I would also like to thank the personnel at the Materials and Manufacturing Technology, especially Eric Tam which helped me with the XPS and Yiming Yao who taught me polishing and mounting.

I would also like to thank the personnel at the Department of Applied Physics who helped with various problems with the SEM.

Peter Svensson, Gothenburg, June 2015

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1

Background and aim

1.1 Background

Roller bearings have been used for centuries and the bearing materials have developed during this time . Research has shown that certain kinds of steel are favorable in these applications. One type of steel which have been widely used is the AISI 52100 steel (also known as 100Cr6). This steel contains a carbon content about 1 wt.% and a chromium content of around 0.5 wt.% and the steel is hard compared to conventional carbon and stainless steels [1]. The life time of this steel in rolling contact environments have shown to be longer than for many other steels[2]

In some applications the roller bearing fail prior to their expected life time. The processes of these failures are not fully understood and there are many different factors which affect the lifetime [3]. One phenomenon which could affect the life time is the corrosion mechanisms of the steel [4]. The macroscopic corrosion processes are generally not a problem in bearings because of the dynamic working environment. However, all components are not used continuously which makes the corrosion environment different during this pause in operation. The parts will also be worn which creates defects on the components[1]. On defects and inclusions corrosion might be initiated even though the material does not corrode on macroscopic level [5].

The corrosion process on macroscopic level is a subject which have been studied thoroughly and there is data on the corrosion rate of steel in several mediums [6]. The data on the microscopic changes is not as extensive but studies on the corrosion around inclusions have been performed since the early 20th century [5].The focus of the investigations have been on the influence of sulphide inclusions which have shown to initiate localized corrosion [5][7][8][9].Theses studies have been performed on both stainless and carbon steel which seem to show different mechanisms in the corrosion process. The difference has been explained by the different nobleness of the materials compared to the inclusions[5].

The research also showed indications that there are some inclusions which initiate corrosion while other inclusions of the same composition do not. The two kinds of the inclusions were therefor named active and inactive, where the active are the ones which do initiate corrosion[5]. The reason for the difference between the inclusions was proposed to be dependent on the composition of the matrix surrounding the inclusions[7]. This theory has been proved to some extent but it is hard to measure the chemical composition near the sulphides[8]. The matrix close to the inclusions will vary dependent on the solubility of different elements in the steel and how the steel is manufactured [5].

Investigation as those mentioned for stainless steel and general carbon steel have not been performed for bearing steel. The mechanisms could be the same which makes similar inves-

tigations interesting. Bearing steel is a kind of carbon steel and the earlier studies performed should be similar even though the content of the alloying elements differ a bit. This project will focus on the investigation of the initial corrosion of bearing steel.

1.2 Aim

Study the initial aqueous corrosion on bearing steel with electron microscopy to see when and where corrosion starts. The focus will be on the influence of different inclusions and how they affect the corrosion initiation. The investigation will be performed on samples emerged in deionised water for a few minutes.

1.3 Limitations

The project only aims to investigate the corrosion of martensitic AISI 52100 steel. The project does not aim to evaluate the corrosion potential of the steel but characterize the corrosion on a microscopic level.

2

Introduction

2.1 Bearings

Roller bearings are used to lower the friction between rotating parts. The two main parts of a bearing are the rolling elements and the raceways. The rolling elements can be balls, rollers and the raceways are rings placed on both sides of the rolling elements [1]. Information on the steel used in bearings is found in section 2.3.

2.2 General about corrosion

The problem of corrosion originates from the fact that mankind reforms materials and then wants them to keep the shape we create. The thermodynamics fight against this phenomenon since it makes all matter strive for the most thermodynamically favorable state. Corrosion is a subject which mainly is discussed regarding metals which are generally taken as ore from mines. In the mine the iron is in the form of oxide or sulphide e.g. chemical form of Fe_3O_4 (magnetite). The iron in this ore are in the oxidation state of II+ or III+ which makes a reducing agent necessary to get elemental iron which can be used to produce usable materials like steel. The corrosion process which occurs in the environment is the opposite where the elemental iron goes back to the more thermodynamically favored species of Fe^{II+} , see equation 2.1.



Some materials tend to go to their oxidized states more easily than others which is the background for the term nobleness of metals. The less noble a material is the easier it will go to an oxidized state. The difference in nobleness of different materials is a very important phenomenon to consider when using materials together. When two conductive materials are connected it is possible for a current of electrons to transfer between the materials, a galvanic cell is created. The material which is more noble will not be oxidized, instead, only the less noble metal will suffer from this. This property can also be used to protect materials from corrosion where a less noble material is introduced as a sacrificial anode[10].

Uniform corrosion is when a material suffers from corrosion all over the surface independent of position. Since very few products consist of identical components and most materials have some flaws the corrosion process might occur differently on different positions on the component. This phenomenon is called localized corrosion which will be described more in detail in the following part[11].

2.2.1 Passivity

Under certain conditions some metals can be resistance to corrosion. The reason is that metals like aluminum and stainless steel are able to form a oxide film on top of the material which slows down the corrosion rate [12]. This oxide film can be able to stop the corrosion process in some environments, but it can also be destroyed in more aggressive environments and then the corrosion rate will increase. The reason the passive film hinders the corrosion is that the diffusion rate of metals and oxygen through the oxide is low and that it can be insulating which hinder the electron transfer. These two phenomena reduce the corrosion rate[11].

2.2.2 Difference between carbon steel and stainless steel

Stainless steel is resistant to corrosion in environments where normal carbon steel corrodes rapidly. The reason is the high chromium content, more than 11%, which makes formation of a thin and dense passive film possible. In carbon steel the chromium content is too low for a similar passive film to be formed [12]. The difference in corrosion resistance is often measured in corrosion potentials where a higher potential gives a more noble and therefore more resistant material.

2.2.3 Corrosion in general water compared to deionised water

The corrosion process in an aqueous media is affected by the content of the water. The conductivity of water will increase with the ion content and therefore deionised water has a very low conductivity. This means the corrosion velocity in deionised water is lower than in tap water since the conductivity is essential for the cathode and anode reaction in the corrosion process [13].

2.2.4 Localized corrosion

Localised corrosion is a phenomenon where some part of a material corrodes but other regions, e.g. the bulk, remain unaffected. There are several different mechanisms of localized corrosion, there can be changes in the environment, the product design or the purity of the material [10]. Two different kinds of localised corrosion are pitting corrosion and microgalvanic corrosion which will be described in section 2.2.4.1 and 2.2.4.2 respectively.

2.2.4.1 Pitting corrosion

One phenomenon which is a common problem with the materials is pitting corrosion. The results is a preferential dissolution of the materials on certain spots on the surface which creates holes, or pits, on the component [10]. This problem can occur on many different kinds of materials, e.g. stainless steel, which can be passive to other forms of destructive corrosion[8]. There are many theories for the formation of pitting corrosion and some environmental aspects of the phenomenon have been confirmed. The most discussed compound which is known to increase the risk for pitting is the presence of chloride ions in the environment [11]. There are also some theories on where the pitting corrosion will occur and

several articles have shown that pitting corrosion of stainless steel have a tendency to start at inclusions in the steel, see section 2.4.3.2 [8][7][5].

2.2.4.2 Micro-galvanic corrosion

Galvanic corrosion occurs when materials with different nobleness are in contact. The more noble material will be able to avoid being oxidised by acting as a cathode for the other metal. The less noble of the metals will therefore corrode while the other will keep its metallic form [12]. In some alloys, e.g. Magnesium alloys, the different phases in the material can have different nobleness which enables galvanic corrosion on a microscopic level [14]. This means that one phase can be dissolved while the rest of the material is unaffected [15]. In figure 2.1 a schematic image of the phenomenon is presented where oxygen reduction is given as an example of cathode reaction.

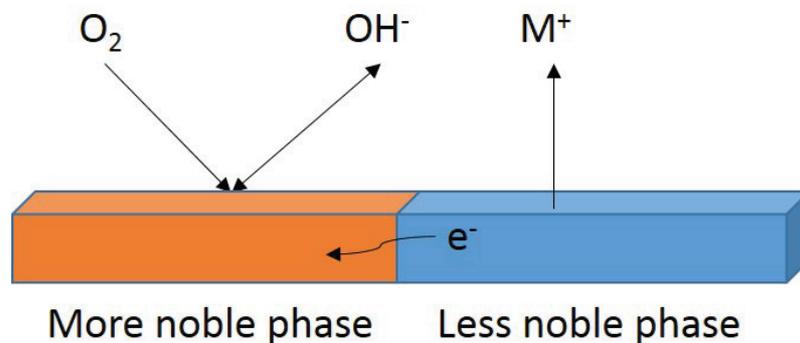


Figure 2.1: Schematic image of micro-galvanic corrosion

2.3 The steel: AISI 52100/100Cr6

The general composition of AISI 52100 steel is given in table 2.1.

Table 2.1: Composition of standard AISI 52100 bearing steel used by SKF , (wt.%)

Material	C	Si	Mn)	S max	Cr
100Cr6	0.97	0.25	0.35	0.0015	1.5

The steel processing affects the content of the inclusions and different kinds of inclusions will appear and be eliminated in different steps. Therefore, it is important to consider how the steel is produced. There are two main techniques for producing bearing steel: ingot casting and continuous casting. The first is the traditional technique which has dominated the manufacturing the last century due to the better quality of the steel. Continuous casting has increased in latter years since the improvements of the process have enhanced the quality of the product, which have made it comparable to the quality of the ingot cast steel[16].

The raw product in both processes is scrap metals and some additional alloy elements. The material is melted in an electric arc furnace or a blast furnace [1]. The melt is treated in different ways to control the alloy content, remove oxygen and sulphur[16]. This process is

often called secondary metallurgy or ladle metallurgy where the stirring of the metal is very important to create a homogeneous metal. A common method is to use induction stirring and argon bubbling[16]. When the secondary metallurgy is finished the two methods take different paths. For ingot casting the melt is transferred into a mold to produce a metal bar. The shape of the ingot and the process of filling it have been optimized to reduce the oxidation and the inclusion content of the steel. In continuous casting the metal bars are produced through a die to get a constant flow of metal bars which are cut into the desired length. In both processes the metal bars are rolled while hot to form the final products (bars) from the steel mill. The bars can be rolled again to a certain shape in the process of secondary rolling[16].

Bearing steel has been manufactured with the as clean as possible philosophy for a long time but the presence of inclusions is a complex phenomenon. An addition of sulphur can be favorable to increase the machinability of the steel, but harmful in a later part of the bearing life as a contribution to premature failure and fatigue [17]. Reducing the amount of inclusions is expensive but will produce a bearing with a longer life-time. That makes the bearing steel a compromise between these factors and it would be possible with the techniques available to produce a steel with less inclusions than today, but it will be hard in economical and processing perspective.

The steel used in bearings is typically heat treated to get a martensitic or bainitic structure. For some bearings which are produced in large geometries e.g. for use in wind turbines, it can be favorable with a bainitic structure while a martensitic structure is sufficient for smaller bearings. These two structures are obtained by different heat treatments[1]. For both martensitic and bainitic heat treatments, the steel is first austenitized at about 840°C) to dissolve the cementite and bring alloy elements into solution. For martensite, the steel is then quenched to below the martensite start (Ms) temperature to obtain the martensitic structure. This is most often followed by tempering at an intermediate temperature (e.g. 160°C)) to increase ductility and reduce the amount of retained austenite. Bainite on the other hand is obtained by quenching the steel to a temperature above the Ms (e.g. 200°C)) and then holding it at a slightly higher temperature of e.g. 250°C) for a longer period of time under which the austenite transforms to bainite. For a full bainitic transformation there is no need for tempering as the ductility is good and retained austenite does not occur in great extent, given that it has already transformed to bainite.

2.4 Inclusions and their origin

In steel some impurities and unwanted particles can get stuck in the steel matrix. These particles are usually called inclusions and are divided into two categories: Endogenous and exogenous inclusions. Endogenous are particles which originates from reactions in the melt or solidification of the steel. Exogenous inclusions comes from mechanical incorporation of slags or particles from equipment materials in the process[17]. Some inclusions, like oxides, can be of either endogenous or exogenous origin but some differences can be seen. Exogenous inclusions are generally larger, uneven and complex (composition). The division is not always relevant since there are studies which show that inclusions with endogenous origin can precipitate on exogenous particles. This leads to a continuous change of the composition of the inclusions in the molten steel.[1]

The main idea about inclusions is that they should be avoided as much as possible. When

discussing exogenous inclusions this theory is completely true but not always for endogenous. The reason some inclusions are wanted is that they may improve machinability or other properties of the steel. This will be discussed some more regarding the different kinds of inclusions.

The process of oxygen reduction in the melted steel is a process which can create inclusions. There are several ways to reduce the oxygen content in the steel and common ways is the addition of aluminium or silicon. Addition of aluminum or silicon will lead to the formation of the alumina (AlO_2) and silica (SiO_2) respectively. Most of these will be removed during the ladle treatment but some will be present in the final product as inclusions[1].

2.4.1 Sulphide inclusions MnS-FeS

Sulphur had been used in steel due to the improvements of the machinability[17]. In the molten steel the solubility of sulphur is high but not in the solid metal. This leads to the precipitation of sulphide with metals. The most common metallic sulphides are FeS and MnS. FeS will create some problems during the solidification of the steel. The FeS can precipitate in the steel as a eutectic of sulphur and iron and the melting point of this structure is low compared to the steel. This makes the eutectic wet the grain boundaries in the solidifying steel, which can create cracking in final steel product. This problem is called hot-shortness which is avoided in steel by adding Manganese. MnS forms preferentially before FeS which solves the problem since the melting point of MnS is higher than for the eutectic iron sulphur system. The deformability of MnS inclusions is similar to the one of the steel in a large temperature interval which is good since this reduces the risk of creation of defects in the steel matrix. These defects could later in the components life be the origin of the cracks and failures. A result of this is also that the MnS inclusions are plastically deformed during the steel processing and get elongated [17].

2.4.2 Aluminum oxides

Aluminum oxides exist in many steels because of the use of the element as a deoxidizer. The Aluminum is often present in a complex phase with other elements. Two common phases are the MnO-SiO₂-Al₂O₃ and CaO-SiO₂-Al₂O₃ systems. The phase can consist solely of Al₂O₃ but in both systems combinations of the three part creates different phase, the relation is often described by ternary phase diagrams[17]. Pure Al₂O₃ is not able to deform plastically during the steel processing and is therefore not used to improve the machinability of the steel[17]. Some of the phases in the ternary phase diagrams are able to do this though. Oxide inclusions are generally bad for fatigue properties of the steel but the origin is important to know if the inclusion will affect the properties. Exogenous oxide inclusions, which generally are large, are the most harmful to the fatigue properties[17].

2.4.3 Inclusions and corrosion

In the 1970s some studies on the influence of the inclusions on the localized corrosion process were performed. There are studies which have been performed on both stainless and carbon steel. For this project the focus is on carbon steel but both steels will be discussed in the following sections.

2.4.3.1 Carbon steel

The theory of corrosion of carbon steel differs from that of stainless steel since the chromium content in the steel is not sufficient to create a stable passive film that will reduce the corrosion rate. The studies of inclusions and their roll in the corrosion process on steel were studied in the 1970s by two authors and their work will be described below. Few recent articles concerning inclusions and corrosion has been found but one recent article regarding MnS and corrosion in an environment with sulphea bacteria was found. It should also be noted that in a corrosion perspective bearing steel should behave in a similar way as carbon steel. The difference is mainly the carbon content which does not affect the corrosion.

According to Eklund[5] (PhD thesis based on [18],[19] and [20]) the studies of the influence of inclusions on the corrosion properties of carbon steel started with the investigation issued by the Corrosion Committee of the Iron and Steel institute in 1932. The investigation aimed to study if there was any correlation between localized corrosion and the presence of different kinds of inclusions. The results showed that localized corrosion started at sulphide inclusions while silicates and alumina seemed to be inert in that matter. The results also indicated that only some of the sulphide inclusions of the same composition initiated corrosion but other did not. The study could not explain this difference. [5]

Several theories were later proposed in order to explain the reason the sulphide inclusions affected the corrosion. One theory was that the inclusion might act as cathode to the corroding metal. Another reason could be that crevices might appear around the inclusions under the processing of the metal, corrosion would then start around these crevices[5].

The phenomenon where only some inclusions create corrosion has created the naming of active and inactive inclusions, where the active inclusions promote corrosion quickly while inactive do not. The reason this phenomenon is observed have been explained by several theories. Wranglen[7] proposed that some MnS inclusions could have a sulphur infected matrix close to the inclusions, which then easily form anodic sites where the iron corrodes. The cathodic reaction would take place in the matrix further away from the inclusion where no sulphur contamination is present.

In Wranglens [7] studies he also concluded that all sulphides did corrode if the experiment was performed long enough and that the corrosion sometimes started at crevices between the steel and the inclusion that were there before the experiment started. The results also proposed that the MnS inclusions are cathodic compared to the steel surface. Another theory proposed by Wranglen was that submicroscopic precipitates could form around the inclusions during the steel processing. These precipitates would then explain the increase of activity close to the active inclusions. Eklund [5] found that the active inclusions in his experiments consisted of calcium sulphides shells around aluminate particles with some manganese dissolved, while the inactive were manganese sulphides with or without calcium.

Recent studies regarding pitting corrosion of carbon steel in the presence of sulfate reducing bacteria showed interesting results regarding MnS inclusions [21]. The article by Avci[21] indicated that the manufacturing process of the steel greatly affect the activity of the inclusions due to contamination and residual strain in the matrix close to the inclusion. Some MnS inclusions suffered from corrosion early and for those it was the material around the inclusions which dissolved and started the pit initiation and not the inclusion itself.

2.4.3.2 Stainless steel

Stainless steel is passivated in most environments and the corrosion potential is higher than for carbon steel. The nobleness is also different and the corrosion around inclusions could be affected by this. Stainless steel does not corrode in an aqueous solution but in some environments localized corrosion might be initiated. This phenomenon has been studied to be able to improve the resistance of the steel. It is mainly pitting corrosion which has been observed and much research has focused on the matter[5]. Both Wranglen and Eklund discussed the influence of the sulphide inclusions on the pitting corrosion. A more recent article by M.P. Ryan et al [8], showed that the matrix close to the inclusions were depleted in Chromium. This can explain the corrosion in the matrix near the inclusions since the passive film can be weaker because of the loss in the chromium content[8]. D. E. Williams et. al [22]. proposed chromium depletion to be the reason for pitting initiation in stainless steel in an article 2 years earlier. During the cooling of the steel in the processing the composition of the sulphide will change which can generate the zone with depleted chromium[22].

2.4.4 Inclusions and fatigue

The connection between inclusions and fatigue had been known for a long time and many studies have investigated this phenomenon. Some inclusions have been confirmed by studying fracture surfaces and investigating the chemical composition of inclusions present there. In an article by A. Melander et.al.[23] it was found that MnS and TiN did not affect the fatigue properties of 100Cr6 steel while both alumina and silica particles were present on fracture surfaces. Another fact was that it was only small inclusions with a diameter below 30 μm which were found on the fracture surfaces[23]. The general approach on inclusions in steel is that the larger the inclusion the worse it is for the fatigue properties.

3

Analysis methods

In this chapter the different analysis methods used in the project will be described. The focus will be on a short description of the technique and what information it can give to this project.

3.1 Scanning Electron Microscopy

Scanning electron microscopy is a instrument that enables studies of the topography and chemical composition of a surface at high magnification. The instruments consist of a electron gun which emits electrons which are scanned over the surface and focused on the sample with electromagnetic lenses [24]. The electrons will hit the sample and interact with the material in several ways. Some electrons will back scatter elastically which can be detected and give images with compositional contrast since heavy elements (High Z) will lead to more scattering. The incoming electrons will also generate secondary electrons from inelastic scattering which gives good imaging of the topography with a large depth of focus[25].

3.1.1 Energy selective back scattered detection (ESB)

To improve the surface sensitivity of imaging with back scattered electrons a energy selective backscattering detector can be used. The detector is placed in an inlens position and is able to filter out electrons which have lost too much energy in the scattering process. This is done by controlling the energy difference between the incoming electrons and those used for imaging. A grid is placed in the detector inlet and a positive voltage is applied in it [26]. In this project the incoming electrons had an energy of 1kV and the grid was set to 0.925kV which means only electrons which has lost less than 75V in the process will be used in the imaging. When studying initial corrosion this is beneficial since the oxide films are very thin. ESB can give good contrast between different material phases even though the films are thin which is not possible because of the larger interacting volume in regular back scattering detector[26].

3.1.2 Energy dispersive X-ray spectroscopy (EDX)

When the incoming electrons hit the surface some electrons in the sample are excited due to inelastic scattering. This leads to a vacancy in one of the inner shells in the atoms which will be filled by an electron from an other shell. In this process a photon with an energy corresponding to the difference between the shells will be released [25]. Since the energy levels in an atom are discrete the X-rays emitted will be characteristic for each element. This makes it possible to determine the elemental composition of a sample in the SEM[24].

3.1.3 Focused Ion Beam SEM (FIB-SEM)

Focused ion beam SEM (FIB SEM) have two guns, one ion gun and one electron gun [27]. Imaging can be obtained both from electrons generated by interaction of either gun but also from ions emerging from the sample. The ion gun often use Gallium ions to machine the surface to do cross sections and cut outs. Other ions like platinum can be used to cover the surface and protect it during the machining. Platinum can be deposited either by electron deposition where electrons are sputtered on the surface and platinum ions adsorb from the atmosphere due to charge balancing. Platinum can also be adsorb by sputtering of the platinum ions only[27].

3.2 X-ray photoelectron spectroscopy (XPS)

When X-rays (photons) hit a surface the beam will interact with the atoms on the sample. If an incoming X-ray contains enough energy it might excite the atoms by knocking out one of the electrons in the inner shells of the element. Since the energy levels in each elements are quantified the energy of the knocked out electron will be special for each element. This is the background for the XPS where X-rays are bombardment on a sample and the energy of the knocked out electrons are measured. The advantages of the technique is that it is able to detect all elements except hydrogen and that it also can detect the chemical state of the elements. Since electrons can not escape from large depths without losing energy, the technique is also surface sensitive and only collect information down to a depth of 2-20 atomic layers (up to 10nm)[28].

The instrument is often equipped with an ion gun which enables milling of the surface. This is important for cleaning of the surface. It can also be used to do depth profiling and trace how thick different layers on a material are, e.g. the thickness of an oxide on a metal. Depth profiling can also be done by tilting the sample which will affect the information depth [29].

4

Experimental

In this chapter the sample preparation, exposure and analyses of the project will be described.

4.1 The steel and the initial sample preparation

The composition of the analysed steel is given in section 2.3. The steel was heat treated by SKF to get a martensitic structure and then cut with electric discharge machining, this was also performed by SKF. In this project a steel rod with a diameter of 12 mm was cut to discs with a height of 4 mm.

4.2 Microstructure

The analysis of the microstructure of the steel was carried out to have a reference on the microstructure of the steel. The samples were mounted in a thermosetting conductive resin and then grinded and polished. The sample was etched with 3 % nital and then studied in the SEM.

4.2.1 Microstructure - sample preparation

The samples were mounted in a thermosetting conductive resin called Polyfast which consists of Bakelite and carbon filler and is produced by Struers. The samples were marked and numbered to be able to distinguish them.

The polishing procedure used was designed for high alloy tool steel which should have similar hardness to bearing steel. This procedure is presented in table 4.1 and is based on the manual from Struers. The procedure was carried out in a polishing machine where the given force was applied to each sample individually. Between the polishing steps the samples were rinsed with deionised water, ethanol and compressed air to remove all particles from the last step.

Table 4.1: Grinding and polishing steps used in the preparation of the sample for the analysis of the microstructure

Step	Surface	Suspension	Rotation (Holder/Disc)	Force	Time
First	Fuga+220 μ m SiC	Water	300/150 RPM	30 N	1 min
Second	MD-Allegro	DiaPro Allegro/Largo (9 μ m)	150/150 RPM	35 N	7 min
Third	MD-Dac	DiaPro Dac (3 μ m)	150/150 RPM	25 N	6 min
Fourth	MD-Nap	DiaPro Nap B (1 μ m)	150/150 RPM	25 N	1 min

The etching of the sample was carried out in 3 % nital for 4 + 2 seconds. The sample was immersed into the etchant for 4 seconds and then immersed into ethanol to stop the process. Then the sample was rinsed with deionised water and flushed with compressed nitrogen. The sample was then immersed in nital for 2 seconds and the same rinsing procedure was used again. The procedure described was the final etching but several other etching times were tried. After the etching the sample was investigated in an optical microscope to see if the etching was successful. Several samples got over-etched and the final polishing step in table 4.1 was then performed again to get a fresh surface which could be etched again.

4.2.2 Microstructure - analysis

The sample was investigated in SEM with an acceleration voltage of 10kV and detection of secondary electrons. Micro-graphs were taken in different magnifications to get a good evaluation of the microstructure.

4.3 Corrosion tests

Samples were moulded in resin, grinded and polished and then immersed in deionised water for different exposure times. The samples were investigated in SEM to see how the samples had corroded and see where the corrosion started. Some samples were also investigated with a FIB-SEM.

4.3.1 Corrosion tests - SEM

4.3.1.1 Corrosion tests - SEM - sample preparation

The samples were moulded with the same procedure as described in section 4.2.1 but the polishing procedure was different. The first step described in table 4.1 was removed and two steps with smaller SiC particles was used to reduce the deformation the rough grinding can introduce to the surface, see table 4.2 for details. After the polishing the samples were stored in a desiccator until the samples were to be studied. Before the samples were exposed a final step of polishing with 1 μm diamond particles were performed for 1 minute. This was done by manual polishing on a surface of MD-Nap and a rotation of 150 rpm for one minute. The cleaning process consisted of rinsing with ethanol and then flushing with compressed nitrogen. This final cleaning procedure changed during the project, see section 4.4

Table 4.2: Grinding and polishing steps used in the preparation of the sample to be exposed to deionised water

Step	Surface	Suspension	Rotation (Holder/Disc)	Force	Time
First	Fuga + 500 SiC	Water	300/150 RPM	20 N	1.5 min
Second	Fuga + 1000 SiC	Water	300/150 RPM	30 N	3 min
Third	MD-Allegro	DiaPro Allegro/Largo (9 μm)	150/150 RPM	35 N	7 min
Fourth	MD-Dac	DiaPro Dac (3 μm)	150/150 RPM	25 N	6 min
Fifth	MD-Nap	DiaPro Nap B (1 μm)	150/150 RPM	25 N	1 min

4.3.1.2 Corrosion tests - SEM - exposure

The samples were placed in a container with deionized water for a controlled period of time, see figure 4.1. Different exposure times were tried during the project to be able to see different sequences of the corrosion process. The exposure times used in the project were 1 minute, 2 minutes, 5 minutes and 10 minutes. Directly after the samples were withdrawn from the distilled water the surfaces were flushed thoroughly with compressed nitrogen to remove all water from the specimen. This was done to be able to stop the corrosion process on the surface. The samples were then put in the desiccator until the sample was put in the SEM. The time after the exposure until the sample was put in the SEM was always less than 15 minutes and in cases immediate.

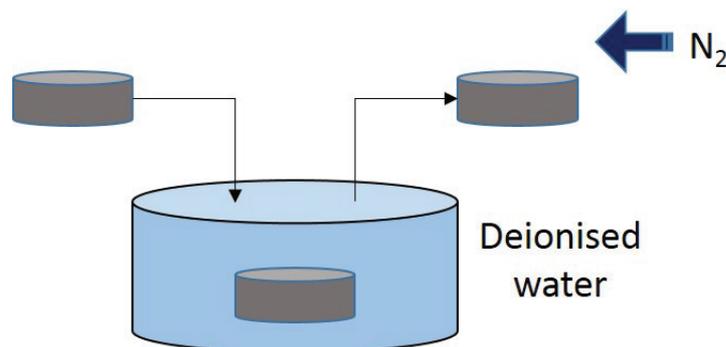


Figure 4.1: Schematic image of the exposure in the corrosion test.

4.3.1.3 Corrosion tests - SEM - analysis

4.3.1.3.1 Corrosion tests - SEM - analysis - SEM In the project several different acceleration voltages and detectors were used. The investigation started at 1 kV accelerating voltage, working distance of 3-4 mm and with imaging with the inlens detector (secondary electrons) with the aim to find interesting areas on the sample. When something interesting was found an image with a slow scan speed was taken and the detector was switched to ESB. Another image of the same region was taken with the ESB detector with the grid set on 0.925 kV. This process where two images were taken on each site gives both topographic and phase information on each region. When chemical information was wanted on a region the working distance was changed to 10 mm and the acceleration voltage to 10 kV. EDX analysis was then performed, generally with an initial mapping of the site and then with some point analysis on interesting parts.

4.3.1.3.2 Corrosion tests - SEM - analysis - FIB-SEM FIB-SEM was used on two samples to be able to do a local (micron-scale) cross section through some inclusions. The studied sample were samples exposed for 5 minutes and 10 minutes respectively. The sample was mounted, polished and exposed according to the scheme in section 4.3.1.1 and 4.3.1.2. The procedure in the FIB-SEM started with a search for interesting areas on the samples to find inclusions where corrosion has started. Some imaging with secondary electrons were also performed. Where a cross section was to be performed platinum deposition of roughly $0.3\mu\text{m}$ was applied to protect the near-surface region from unwanted milling, see figure 4.2. The deposition started with charging of the surface with electrons which attracts platinum ions

from the atmosphere that adsorb to the surface. Then the area was sputtered with platinum ions to create a thicker film. The cross section was made by bombardment by gallium ions which was set to create a rectangular pit which is deepest close to the platinum deposition . Images of the cross section was taken and the sample was then transferred to an SEM with and EDX so chemical information could be obtained.

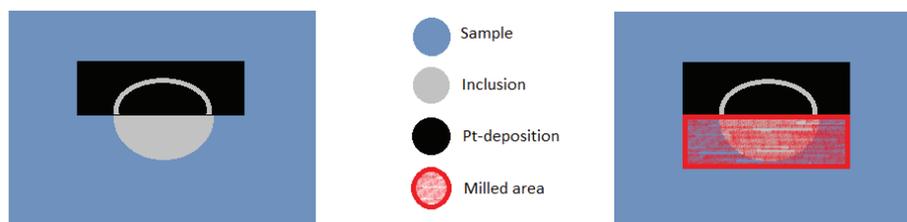


Figure 4.2: Schematic image of the Pt-deposition and milling, seen from top view

4.3.2 Corrosion test - XPS

It is not possible to study moulded samples in the XPS and the sample preparation was a bit different for those samples. The samples were moulded in the same resin but the metal disc was attired in aluminum foil to make it easier to release the disc from the resin later on. When the samples were moulded they were polished according to the scheme in table 4.2. The metal discs were then released from the resin by compression in a vice, the samples were kept in a small plastic bag to avoid it from being shot away. The samples were then kept in a desiccator until they were to be studied in the XPS. Before the samples were put in the XPS they were polished by manual polishing on MD-Nap and 1 μ m diamond suspension for 1 minute. The samples were then immersed in deionised water for 5 minutes or just put directly in the desiccator and transferred to the XPS. The time in the desiccator before the XPS was less than 15 minutes.

In the XPS the vacuum was pumped and then a survey for oxygen and iron was performed. The samples were then milled 10 Å and 50Å respectively with control of the iron and oxygen composition in between.

4.4 The effect of sample preparation on the corrosion process

In the cleaning procedure after the final manual polishing, described in section 4.3.1.1, deionised water was initially used to rinse the sample to remove the diamond suspension. This can affect the corrosion process and a test was done to see if the deionised water in the cleaning process affected the results. Two samples were prepared according to the scheme in table 4.2 but the rinsing after the manual polishing step was different. One sample was first rinsed with deionised water and then with ethanol, the other was only rinsed with ethanol. It should be noted that the sample was not exposed before the final manual polishing step was performed. The samples was investigated in the same way as described in section 4.3.1.3.1.

4.5 Investigation of samples exposed in deionised water with anti-corrosion oil applied

A sample with anti-corrosion oil, provided by SKF, was exposed and then studied in the SEM to get an indicative comparison with the unprotected samples.

The anticorrosion liquid was applied to sample polished with the scheme presented in table 4.2 and was left to set/dry for 1 hour. The samples was then immersed into a beaker with deionised water for 160 hours. After the exposure the sample was cleaned with isopropanol and ethanol. The sample was then investigated in the SEM.

5

Results

5.1 Microstructure

The analysis of the microstructure of the steel is presented in figure 5.1 . The images shows the spheroidized carbides in the microstructure and the martensitic needles .

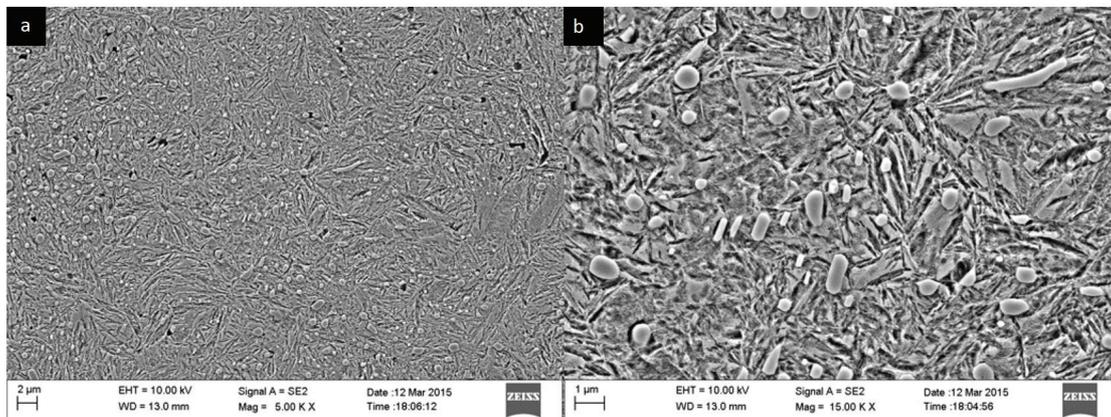


Figure 5.1: SEM image of etched sample imaged with secondary electrons, a and b are with different magnifications

5.2 XPS

In figure 5.2 the overall spectrum for non exposed sample can be seen and in table 5.1 the chemical composition on the different depths are presented. The same information for a sample exposed for 5 minutes can be found in figure 5.3 and table 5.2.

The XPS analysis showed that there is no difference in oxide films on the exposed and non exposed samples, both regarding thickness and composition. Given the large analysis area (diameter 0.8 mm) and the limited coverage of localized corrosion exemplified below, the XPS results will represent the some few nm thin oxide film covering most of the surface. This indicates that the corrosion process during the 5 minute exposures does not generate a general oxide film that is thicker than the one formed in air. A prolonged exposure with rinsing of the sample in deionised water was also performed, but the results were the same. The XPS was not able to detect manganese or sulphur signals that were strong enough to be able to study the peak shifts of the elements. In a case where the manganese or sulphur signals would be strong enough it would be interesting to see if a peak shift could

be identified since this could give the chemical state of elements and then give some hints about the corrosion reactions.

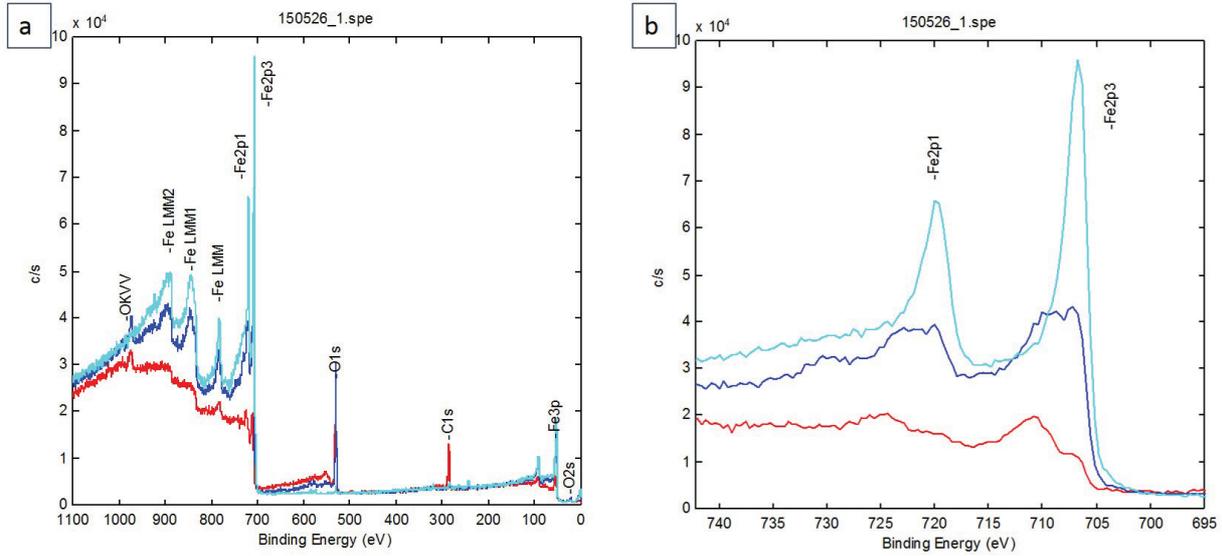


Figure 5.2: XPS spectra for non exposed sample, a) is the general spectrum and b) the iron spectrum. The red lines are from the depth of 0 Å, dark blue from 10 Å and light blue from 50 Å.

Table 5.1: Chemical composition on different sputtered depths of non exposed sample studied with XPS. (at%)

Depth	C	O	Fe
0 Å	32.32	41.44	26.25
10 Å	1.42	30.94	67.63
50 Å	4.43	1.29	94.28

Table 5.2: Chemical composition on different sputtered depths of sample exposed for 5 minutes studied with XPS. (at%)

Depth	C	O	Fe
0 Å	33.54	36.55	29.91
10 Å	4.86	27.92	67.21
50 Å	4.06	1.33	94.61

5.3 Reference of inclusions on unexposed samples

Images of inclusions from samples that have not been exposed are presented to get a reference. Images of one MnS inclusion that has been affected by the polishing is seen in figure 5.4.

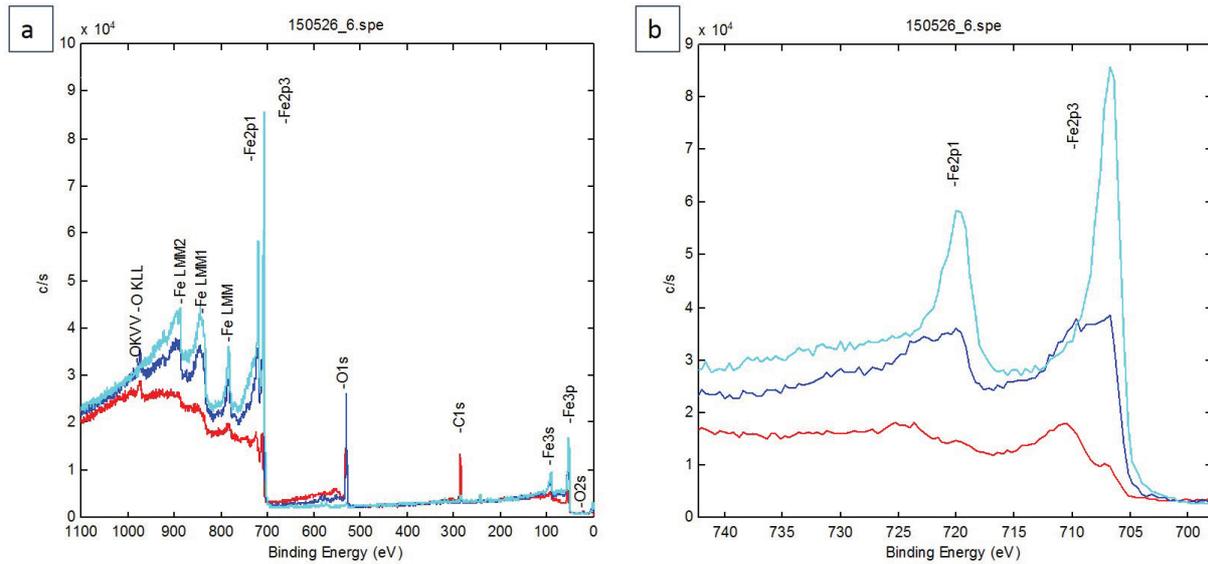


Figure 5.3: XPS spectra for sample exposed for 5 minutes, a) is the general spectrum and b) the iron spectrum. The red lines are from the depth of 0 Å, dark blue from 10 Å and light blue from 50 Å.

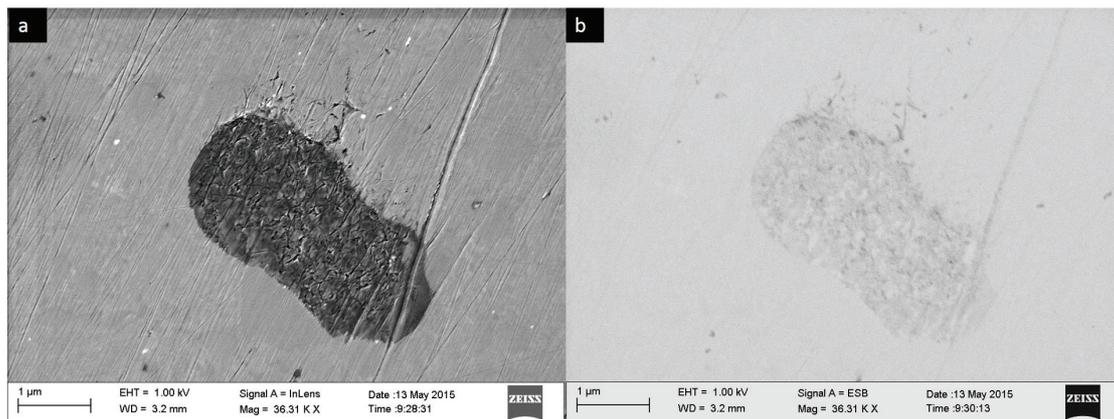


Figure 5.4: SEM image (1kV) of a MnS inclusions from unexposed sample, a inlens, b ESB detector. The image show that the inclusions is affected by the sample preparation and get some scratches from the polishing.

The image show how the surface of the inclusion is affected by the polishing and sample preparation.

A MnS inclusion that has not been as affected can be seen in figure 5.5. In this image the inclusion do not show deep scratch marks on the surface but the surface of the inclusion is not completely smooth.

The composition of three studied MnS inclusions from the non exposed samples can be seen in table 5.3. The table shows that the composition of the inclusion differ. The analysis in this report will discuss all inclusions with mainly Mn and S as the same kind even though a difference in the composition can be seen. The number of studied inclusions is too small to be able to do any comparison between different kinds The detection of fluoride ($K \alpha$ 0.67keV) in some inclusions was unexpected and very likely an artefact of the interference between

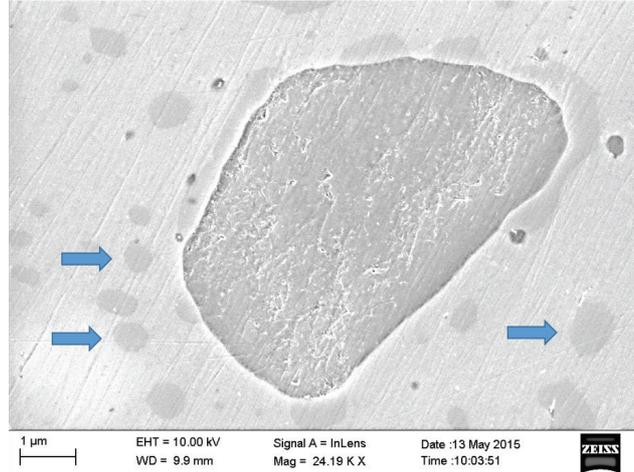


Figure 5.5: SEM image (10kV) of a MnS inclusions from unexposed sample. The image shows that the inclusions do not have a completely smooth surface appearance even though few scratch marks can be observed. Note the presence of carbides around the inclusion, see arrows

Mn K α 0.637 keV-energy and Fe L α 0.705 keV -energy. The results confirm that inclusions with similar appearance as seen in figure 5.4 and 5.5 are MnS inclusion with some iron.

Table 5.3: Composition of three MnS inclusions in non exposed samples. (wt.%)

Inclusion	S	Mn	Mg	F
1	38.10	60.87	1.03	-
2	37.85	56.34	0.74	5.08
3	36.84	55.35	-	7.81

5.4 SEM and FIB-SEM

In this section the results from the samples which have been emerged into a beaker with deionised water for various exposure times are presented. The results are divided into subsections based on the time of the exposure. First the shortest exposure times will be presented and the results will follow in order of increasing exposure times.

5.4.1 1 min

There are no clear signs of corrosion after 1 min exposure. The discernible effects of the exposure are limited to what are believed to be effects from sample preparation and some contamination. This is exemplified in figure 5.6 and is supported by EDX analyses seen in figure 5.7 where any signal from oxides or inclusions are lacking.

Even though no inclusions that showed signs of corrosion were observed areas with possible corrosion on the matrix could be observed, see figure 5.8. The image shows that the surface appearance is different which means that the sample could have corroded.

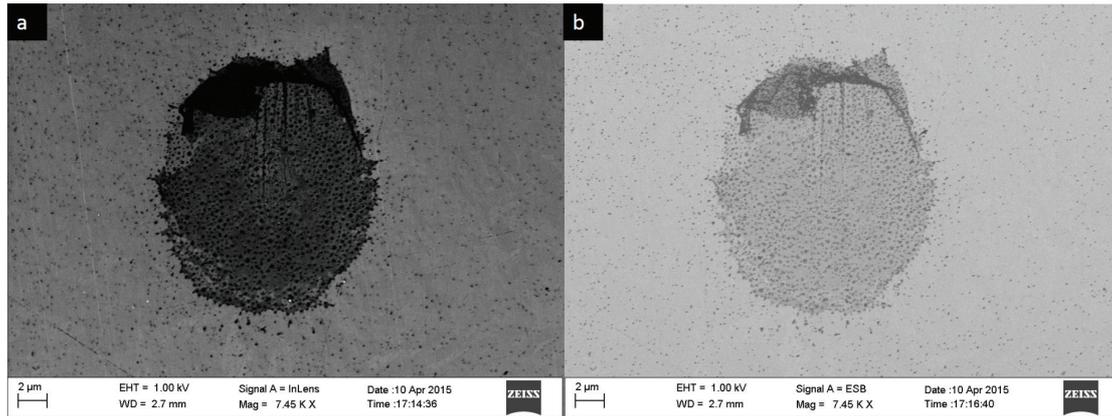


Figure 5.6: SEM image (1kV) sample exposed for 1 minute, a inlens b ESB . The image show an area which could be an inclusions covered with diamond or just a mark from the drying.

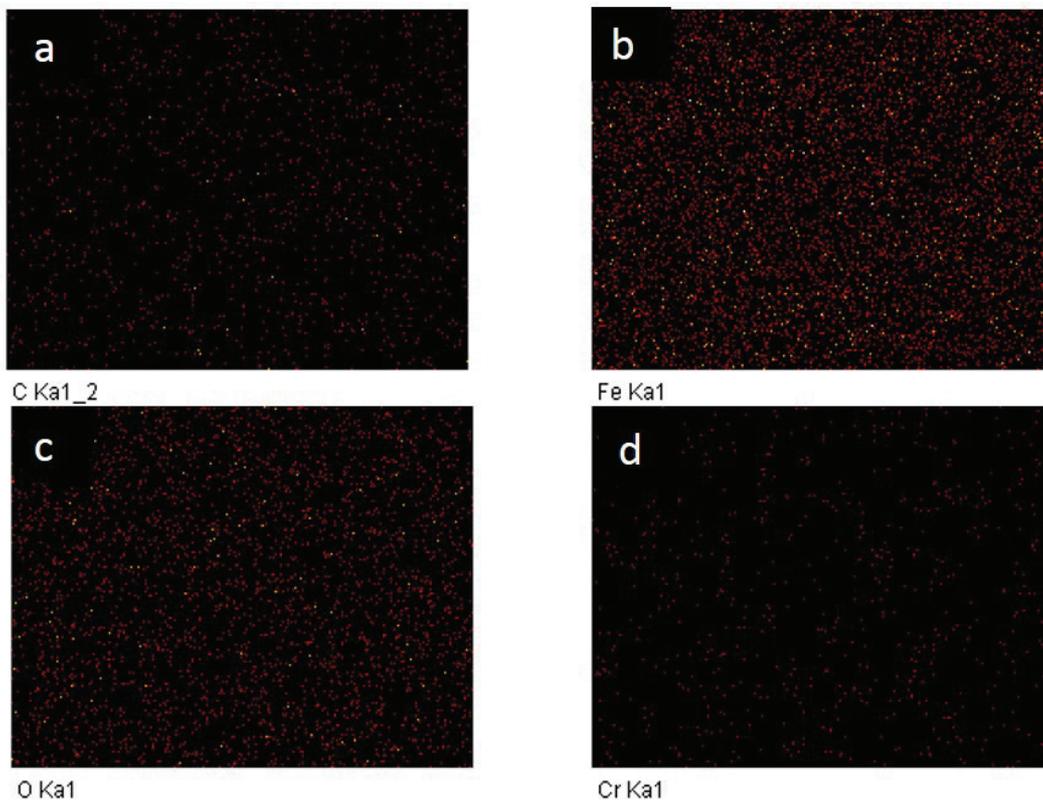


Figure 5.7: EDX mapping of area in figure 5.6, a-d are mappings of different elements significant for oxides or inclusions

Another example is shown in figure 5.9 where the composition of the analyses spectrum are presented in table 5.4 which show that some oxygen was found in the region, but also some carbon. This indicates that the region can either be thin oxides or contaminants but it is not possible to tell which with this technique.

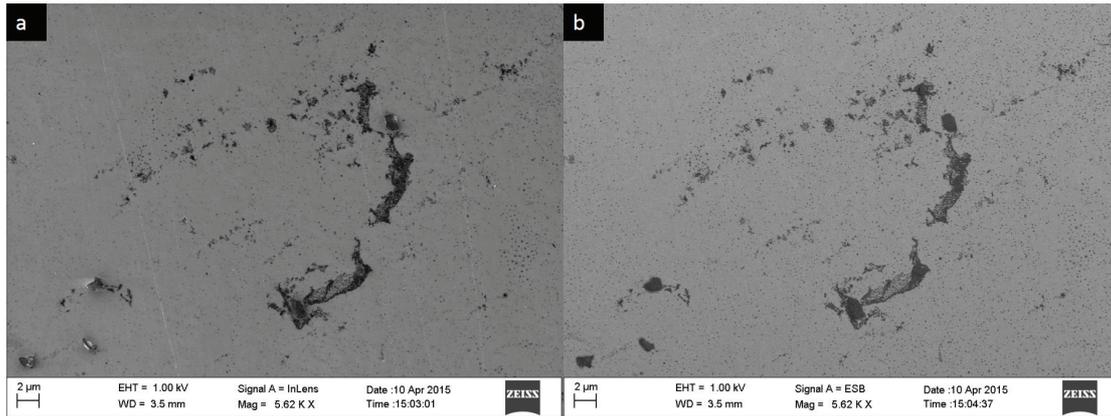


Figure 5.8: SEM image (1kV) of a area on sample exposed in 1 minute, a inlens b ESB. The image shows an area which could be mild localcorrosion on the matrix or possibly dirt.

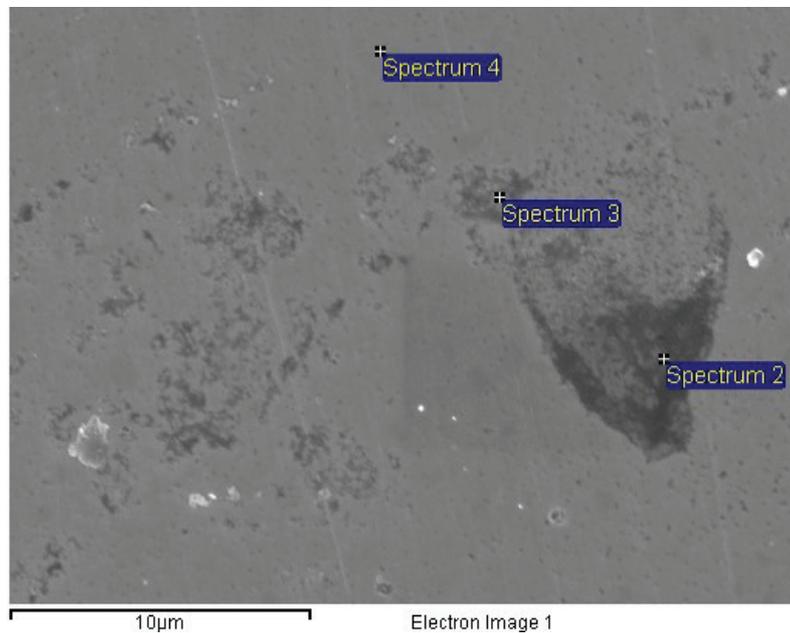


Figure 5.9: SEM image (10kV) sample exposed for 1 minute, The image shows an area which could be corrosion on the matrix.

5.4.2 2 min

After 2 minutes some signs of corrosion were observed. A complex inclusion where corrosion has initiated can be seen in figure 5.10. The region around the inclusion shows changes in surface appearance and the inclusion is uneven which could be due to corrosion of the vary inclusion. The white area is assumed to be some kind of oxide. The particular inclusions was not studied in with EDX and the composition of the inclusion is therefore unknown. The most probable inclusion type is a MnS-AlO based on other observations.

Inclusions which showed minor or no signs of corrosion were found, see figure 5.11 and 5.12. Only small changes in imaging contrast around the interface between the inclusion and the matrix can be observed.

For images where changes in the surface appearance due to corrosion in the matrix was

Table 5.4: EDX analysis of points marked in figure 5.9 (at%)

Spectrum	C	O	Fe	Cr
2	2.30	1.46	90.14	2.21
3	4.91	-	95.09	-
4	3.80	0.62	93.51	2.07

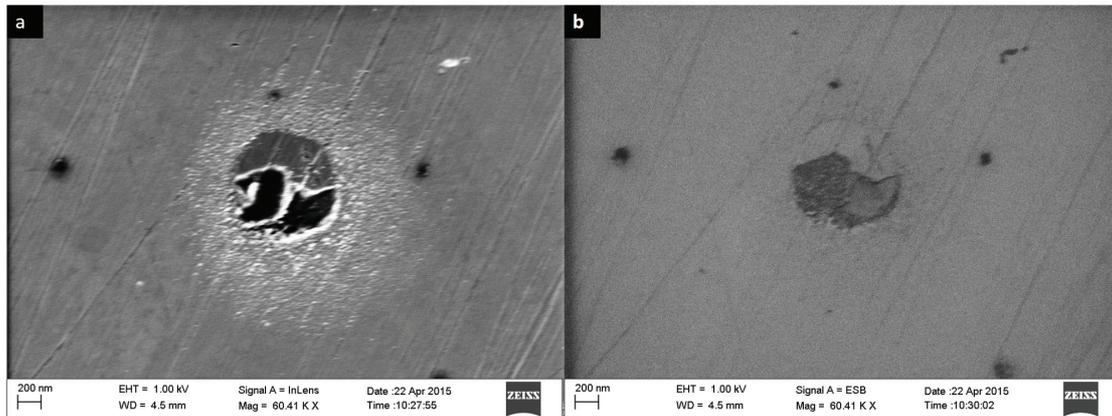


Figure 5.10: SEM image (1kV) sample exposed in 2 minutes, a inlens detector, b ESB detector. The image show a complex inclusion with unknown composition. The region around the inclusion have changes in surface appearance and there crevices can be observed

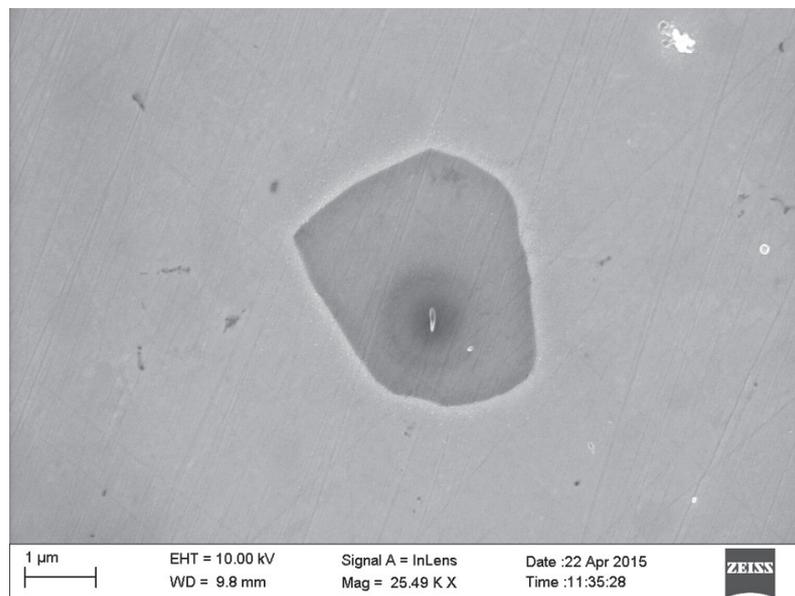


Figure 5.11: SEM image (10kV) sample exposed for 2 minutes. The inclusion show some signs of corrosion around the edges based on the difference in imaging contrast, but no other changes can be observed

observed, see figure 5.13.

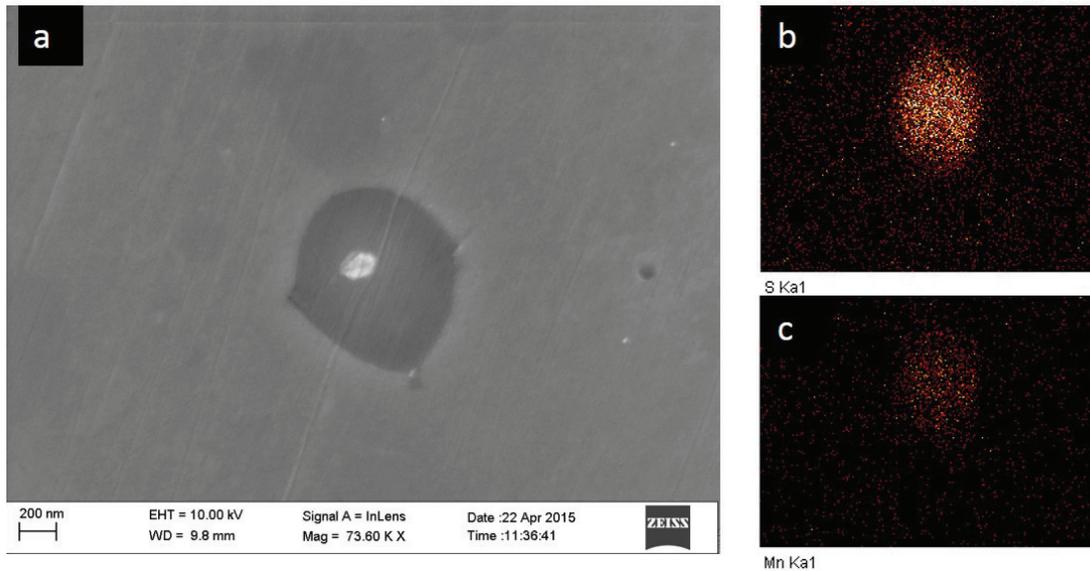


Figure 5.12: SEM image (10kV) sample exposed for 2 minutes, where a is inlens , b sulphur mapping and c the managnese mapping. The inclusion show some signs of corrosion around the edges, and what is believed to be sample preparation effects in the middle, but no other changes can be observed

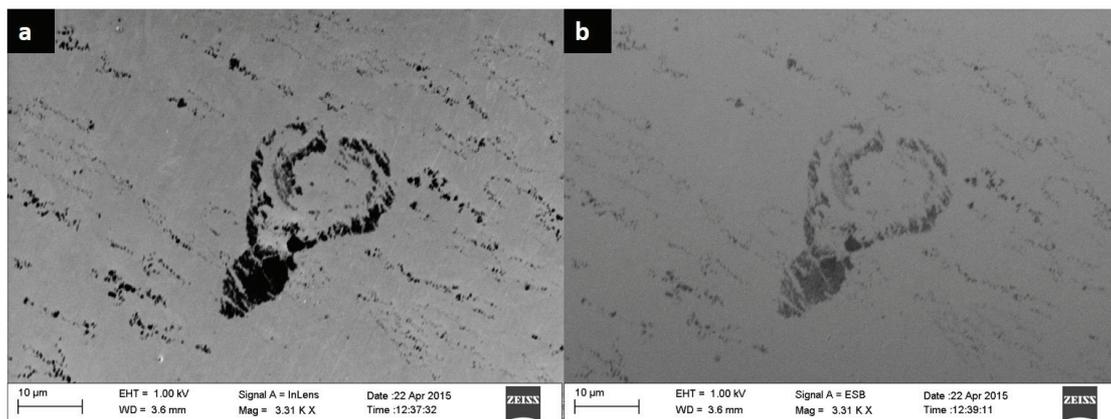


Figure 5.13: SEM image (1kV) of a area on sample exposed in 2 minutes, a inlens detector, b ESB detector. The image show possible corrosion on the matrix of the steel or dirt.

5.4.3 5 minutes

After 5 minutes of exposure corrosion could be observed around several inclusions. The results for the SEM and FIB-SEM images will be presented in different sections.

5.4.3.1 5 minutes - SEM

An example of an inclusions that has corroded can be seen in figure 5.14. The surface of the inclusions is rough and has decomposed (corroded). Compared to the samples that have not been exposed, see figure 5.4 and 5.5, the surface is more rough which means the roughness should not only come from the sample preparation. The matrix close to the inclusion is affected and gives bright edge contrast in the inlens image. A small crevice in the top of

the inclusions can be seen, it can be either a result of the corrosion, sample preparation (partial loss of any factured piece of inclusion), or bad incorporation of the inclusion in the processing. No EDX was performed on the inclusion but based on observations of other inclusions it is most likely a MnS.

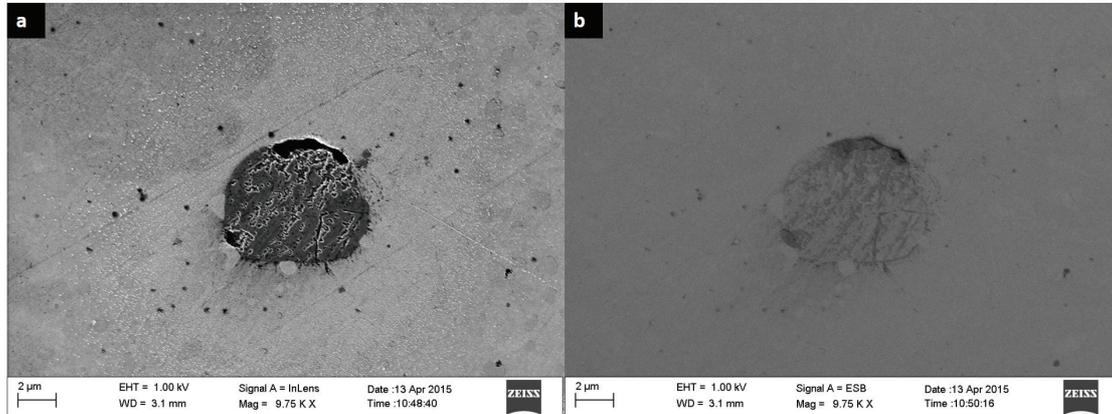


Figure 5.14: SEM image (1kV) sample exposed for 5 minutes, a inlens detector, b ESB detector. The image shows that some of the inclusion have been dissolve due to the increased roughness of the surface. The composition of the inclusion is unknown

More inclusions which show similar signs of corrosion can be seen in figure 5.15. The inclusions have a rough surface and show some signs of crevices in the interface between the inclusion and the matrix. They also show a more distinct region around the inclusion which has changed, this could be some kind of corrosion product.

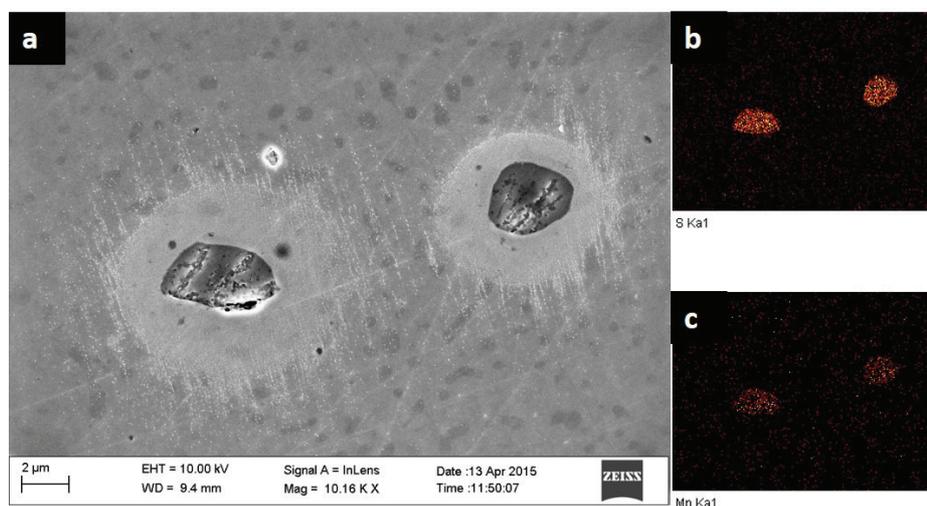


Figure 5.15: SEM image (10kV) sample exposed for 5 minutes with S and Mn mapping. a inlens , b S- mapping and c Mn-mapping. The image shows that some of the inclusion has decomposed (corroded) due to the increased roughness of the surface

In figure 5.16 carbides can be seen (some are marked by arrows) and no changes close to them can be seen which means corrosion has not initiated at them.

A complex inclusion with a crevice formed around one side can be seen in figure 5.17. Since the crevice is formed on one side it could mean that one part of the inclusion is preferentially

5. Results

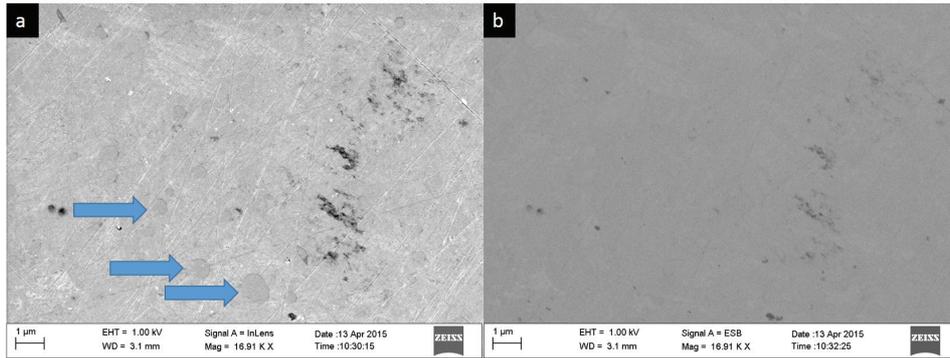


Figure 5.16: SEM image (1kV) sample exposed for 5 minutes, a inlens and b ESB. The image show that the carbides (marked by arrows) are not affected of the corrosion process but are inert.

decomposed or that it has been effected by sample preparation. The region around the inclusion show similar effect as observed in figure 5.14. No EDX was performed on the inclusion which makes the composition unknown.

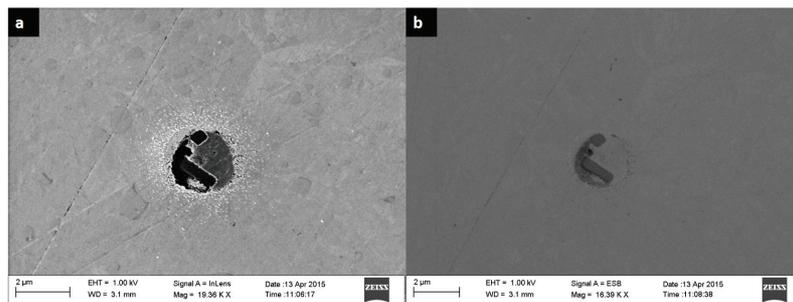


Figure 5.17: SEM image (1kV) sample exposed for 5 minutes, a inlens , b ESB . The image shows a image of a complex inclusions with a crevice on the left side.

Some areas showed changes in the surface appearance as seen in the shorter exposures were also observed. In figure 5.18 this phenomenon can be observed.

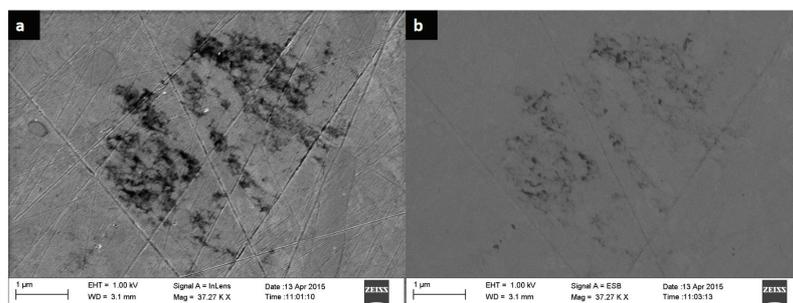


Figure 5.18: SEM image (1kV) sample exposed in 5 minutes, a inlens , b ESB. The image shows corrosion on the matrix on the steel or dirt.

5.4.3.2 5 minutes - FIB-SEM

Two cross sections were done in the FIB SEM on a sample exposed for 5 minutes. One of the inclusions is presented in figure 5.19. The images show that the surface of the inclusion is rough and that a circular region of matrix around the inclusion is changed due to the corrosion. It is also possible to detect a increased roughness in one spot in this circular region to the right of the inclusion. The cross section of the inclusion shows that the surface of the inclusion is lower than at the surrounding matrix. No EDX analysis was performed on the inclusion.

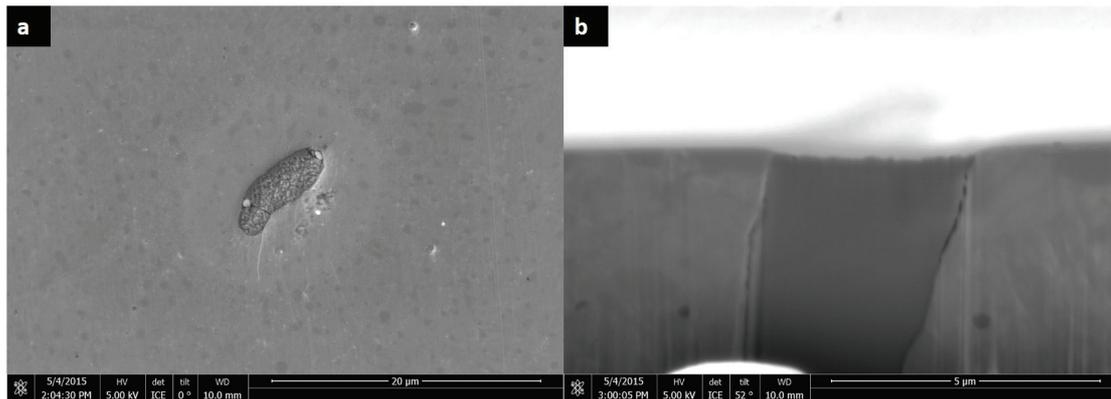


Figure 5.19: SEM image of an inclusion with cross section. a before cross section and b after cross section. The surface of the inclusion is rough and the cross section show that the very inclusion had corroded (decomposed).

The other inclusion studied in the FIB SEM is presented in figure 5.20. The inclusion shows the same characteristics as described for the inclusion in figure 5.19. The inclusion also show some signs of poor incorporation in the matrix on the left side in the cross section. This inclusion was studied with the EDX which showed that the inclusion is a MnS.

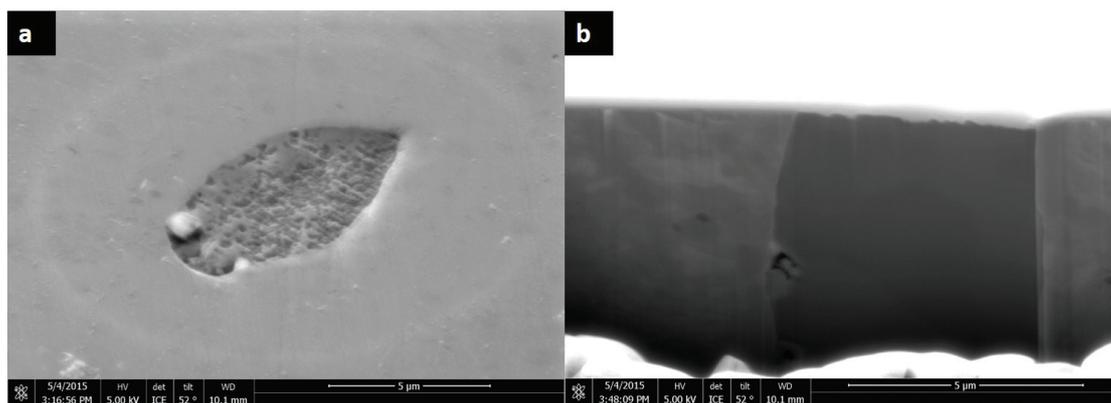


Figure 5.20: SEM image (5kV) of a MnS inclusion with cross section. a shows the inclusion before the cross section and b shows it after the cross section. The surface of the inclusion is rough and the cross section show that the very inclusion had corroded (decomposed).

5.4.4 10 minute exposure

The 10 min exposure caused significant corrosion, most pronounced at manganese sulphides. Samples exposed for 10 minute were studied in two separate occasions in the FIB SEM, one studied inclusion from the first session can be seen in figure 5.21. The surface of the inclusion is rough which indicates that the inclusion has decomposed (corroded). It was not possible to determine if the inclusion is more or less decomposed than in the 5 min exposed samples.

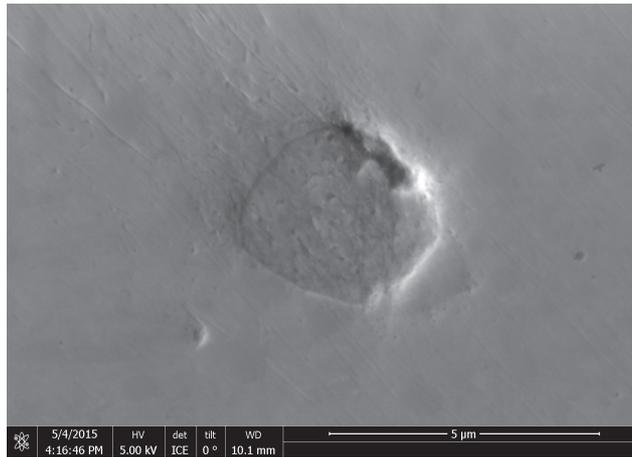


Figure 5.21: SEM image (5kV) of inclusion in 10 min exposed sample. The surface is rough which indicates that the inclusion has decomposed. Scratches from sample preparation are visible towards the top-left corner

In the second session more extensive investigations were performed. The samples showed more effects of corrosion than in the earlier session and the inclusions had corroded in a similar way as for the first samples when deionised water was used for rinsing in the sample preparation. The difference in perceived corrosion effect highlights the delicacy of sample preparation and exposure, that can have slight variation between each other.

Below some images from the FIB/SEM are presented. Three micro cross sections were performed and will also be presented. The two inclusions in figure 5.22 show similar results where an area around the inclusion is darker and is covered by something assumed to be a thicker oxide film with cracks, the area outside the dark oxide is smoother than the bulk steel matrix. This area will further on be mentioned as oxide.

Figure 5.23a shows an inclusion that has partially decomposed and the oxide film shows no signs of cracks, figure 5.23b shows a region where whiskers are growing inside a pit or on top of an inclusion as well as around it. Figure 5.24 shows the same characteristics as seen in figure 5.22 but the cracked area is larger and more cracks can be observed. It is also possible to see that the dark oxide film has started to flake from the material.

Three micro cross sections were performed and are presented below. In figure 5.25 an inclusion and corroded area are presented in two different angles and the FIB micro cross sections are shown in figure 5.26. The figures show that an oxide film has formed close to the inclusions and that several cracks have formed. The surface of the film is flaking and it is possible to see that the film is not completely adhered to the metal. The micro cross section shows that the crevices go down in the material and that a part of the material close to the inclusion has started to spall since the cracks surround this part.

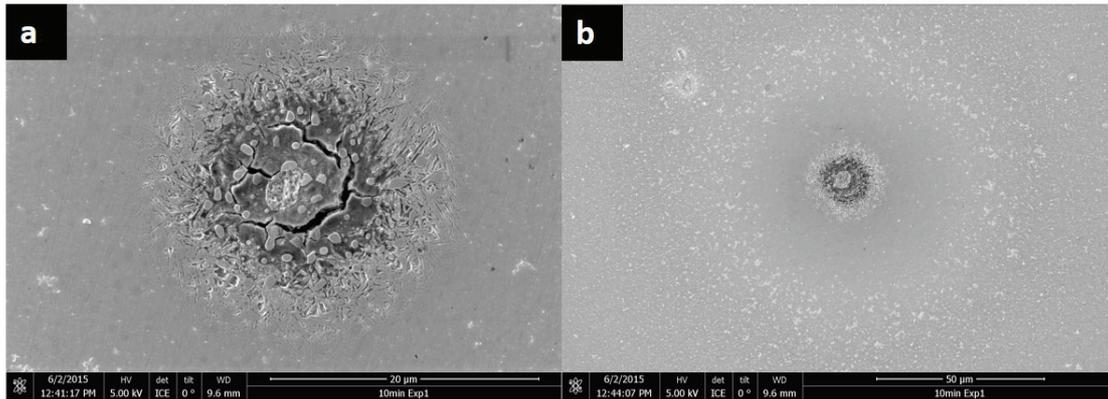


Figure 5.22: SEM image of inclusions and corroded areas in the 10 min exposed sample studied in the FIB/SEM. a-b are different inclusions observed

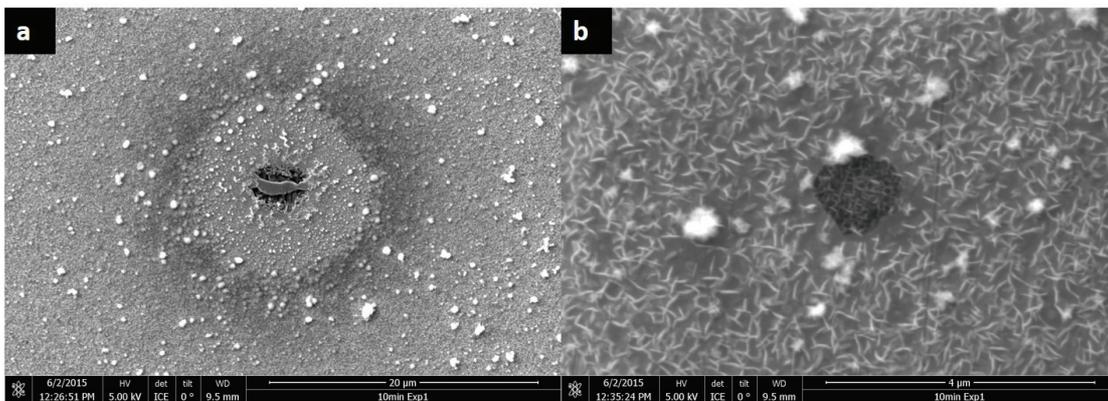


Figure 5.23: SEM image of inclusions and corroded areas in the 10 min exposed sample studied in the FIB/SEM. a-b are different inclusions observed

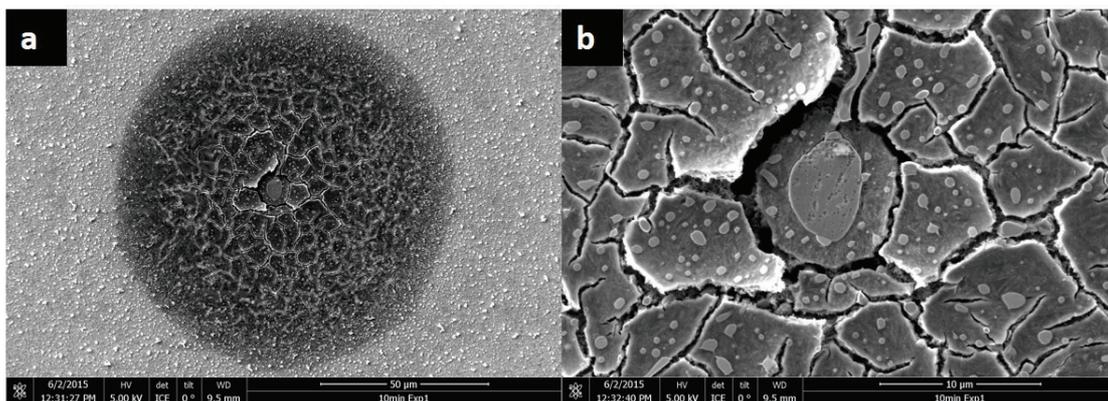


Figure 5.24: SEM image of inclusion and corroded area in the 10 min exposed sample studied in the FIB/SEM. a and b are imaged with different magnification

In figure 5.27 a corroded area but no clear center with an inclusion can be seen. The area is covered by an oxide with cracks and the surface has started to flake. The micro cross section, figure 5.28 reveal cracks below the surface and similar characteristics as observed earlier when crevices form around a certain area. No inclusion can be seen in the image but

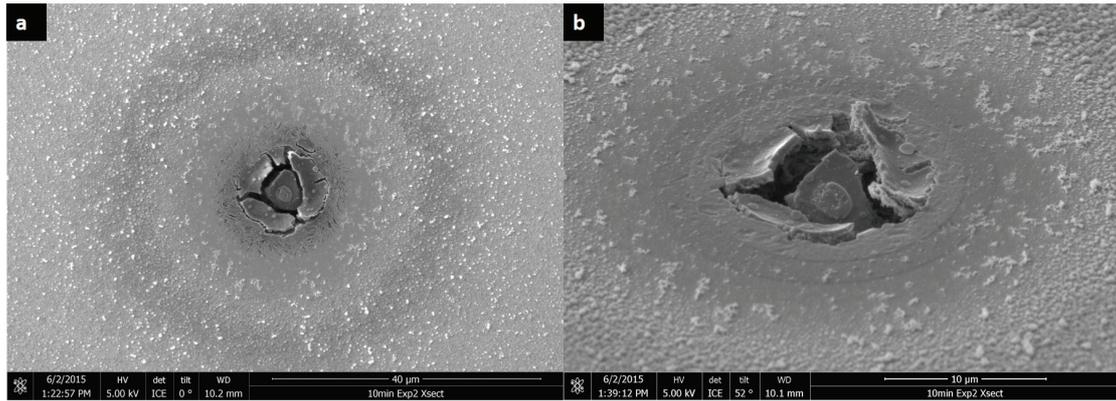


Figure 5.25: SEM image of inclusions and corroded areas the in 10 min exposed sample studied in the FIB/SEM. a is taken perpendicular to the surface and b is with a tilted sample (some Pt is deposited in a circle over the inclusion in b).

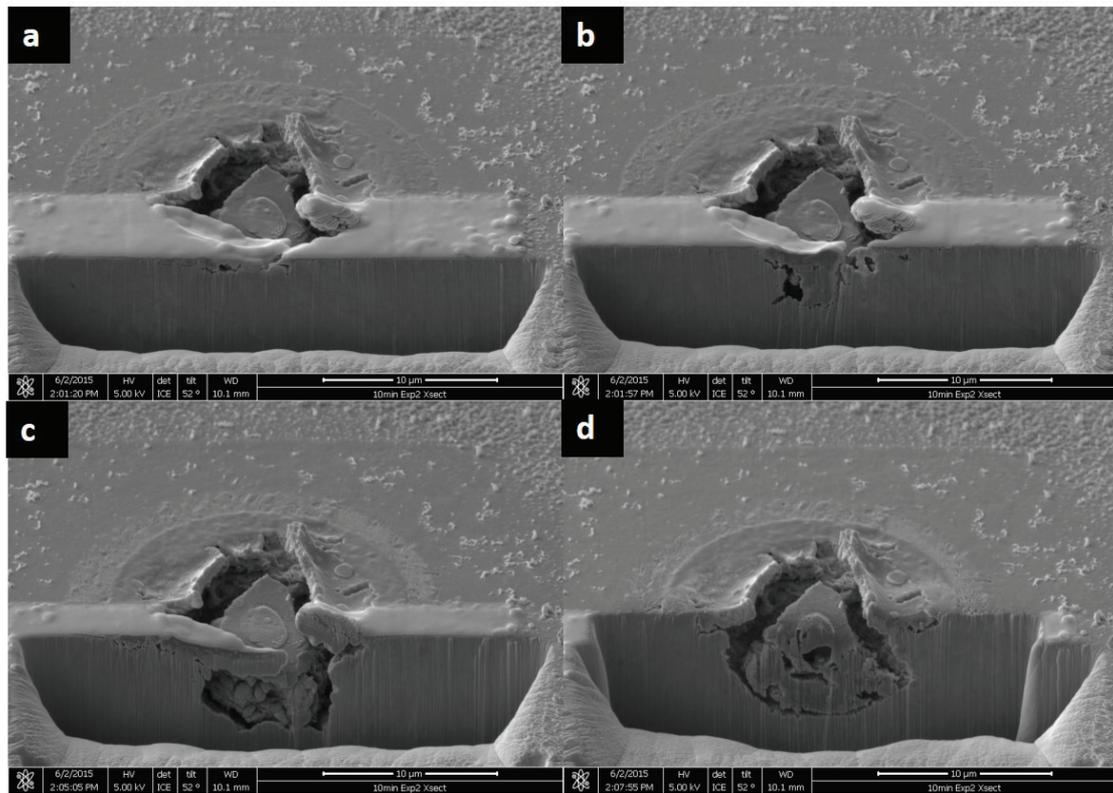


Figure 5.26: SEM image of the etching process of region in figure 5.25, a-d show different times of the ion milling.

could be incorporated somewhere in the area inside the crevices.

In figure 5.29a an inclusion with less signs of corrosion than the other studied inclusions is presented, in figure 5.29b-d the micro cross section is presented. The inclusion show several grains and the inclusion does not look well incorporated to the steel. A border with porous material can be seen between the inclusion and the steel. The micro cross section was also studied with EDX and the results of this is shown in figure 5.30. The inclusion consist mainly of Al, Mg and O.

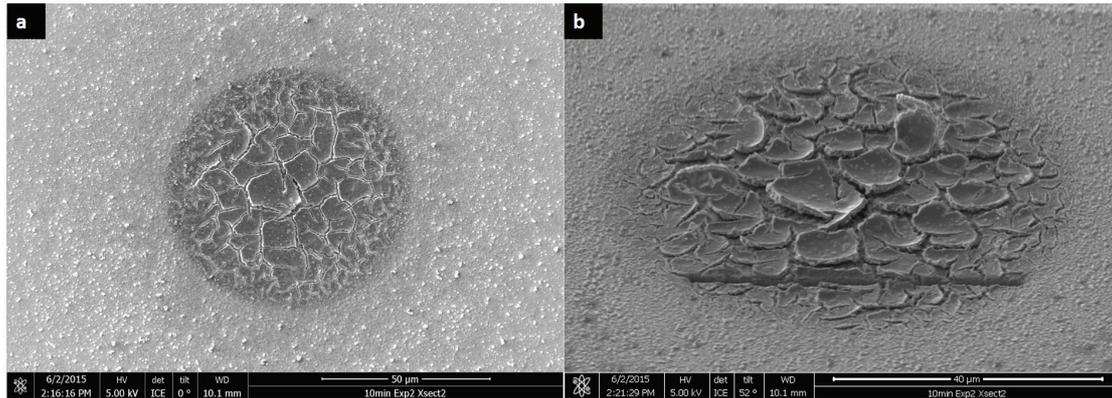


Figure 5.27: SEM image of inclusions and corroded areas in the 10 min exposed sample studied in the FIB/SEM. a is taken directly over the surface and b is with a tilted sample where also the first ion mill region is visible (line).

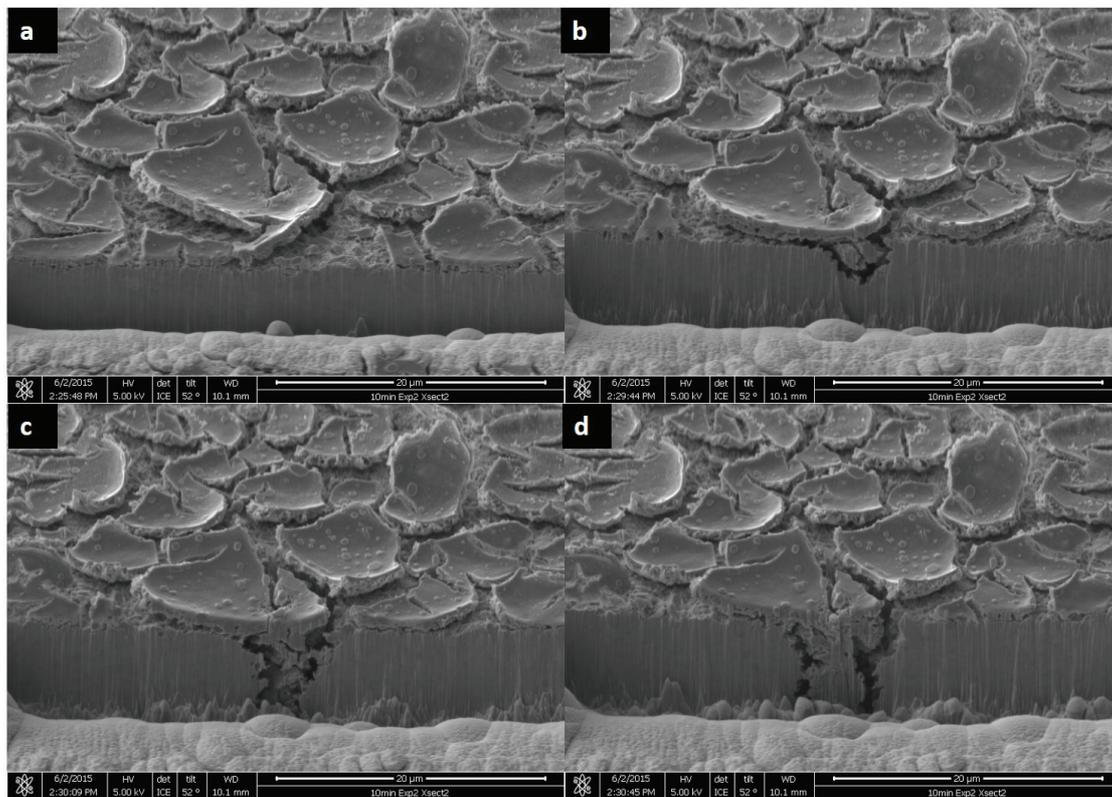


Figure 5.28: SEM image of the etching process of region in figure 5.27, a-d show different times of the ion milling where flaking of the area of assumed oxide can be seen.

More EDX analysis was performed on the 10 min exposed sample, in figure 5.31 an inclusion with similar characteristics as e.g. figure 5.25. A pseudo phase diagram (Oxford INCA software, where the ratios of three elements are set as indicative of a phase) between iron oxygen and chromium was performed which is presented together with the element maps in figure 5.32, the mean composition of the phases is found in table 5.5.

The EDX results show that the region around the inclusion is oxidised, that the iron content is low close to the inclusion and that the chromium content is higher close to the inclusion. The

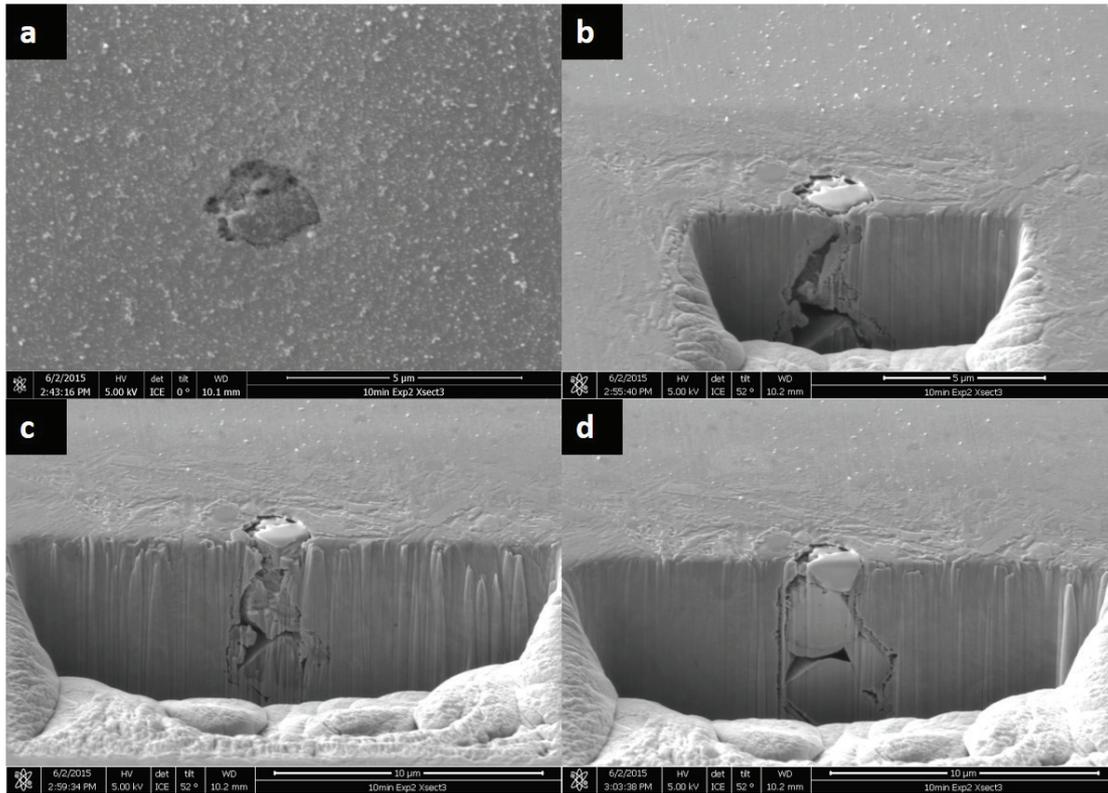


Figure 5.29: SEM image of inclusions in 10 min exposed sample, a is a overview and b-d different times of the ion milling in the micro cross section

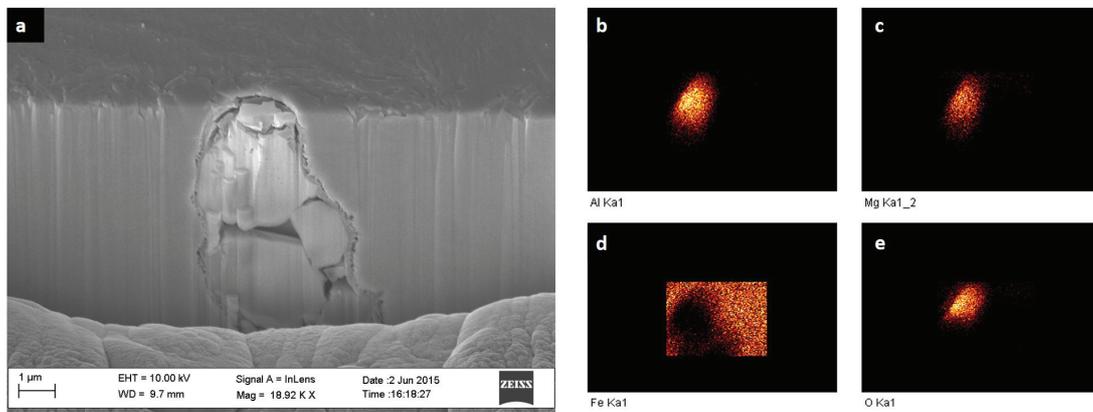


Figure 5.30: SEM image of inclusions in 10 min exposed sample, a is a overview and b-e different different element maps

reason that the chromium content is higher close to the inclusion might be due to corrosion of the iron which then will make the relative chromium content higher. The pseudo phase diagram show that the there is more oxygen in the middle which indicates that this part has corroded the most as a thicker oxide would yield higher O signal. It is also possible to detect region outside the heavily oxidised part (red-green) where very little oxygen compared to iron is found.

In figure 5.33-5.34 an inclusion of mainly Mn, S and Mg is studied. The inclusion also have

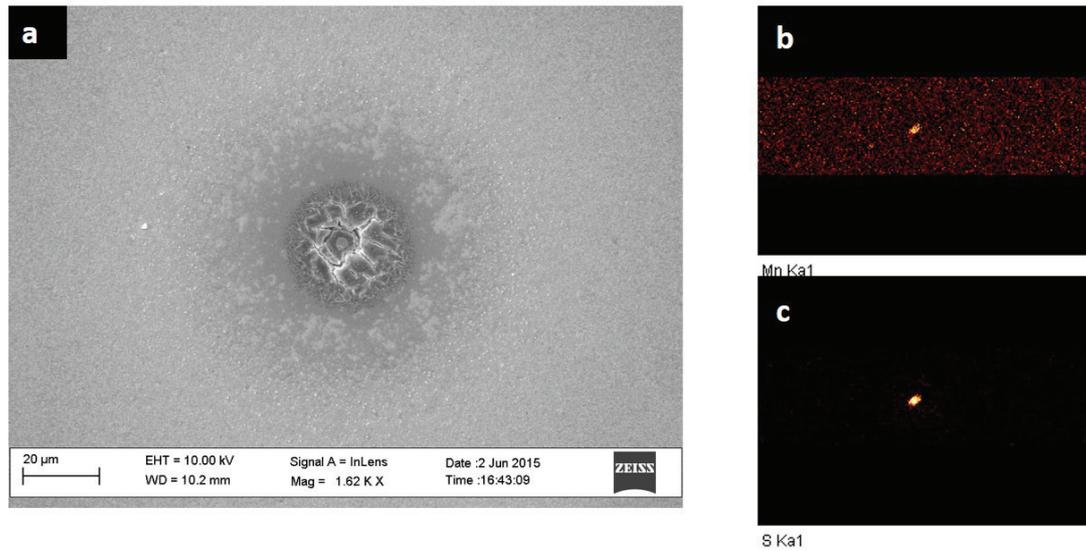


Figure 5.31: SEM and EDX analysis of inclusions in 10 min exposed sample, a is a overview and b-e different different element maps

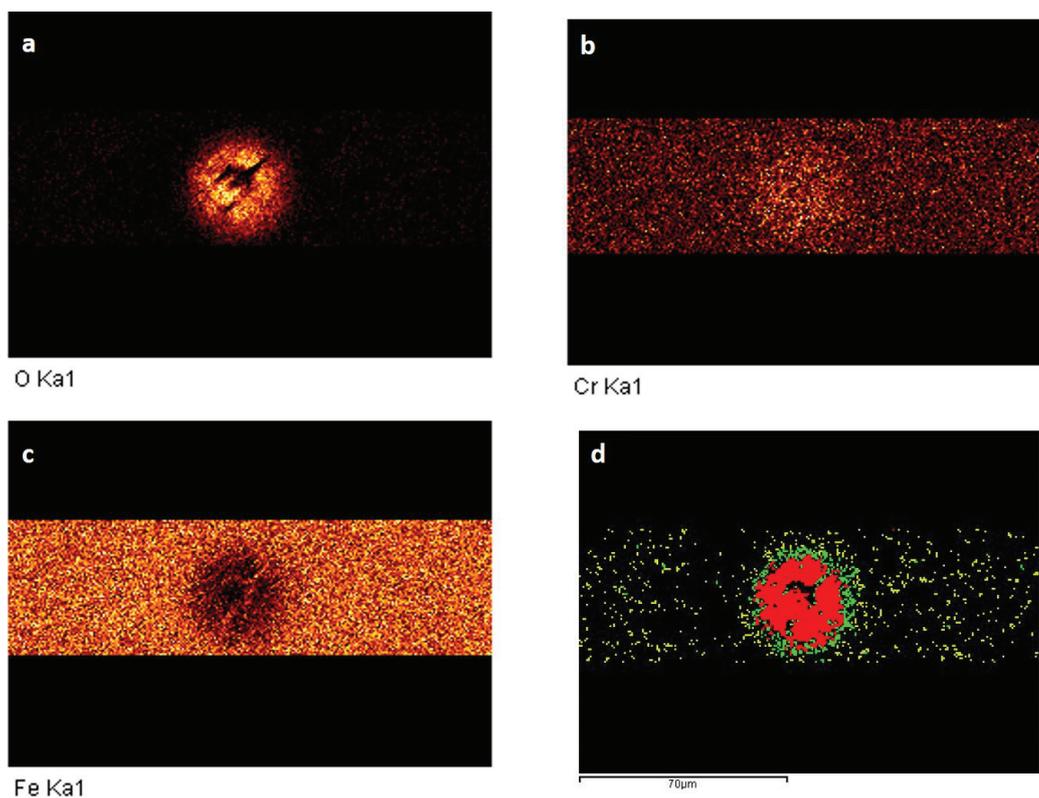


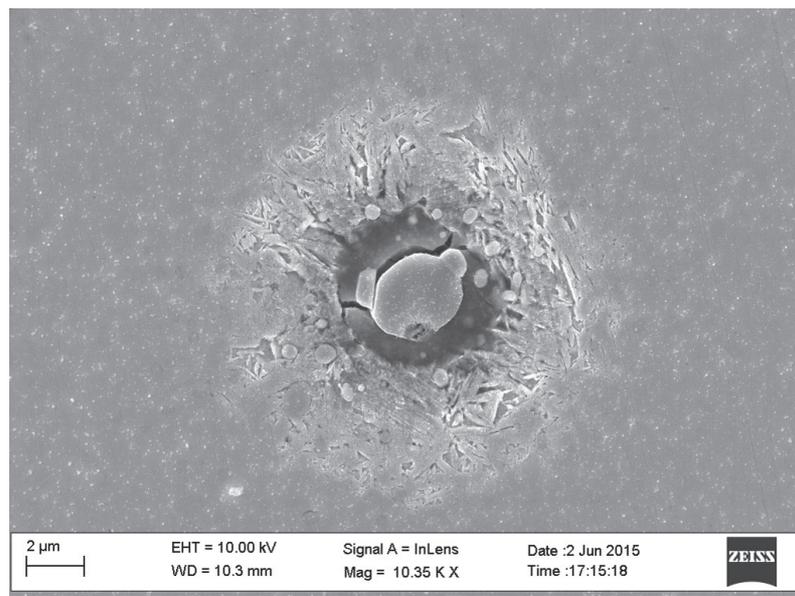
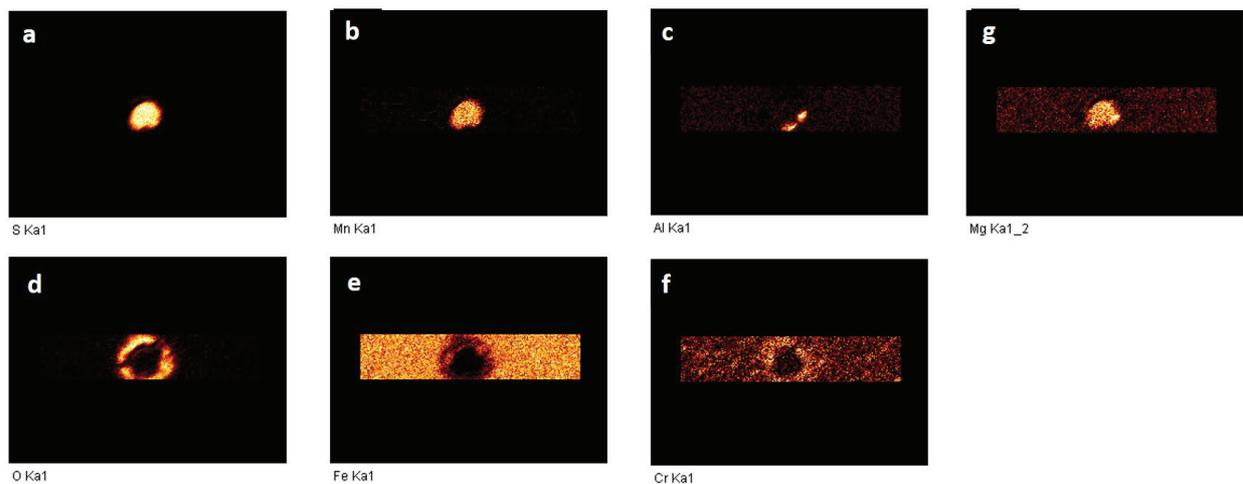
Figure 5.32: Pseudo phase map and EDX analysis of inclusions in 10 min exposed sample, a-c are element maps and d the pseudo phase digram where the red is the most oxygen rich, green roughly equal parts oxygen and iron, and yellow most iron rich parts of the oxide

some aluminum in one part and is a complex inclusion. The area around the inclusion is oxidised but no oxide films with cracks can be observed. This could mean that the corrosion at this inclusion is in a earlier phase in the process than the other studied inclusions in the

Table 5.5: Mean composition for phases in figure 5.32 (wt%)

Phase	O	Fe	Cr	S
Red	14.13	59.76	24.59	1.69
Green	7.64	82.77	8.68	0.08
Yellow	2.27	93.32	4.93	0.14

10 min exposure.

**Figure 5.33:** SEM image of inclusions in 10 min exposed sample**Figure 5.34:** EDX analysis of inclusions in figure 5.33, a-f is maps for different elements

5.4.5 10 minute exposure and rinsing with deionised water

Some samples from the first exposures when rinsing with deionised water was used in the sample preparation showed some heavily oxidised areas. One inclusion where a thick oxide was formed can be seen in figure 5.35. The EDX analysis showed that the surface around the inclusion is oxidised and that the inclusion contain sulphur.

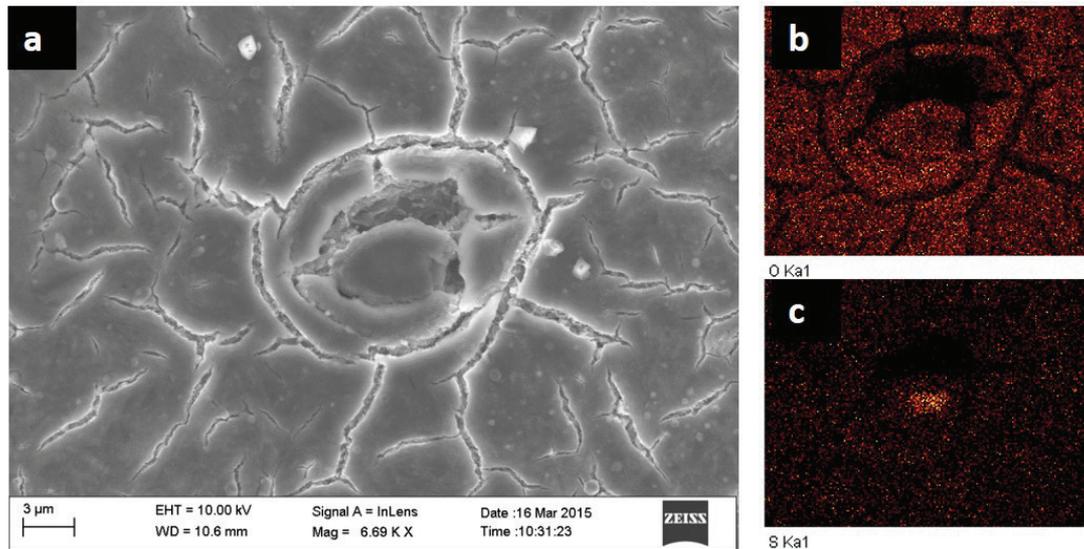


Figure 5.35: SEM image of inclusion the in 10 min exposed sample with old rinsing method. a is the inlens image, b the oxygen mapping and c the sulphur mapping.

5.5 The effect of sample preparation on the corrosion process

The results of the study of sample preparation in the SEM is presented in figure 5.36. The images show that the the sample that was rinsed with deionised water have corroded. The black areas in figure 5.36a is an attack on the steel since no large topographic difference can be seen, this means that it is not dirt. The black areas on figure 5.36b must be dirt since it is laying on top of the metal and bear no resemblance to known corrosion products. In all images from the sample only rinsed with ethanol no signs of corrosion could be observed, only changes on the surface as observed in image B could be seen. This means that there is a difference between the samples depending on the rinsing method and that the samples that was rinsed with deionsed water before the corrosion experiment will have corroded more than originally planned.

It should be noted that all samples in section 5.4 were only rinsed with ethanol.

5.6 Samples with anti corrosion oil

The samples with anti corrosion oil showed no sign of corrosion, only areas of residuals of the oil could be found after cleaning the sample, see figure 5.37. Many similar spots were

5. Results

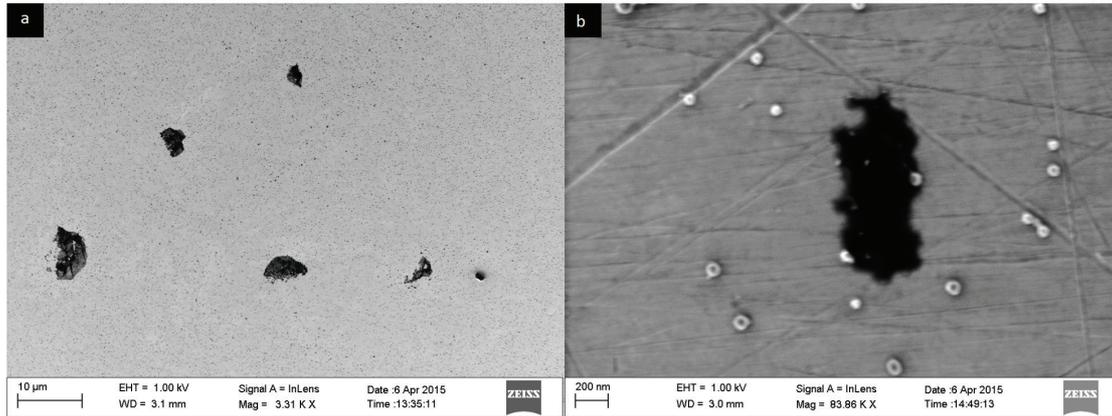


Figure 5.36: SEM image of samples where different cleaning the in the sample preparation, a is rinsed with deionised water and ethanol, b is only rinsed with ethanol. In a corrosion can be observed but not in b where the black area is dirt.

observed and covered most of the surface. Thus the protection worked in this environment since no corrosion could be observed, but it would be more certain if inclusions were found and then compared to the ones in the corroded samples.

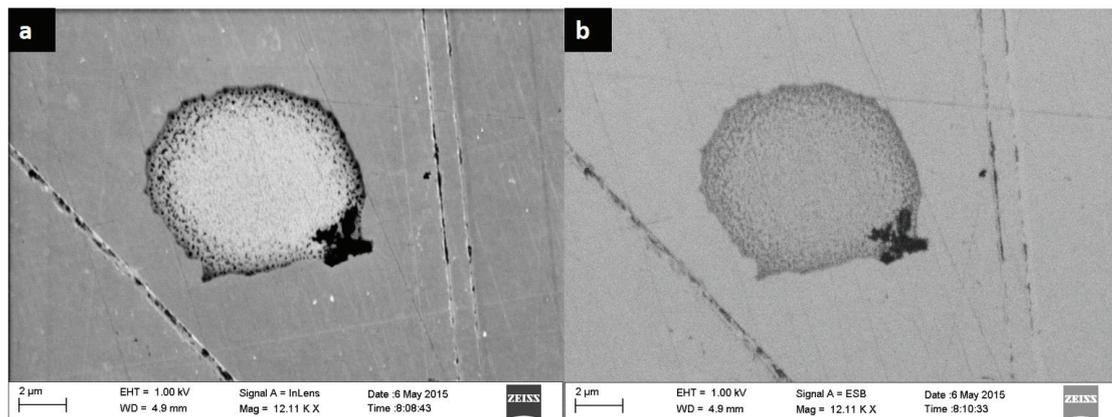


Figure 5.37: SEM image of sample with anti corrosion liquid applied. Corrosion was not found on this sample. The image show residuals of the anti corrosion oil.

6

Discussion

6.1 Summary of observations

The observations showed that the corrosion has occurred on the whole surface even though the most severe corrosion could be seen close to inclusions. The results from the short exposures, 1-2 minutes, only showed minor corrosion. Several inclusion exposed for 5 minutes had rough surfaces which indicates that it has started to decompose (the very inclusion corrode). The micro cross section also showed that the surface of the inclusion was lower than the steel which also proposed the inclusion has decomposed. The samples exposed for 10 minutes showed several inclusions with circular regions, assumed to be oxide, around inclusions. This region was often cracked and sometimes flaking could be observed.

6.2 Corrosion initiation

The results obtained from the 5 min exposure propose that the inclusions are decomposed due to some form of micro galvanic corrosion. The steel around the inclusion is covered by a oxide film but it is not possible with these results to determine what the oxide film consists of. One theory is that when the inclusion is dissolved it will act as an anode to the steel which then will be protected from corrosion and act as a cathode. One way to confirm this theory would be to compare the corrosion rate of the steel close to the inclusions and the steel further away. But the corrosion environment in this study might not have been strong enough to be able to see this phenomenon even though general corrosion have been observed on the steel matrix. The more corroded samples in the 10 min exposures also show circular areas where a difference in surface appearance can be seen (e.g. see figure 5.22), this could lend some support to the theory that some part of the matrix close to the inclusion is protected.

The results from the FIB/SEM in the 10 minute exposures might be of most interest in this report. Several corroded areas was observed close to MnS and it was possible to see an oxide film with cracks on top of the surface and cracks further down in the material. The cross sections showed that the cracks in the material had formed not only around the inclusion it self but around a region of the steel close to the inclusions. These results are similar to the ones of Wranglen[7] which he explains by sulphur infection of the matrix close to the inclusion. If this is the case the processing of the steel is very important if one would like to reduce the negative effect of the inclusions.

The other cross section which was of an inclusion with Al, O and Mg do not show the oxide films with cracks which was observed around several other inclusions. The reason could be that the corrosion has not proceeded long enough or that the corrosion at this kind of

inclusion is different. The area around the inclusion is affected here and it is possible to detect an increase in oxygen content which indicate that corrosion has occurred, this area also look more porous than the other part and do show little different contrast than the rest of the inclusions. One possible reason is that the coherence between the inclusions and the steel matrix could be insufficient and therefore cracks form prior to the corrosion experiments, these cracks would then be more sensitive to corrosion.

Two main observations are one where the inclusion is decomposed (5min) and one where the area around the inclusion have started to crack and sometimes flake (10min), see figure 6.1 for schematic figure. These two theories could be different part of the same corrosion process or just two different processes.

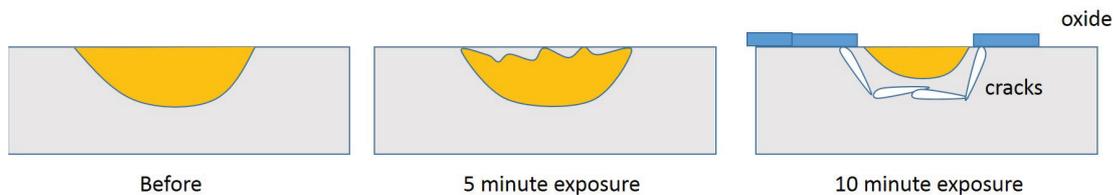


Figure 6.1: Schematic figure of the two processes discussed in this report

6.3 Earlier work

Throughout the project it was very hard to find relevant articles on the subject. The most interesting articles were from the 70s and used references from the 1930s which could not be found in the digitalised archives. Recent articles also use Wranglen and Eklund as references which proves the importance of these work and that some of their theories is still under evaluation. One major problem was that most of the articles found also solely discussed the problems with stainless steel. The problems with pitting corrosion in stainless steel have been under much discussion which has funded many project about this phenomena. Carbon steel on the other hand have been used with the knowledge that it does corrode if its not protected an therefore the understanding of the initial corrosion have been overseen.

6.4 Problems with the method

During the project there was a difference in how much the samples corroded even when the same exposure time was used. The reason the results of the exposure differs is not known, but the most probable reason is difference in the quality of the deionised water, mainly difference in oxygen content and conductivity. One reason could also be that the polishing involves a manual step which will make it vary between different times. The time the samples were kept in the desiccator before the final polishing and exposure was performed, although attempted to minimize, could also affect the outcome. Moreover, the mechanical damage induced during polishing can also have an effect on corrosion rates. An improved cleaning of the samples may be considered to limit any confusion of corrosion products with dirt.

7

Conclusion

Preferential corrosion initiates around MnS inclusions and complex inclusions. General corrosion could also be found on the whole surface. The data in this report suggest that 10 min exposure to deionised water is sufficient to cause decomposition of the inclusions and formation of crevice corrosion in the inclusion/matrix interface. This could be because of a difference in nobleness between the inclusions and the steel matrix or because of poor coherence between the inclusions and the steel matrix.

The study of a sample which exposed with anticorrosion liquid applied did not show any clear indication of corrosion.

Based on the observations in the XPS it can be concluded that no difference in the general surface oxide can be seen between non exposed and exposed sample.

7. Conclusion

8

Future work

- TOF-SIMS to study the matrix close to the inclusion and see if there is sulphur and other contaminants
- Cross sections and study more thoroughly with EDX, maybe even in TEM-EDS
- More focus on quantitative information about which inclusion that corrode
- Change corrosion medium and see if the corrosion process remain the same
- Surface analysis of thin surface oxides

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