Intergranular and transgranular stress corrosion cracking of carbon steel in fuel-grade ethanol

Janne Johannes Torkkeli
Intergranular and transgranular stress corrosion cracking of carbon steel in fuel-grade ethanol

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A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Engineering, at a public examination held at the lecture hall 216 of the school on 22 August 2017 at 12:00 pm.

Aalto University
School of Engineering
Department of Mechanical Engineering
Abstract

The SCC mechanisms in FGE are studied by making slow-strain rate testing (SSRT) and notched constant tensile load testing (NCTL) in fuel-grade ethanol (FGE) with carbon steel SA-106 and St35 test specimens machined from pipeline samples. The test specimens with SCC were characterized and compared to failed pipeline samples from FGE service. The effect how impurities or microstructure of the carbon steel affect the SCC mechanisms were studied by making experiments with pure compounds and by comparing the results to the observations from the SSR and NCTL testing or from the failed pipeline samples. The selective dissolution of manganese sulfide (MnS) inclusions was studied by making dissolution tests with pure MnS. The selective dissolution of pearlite nodules was studied by making cathodic polarization measurements with pure iron and cementite.

Clear differences were found between the intergranular and transgranular SCC mechanisms. With negligible chloride concentrations the transgranular SCC initiates only at the pearlite nodules while the intergranular SCC initiates only at the ferrite phase. With chloride concentrations of approx. 2 mg/l or more, intergranular SCC does not initiate and transgranular SCC can initiate in ferrite and pearlite phases. Conditions inside intergranular SCC crack are not acidic. Selective dissolution of the pearlite nodules, which can be catalyzed by chlorides, occurs in FGE and this effect stops the propagation of the intergranular SCC crack leading to a localized corrosion at the pearlite nodule. With high enough stress level the intergranular SCC mechanism can change to transgranular SCC cracking at the pearlite nodules.

The penetration rate of MnS inclusion dissolution front was measured to vary from 11 μm/year up to 127 μm/year inside the intergranular SCC cracks but it is most likely higher inside the transgranular SCC cracks due to more acidic conditions. The sulfur species formed due to selective dissolution of the MnS inclusions are HS⁻ and S₂O₃²⁻ in acidic conditions with chlorides and SO₄²⁻ in conditions with negligible chloride concentrations and acetic acid. These results indicate that there can be HS⁻ and S₂O₃²⁻ ions inside the transgranular SCC cracks but only SO₄²⁻ inside the intergranular SCC crack.

There is an apparent microgalvanic coupling between cementite and ferrite of pearlite phase. The cementite is more favourable cathode as the OCP of cementite is higher than for pure iron. The OCP of cementite is approximately 120 mV higher in aerated FGE and approximately 40 mV higher in unaerated FGE. CO and CO₂ can form in the cathodic reactions at cementite surface and react into carbonate. There are a lot of similarities with the intergranular and transgranular SCC mechanisms occurring in FGE compared to carbonate solutions.

Keywords Carbon steel, fuel-grade ethanol, stress corrosion cracking, manganese sulfide, pearlite, electrochemical polarization
Preface

The present thesis was done at Aalto University School of Engineering in the research group of Engineering Materials at the Department of Mechanical Engineering during 2011 - 2016. The Publications I, II, III, and IV were funded by Neste Oy. The FGE and steel samples used in Publications V and VI were also provided by Neste Oy.

This project has been long and demanding as big portion of it was done as a personal hobby during evenings and nights. I would like to thank my supervisor professor Hannu Hänninen, who did not turn me down although there was no funding for the project, and who took the time to carefully read through all the work and gave me guidance when needed.

Big thanks go for the materials engineering team of Neste Jacobs Oy for the speculations and especially for Olli Kortelainen, who originally brought the problem to my table. Special thanks go for the researchers at Neste Oy Leena Rantanen-Kolehmainen and Ulla Kiiski and the motor laboratory team, and for Rauno Silvennoinen from the maintenance team.

Finally I want to thank professor Preet M. Singh and Sannakaisa Virtanen for the premilinary examination of the dissertation and for the valuable comments given.

I would also like to acknowledge the laboratory personnel at Aalto University especially Tapio Saukkonen for SEM observations, Kim Widell for organizing the test equipment and Valtteri Hirsi, for the work done for Publications I, II and III.

The biggest thanks go for my wife PhD Nguyet Doan for patience and understanding during this project as well as for our children Lac Onni, Tue Aatos and Sen Tyyni.

Espoo, June 29, 2017,

Janne Johannes Torkkeli
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List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Stress corrosion cracking of carbon steel in ethanol”

The author was supervising the work and participated in the design of the SSRT tests done. The author also participated in the characterization of the SSRT test specimens. Checking of the manuscript of the article was done by the author.

Publication II: “Evaluation of PWHT as a Method to Prevent SCC of Carbon Steel in FGE by Notched Constant Tensile Load Testing”

The author was supervising the testing done and participated in the design of the SSRT and NCTLT tests done. The author also participated in the characterization of the SSRT and NCTLT test specimens. The manuscript of the article was written by the author.

Publication III: “Mechanistic study for stress corrosion cracking of carbon steel in ethanol”

The author was supervising the testing done and participated in the design of the SSRT and NCTLT tests done. The author also participated in the characterization of the SSRT and NCTLT test specimens. The manuscript of the article was written by the author.
Publication IV: “Stress corrosion cracking of carbon steel in ethanol-gasoline blends”

The author has done all of the experimental work in the article excluding the SEM characterization, which was done together with T. Saukkonen. The author has also written the manuscript for the article.

Publication V: “Effect of MnS inclusion dissolution on carbon steel stress corrosion cracking in fuel-grade ethanol”

The author has done all of the experimental work in the article excluding the SEM characterization, which was done together with T. Saukkonen. The author has also written the manuscript for the article.

Publication VI: “Effect of pearlite phase on SCC cracking of carbon steel in fuel-grade ethanol”

The author has done all of the experimental work in the article excluding the SEM characterization, which was done together with T. Saukkonen. The author has also written the manuscript for the article.
In this study stress corrosion cracking (SCC) of carbon steel in fuel-grade ethanol (FGE) is examined by laboratory testing using slow strain rate testing (SSRT) and notched constant tensile load testing (NCTLT) and by characterizing field failure samples. The SSRT and NCTLT specimens for the study were prepared from FGE pipeline samples and SCC testing is performed in FGE received from a refinery. The work was started with a general study to demonstrate, that the FGE received from the refinery causes SCC of the carbon steel pipelines. Then NCTLT testing was performed to study, whether the post-weld heat treatment (PWHT) is able to prevent the SCC phenomenon. The work was continued by making series of SSRT testing to examine how much ethanol blended to gasoline is needed to cause SCC. In this study the transgranular and intergranular SCC mechanisms were distinguished as different mechanisms, which have different kinds of behavior. The focus was then put to the unit processes occurring inside the SCC cracks. The dissolution of manganese sulfide (MnS) inclusions of carbon steel was studied in FGE by making dissolution rate measurements with pure MnS in FGE with various pH controlled by hydrochloric acid (HCl) or acetic acid. The dissolution rates were compared with MnS inclusion dissolution rates measured from the failed field samples. Finally the selective dissolution of the pearlite phase of carbon steel was studied by reviewing of all findings from the previous studies. Cathodic polarization curves were measured with pure iron and cementite to examine the differences in electrochemical properties between these to phases of pearlite. The following features are considered to be original:

1. The effectiveness of PWHT as a method to mitigate the transgranular SCC of carbon steel in FGE was demonstrated. It is still unclear
whether PWHT is applicable against the intergranular SCC.

2. It was shown that only 2 mg/l of chlorides prevents the intergranular SCC mechanism and causes the SCC of carbon steel in FGE to be fully transgranular.

3. The transgranular and intergranular SCC mechanisms of carbon steel in FGE were distinguished and shown to exhibit different behavior.

4. The dissolution rate of MnS inclusions of carbon steel was measured for the first time in FGE. The MnS inclusion dissolution rate varied from 11 μm/year up to 127 μm/year.

5. As the MnS inclusions dissolve $HS^-$ and $S_2O_3^{2−}$ form as the dissolution product in acidic FGE conditions containing chlorides, while only $SO_4^{2−}$ forms in FGE with acetic acid.

6. It was shown that the conditions inside the intergranular SCC are most likely not very acidic and the sulfate concentration is near 1 wt.-ppm.

7. It was shown that the conditions inside the transgranular crack can be acidified and there can be $HS^-$ present.

8. The selective dissolution of pearlite nodules of carbon steel in FGE was fully characterized for the first time. This includes characterization of the phenomena occurring on the external surfaces and inside the transgranular and intergranular SCC cracks.

9. It was shown that the selective dissolution of the pearlite phase affects the SCC mechanism.

10. The intergranular SCC mechanism of carbon steel in FGE stops at the pearlite phase, but can change to transgranular SCC at high stress/strain levels in SSRT testing. Usually this type of transition does not occur in the field process conditions with lower stress/strain levels, but selective dissolution of pearlite nodules occurs instead.
11. There is microgalvanic coupling between cementite and ferrite of the pearlite phase and the cementite is the more favorable cathode.
### List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>SCC</td>
<td>stress corrosion cracking</td>
</tr>
<tr>
<td>CGR</td>
<td>crack growth rate</td>
</tr>
<tr>
<td>FGE</td>
<td>fuel-grade ethanol</td>
</tr>
<tr>
<td>SFGE</td>
<td>simulated fuel-grade ethanol</td>
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<tr>
<td>HAZ</td>
<td>heat-affected zone</td>
</tr>
<tr>
<td>PWHT</td>
<td>post-weld heat treatment</td>
</tr>
<tr>
<td>SSRT</td>
<td>slow-strain rate testing</td>
</tr>
<tr>
<td>NSSRT</td>
<td>notched slow-strain rate testing</td>
</tr>
<tr>
<td>NCTLT</td>
<td>notched constant tensile load testing</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>EBSD</td>
<td>electron backscatter diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>OCP</td>
<td>open circuit potential</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing Materials</td>
</tr>
<tr>
<td>NACE</td>
<td>National Association of Corrosion Engineers</td>
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<tr>
<td>$k_t$</td>
<td>stress concentration factor</td>
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</table>
List of Abbreviations and Symbols
1. Introduction

Europe has established new goals to increase the share of renewable energy in the transport sector, which may increase the usage of fuel-grade ethanol [FGE] in the near future. It was found by Beavers et al. [1] and confirmed in Publication IV, that only 15 wt-% of ethanol blended to gasoline is enough to cause SCC of carbon steel. This is significant as most of the gasoline infrastructure is made of carbon steel. Earliest publications relevant to the topic were published before any failures were reported from the industry [3, 4, 5]. American Petroleum Institute was the first to publish an extensive study on the subject, which shows that SCC of carbon steel has been observed in ethanol pipelines as well as ethanol storage tanks [2].

The SCC of carbon steel in FGE occurs typically near welds in a region between the weld heat-affected zone (HAZ) to about 1 inch into the base metal [2]. Vast majority of the laboratory studies has been done since late 1990s and most common method to study SCC has been the slow strain rate testing (SSRT). In laboratory studies the SCC fracture mode has been mainly transgranular while in industrial cases fracture mode has been intergranular [2]. It was originally speculated that the main reason for transgranular SCC mode in laboratory studies is the SSRT method which promotes transgranular cracking [6]. This is partially true as it was shown in Publication IV and VI that only 2 mg/l of chlorides will prevent the intergranular SCC mechanism and cause trangranular SCC instead and also even without measurable chlorides the intergranular SCC can change fracture mode to transgranular SCC at the pearlite nodules of the steel with sufficient amount of stress. It was also highlighted that these two SCC mechanisms should be separated and not treated as a single mechanism.

Environmental parameters affecting the SCC susceptibility have been
studied quite extensively. It should be noted that during most of the labora-
tory testing, corrosion potential has been measured with the help of
Ag/AgCl EtOH-reference electrode. This practice has been questioned by
Lou et al. [7] because of chloride leakage from the reference electrode and
the effect of chloride on susceptibility to SCC. As mentioned above it was
also shown in Publications IV and VI that chlorides prevent the intergran-
ular SCC and lead to trangranular SCC instead and there are differences
between these two mechanisms. It has also been found by Abel and Virta-
nen that extremely low chloride concentrations in ethanol-gasoline blends
induce pitting of martensitic stainless steel, while pitting did not occur in
purely aqueous solution [8]. Also most of the laboratory testing has been
done with simulated FGE with added chlorides. Due to this reason there
may be a risk that the same environmental parameters do not apply with
the intergranular SCC mechanism, which should be taken into account
when considering the environmental parameters published.

It was shown that SCC of carbon steel can occur in fuel-grade ethanol
(FGE) meeting the specification ASTM D 4806. Oxygen, chloride, water,
and galvanic contact between new carbon steel and old rusted carbon steel
were shown to have the strongest influence and methanol a minor influ-
ence on the SCC susceptibility [2]. SCC of carbon steel occurs most likely
when the corrosion potential is above 25 mV and below 600 mV versus
SCE [9, 10]. Oxygen in ethanol promotes SCC and without oxygen SCC
is mitigated in ethanol environment [2, 7, 11]. Oxygen concentration in
ethanol can be as high as 80 ppm which is a much higher value than the
oxygen concentration in air-saturated water [11]. Oxygen can be removed
from ethanol by chemical agent, nitrogen purging or steel wool [1, 13].
Significant metal dissolution can occur in deaerated ethanol [7]. Addition
of 4.5 wt% or higher water to ethanol prevents SCC of carbon steel [7]
although significant pitting attack has been observed in this environment
[9, 12]. Also pH of ethanol influences the SCC susceptibility and alkaline
ethanol environment does not promote SCC of carbon steel [7]. In addition
to the environmental parameters above, there are numerous publications
discussing the environmental parameters affecting the carbon steel SCC
mechanism in FGE [13-30]. Lately also microbially influenced corrosion
in FGE environments have been studied [32, 33]. Sulfate reducing bacte-
ria can increase the hydrogen sulfide concentrations and acid-producing
bacteria can increase the acetic acid concentrations in FGE [33].

Beavers et al. [1] proposed a qualitative model for the transgranular
SCC of carbon steel in ethanol. This model is based on anodic polarization measurements with microelectrodes in ethanol purged with nitrogen–oxygen mixtures. The measurements showed that oxygen increases the passivity of the carbon steel in ethanol additionally increasing its corrosion potential. Anodic dissolution rate of the carbon steel increased, when the oxygen concentration was decreased. Other observations were that an addition of chloride increased the anodic dissolution, while an addition of gasoline decreased the dissolution rate. According to the proposed model, the enhanced anodic metal dissolution at the deaerated crack tip can lead to SCC of carbon steel in ethanol [1]. According to the proposed model [1] outside the crack and along the crack walls, occur the cathodic reduction of oxygen and passivation of steel due to the dissolved oxygen. At the crack tip fresh metal is exposed by plastic deformation. Oxidation of the exposed steel consumes the dissolved oxygen rapidly and creates a fully deoxygenated environment near the crack tip. The coupling of the passivated steel in oxygenated environment outside the crack to the exposed steel surface in the deaerated environment at the crack tip leads to crack tip dissolution and subsequent crack advance. In this situation, there should be a zone of active steel surface near the crack tip and passivated oxide covered steel surface on the crack walls and outside the crack [1]. Results from a study by Lou et al. [14] indicated that the initiation of the transgranular SCC cracks is associated with plastic deformation in the steel, which leads to a surface film breakdown and to the propagation of the cracks controlled by the competition between active anodic dissolution and repassivation at the crack tip as proposed by Beavers et al. [1]. This may explain the effect of galvanic coupling to corroded steel increasing the susceptibility to SCC in FGE. It should be noted that this model does not necessarily apply for the intergranular SCC mechanism, which behaves in a different way.

In this work more focus is put on the topics, which have not been discussed as much. There has been only few publications related on how to prevent the SCC mechanism from occurring [34, 35], but without any practical results. In this work post-weld heat treatment (PWHT) is discussed as one method to prevent the SCC of carbon steel from occurring in FGE. The differences between the intergranular and transgranular SCC mechanisms are studied in details including the conditions within the SCC cracks. The comparison is done by investigating selective dissolution of manganese sulfide (MnS) inclusions and pearlite nodules of carbon
steel in FGE conditions. Both of these phenomena were observed during the work done for Publications I - VI.

1.1 Selective dissolution of MnS inclusions

One way to get information of the conditions within the SCC crack is to study the dissolution of the MnS inclusions. MnS inclusions are known to act as pitting corrosion nucleation sites for stainless steels and therefore the dissolution process of the MnS inclusions in aqueous conditions has been studied extensively [36, 37, 38, 62, 40, 41, 42, 43]. MnS inclusions have also been found to affect environmentally assisted cracking of pressure vessel steels in high-temperature water [44, 45, 46, 47, 48, 49, 50, 51, 52, 53]. Dissolution rate of MnS has not yet been directly measured but the chemical dissolution rate of MnS inclusions of stainless steels in acidic conditions containing NaCl has been estimated between 0.01 and 0.19 µm³/min by using in situ atomic force microscopy [36]. It has not been studied whether the sulfur species released during the dissolution of the MnS inclusions can affect the ethanol SCC mechanism or to what extent the MnS inclusions dissolve in FGE.

1.2 Selective dissolution of pearlite nodules

Selective dissolution of ferrite from the pearlite phase has been previously studied in aqueous solutions. The role of cementite in the acidic corrosion of steel was studied by Staicopolus by making electrochemical measurements with cementite isolated from specially made steel [54]. It was found that cementite is an active cathodic site in corrosion of steel as it does not polarize at low current densities. At high current densities cementite polarizes to the potential of iron in similar conditions. This was considered to be due to chemical decomposition of cementite to iron and predominantly methane and carbon monoxide under the influence of cathodically evolving hydrogen. Galvanic coupling between the steel and a layer of undissolved Fe₃C was studied by Crolet et al. [55, 56]. According to the studies galvanic coupling of steel and cementite is considered to affect the carbon dioxide corrosion of steels. The galvanic coupling can lead to acidification inside the oxide layers and breakdown of uniform corrosion and the onset of localized corrosion attack.
1.3 Aims of the study

Originally the aim of the study was to provide specifications for Neste Porvoo refinery on how to safely handle FGE and ethanol-gasoline blends but the study was continued due to personal interest on the emerging new phenomena. The focus was moved from safe handling to the differences between the intergranular and transgranular SCC mechanisms and on how the steel microstructure and properties affect these mechanisms. This environment was considered as a great opportunity as the corrosion reactions in ethanol solutions occur at a slow rate, which makes it a tool to study the transgranular and intergranular SCC mechanisms in slow motion compared to aqueous solutions. But it was found out that in reality these mechanisms do not necessarily occur slower in ethanol than in aqueous solutions.
Introduction
2. Experimental

In this chapter the studied materials and the main experimental methods and techniques used are described. Some specific analysis methods or experimental details are explained in details in Publications I - VI.

2.1 Materials

All of the carbon steel pipeline materials including the failed pipeline samples and the fuel-grade ethanol (FGE) or gasoline samples have been received from the Neste Porvoo refinery in Finland. The FGE samples used were conformable to specification EN 15376. Test specimens for slow strain rate (SSR) and notched constant tensile load (NCTL) tests were machined from seamless carbon steel pipes conformable to specifications ASTM A106 Grade B and DIN 2391-2 St35 according to standard ASTM E8. The designations and typical compositions of the test materials used are shown in Table 2.1. The test specimens had gauge length of 32 mm, width of 5 mm, and thickness of 1.5 mm. The notch was made on the thin side of the test specimen with depth of 0.57 mm and radius $0.3 \pm 0.01$ mm, respectively (the stress concentration factor, $k_t$, was 2.3). Schematic of the notched test specimens including optical micrographs of the microstructure for both materials tested and from both sides is shown in Figure 2.1. The dark area in the micrograph is the banded pearlite phase and the light area is the ferrite phase. All the surfaces were first ground up to 1200 grit longitudinally, then degreased with ethanol and acetone and finally dried in blowing air. During preparations for the Publications I and II several SSR tests were made with test specimens without pre-oxidation and no SCC was observed with any of the samples. After these preliminary tests, more SSR testing was done with pre-oxidized test specimens and SCC was observed with all samples in the same environ-
Table 2.1. Chemical compositions (wt%) of the tested carbon steels.

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<th>C</th>
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<th>S</th>
<th>Cr</th>
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<tr>
<td>Fe</td>
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<td>0.136</td>
<td>0.161</td>
<td>0.491</td>
<td>0.048</td>
<td>0.027</td>
<td>0.018</td>
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<tr>
<td>ASTM A106 Grade B</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>98.140</td>
<td>0.197</td>
<td>0.211</td>
<td>0.985</td>
<td>0.048</td>
<td>0.013</td>
<td>0.063</td>
<td>0.027</td>
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<tr>
<td>Ni</td>
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<td>0.029</td>
<td>0.012</td>
<td>0.152</td>
<td>0.003</td>
<td>0.002</td>
<td>0.010</td>
<td>0.013</td>
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ment. Due to these preliminary tests, the oxide film on the carbon steel surface, which is usually formed in the water phase, is considered as an important factor contributing to the SCC susceptibility. It was decided that before the SSR and NCTL tests, a corrosion film was formed on the surface of the test specimens by a potentiostatic method in naturally aerated water environment. Potential during the oxidation was 640 mV and pH of the water was adjusted to be 10.5 with sodium hydroxide (NaOH). The oxidation was continued for 12 h and the pH decreased during the oxidation. The potential and pH were selected after some empirical testing to confirm that uniform oxide film was formed on the test specimen. The pre-oxidized sample surface was used to simulate a rusted pipe wall more closely and the process resulted in a surface with corrosion potential range where SCC occurs in FGE. The specific details of the materials and chemicals used for the tests are given in the Publications I - VI.

2.2 Mechanical tests

All of the SSR and N–SSR tests were performed according to NACE standard TM0111-2011 with the exceptions that pre-oxidized test specimens were used and the dimensions were different from the standard values due to practical reasons. A displacement rate of $2.2 \times 10^{-5}$ mm/s was used for all the SSRTs and N–SSRTs. All of the NCTL tests were done using the same test setup, where the constant stress level was set using an ini-
Experimental

Figure 2.1. Schematic of the notched test specimens including optical micrographs of the microstructure for both materials tested and from both directions. The dark area in the micrographs is the pearlite phase and the light area is the ferrite phase.

Patial displacement rate of $2.2 \times 10^{-5}$ mm/s. All tests were performed in the environmental cell. Body of the cell was made from glass. Bottom and top of the cell were made from Teflon. The FGE was circulated between the cell and a beaker, where the FGE solution was actively purged with dry air or nitrogen and stirred slowly. Composition of the air was 20 vol% of oxygen and 80 vol% of nitrogen. Air or nitrogen purging was started 2 h before the tests and continued throughout the test.

2.3 Electrochemical measurements

All the potentiodynamic polarization curves were measured using potentiostat (PCI4, Gamry Instruments) in a sealed three-electrode electrochemical testing cell. The reference electrode used was a silver-silver chloride based reference electrode Ag/AgCl/1M LiCl, EtOH. The purging gas used for unaerated measurements was dry nitrogen and for aerated measurements dry air. The electrochemical measurements in pure FGE were not possible due to very low conductivity, which is why some chlorides were added to the FGE for the measurement. Due to the very low
Experimental

conductivity, IR compensation was needed for the measurements. For IR compensation positive feedback and current interrupt methods were both evaluated. Positive feedback method could have been used with lower conductivity than current interrupt method, but it does not take into account that the conductivity of the solution may change quite significantly during the long measurement. Due to this reason the current interrupt method by Gamry Instruments was used for the IR compensation. During testing it was noticed that at least 50 wt.-ppm of chlorides was required for the current interrupt method to work reliably down to the target potential of -1.2 V.

2.4 Intrinsic dissolution rate

The intrinsic dissolution rate measurement is standard method used in the pharmaceutics to measure dissolution rate of pure solid substances having null porosity, which is defined as intrinsic dissolution rate. The principle is that compacting the powder removes all porosity restricting the surface area to the visible sample surface. Because very small amount of the substance is dissolved during the dissolution rate measurement, the conditions of surface area are considered as constant. The surface area of the sample used depends on the surface plate used to compress the powder.

The intrinsic dissolution rate of MnS was measured in FGE with various concentrations of acetic acid and hydrochloric acid. The intrinsic dissolution rate was measured using rotating disk system (USP Wood apparatus), which is commonly used in the pharmaceutical industry [60]. This method was selected because there are lots of reference values available in the literature and the dissolution tests are easy to reproduce as identical test equipment is readily available.

2.5 Fractography

Scanning electron microscopy (SEM) and electron backscattering diffraction (EBSD) measurements were done with Zeiss Ultra 55 FEG-SEM equipped with Nordlys F+ camera and Channel 5 software from Oxford Instruments. In EBSD measurements misorientation angle of 10° was used for defining the grain boundaries. Chemical composition of non-
metallic inclusions was analyzed by energy dispersive X-ray spectroscopy (EDS).
Experimental
3. Prevention of SCC of carbon steel in FGE or ethanol-gasoline blends by PWHT

In this chapter post-weld heat treatment is considered as a method to prevent the transgranular and intergranular SCC of carbon steel in FGE or ethanol-gasoline blends. One of the requirement for SCC is that tensile stress above the threshold for the SCC is applied to the material. It is well known that one source for stress is the residual stress from fabrication e.g. from welding or cold working. One common method to prevent SCC from occurring is to apply post-weld heat treatment (PWHT) for welds and cold formed components to reduce the residual stresses below the threshold of the SCC. It can be considered that the residual stresses due to welding or cold working are at the yield strength level of the steel and by PWHT the residual stresses can be reduced approximately to 80% of the yield strength. PWHT will prevent SCC from occurring only if the threshold stress level of the SCC is above the residual stress level achieved by the PWHT. As the threshold stress level for SCC depends on the SCC mechanism, the PWHT does not necessarily prevent the SCC of carbon steel in FGE. Due to this reason it is important to separately study whether specific SCC mechanism can be prevented by PWHT.

3.1 Transgranular SCC

The effect of PWHT on the SCC susceptibility of carbon steel in FGE was studied in Publication II by using notched constant tensile load testing (NCTL). The NCTL testing was done with notched test specimens machined from pipeline steels St35 and SA-106 in FGE, which was confirmed to cause SCC by slow-strain rate testing (SSRT). It is important to note that the testing was done in chloride containing environment due to chloride leakage from the reference electrode used. The NCTL testing was done with stress level near the yield strength to simulate the conditions
Prevention of SCC of carbon steel in FGE or ethanol-gasoline blends by PWHT

Figure 3.1. Fracture surface of notched St35 test specimen from NCTLT testing in FGE with stress near the yield strength of the steel.

Figure 3.2. Fracture surface of notched SA-106 test specimen from NCTLT testing in FGE with stress near the yield strength of the steel.

of a weld in a pipeline and with stress level of 80% of the yield strength to simulate the conditions of a pipeline weld with PWHT. SCC was observed only with stress level near the yield strength of the steel. SEM images of fracture surface of the notched test specimen from the NCTLT testing with stress at the yield strength of the steel are shown for St35 and SA-106 in Figure 3.1 and 3.2, respectively. SEM images of the notch bottom of the test specimen from NCTLT testing with stress level of 80% of the yield strength of the steel are shown for St35 and SA-106 in Figure 3.3 and 3.4, respectively. It is very important to note that the fracture mode was fully transgranular as can be seen from the SEM fractographs of both steels. Summary of all results are shown in Table 3.1.

As seen from Figures 3.1 - 3.4 and from the summary given in Table 3.1, it was found that transgranular SCC occurs at the yield strength stress level but with stress level of 80% of the yield strength only nuclei of SCC cracks were observed on the steel surface after 20 days for St35 and 30 days for SA-106. Considering these results it is relatively safe to claim that transgranular SCC can be prevented by PWHT in case the residual
Figure 3.3. SEM images of the notch surface of ST35 test specimen from the NCTL test at 80% of the yield strength stress level and a SCC crack initiation on the surface.

Figure 3.4. SEM images of the notch surface of SA106 test specimen from the NCTL test at 80% of the yield strength stress level and a SCC crack initiation on the surface.

Table 3.1. Summary of the SSR and NCTL test results.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Displacement rate</th>
<th>Duration</th>
<th>Avg. corrosion potential</th>
<th>Stress</th>
<th>Crack growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIN 2391-2 ST35</td>
<td>N-SSRT</td>
<td>2.2 x 10-5 mm/s</td>
<td>24 hours</td>
<td>173 mV vs SCE</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>NCTL</td>
<td>2.2 x 10-5 mm/s</td>
<td>30 days</td>
<td>149 mV vs SCE</td>
<td>353 MPa</td>
<td>1.8 mm/year</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2 x 10-5 mm/s</td>
<td>20 days</td>
<td>Failed</td>
<td>300 MPa</td>
<td>Nuclei</td>
</tr>
<tr>
<td>ASTM A106 Gr. B</td>
<td>N-SSRT</td>
<td>2.2 x 10-5 mm/s</td>
<td>26 hours</td>
<td>Failed</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>NCTL</td>
<td>2.2 x 10-5 mm/s</td>
<td>30 days</td>
<td>190 mV vs SCE</td>
<td>373 MPa</td>
<td>1.8 mm/year</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.2 x 10-5 mm/s</td>
<td>30 days</td>
<td>134 mV vs SCE</td>
<td>236 MPa</td>
<td>Nuclei</td>
</tr>
</tbody>
</table>

* This was the initial displacement rate used to set the constant stress level.
stresses can be reduced to 80% of yield strength. Transgranular SCC cracks can still initiate but the crack growth rate is insignificant and it is possible that localized corrosion would occur instead of SCC propagation.

### 3.2 Intergranular SCC

It is important to note that the results given above cannot be directly applied for the intergranular SCC mechanism of carbon steel in FGE as the threshold stress for intergranular SCC can be different than the threshold stress for transgranular SCC. Due to this reason use of PWHT as a method to prevent the intergranular SCC needs to be considered separately. This consideration was done partially while SCC was studied in ethanol-gasoline blends by making notched SSRT (N-SSRT) for Publication IV. The testing was done in ethanol-gasoline blends without chlorides and mainly intergranular SCC was observed. The intergranular SCC was observed on the notch bottom as well as relatively far away from the notch as shown in Figure 3.5 and 3.6.

The evaluation whether PWHT can be used to prevent the intergranular SCC of carbon steel in FGE can be done by looking at the notched test specimens used in the N-SSRT testing. The test specimens had gauge length of 32 mm, width of 5 mm, and thickness of 1.5 mm. The notch was made on the thin side of the test specimen with depth of 0.57 mm and radius $0.3 \pm 0.02$ mm, respectively (the stress concentration factor, $k_t$, was 2.3). The gauge section cross-sectional surface area was $7.5 \text{ mm}^2$ and the cross-sectional surface area at the notch was $5.79 \text{ mm}^2$, which means the surface area at gauge was 29.5% higher. Considering only the cross-sectional surface areas the stress at the gauge section of the test specimen was approximately 77% of the stress at the notch. It can be considered that the stress at the notch was at or above the yield strength of the material during the SSRT. This means that the stress level at the gauge section of the test specimen could simulate the conditions of weld with PWHT. If we consider the stress concentration factor the stress level at the gauge section is only 43.5% of the stress level at the notch. This means that the stress level is low and most likely below the level, which could practically be achieved by PWHT. In any case since intergranular SCC has initiated relatively far away from the notch as shown in Figures 3.5 and 3.6, the PWHT does not necessarily prevent the intergranular SCC mechanism as effectively as it does the transgranular SCC mechanism. It is clear by
Figure 3.5. SEM images from side surface of N-SSRT specimen tested in ethanol-gasoline blend with 20 wt-% of ethanol. Grain boundaries are attacked over the whole surface and initiation sites of intergranular SCC as shown in detail A were found on the whole surface.

Figure 3.6. SEM images from side surface of N-SSRT specimen near the final fracture at the notch bottom. The sample was tested in ethanol-gasoline blend with 20 wt-% of ethanol.
looking at Figures 3.5 and 3.6 that the intergranular SCC crack growth rate depends strongly on the stress level, but it is difficult to say whether PWHT would reduce the crack growth rate of intergranular SCC enough. This would require additional NCTLT testing.
4. SCC of carbon steel in ethanol-gasoline blends

As the transgranular and intergranular SCC mechanisms of carbon steel in FGE or in ethanol-gasoline blends are both electrochemical processes, they require an electrolyte for the reactions to occur. It is important to understand how strong electrolyte a typical FGE or ethanol-gasoline blend is compared to e.g. water solutions. The conductivity of sea water can be 50000 μS/cm, drinking water 50 μS/cm, and distilled water 10 μS/cm. Depending on the purification process deionized water can have conductivity from ultra-pure levels below 0.1 μS/cm up to 10 μS/cm. The conductivity of typical FGE used in the refinery in Finland is 1.5 μS/m, which is near the conductivity of ultra-pure water. The conductivity of ethanol-gasoline blends is even lower. The conductivities of the ethanol-gasoline blends used in our studies are given in Table 4.1. The conductivity of the FGE and ethanol-gasoline blend are of course affected by the water content and the impurities, but generally it is much lower than the conductivity of any water solutions. Also the water content in FGE is very low.

As the conductivity and water content of the FGE and ethanol-gasoline solutions are very low, the electrochemical or water reactions will occur at much lower rate than in aqueous solutions at least in the bulk solution. The susceptibility of carbon steel for SCC in ethanol-gasoline blends shown in Table 4.1 was tested with N-SSRT testing. SCC occurred in ethanol-gasoline blend with only 15 wt-% of ethanol. This type of ethanol-

<table>
<thead>
<tr>
<th>Component</th>
<th>E85</th>
<th>E30</th>
<th>E25</th>
<th>E20</th>
<th>E15</th>
<th>E10</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol 1</td>
<td>82.2</td>
<td>32.3</td>
<td>27.0</td>
<td>20.9</td>
<td>17.9</td>
<td>10.4</td>
<td>wt-%</td>
</tr>
<tr>
<td>Water 2</td>
<td>0.190</td>
<td>0.091</td>
<td>0.110</td>
<td>0.064</td>
<td>0.074</td>
<td>0.044</td>
<td>wt-%</td>
</tr>
<tr>
<td>Conductivity 3</td>
<td>0.74</td>
<td>0.17</td>
<td>0.10</td>
<td>0.02</td>
<td>0.01</td>
<td>&lt; 0.01</td>
<td>μS/cm</td>
</tr>
</tbody>
</table>

*Measured using methods, 1NM40, 2EN15489 and 3EN15938.*
gasoline blend has very low conductivity and water concentration. It is quite surprising to have this kind of relatively fast electrochemical process occurring in such a poor electrolyte, where the ion transfer and concentrations should be quite low. Summary of all the results is given in Table 4.2.

Although the FGE or ethanol-gasoline blends are such poor electrolytes the crack growth rates do not seem to be lower than what have been reported for other SCC mechanisms in similar tests made in aqueous solutions [57, 58]. This indicates that the propagation of the SCC crack does not necessarily depend strongly on the properties of the bulk solution. This is why it is important to consider the conditions on the steel surface under the oxide layer or within the SCC cracks, where the local condi-

Table 4.2. Stress corrosion cracking in ethanol-gasoline blends.

| Ethanol, Water, Conductivity, | ACGR$^1$, | Ethanol, | Water, | Conductivity, | ACGR$^1$, |
|-------------------------------|------------|--|--|--|--|---|
| wt-% | wt-% | $\mu S/cm$ | mm/year | | | |
| E85  | 82.2 | 0.190 | 0.74 | - | | |
| 1E85 | 83.0 | 0.232 | 1.42 | 22.80 ± 5.07 | | |
| 2E85 | 83.0 | 0.237 | 3.56 | 14.37 ± 3.72 | | |
| E30  | 32.3 | 0.091 | 0.17 | - | | |
| 1E30 | 56.0 | 0.460 | 2.27 | 8.56 ± 1.37 | | |
| 2E30 | 42.3 | 0.200 | 0.30 | 10.86 ± 5.36 | | |
| E25  | 27.0 | 0.110 | 0.10 | - | | |
| 1E25 | 41.1 | 0.253 | 0.57 | 9.89 ± 1.32 | | |
| 2E25 | 39.9 | 0.215 | 0.41 | 5.01 ± 0.32 | | |
| E20  | 20.9 | 0.064 | 0.02 | - | | |
| 1E20 | 31.0 | 0.175 | 0.21 | 8.11 ± 2.04 | | |
| 2E20 | 31.2 | 0.161 | 0.20 | 4.22 ± 0.92 | | |
| E15  | 17.9 | 0.074 | 0.01 | - | | |
| 1E15 | 23.5 | 0.196 | 0.09 | No SCC | | |
| 2E15 | 18.7 | 0.168 | 0.02 | 3.45 ± 1.78 | | |
| E10  | 10.4 | 0.044 | < 0.01 | - | | |
| 1E10 | 15.5 | 0.150 | 0.01 | 2.53 ± 0.67 | | |
| 2E10 | 19.8 | 0.185 | 0.03 | No SCC | | |

$^1$ Average crack growth rate.

$^2$ Contained 2 mg/dm$^3$ of chlorides.
tions are most likely completely different than in the bulk solution. Only 10 to 15 wt-% ethanol in gasoline is enough for carbon steel to become susceptible for SCC in ethanol-gasoline blends.
SCC of carbon steel in ethanol-gasoline blends
5. pHe inside intergranular SCC

It is generally very difficult to study conditions within the SCC crack while crack propagation takes place as you cannot open the crack or take a sample without disturbing the process and it is not possible to make electrochemical measurements inside a single crack and between the local anodes and cathodes on the steel surfaces. One way to get information of the conditions within the SCC crack is to study the unit processes occurring inside the SCC crack. In this chapter pHe inside the intergranular SCC crack is studied by looking at the selective dissolution of the manganese sulfide (MnS) inclusions, which have been observed in all of the studies related to Publications I - VI.

The dissolution of MnS inclusions has been studied a lot in aqueous environments but not in FGE environments. During our studies the selective dissolution of MnS inclusions was observed on the fracture surfaces of the SSRT and NCTLT test specimens as well as on the failed pipeline samples. An example of partially dissolved MnS inclusion is shown in Figure 5.1 showing a) cross-section image of an intergranular SCC crack in failed pipeline sample and b) SEM-EDS map of oxygen and sulfur from the dissolution front of the MnS inclusion.

The dissolution reactions and rate depend on the environment. The most important factors apart from temperature is the pH or pHe for ethanol and the redox potential of the solution. It is possible to measure the dissolution rate of MnS inclusions from failed pipeline samples from FGE service as shown in Figure 5.1 or from the SSRT and NCTLT test specimens tested in FGE as long as the service history is well known. This way we get an estimate of the MnS dissolution rate inside the SCC crack. We can then use this value to get information of the environment inside the SCC crack, because we know what affects the dissolution rate of MnS. We also have the knowledge of what impurities can exist inside the SCC
pHe inside intergranular SCC

**Figure 5.1.** Partially dissolved MnS inclusion inside an intergranular SCC crack of failed carbon steel pipeline sample.
Table 5.1. Chemical composition (wt-%) of the carbon steel pipeline sample studied.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>2391-2</td>
<td>98.880</td>
<td>0.136</td>
<td>0.161</td>
<td>0.491</td>
<td>0.048</td>
<td>0.027</td>
<td>0.018</td>
<td>0.004</td>
</tr>
<tr>
<td>Ni</td>
<td>0.053</td>
<td>0.016</td>
<td>0.020</td>
<td>0.091</td>
<td>0.003</td>
<td>0.028</td>
<td>0.003</td>
<td>0.025</td>
</tr>
</tbody>
</table>

The dissolution rate of MnS inclusions inside intergranular SCC crack was measured from failed carbon steel pipeline samples from FGE service from Neste refinery in Finland. The final cracking occurred during routine hydrostatic testing after some changes were made to the pipeline. The pipeline affected was a FGE transfer line from harbor to storage tanks. Failure analysis was made for the cracked pipeline and the cracking was caused by environmentally assisted cracking. The pipeline was taken into FGE service in 2001. The first cracks occurred in 2007. One representative sample taken from the pipeline while it was replaced in 2010 is characterized using SEM and SEM-EDS. The SCC cracks in this particular sample were detected using non-destructive testing during normal operation, which means that the SCC cracks were exposed to the FGE for at least one year. Chemical composition of the carbon steel studied is given in Table 5.1. A piece of the pipeline characterized here is in Figure 5.2 and locations of the SCC cracks were measured with SEM and are indicated with arrows.

Partially dissolved MnS inclusions were found from the fracture surface as well as from the cross-sections of the SCC cracks of the sample in Figure 5.2. Representative partially dissolved MnS inclusion was measured together with the SCC crack depth and SEM-EDS map was made to get a profile of the dissolution front of the selected MnS inclusion. The results are shown in Figure 5.3.

Considering this particular failure case we can estimate the limits for
the crack growth rate by taking into account the operating history and the wall thickness of the failed pipeline. The wall thickness of the pipeline is 8.8 mm and the first crack occurred after operating for 6 years in the FGE service. The depth of the crack studied in this case is 1180 μm as seen from Figure 5.3. If we assume that all cracks have initiated quickly after the pipeline was taken into FGE service we can calculate the crack growth rates (CGR) to be from 130 μm/year up to 1467 μm/year. Even though it seems that the MnS near the interface between the MnS inclusion and the steel dissolves somewhat faster, the MnS inclusion dissolution front is still relatively flat, which means that it can be used to estimate the dissolution rate of the MnS inclusion. As seen from Figure 5.3 the MnS inclusion dissolution front has penetrated 57 μm to the MnS inclusion, while the SCC has propagated 660 μm after reaching the MnS inclusion. By using this information and the CGRs we can estimate that the dissolution rate of the MnS inclusion has been from 11 μm/year up to 127 μm/year. These measurements apply only for St35 or SA-106 steels. The size and volume of the MnS inclusions may vary for other steels, which affects the results.

5.2 Dissolution rate of MnS in FGE solutions

In Publication V the intrinsic dissolution rate of pure MnS was measured. The intrinsic dissolution rate measurement is standard method used in the pharmaceutics to measure dissolution rate of pure solid substances having null porosity, which is defined as intrinsic dissolution rate [59].
Figure 5.3. Partially dissolved MnS inclusion in the middle of an intergranular SCC crack. (a) The MnS inclusion is located in the middle of the quadrangle. The distance from the crack tip up to the MnS inclusion was measured as 660 μm. (b) Higher magnification of the MnS inclusion. The MnS dissolution front had penetrated approximately 57 μm of the MnS inclusion. (c) SEM-EDS maps of the MnS inclusion.
The principle is that compacting the MnS powder removes all porosity restricting the surface area to the visible sample surface. The intrinsic dissolution rate of MnS was measured using rotating disk system (USP Wood apparatus), which is commonly used in the pharmaceutical industry [60]. This method was selected because there are lots of reference values available in the literature and the dissolution tests are easy to reproduce as identical test equipment is readily available. The intrinsic dissolution rate of MnS is used for evaluation of the conditions inside the intergranular SCC cracks by examining partially dissolved MnS inclusions on the fracture surface of failed carbon steel piping handling FGE. The failure case is also presented as a background for the study.

It is difficult to estimate the composition of the FGE solutions inside the SCC crack as there can be impurities from the FGE or the steel, which can get concentrated inside the SCC crack. The FGE can contain small amounts of acetic acid as impurity, which can affect the pH of the FGE. There can also be traces of chlorides as impurity in FGE. The chlorides can get concentrated and cause acidification of the solution to very low pH levels at local anodic sites on the steel surface. Because the pH apart from temperature has the strongest effect on the MnS dissolution rate, the two known impurities affecting pH were considered while measuring the MnS dissolution rates in FGE. The acidification by chlorides was simulated by using hydrochloric acid. The measurements were made considering as wide pH range as possible, because the results were used to evaluate the pH inside the SCC cracks. The intrinsic dissolution rates of MnS in FGE with various concentrations of acetic acid and hydrochloric acid were measured and the results are shown in Figure 5.1.

By using density of 3.99 g/cm$^3$ and the equations for the dissolution rates from Figure 5.4, we observe that to yield similar dissolution rates the hydrochloric acid concentration shall be below 0.1 mg/dm$^3$. In terms of acetic acid even the bulk solution has higher dissolution rate. These estimations indicate that the conditions within the intergranular SCC are not acidified in any way.

Partially dissolved MnS inclusions were observed on the transgranular SCC fracture surfaces of St35 N-SSR test specimens studied in Publication III. Because the duration of the N-SSR tests is only few days, only minimal MnS dissolution is expected. The only difference in the conditions comes from the water content or the chlorides leaked from the reference electrode. It can be that the chlorides cause acidification of the SCC
Figure 5.4. The intrinsic dissolution rate of MnS in FGE with various hydrochloric acid and acetic acid concentrations. (a) The intrinsic dissolution rate of MnS vs. hydrochloric acid concentration in FGE. (b) The intrinsic dissolution rate of MnS vs. acetic acid concentration in FGE.
pHe inside intergranular SCC cracks during N-SSR testing, which explains the high MnS dissolution rate. It has been reported that chlorides are needed to initiate pitting in FGE [7, 20]. This also supports the idea that chlorides acidify the SCC crack and the pHe within the SCC crack depends on the chloride concentration. This makes it more difficult to estimate the dissolution rate of MnS inclusions within the SCC crack in FGE containing chlorides.
6. The sulfur species inside the SCC cracks

In addition to the impurities in the bulk FGE solution, the steel itself can have impurities, which affect the conditions on the steel surface under the oxide layer or inside the SCC cracks. One common impurity of steel is MnS inclusions, which can provide sulfur species as it dissolves. The dissolution rate of MnS gives some information of the possible dissolution reactions occurring inside the SCC crack, which can be used to evaluate what type of sulfur species are formed. This idea was applied in Publication V to get information of the sulfur species inside the intergranular SCC cracks.

6.1 MnS dissolution reactions in FGE

The selective dissolution of MnS inclusions has not been studied in ethanol environments but according to the previous studies in aqueous conditions the dissolution of MnS inclusions can proceed either by chemical dissolution or electrochemical dissolution path. According to dissolution tests made by Eklund $SO_4^{2-}$ ions are formed, when MnS dissolves while polarized to +200 mV vs. SHE in deaerated aqueous solution with 0.1 M NaCl [42]. Sulfur particles were formed on the MnS surface during the tests. Based on the thermodynamical calculations Eklund suggested that the MnS dissolution proceeds according to reactions:

$$MnS + 4H_2O \rightarrow Mn^{2+} + SO_4^{2-} + 8H^+ + 8e^- \quad (6.1)$$

$$MnS + 2H^+ \rightarrow Mn^{2+} + H_2S \quad (6.2)$$

$$H_2S = S + 2H^+ + 2e^- \quad (6.3)$$
Lott and Alkire made dissolution tests in similar conditions, but only \( S_2O_3^{2-} \) ions were detected, when MnS electrode dissolved in deaerated aqueous 0.1 N NaCl solutions while anodically polarized from -125 to 0 mV vs. SCE [40]. Sulfur was detected on the MnS surface. Some additional dissolution tests were made and it was confirmed that sulfur can be produced from MnS with the consumption of \( H^+ \) and without net passage of current when pH was 4, 5 and 6. Based on the results Lott and Alkire proposed that the MnS dissolution proceeds with reactions:

\[
2 MnS + 3H_2O \rightarrow 2 Mn^{2+} + S_2O_3^{2-} + 6H^+ + 8e^- \quad (6.4)
\]

\[
2H^+ + MnS = Mn^{2+} + S + H_2 \quad (6.5)
\]

Williams et al. made tests with scanning electrochemical microscopy, where MnS inclusions dissolved in mixtures of NaClO\(_4\) and NaCl [37]. It was suggested that in aqueous conditions containing chlorides the MnS inclusions dissolve according to reactions:

\[
MnS + 2Cl^- \rightarrow MnCl_2 + S^{2-} \quad (6.6)
\]

\[
S^{2-} + H^+ = HS^- \quad (6.7)
\]

\[
HS^- \rightarrow S + H^+ + 2e^- \quad (6.8)
\]

or

\[
2 MnS + 4Cl^- + H_2O \rightarrow S_2O_3^{2-} + 2MnCl_2 + 6H^+ + 8e^- \quad (6.9)
\]

\[
S_2O_3^{2-} \rightarrow S + SO_3^{2-} \quad (6.10)
\]

Webb et al. used the reactivity of Ag with hydrosulfide to distinguish the sulfur species dissolving from the MnS inclusions [62]. The \( HS^- \) ions were detected, when MnS inclusion dissolved chemically in an aqueous acidic 0.1 M \( Na_2SO_4 \) solution with pH of 2 at the corrosion potential. It was proposed that in acidic conditions and low potentials, the MnS inclusion dissolves chemically according to reaction:

\[
MnS + H^+ \rightarrow Mn^{2+} + HS^- \quad (6.11)
\]
The sulfur species inside the SCC cracks

All of the MnS dissolution reactions with hydrogen ions listed above can also occur with ethanol as ethanol can also go through self-ionization but to much lesser extent. The reactions with water can also occur to lesser extent as FGE always has very small amount of water. Because ethanol can dissolve ten times more oxygen, more oxygen based reactions could occur in ethanol, which are not yet known. By looking at the MnS dissolution reactions it is likely that apart from temperature the hydrogen ion activity has strongest effect on the dissolution rate of MnS in ethanol. In water solution pH is the measure for hydrogen ion activity but the scale is different in ethanol so pHe is used instead to distinguish these values from each other as they are not comparable.

The FGE can contain small amounts of acetic acid as impurity, which can affect the pHe of the FGE. There can also be traces of chlorides as impurity in FGE. The chlorides can get concentrated and cause acidification of the solution to very low pHe levels at local anodic sites on the steel surface. Because the pHe apart from temperature has the strongest effect on the MnS dissolution rate, these two known impurities were considered while measuring the MnS dissolution rates in FGE. The acidification by chlorides was simulated by using hydrochloric acid. To get better understanding of the pHe scale of ethanol compared to pH of water, the pHe values of the FGE used in the MnS dissolution tests were measured according to standard test method ASTM D6423 with various acetic acid and hydrochloric acid concentrations. The results are shown in Figure 6.1.

The MnS dissolution reactions in FGE solutions with hydrochloric acid (HCl) and acetic acid were studied by detecting the sulfur compounds from the FGE dissolution medium. The \( SO_4^{2-} \), \( SO_3^{2-} \) and \( S_2O_3^{2-} \) ions were detected with standard qualitative methods [61] and the \( HS^- \) ions by using the electrochemical method introduced by Webb et al. [62]. In this method the reactivity of Ag with \( HS^- \) is used to distinguish the \( HS^- \) ions from the dissolution medium. The sulfur compounds detected during the dissolution of MnS were \( HS^- \) and \( S_2O_3^{2-} \) in FGE with HCl and \( SO_4^{2-} \) in FGE with acetic acid. The voltammetric responses of silver wire in the dissolution mediums are shown in Figure 6.2.

The results show that in FGE with acetic acid having pHe from 8 down to approx. 3.6, the dissolution reaction product is \( SO_4^{2-} \), which points to the dissolution reaction 6.1 proposed by Eklund. The FGE has very low amounts of water so it is not likely that the MnS dissolution in these
The sulfur species inside the SCC cracks

Figure 6.1. The pHe of the FGE vs. acid concentration. Notice how the hydrochloric acid has stronger and acetic acid weaker effect on the pHe than what would be expected for pH in water.

conditions would proceed only with this reaction. Instead the MnS dissolution most likely proceeds also with other reactions and the product is subsequently oxidized to $SO_4^{2-}$. There could also be some reactions with oxygen as FGE can have ten times more oxygen than water. The pHe increased during the dissolution of MnS, while the pHe should decrease in case the dissolution would proceed with reaction 6.1. To obtain the order of the dissolution reaction the logarithm of dissolution rate was plotted vs. the logarithm of the acetic acid concentration and linear fit was made. The results are shown in Figure 6.3.

It appears that the dissolution reaction with lower acetic acid concentrations is controlled by first order reaction, which is not as effective with higher acetic acid concentrations. By making the linear fit for all data points in Figure 6.3, the slope of the curve was 0.5872. Water content of the dissolution medium due to contamination from the acetic acid may have affected the results with higher acetic acid concentrations.

In FGE with HCl having pH from approx. 3.6 down to as low as -1.6, the dissolution reaction products were $HS^-$ and $S_2O_3^{2-}$, which points to reactions 6.4 - 6.11. Because there is only small amount of water in FGE and the pHe increased during the dissolution, it is likely that the MnS
The sulfur species inside the SCC cracks

Figure 6.2. Voltammetric responses of a Ag wire in the dissolution solutions with sweep rate of 20 $mV_s^{-1}$: (a) in water solution with 0.1 M of hydrochloric acid without MnS, (b) in water solution with 0.1 M of hydrochloric acid with dissolved MnS, (c) in FGE solution with 0.1 M of hydrochloric acid without MnS, (d) in FGE solution with 0.1 M of hydrochloric acid with dissolved MnS, (e) in FGE solution with 0.1 M of acetic acid without MnS and (f) in FGE solution with 0.1 M of acetic acid with dissolved MnS.
dissolution occurs mostly with reaction 6.11 and can also occur in some proportions with reactions 6.4 and 6.9.

As seen from Figure 5.4 the MnS dissolution rate appears to be perfectly linear in terms of HCl concentration with slope of 0.69. Slope of the logarithm of dissolution rate vs. the logarithm of HCl concentration was 0.99 with $R^2$ value of 1, which indicates that the dissolution reaction is controlled by first order reaction. This supports the idea that in FGE with very low pH and chlorides the MnS dissolution reaction is 6.11.

In all cases the dissolution medium was naturally aerated. It is not likely that oxygen affects the MnS dissolution rate as the oxygen concentration was constant during the dissolution tests and the dissolution rate depends on the acid concentration. It is possible that oxygen participates in the MnS dissolution reactions, as the dissolution product is $SO_4^{2-}$ with acetic acid or can be $S_2O_3^{2-}$ with hydrochloric acid. If we consider the whole SCC crack to be fully deaerated, the dissolution rate can be affected, as the dissolution reactions are not identical in the absence of oxygen. But as mentioned this is not likely as the dissolution rate depends on the acid concentration while the oxygen concentration is relatively constant between the dissolution tests. Because oxygen strongly affects the SCC susceptibility of the carbon steel in FGE, this effect most likely re-
results from oxygen concentration gradient within the SCC crack. It is not clear whether the SCC crack tip only or the whole SCC crack is deaerated. This means that some MnS dissolution occurs in deaerated as well as in aerated conditions during the SCC crack propagation.

6.2 Concentration of the sulfur species

The dissolution rate of the MnS inclusions in FGE is slow but can still provide sulfur species inside the SCC crack. The main sulfur compound formed in acidic FGE with acetic acid is $SO_4^{2-}$ and with hydrochloric acid it is $HS^-$. As we can see from the SEM-EDS map in Figures 5.1 and 5.3, there are no iron sulfides present near the dissolved MnS inclusions. During the dissolution tests in aqueous conditions as well as in FGE with high concentration of hydrochloric acid, black sulfide layer was formed on the 316L steel sample holder surface around the MnS. This sulfide layer forms due to the severe acidic conditions containing $HS^-$, which is formed on the MnS surface. Similar layer was not formed during the dissolution tests in FGE with acetic acid. If we consider the conditions near the MnS inclusion within the intergranular SCC crack, some iron sulfides can be expected near the MnS inclusions, if $HS^-$ are formed while MnS inclusion dissolves. However, there are no iron sulfides near the MnS inclusions. This indicates that all the sulfur compounds formed in the MnS inclusion dissolution remain in the solution within the intergranular SCC cracks.

The conditions in the transgranular SCC cracks in FGE with chlorides are different. The chlorides most likely increase the iron dissolution within the transgranular SCC cracks leading to the acidification of the crack due to iron hydrolysis as the FGE always contains some water. Then the conditions within the transgranular SCC cracks become acidic, $HS^-$ ions most likely form in the MnS inclusion dissolution. In this way the dissolution of the MnS inclusions provides one source of $HS^-$ ions, which can affect the transgranular SCC mechanism. With negligible chloride concentration the dissolution of the MnS inclusions can provide $SO_4^{2-}$ ions inside the intergranular SCC crack. It is not obvious if the $SO_4^{2-}$ ions can affect the cracking mechanism.

We can estimate the surface area of all MnS inclusions on the SCC fracture surfaces. If the density of the steel is 7.85 $g/cm^3$, the relation between the densities of the steel and the MnS inclusions is 0.51. The steel studied here contains 0.027 wt% sulfur, which means that the MnS con-
The sulfur species inside the SCC cracks

Figure 6.4. Model for calculating the increase rate of sulfur species concentration inside SCC crack.

Figure 6.4. Model for calculating the increase rate of sulfur species concentration inside SCC crack.

\[ v_{\text{Sulf}}, \quad \text{MnS dissolution rate} \]
\[ A, \quad \text{fracture surface area} \]
\[ p, \quad \text{MnS proportion} \]
\[ V, \quad \text{SCC crack volume} \]
\[ w, \quad \text{crack opening} \]
\[ v_{c\text{,Sulf}}, \quad \text{increase rate of sulfur species concentration} \]
\[ M_{\text{Sulf}}, \quad \text{molar mass of MnS} \]
\[ M_{\text{Sulf}}, \quad \text{molar mass of the sulfur species formed} \]

\[ v_{c\text{,Sulf}} = \frac{2Apv_{\text{MnS}}}{V} \]
\[ M_{\text{Sulf}} = \frac{2Apv_{\text{MnS}}}{M_{\text{MnS}}} \]
\[ M_{\text{Sulf}} = \frac{2pv_{\text{MnS}} M_{\text{Sulf}}}{w} \]

The sulfur species inside the SCC cracks

tent is 0.073 wt%. By dividing the MnS content with the relation between the densities of the steel and MnS, we get that approximately 0.14% of the SCC fracture surface is covered by MnS inclusions. Conservative estimate of the crack opening of the intergranular SCC crack studied here was approximately 3 \( \mu m \). Near the surface of the steel the crack opening was higher while near the crack tip and in the middle of the SCC crack the crack opening was small. By using this information and the results from the dissolution rate measurements shown in Figure 5.4 we can estimate how the concentration of the sulfur species develops over time due to the dissolution of the MnS inclusions inside the SCC crack. How this estimate is calculated is shown in Figure 6.4. The model for calculating the increase rate of the sulfur species inside the SCC crack shown in Figure 6.4 assumes constant SCC crack opening and flat surfaces. In reality the crack opening is not constant. The value of 3 \( \mu m \) used for the crack opening is conservative value for this particular SCC crack.

The model does not take into account the geometry of the MnS inclusions or the fact that the fracture surface is not flat, which affects the dissolution process. The model, however, gives a conservative estimate of how fast the concentration of the sulfur species increases inside the SCC crack assuming that all sulfur species stay inside the SCC crack. Using the estimated dissolution rate of the MnS inclusions of the field pipeline sample, we calculate \( SO_{2}^{2−} \) concentration increase rate inside the intergranular SCC crack to be from \( 4.5 \times 10^{-5} \) to \( 5.2 \times 10^{-4} \) mg/dm\(^{3}\) min. By using the estimated MnS dissolution rates from the field sample as reference points and considering that the relation between the acid concentration and dis-
solution rate remains the same inside SCC crack, the limits for the sulfur species concentration increase rate inside the SCC crack with various acid concentrations are obtained. The results are shown in Figure 6.5.

It is not likely that the conditions within the SCC cracks are as severe as the conditions used in the dissolution rate measurements. Still because the relation between the dissolution rate and the acid concentration was linear, some estimates of how the concentration of the sulfur species develops within the SCC crack can be made by extrapolating the results using the linear fit functions in Figure 6.5. Considering the field sample it takes from 32 to 370 h to reach $SO_4^{2-}$ concentration of 1 mg/dm$^3$ within the intergranular SCC crack, if only $SO_4^{2-}$ is formed. Andresen and
Young measured the concentration of the sulfur species inside EAC crack of low alloy steel in high-temperature water using crack tip microsampling [44]. The concentration of the sulfur species was between 1 ppm and 2 ppm and sulfur concentrations above 0.5 ppm induced high crack growth rates. Only $SO_4^{2-}$ ions were detected inside the crack tip, but this was assumed to be due to oxidation of the sulfur species while the samples were cooled down. According to the thermodynamics the dominant sulfur species expected was $HS^-$ ion. According to the results shown here it is clear that due to the dissolution of the MnS inclusions sulfur species exist within the SCC crack of carbon steel in FGE. The concentration of these sulfur species is most likely constant inside intergranular SCC crack but can vary inside the transgranular SCC crack, if the conditions within the transgranular SCC crack in FGE with chlorides are acidified. The dissolution of MnS inclusions in acidic conditions and most likely in deaerated conditions provides $HS^-$ ions inside the SCC crack, which affects the CGR or even changes the cracking mechanism in case the dissolution rate is sufficient. According to this information it can be that carbon steels with low sulfur content are less susceptible for stress corrosion cracking in fuel-grade ethanol especially in conditions containing chlorides.
7. Differences between intergranular and transgranular SCC mechanisms

During our studies for Publications I - VI, differences were observed on the behaviour of the intergranular and transgranular SCC mechanisms. One important difference was that the intergranular SCC does not appear to require as much stress as the transgranular SCC as explained in Chapter 3. This indicates that the cracking mechanisms are not identical. It was shown in previous studies by others that the transgranular SCC mechanism is most likely anodic dissolution process at the crack tip [1, 12]. It could be considered that this type of mechanism would require high strain rate for the oxide layer to break at the crack tip leading to anodic dissolution of the bare steel coupled to the oxidized steel behind the crack tip. The intergranular cracking mechanism is most likely not similar, as it does not require as much stress. It has also been observed that there is not any oxides on the intergranular fracture surfaces after the SSRT testing, while oxides have been seen on the transgranular fracture surfaces. The transgranular SCC occurs only in FGE with chlorides as was shown in Publication IV. Selective dissolution of pearlite nodules has also been observed in all of our studies for Publications I-V, especially when tests haven been done in FGE containing chlorides. Due to this reason the differences between the intergranular and transgranular SCC mechanisms are studied by looking at how the selective dissolution of pearlite nodules affects the cracking mechanisms.

Pearlite nodule consists of alternating layers of ferrite and cementite. Typical pearlite nodule from steel SA-106 is shown in Figure 7.1. As the ferrite lamellaes are selectively dissolving from the pearlite nodule, structures of cementite lamellae are left on the steel surface like shown in Figure 7.2. This selective dissolution process appears to be catalyzed by chlorides as was shown in Publication VI. It is most likely because the cementite acts as cathode while the ferrite lamellaes are dissolving as
Differences between intergranular and transgranular SCC mechanisms

Figure 7.1. a) Single pearlite nodule in SA-106 steel. b) The pearlite structure showing the distribution of ferrite and cementite lamellae in pearlite phase. Average thickness of the cementite lamellae is approx. 70 nm and ferrite lamellae approx. 110 nm.

The anodes, which leaves crevices between the cementite lamellae where the chlorides can get concentrated. This can lead to acidification of these crevices and what makes the conditions even more aggressive is that the relative surface area of the cementite lamellae around these crevices increases as the mechanism proceeds. As this selective dissolution process has been observed on the external surface of the steels as well as on the fracture surfaces, it can be used as another tool like the MnS inclusions to study the conditions inside the SCC cracks. As it occurs in conditions inducing intergranular SCC as well as in conditions inducing transgranular SCC, it can be used to compare the differences between these two mechanisms, which was done in Publication VI.
Differences between intergranular and transgranular SCC mechanisms

7.1 Initiation of intergranular and transgranular SCC

It was shown in Publications IV and VI that in FGE with chloride content below the analysis limit SCC initiates as transgranular cracking in the pearlite phase and intergranular cracking in the ferrite phase. This can be seen from Figure 7.3 a) showing transgranular SCC cracking initiated at the pearlite phase of SA-106 steel surface during SSRT in 20% ethanol-gasoline blend and Figure 7.3 b) showing intergranular SCC cracking initiated at the ferrite phase of the same steel. With chloride content above 2 mg/l the intergranular SCC does not initiate anymore and only transgranular SCC occurs.

In Publication VI it was observed that selective dissolution of the pearlite nodules occurs also in conditions with negligible chloride concentrations as partially dissolved pearlite nodules were observed on the steel surface under the oxide layer of failed pipeline sample from FGE service with no chlorides. The cross-section of oxide layer with partially dissolved pearlite nodule on the steel surface and empty spaces left by the cementite inside the oxide layer is shown in Figure 7.4. It has been shown that chlorides catalyze the localized corrosion at the pearlite nodules near the cementite lamellae. This effect can be clearly seen in Figure 7.5.

It is not clear why the intergranular SCC cannot initiate in conditions with chlorides but it is likely to be related to the localized corrosion phenomenon occurring at the pearlite nodules. The transgranular SCC mechanism considered to be anodic dissolution process at the crack tip can initiate in conditions with chlorides and prefers the pearlite nodules, where
Figure 7.3. Transgranular SCC cracking of SA-106 steel initiated at pearlite phase during SSRT in 20% fuel-grade ethanol and gasoline blend. b) Intergranular SCC cracking of SA-106 steel initiated at the ferrite phase in the same test.
Differences between intergranular and transgranular SCC mechanisms

Figure 7.4. a) Cross-section of oxide layer on the pipeline steel surface from FGE service. b) Some cementite left on the steel surface and empty sites inside the oxide layer are most likely due to the cementite based on their dimensions.

Figure 7.5. Fracture surface of transgranular SCC initiated at pearlite nodule in SA-106 N-SSR test specimen tested in ethanol-gasoline blend with 85 % of ethanol containing 2 mg/l chlorides. Corroded zone consisting of crystallographic pits is present on the fracture surface in locations, where cementite is covering the steel outer surface.
more localized corrosion occurs. This shows that there is clear difference between the intergranular and transgranular SCC initiation. Also as explained in Chapter 3, the intergranular SCC initiation does not appear to require as much stress as the transgranular SCC initiation.

### 7.2 Intergranular and transgranular SCC crack propagation

Review of observations from all of the failed pipeline samples characterized in Publications I - IV as well as for one new sample was made in Publication VI. Selective dissolution of the pearlite nodules was observed inside the intergranular cracks on the failed pipeline samples. It was also observed that the propagation of the intergranular SCC crack stops at the pearlite nodules and the selective dissolution of the pearlite nodule occurs instead. These observations are shown for two different samples in Figures 7.6 and 7.7. As a result empty spaces filled with oxides are left in place of the dissolved pearlite nodules inside the intergranular SCC crack.

Review of all the SSRT and NCTLT testing was also made in Publication VI. It was observed that in ethanol-gasoline blends with chloride concentrations below the analysis limit, the SCC fracture mode changes from fully intergranular cracking to transgranular cracking at the pearlite phase. This effect is clearly seen with the SA-106 steel sample with banded pearlite microstructure in Figure 7.8, on the SSRT SCC fracture surface formed in 25% ethanol-gasoline blend with chloride concentrations below the analysis limit. Fully intergranular SCC cracking initiated at the ferrite phase changes to transgranular SCC cracking in the first pearlite band perpendicular to the direction of crack propagation. The difference in the SSRT testing compared to the field samples is, that in the SSRT testing the stress level is much higher. So even though the intergranular SCC mechanism stops at the pearlite phase with lower stress levels based on the field samples, it can continue as transgranular SCC with higher stress levels of the SSRT samples.

These observations give some information of the differences between the intergranular and transgranular SCC. As the propagation of the intergranular SCC cracks stops at the pearlite nodules and changes to localized corrosion at the pearlite nodule, it indicates that there is a microgalvanic coupling between the cementite and ferrite lamellas of the pearlite nodule. Due to the microgalvanic coupling the cementite becomes the
Differences between intergranular and transgranular SCC mechanisms

Figure 7.6. Intergranular SCC crack in SA-106 carbon steel pipe sample from FGE service. a) The intergranular crack propagation stops at the pearlite nodule. b) Partially dissolved pearlite nodules.
Differences between intergranular and transgranular SCC mechanisms

Figure 7.7. Intergranular SCC cracking in a carbon steel pipe sample from FGE service. a) The intergranular SCC crack propagation stops at the pearlite nodules. b) A partially dissolved pearlite nodule inside the crack.

Figure 7.8. Fracture surface of SCC crack of SA-106 steel SSRT sample tested in 25% ethanol-gasoline blend with chloride concentration below the analysis limit. Fully intergranular SCC cracking changes fracture mode to transgranular cracking at the pearlite band perpendicular to the direction of crack propagation.
Differences between intergranular and transgranular SCC mechanisms

cathode, which affects the potential at the intergranular crack tip enough to stop the crack propagation. This also explains why the intergranular SCC cannot initiate in conditions containing chlorides. This is because the chlorides catalyze the effect of the microgalvanic coupling by increasing the localized corrosion and conductivity of the solution, and the cementite lamellae on the steel surface become stronger cathodes. As the conductivity of the solution increases the galvanic coupling between the cementite and ferrite affects a wider area around the pearlite bands preventing the propagation and initiation of the intergranular SCC.

It is unclear, whether something formed at the pearlite phase, for example in the cathodic reaction, can change the SCC mechanism from intergranular to transgranular cracking. An attempt to measure the compounds formed at the cementite during acidic corrosion of steel in aqueous conditions was made by Staicopolus [54] by using mass spectrometric techniques and the results were: $H_2$, 87.8%; $CH_4$, 4.5%; $CO$, 3.2%; $C_3H_8$ and $C_4H_8$ (each), less than 1.0%; $C_2H_2$, $C_2H_6$, $C_4H_10$, and $H_2O$ (each) less than 0.5%; and traces of $CO_2$. This shows that quite high amounts of carbon monoxide can form at the cementite. The corresponding cathodic reactions were considered to be

$$2Fe_3C + H_2O \rightarrow 6Fe + -CH_2- + CO$$  \hspace{1cm} (7.1)

$$Fe_3C + -CH_2- + H_2O \rightarrow 3Fe + CH_4 + CO$$  \hspace{1cm} (7.2)

Hypothesis made by Newman related the transgranular SCC mechanism to $CO-CO_2$ SCC and the intergranular SCC to a mechanism caused by the incomplete electrochemical oxidation products of ethanol [6]. It is well known that $CO-CO_2$ can cause transgranular SCC of carbon steel [63]. Depending on the $CO-CO_2$ concentrations and pHe conditions the SCC mechanism could also be a form of carbonate cracking. The similarities between the mechanisms observed here and the SCC mechanisms in carbonate solutions are clear. The SCC mechanisms in carbonate solutions can be divided into high pH intergranular SCC and near neutral transgranular SCC [64, 65, 66, 67]. Selective dissolution of pearlite nodules has been observed in carbonate solutions at specific potential range, which is also the potential range where the high pH intergranular SCC occurs [64]. In these conditions a more dense oxide layer containing magnetite and iron carbonate forms. It could also be the potential range where iron carbonate and magnetite have stability.
boundary, which is where intergranular SCC has been observed in DI-isopropanolamine (DIPA) solutions used in refinery amine systems containing sulfur [69, 70]. The near neutral transgranular SCC prefers to initiate at the pearlite bands as shown in Figure 7.9 [66]. It was also found that the steels with ferrite-pearlite structures are more susceptible for both SCC mechanisms [65]. The near neutral transgranular SCC occurs often in dilute bicarbonate–carbonate groundwater containing small quantities of chloride in coating disbonding of pipelines [68]. All the mechanistic findings related to the SCC mechanisms in carbonate solutions are very similar if not identical to our observations on the SCC mechanisms in FGE solutions. This supports the hypothesis made by Newman that the carbon steel SCC in FGE can be a form of CO – CO$_2$ or carbonate cracking. During our studies some SEM-EDS analyses were made of the oxide films of failed pipeline samples. SEM-EDS maps of iron, carbon and oxygen from cross-section of the oxide layer on the steel surface are shown in Figure 7.10 and from cross-section of an intergranular SCC crack in Figure 7.11. It has to be taken into account, that carbon analysis with SEM-EDS is not accurate, so these results are only indicative but there appears to be relatively high amounts of carbon in the oxide films near the steel surface and inside the intergranular SCC crack.

The SCC can occur if sufficient amounts of CO and CO$_2$ is either dissolved in the FGE from air or formed in the cathodic reaction at the steel surface or by ethanol oxidation. The susceptibility for SCC in carbonate solutions is controlled by the partial pressure of CO$_2$ and the pH of the solution [64, 65]. In FGE solutions the CO and CO$_2$ content and pH are
Differences between intergranular and transgranular SCC mechanisms

Figure 7.10. SEM-EDS maps of carbon, oxygen, sulfur and iron from a cross-section of oxide layer on failed SA-106 pipelines surface from FGE service.
Differences between intergranular and transgranular SCC mechanisms

Figure 7.11. SEM-EDS maps of carbon, oxygen, sulfur, manganese and iron from a cross-section of intergranular SCC cracks of failed SA-106 pipe sample from FGE service.
controlled by the reactions at the steel surface, as we can consider them to be relatively constant at the bulk solution, which is usually according to the used FGE standard. It was shown that the pHe conditions within the SCC crack are not acidic. Based on the MnS dissolution rate, the pHe can actually be quite high inside the intergranular SCC cracks, which could make intergranular carbonate SCC mechanism possible. It was shown that the transgranular SCC mechanism favors the pearlite phase, which is selectively dissolving by an electrochemical process. As proposed by R.C. Newman the chlorides catalyze the localized corrosion reactions at the pearlite nodules, which can also increase the electrochemical oxidation of ethanol to CO and CO$_2$ at these locations leading to the transgranular SCC mechanism. Chlorides can also decrease the pHe to levels required by the transgranular SCC mechanism but the pHe levels inside the transgranular SCC crack are not clear. Oxygen is needed for the oxidizing potentials and it can also participate in some of the reactions. All these findings together point to the direction of a SCC mechanism controlled by CO – CO$_2$ or carbonates, but more evidence has to be found to support this hypothesis.

7.3 Electrochemical differences between cementite and pure iron

To get a better understanding of the electrochemical differences between the ferrite and cementite phases, cathodic potentiodynamic polarization curves were measured with pure iron and cementite in various aerated and unaerated FGE solutions containing chlorides and HCl. The results are shown in Figures 7.12 and 7.13.

According to the electrochemical measurements the electrochemical differences between cementite and pure iron are not that clear. The OCP of cementite was always higher than that for pure iron. In aerated conditions the OCP of cementite was approximately 120 mV higher and in unaerated conditions approximately 40 mV higher than that for pure iron. Also, as seen from Figure 7.12, the cementite phase has more positive potentials for the cathodic reactions than pure iron. This indicates that the cementite phase can be the more favorable cathode compared to pure iron, but this is not clear when looking at the Tafel slopes. Possibly four linear regions are seen on the cathodic polarization curves shown in Figure 7.12. The behavior of the four regions is compared by using Tafel slopes. It is seen that the Tafel slope for Region I in aerated conditions is lower for
Differences between intergranular and transgranular SCC mechanisms

Figure 7.12. Cathodic potentiodynamic polarization curves of pure iron and cementite measured in a) aerated and b) unaerated FGE with 50 wt.-ppm chlorides added as sodium chloride with scan rate of 1 mV/s.
Figure 7.13. Cathodic potentiodynamic polarization curves of pure iron and cementite measured in a) aerated and b) unaerated FGE with various HCl concentrations with scan rate of 1 mV/s. The cathodic polarization curves are marked as: a. iron, 10 wt-ppm HCl; b. cementite, 10 wt-ppm HCl; c. iron, 30 wt-ppm HCl; d. cementite, 30 wt-ppm HCl; e. iron, 80 wt-ppm HCl; f. cementite, 80 wt-ppm HCl; g. iron, 1000 wt-ppm HCl; h. cementite, 1000 wt-ppm HCl.
cementite while in unaerated conditions it is lower for pure iron. This indicates faster and easier reaction kinetics for the cathodic reactions occurring at Region I for cementite in aerated conditions and for pure iron in unaerated conditions. In Region II the behavior is reversed. The pure iron has lower Tafel slope in aerated conditions and the cementite has lower Tafel slope in unaerated conditions. In Region III the behavior is reversed compared to Region II although the differences in aerated conditions are very small. In Region IV the Tafel slope is always lower for cementite. The Tafel slopes for iron and cementite are much lower in unaerated conditions in Region IV. It is likely that in Region IV the cathodic reaction rates are no longer limited by charge transfer as the current is almost independent of the applied potential. It is likely that the cathodic reactions in Region IV are ionic mass transport controlled, which is also the case with the cathodic polarization curves in acidic conditions seen in Figure 7.13. The current density for the cathodic polarization curves depends mainly on the HCl concentration. The OCP of iron and cementite was similar in aerated conditions with all HCl concentrations tested but in unaerated conditions the OCP of cementite was always approximately 30 mV higher. This can indicate that in the acidic conditions the selective dissolution will be stronger in unaerated conditions.

The cathodic reactions observed are similar to what was obtained by Lou and Singh [22], who measured cathodic polarization curves for carbon steel in SFGE with various impurity levels. The difference is that the SFGE used by them had much higher concentration of water and acetic acid than the FGE used here. Due to this reason the conductivity of our FGE was much lower. This can be the reason for lower limiting current density observed in this study. As acetic acid concentration was much lower in the FGE, the reactions associated with acetic acid and oxygen were not as clearly visible.

The cathodic polarization curves do indicate that the cementite acts as a more favorable cathode in most cases. Still it seems based on the Tafel slopes, that in some specific conditions pure iron can act as a cathode leading to selective dissolution of cementite although this has not been observed, yet. In any case it is difficult to compare the cathodic polarization curves to the conditions at the selectively dissolving pearlite nodule on the steel surface under the oxide layer or inside a SCC crack as the exact solution composition at these locations is not known. As was observed by looking at the dissolution of MnS inclusions during the Publication
V, the conditions inside an intergranular SCC crack are most likely not acidic, while the conditions inside a transgranular SCC crack can be very acidic. There are also impurities, which affect the cathodic or anodic reactions occurring inside the SCC crack, such as the sulfur species from dissolving MnS inclusions or \( CO \) and \( CO_2 \) forming at the cementite acting as the cathode. The conductivity of the solution inside the cracks is most likely much higher than that of the bulk solution due to a higher amount of impurities.
Differences between intergranular and transgranular SCC mechanisms
8. Conclusions and recommendations for future research

Clear differences were found between the intergranular and transgranular SCC mechanisms. With negligible chloride concentrations the transgranular SCC initiates only at the pearlite nodules while the intergranular SCC initiates only at the ferrite phase. With chloride concentrations of approx. 2 mg/l or more, intergranular SCC does not initiate and transgranular SCC can initiate in ferrite and pearlite phases. The initiation and most likely also the propagation of the intergranular SCC mechanism does not require as high stress level as the transgranular SCC mechanism, which is why post-weld heat treatment can prevent the transgranular SCC but not necessarily the intergranular SCC.

Chlorides cause localized corrosion at the pearlite nodules inside the transgranular SCC by selective dissolution of ferrite from the pearlite phase. Due to this reason the chlorides cause acidification inside the transgranular SCC crack while the conditions inside intergranular SCC crack are not very acidic. Selective dissolution of the pearlite nodules also occurs inside intergranular SCC cracks in conditions with negligible chloride concentrations. This effect stops the propagation of the intergranular SCC crack leading to localized corrosion at the pearlite nodule. With high enough stress level the intergranular SCC mechanism can change to transgranular SCC cracking at the pearlite nodules. As the propagation of the intergranular SCC stops at the pearlite nodules but the propagation of the transgranular SCC continues, it can be concluded that the SCC propagation mechanisms are not identical.

The penetration rate of MnS inclusion dissolution front was measured to vary from 11 μm/year up to 127 μm/year inside the intergranular SCC cracks but is most likely higher inside the transgranular SCC cracks due to more acidic conditions. The sulfur species formed due to selective dissolution of the MnS inclusions are $HS^-$ and $S_2O_3^{2-}$ in acidic conditions.
Conclusions and recommendations for future research

with chlorides and $SO_4^{2-}$ in conditions with negligible chloride concentrations and acetic acid. These results indicate that there can be $HS^-$ and $S_2O_3^{2-}$ ions inside the transgranular SCC cracks but only $SO_4^{2-}$ inside the intergranular SCC crack.

It was shown that the selective dissolution of ferrite from pearlite occurs in FGE and chlorides significantly increase this effect. There is apparent microgalvanic coupling between cementite and ferrite of pearlite phase. The cementite is more favourable cathode as the OCP of cementite is higher than for pure iron. The OCP of cementite is approximately 120 mV higher in aerated FGE and approximately 40 mV higher in unaerated FGE. $CO$ and $CO_2$ can form at the cathodic reactions at cementite surface [54] and react to carbonate. There are a lot of similarities with the intergranular and transgranular SCC mechanisms occurring in FGE compared to $CO - CO_2$ or carbonate solutions. This supports the hypothesis originally made by R.C. Newman, that the SCC mechanisms in ethanol is controlled by $CO - CO_2$ or carbonates [6].

The SCC or carbon steel in ethanol environments can be considered as an opportunity to study the differences between the intergranular and transgranular SCC mechanisms. My recommendation for future research is to attempt to replicate the SCC mechanisms known in aqueous solutions in ethanol solutions. If the SCC mechanisms known to occur in aqueous solutions also occur in ethanol solutions, it were an additional proof for these phenomena. To get more information on the SCC mechanisms studied in this thesis, my recommendation is to attempt to measure the species formed in the cathodic reactions including the gaseous components. Another observation during the studies was that no oxide layers were seen on the intergranular fracture surfaces after SSR testing, while some oxides were present on the transgranular fracture surfaces. Measurements should be made to distinguish the type of oxide layers on the SCC fracture surfaces.
Bibliography


