An Experimental Study to Understand the Localized Corrosion and Environment-Assisted Cracking Behavior of AISI 420-Martensitic Stainless Steel

Krishnan Hariramabadran Anantha

Doctoral Thesis

KTH Royal Institute of Technology
School of Engineering Sciences in Chemistry, Biotechnology and Health
Department of Chemistry
Division of Surface and Corrosion Science
Drottning Kristinas Väg 51
SE-100 44 Stockholm, Sweden
The quest who am I is the axe with which to cut off the ego
- Ramana Maharshi
About me

I was born in Chennai, Tamil Nadu, India. After completing my 12 years of formal schooling, I joined Bachelor of Engineering (B.E.), a 4 years degree program in Mechanical engineering at University of Madras and completed the same, obtaining first class with distinction. After a short stint as a production engineer trainee at Pepsi Co India Holdings Pvt. Ltd., I joined a powder metal component manufacturing company (Sundram Fasteners Ltd., India) where I worked as a design and development/R&D engineer for 5.4 years. As an assistant manager in Sundram Fasteners Ltd., India, I was involved in design and development of single level and multi-level powder metallurgical (PM) parts, design of PM process flow for components, conversion of parts from other technologies to PM route and in product costing. To further hone my skills, I joined and completed Master of Science (M.S.), a 2 years degree program in Materials Science at Royal Institute of Technology (KTH), Stockholm, Sweden. During my M.S program, I did a 2 months summer internship where I worked on water atomization, and a 6 months industrial master thesis titled “Study of total oxygen content and oxide composition formed during water atomization of steel powders due to Mn variation” at Höganäs AB, Sweden. Then I earned myself an entry into this industrial PhD program which is a collaborative project between Uddeholms AB, Sweden and Royal Institute of Technology (KTH), Stockholm, Sweden. I am currently working towards the objectives of this research project and also towards my doctoral degree.

Krishnan Hariramabadran Anantha
Hagfors, Sweden.
Abstract

Martensitic stainless steels (MSSs) are presently used for plastic molding applications due to their favorable mechanical properties and corrosion resistance. A higher demand for a relatively enduring molding material is forecasted since automobile industries are opting for a lighter vehicle design where the usage of plastics and polymer composite materials are expected to increase [11]. Currently steel molds are designed with cooling channels to reduce the solidification time of molten plastic within the mold to improve the productivity. As water is generally used as the cooling medium, corrosion and corrosion induced cracking leading towards the dysfunction of mold, which have been observed in some cases, can increase the production downtime. Hence the primary aim of this thesis is to study the corrosion and corrosion induced cracking behavior of a martensitic stainless steel (MSS) to further the current understanding thereby to optimize the existing alloy/s and to design and develop new steel grades.

In this work, by varying the heat treatment, microstructure of AISI 420 modified (a MSS grade, Uddeholm Stavax ESR) was altered and its corresponding localized corrosion and environment-assisted cracking (EAC) behavior in Cl containing environment were studied in detail. The MSS had been austenitised at 1020°C, and successively quenched in nitrogen gas at fast (3°C/s) and slow quenching rates (0.6°C/s). Then tempering was done at 250°C, and 500°C, respectively, twice for two hours.

To identify the stable phases present in the austenitizing condition, Thermo-Calc simulation was performed which predicted the presence of M7C3 carbide and austenite. Dilatometry was performed to investigate the phase transformation during hardening and it showed an increase in martensite start (Ms) temperature for the slow quenched condition compared to fast quenched condition. Dilatation due to pearlitic phase transformation even during slow quenching was not observed. To characterize the retained austenite content after tempering, X-ray diffraction (XRD) was performed, which showed a relatively higher amount for 250°C tempering in both quenching rates. The highest amount was observed on slow quenched samples tempered at 250°C. Light optical microscopy (LOM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) characterization revealed undissolved carbides and tempering carbides in a martensitic matrix. In the slow quenched condition, additionally pearlite was also identified. Energy dispersive X-ray spectroscopy (EDX) confirmed that the undissolved carbides are rich in chromium. Using XRD the carbides were identified as Fe3C, Cr7C3, and Cr23C6 type in fast quenched samples tempered at 250°C and Cr23C6, Cr7C3, Cr3C2, Cr3C, Cr2C, and CrC in fast quenched samples tempered at 500°C.

The corrosion behavior in 0.1M NaCl solution was investigated using standard salt spray test and electrochemical experiments at room temperature. The results showed that, when tempered at 250°C, the slow quenched samples have an inferior corrosion
resistance than the fast quenched ones. When tempered at 500°C, no significant difference in the corrosion behavior was observed for the slow quenched and fast quenched samples. Volta potential mapping by scanning Kelvin probe force microscopy (SKPFM) indicated higher nobility of the undissolved carbides with respect to the martensitic matrix, whereas, regions adjacent to carbides showed lower nobilities due to chromium depletion.

The evolution of localized corrosion process was investigated using in-situ AFM. Measurements on fast quenched 250°C temper revealed selective dissolution of certain undissolved carbide boundary regions and martensitic inter-lath regions, indicating higher propensity to localized corrosion. Measurements on fast quenched 500°C temper revealed a sequence for localized corrosion, in which, the neighboring matrix next to secondary carbides dissolved first, followed by corrosive attack on regions adjacent to undissolved carbides.

For both fast and slow quenched conditions, tempering at 500°C, reduced the corrosion resistance and the ability to passivate, in comparison to tempering at 250°C.

Stress relaxation associated with tempering treatments at 250°C, and 500°C was characterized by a new method for both fast and slow quenched conditions. Based on the findings from the above-mentioned, initial loading levels were altered and the corresponding EAC behavior was investigated in 0.3M NaCl solution at room temperature.

Determination of stress relaxation: As-quenched samples were first plastically deformed under four-point bending to induce significant amount of residual stresses. Using XRD, the tensile residual stresses were measured. Then samples were tempered at 250°C, and 500°C, which was followed by residual tensile stresses measurement using XRD on the same area where residual tensile stresses were measured prior to tempering. Then the percentage stress relaxation associated with tempering was calculated.

EAC loading procedure: Two levels of residual stresses were assumed in the as-quenched conditions – 30%σ_{0.2} and 90%σ_{0.2}, and the measured amount of relieved stresses were subtracted accordingly in the two levels (30%σ_{0.2} and 90%σ_{0.2}) and the retained values were used as the respective loading of EAC samples.

In the fast quenched condition, 250°C temper showed superior resistance to EAC (did not fail after 30 days of exposure) against the 500°C temper, whereas in the slow quenched condition, 500°C temper showed superior resistance to EAC against the 250°C temper. In the fast quenched condition, despite higher stresses, 250°C temper survived longer, indicating the dominant role of resistance to localized corrosion on the total time to failure. In the slow quenched condition, despite a lower resistance to localized corrosion, 500°C temper survived longer, indicating the dominant role of the residual stress on the total time to failure. The fracture surface showed faceted grains,
cleavage striations, and inter- and transgranular cracks, suggesting a mixed hydrogen embrittlement (HE) and stress corrosion cracking (SCC) mechanism as the cause for EAC. Finite element modeling (FEM) on the fast quenched 500°C temper indicated strain/stress localization at the mouth of deep pits and at the bottom of shallow pits, displaying the favored locations for pit-to-crack transition.

Based on this research work, it can be rationalized that in order to have a longer service life, both the localized corrosion behavior and the residual stresses are to be considered while recommending tempering temperature to mold makers.

**Key words:** MSS, Microstructure, Tempering, Residual stress, Localized corrosion, EAC, SEM, XRD, SKPFM, In-situ AFM, Constant load testing, Fracture.
Sammanfattning


I detta arbete varierades värmebehandlingar på ett modifierat AISI 420 (ett MSS, Uddeholm Stavax ESR) som resulterade i olika mikrostrukturer. De olika tillståndens uppförande med avseende på lokalisera korrosion och miljöpåverkad sprickbildning (EAC) i miljö med klor studerades i detalj. Värmebehandlingarna i dessa tester omfattade austenitisering vid 1020°C, snabb eller långsam kylning i kvävgas (3 respektive 0,6°C/s) samt två anlöpningar under två timmar vid antingen 250°C, eller 500°C.

250°C. Efter snabbkylning och anlöpning vid 500°C var karbiderna av typ Cr23C6, Cr7C3, Cr3C2, Cr2C och CrC.

Korrosionsuppträdandet i 0,1 M NaCl-lösning undersöktes genom standardtest med saltspray och elektrokemiska experiment vid rumstemperatur. Resultaten visar att för de prover som anlöpts vid 250°C var korrosionsmotståndet sämre för dem som hade kylts långsamt än för dem som hade kylts snabbt. Däremot kunde ingen signifikant skillnad i korrosionsmotstånd påvisas mellan långsam och snabb kylning när anlöpnigen skedde vid 500°C. Kartläggning av voltapotential med scanning Kelvin probe force microscopy (SKPFM) indikerade att de ouplösta karbiderna uppträdde som ett ädla material än den martensitiska grundmassan, medan området runt karbiderna uppträdde som ett mindre ädelt material på grund av utarmning av krom.

Utvecklingen av en lokalisera korrosionsprocess undersöktes med in-situ AFM. Mätningar på snabbkylda prover anlöpta vid 250°C visade selektiv upplösning av vissa områden på gränstorn mellan matrix och de ouplösta karbiderna och områdena mellan martensitlattor, vilket indikerar större tendens till lokalisera korrosion. Mätningar på snabbkylda prover anlöpta vid 500°C visade en sekvens för lokaliserad korrosion där matrix intill de sekundära karbiderna upplöstes först, vilket följdes av en korrosionsattack mot områden runt ouplösta karbider.

Efter både snabb och långsam kylning gav anlöpning vid 500°C lägre korrosionsmotstånd och förmåga till passivering än anlöpning vid 250°C.

Spänningsrelaxation under anlöpning vid 250°C och 500°C efter både snabb och långsam kylning karakteriserades med en ny metod. Baserat på resultatet från dessa tester sattes startnivån på lasten i en test av EAC i 0,3 M NaCl-lösning vid rumstemperatur.


Lastningsprocedur för EAC: Två nivåer av restspänningar antogs efter släckning, 30 % respektive 60 % av sträckgränsen σ0.2, och den uppmätta andelen spänningsrelaxation subtraherades från dessa värden. Den kvarvarande restspänningen sattes som last på proverna för EAC.

I det snabbkylda tillståndet gav anlöpning vid 250°C gott motstånd mot EAC (ej brott efter 30 dagars exponering). Detta var klart bättre än efter anlöpning vid 500°C. Efter
långsam kylning var det i stället anlöpning vid 500°C som jämfört med anlöpning vid 250°C gav det bästa motståndet mot EAC. Att det efter snabbkylning var de prover som anlöptes vid 250°C trots högre restspänningar fick längre livslängd än prover som anlöptes vid 500°C tyder på att lokaliserad korrosion i detta fall spelar störst roll för livslängden. Att det motsatta gällde efter långsam kylning, att prover som anlöptes vid 500°C trots lägre motstånd mot lokaliserad korrosion fick längre livslängd än prover som anlöptes vid 250°C, tyder på att restspänningarna i detta fall spelar störst roll. Brottytoruppsattade facetterade korn, striktioner samt inter- och transkristallina sprickor, vilket antyder en blandning av väteförsprödning (HE) och spänningskorrosion (SCC) som mekanismer för EAC. Modellering med Finita Elementmetoden (FEM) för den snabbkylda varianten anlöpt vid 500°C indikerade en lokaliserande av spänningar och töjningar till poröppningen för djupa porer och till porens botten för grunda porer. Dessa resultat indikerar sannolikheten att restspänningar i detta fall spelar störst roll för övriga från por till spricka.

Med utgångspunkt från detta forskningsarbete kan slutsatsen dras att maximering av verktygens livslängd kräver att både lokaliserad korrosion och restspänningar beaktas när verktygsmakare ges råd om rekommenderad anlöpningstemperatur.

**Sökord:** MSS, Mikrostruktur, Anlöpning, Restspänning, Lokaliserad korrosion, EAC, SEM, XRD, SKPFM, In-situ AFM, Test vid konstant last, Brott.
This book is my PhD thesis which is written by compiling articles prepared during the years 2014 January –2018 September. This is an industrial relevant research work which was done in collaboration with Department of Research and Development, Uddeholms AB, Hagfors, Sweden and Division of Surface and Corrosion Science, Department of Chemistry, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal institute of Technology, Stockholm, Sweden. The work was carried out under the academic supervision of Professor Jinshan Pan, contribution from post-doctoral fellow Dr. Cem Örnek in the form of significant discussions, and under the industrial supervision of Dr. Johnny Sjöström, Dr. Anna Medvedeva, and Sebastian Ejnermark. Electrochemical, AFM and XRD measurements were performed at KTH Royal institute of Technology. Sample preparation, Microscopy, XRD, Mechanical testing and Environment assisted cracking tests were performed at Uddeholms AB.

The contents in this thesis are primarily structured having metallurgist and corrosion scientist/engineers in mind. It comprises of six chapters. The first chapter gives the reader an outlook as to why this work was instituted, the research objectives, and the technical approaches adopted to address the framed research questions. In the second chapter, diverse topics with substantial background information related to this thesis are given to prepare the reader to have a quicker appreciation of the findings of this work. The details provided in this chapter are surveyed from various sources which are mentioned in the bibliography. The third chapter elaborates on the experimental methods and analytical techniques used in this work, along with a short theoretical background. The theoretical part is written to briefly explain the techniques used in this thesis. Findings regarding the role of microstructure on the corrosion behavior of martensitic stainless steel is presented in chapter four along with a detailed discussion. The content in this chapter is written by compiling paper 1, paper 2, and paper 3. Findings regarding the role of stress on the environment-assisted cracking behavior is presented in chapter five along with a detailed discussion. The content in this chapter is written by compiling paper 4, and paper 5. Finally in chapter 6, overall conclusions and future possible research topics related to this thesis work are described.

I hope that the reader can appreciate that, this research work has contributed to the existing knowledge pool by providing strong evidences which has not been provided before (to the best of my knowledge), as well as some certainly new if not novel knowledge in the concerned field of study. Hope the reader finds this thesis interesting.

Krishnan Hariramabadran Anantha
Hagfors, Sweden
List of papers included in the thesis

**Paper [1]: Corrosion behavior of a martensitic stainless steel AISI 420 modified from a mold size point of view**

Authors: Krishnan Hariramabadran Anantha, Sebastian Ejnermark, Anna Medvedeva, Johnny Sjöström, Jinshan Pan


**Paper [2]: Correlative microstructure analysis and in-situ corrosion study of AISI 420 martensitic stainless steel for plastic molding applications**

Authors: Krishnan Hariramabadran Anantha, Cem Örnek, Sebastian Ejnermark, Anna Medvedeva, Johnny Sjöström, Jinshan Pan


**Paper [3]: In-situ AFM study of localized corrosion processes of tempered AISI 420 martensitic stainless steel: Effect of secondary hardening**

Authors: Krishnan Hariramabadran Anantha, Cem Örnek, Sebastian Ejnermark, Anna Medvedeva, Johnny Sjöström, Jinshan Pan


**Paper [4]: Experimental and modelling study of the effects of tempering on the susceptibility to environment-assisted cracking of AISI 420 martensitic stainless steel**

Authors: Krishnan Hariramabadran Anantha, Cem Örnek, Sebastian Ejnermark, Anders Thuvander, Anna Medvedeva, Johnny Sjöström, Jinshan Pan

Status: Revised as per reviewer’s comments and submitted to Corrosion Science, 2018.

**Paper [5]: Effect of residual stress on environmentally assisted cracking behavior of slow quenched AISI 420 martensitic stainless steel tempered at 250°C and 500°C.**

Authors: Krishnan Hariramabadran Anantha, Cem Örnek, Sebastian Ejnermark, Anna Medvedeva, Johnny Sjöström, Jinshan Pan

Status: In manuscript.
Contribution

The contribution of the respondent to the papers is listed below

**Paper 1**: I did the planning, experimental work, analysis and wrote the first version of the manuscript.

**Paper 2**: I did the planning, major part of the experimental work, analysis and wrote the first version of the manuscript. Dilatometry was performed with the help of Amanda Forsberg and SKPFM measurement was performed by one of the co-author Dr. Cem Örnek.

**Paper 3**: I did the planning, major part of the experimental work, analysis and wrote the first version of the manuscript. XRD measurements were performed by Assistant Professor Peter Hedström at Materials science department at KTH.

**Paper 4**: I did the major part of planning, experimental work, analysis and wrote the first version of the manuscript. Bending test idea was proposed by one of the co-author Sebastian Ejnermark. Finite element analysis was performed by one of the co-author Dr. Anders Thuvander.

**Paper 5**: I did the major part of planning, experimental work, analysis and wrote the first version of the manuscript. Bending test idea was proposed by one of the co-author Sebastian Ejnermark.
Conference oral presentations based on this thesis

[1] Presentation title: Effect of heat treatment on corrosion behavior of martensitic stainless steel
Conference title: 16th Nordic Corrosion Congress

[2] Presentation title: Local probing study of corrosion behavior of a martensitic stainless steel
Conference title: Eurocorr 2016
Venue: Montpellier, France, 11-15 September, 2016.

[3] Presentation title: Corrosion behavior of a martensitic stainless steel AISI 420 modified from a mold size point of view
Conference title: 10th Tool Conference
Symbols/Abbreviations/Acronyms

(e-2m) Temperature factor
\( \mu_{em} \) Electrochemical chemical potential of the electrode
\( \mu_{es} \) Electrochemical chemical potential of the electrolyte
\( \mu_m \) (Electrochemistry) Chemical potential of the electrode
\( \mu_m \) (XRD) Linear absorption coefficient
\( \mu_s \) Chemical potential of the electrolyte
A Unit area
A\(_1\) Onset temperature of austenite formation on heating
A\(_3\) Completion temperature of austenite formation on heating for hypoeutectoid steels
A\(_cm\) Completion temperature of austenite formation on heating for hypereutectoid steels
\( \dot{a}_m \) Atomic weight of the metal dissolving
BCC Body-Centered Cubic
BCT Body-Centered Tetragonal
BSE Backscattered electrons
\( c_\alpha \) Volume fraction of martensite phase
\( c_\gamma \) Volume fraction of austenite phase
CCT Continuous-Cooling-Transformation
d (Microscopy) Minimum distance that is resolved
d (XRD) Interplanar spacing
d\(_\perp\) Interplanar spacing of planes perpendicular to the incident x-rays
d\(_0\) Interplanar spacing of the same planes in the unstrained condition
d\(_c/d_\ell\) Change in capacitance with respect to change in distance between the tip and the sample.
dw Mass of metal dissolved
d\(_{\varphi\psi}\) Interplanar spacing of planes perpendicular to the incident X-rays
E (Electrochemistry) Electrode potential difference at non-equilibrium condition
E (Material constant) Young’s modulus
E\(_0\) Electrode potential difference at equilibrium condition
E\(_{corr}/E_0\) Corrosion potential
E\(_M\) Relative electrode potential difference
E\(_{pit}\) Pitting/Breakdown potential
E\(_{pp}\) Primary passive potential
E\(_{rp}\) Re-passivation potential
F (Electrochemistry) Faradays constant (96500 C/mol)
F (AFM) Electrostatic force between the tip and the sample
F (XRD) Structure factor (diffraction that is taking place from a single unit cell)
    f Volume fraction of martensite transformed
FCC Face-Centered Cubic
h Planck’s constant
HV Vickers Hardness
i Current density involved in corrosion process
I (XRD) Integrated intensities of a particular hkl plane
    i_o Exchange current density
    i_c Critical anodic current density for passivation
    i_corr/i_o Corrosion current density
    i_p Passive current density
K Constant independent of the kind and amount of the diffracting phase/substance
L Average length of the diagonals
LT Long Transverse
M_f Martensite finish temperature
M_s Martensite start temperature
m_v Momentum of the electrons
\( \Delta S^\chi \) Surface potential/Dipole potential difference between electrode and electrolyte
\( \Delta S^\Psi \) Outer potential/Volta potential difference between electrode and electrolyte
n (Electrochemistry) Number of valence electrons
    n (Microscopy) Refractive index of the medium between the sample surface and the objective lens
    n (XRD) Order of reflection
NA Numerical aperture
OCP Open circuit potential
P Applied Load
p Multiplicity factor
pH Measure of concentration of dissociated hydronium ions
R Universal gas constant (8.314 J/mol. K)
R(hkl) Depends on \( \theta \), hkl and the kind of substance
SE Secondary electrons
T Temperature in K
t Unit time
TTT Time-Temperature-Transformation
V Applied Voltage
\( v \) Volume of the unit cell

\( V_0 \sin (\omega_1 t) \) AC voltage applied

\( V_{dc} \) DC voltage applied

\( \alpha_{1, 2, 3} \) Direction cosines with respect to principal strain and stress axes.

\( \beta_{\text{anodic}} \) Anodic Tafel coefficient

\( \beta_{\text{cathodic}} \) Cathodic Tafel coefficient

\( \Delta T \) Undercooling below \( M_s \) in °C

\( \Delta V \) Contact potential difference between the tip and the sample.

\( \Delta \phi \) Inner potential/Galvani potential difference between electrode and electrolyte

\( \epsilon_{1, 2, 3} \) Strains along principal axes

\( \epsilon_{\phi \psi} \) Strain along the oblique axis

\( \eta \) Overpotential

\( \theta \) (Microscopy) Half angle of the cone of light from the specimen which is accepted by the objective

\( \theta \) (XRD) Diffracted angle

\( \lambda \) (Microscopy) Wavelength of the illuminating source

\( \lambda \) (XRD) Wavelength of the X-ray used

\( \sigma_{1, 2, 3} \) Stresses along principal axes

\( \sigma_{\phi \psi} \) Stress along the oblique axis

\( \nu \) Poisson’s ratio

\( \varphi \) Inner potential/Galvani potential

\( \Phi \) Work function

\( \varphi_{H_2} \) Absolute electrode potential difference of hydrogen electrode

\( \varphi_M \) Absolute electrode potential difference of metal electrode

\( \chi_M \) Surface potential/Dipole potential of the electrode

\( \chi_S \) Surface potential/Dipole potential of the electrolyte

\( \Psi_M \) Outer potential/Volta potential of the electrode

\( \Psi_S \) Outer potential/Volta potential of the electrolyte

\( \frac{1 + \cos^2 2\theta}{\sin^2 \theta} \) Lorentz polarization factor

\( \Delta \) AlN Aluminum nitride

\( \text{Cr}_{23}C_6 \) Chromium Carbide

\( \text{Cr}_2C \)
<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)$_2$</td>
<td>Iron (II) hydroxide/Ferrous hydroxide</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>Iron (III) hydroxide/Ferric hydroxide</td>
</tr>
<tr>
<td>Fe$_{2.3}$C</td>
<td>ε Carbide</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Iron (III) oxide/Ferric oxide/Hematite</td>
</tr>
<tr>
<td>Fe$_3$C</td>
<td>Cementite</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Iron (II, III) oxide/Ferrous Ferric oxide/Magnetite</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>Iron (III) chloride</td>
</tr>
<tr>
<td>FeOOH</td>
<td>Iron (III) oxide-hydroxide</td>
</tr>
<tr>
<td>M$_{23}$C$_6$</td>
<td>Cr rich carbide</td>
</tr>
<tr>
<td>M$_3$C</td>
<td>Fe rich carbide</td>
</tr>
<tr>
<td>M$_7$C$_3$</td>
<td>Cr rich carbide</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>VC</td>
<td>Vanadium carbide</td>
</tr>
<tr>
<td>α-FeOOH</td>
<td>Goethite</td>
</tr>
<tr>
<td>β-FeOOH</td>
<td>Akaganeite</td>
</tr>
<tr>
<td>γ-FeOOH</td>
<td>Lepidocrocite</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AIDE</td>
<td>Adsorption induced dislocation emission</td>
</tr>
<tr>
<td>AISI</td>
<td>American Iron and Steel Institute</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BOF</td>
<td>Basic Oxygen Furnace</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>EAC</td>
<td>Environment-Assisted Cracking</td>
</tr>
<tr>
<td>EAF</td>
<td>Electric Arc Furnace</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>ESR</td>
<td>Electro-Slag Refining</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Modeling</td>
</tr>
<tr>
<td>HE</td>
<td>Hydrogen Embrittlement</td>
</tr>
<tr>
<td>HEDE</td>
<td>Hydrogen enhanced de-cohesion</td>
</tr>
<tr>
<td>HELP</td>
<td>Hydrogen enhanced localized plasticity</td>
</tr>
<tr>
<td>HIP</td>
<td>Hot Iso Static Processing</td>
</tr>
<tr>
<td>LOM</td>
<td>Light Optical Microscopy</td>
</tr>
<tr>
<td>LVDT</td>
<td>Linear variable displacement transducers</td>
</tr>
<tr>
<td>MSSs</td>
<td>Martensitic Stainless Steels</td>
</tr>
<tr>
<td>MSS</td>
<td>Martensitic Stainless Steel</td>
</tr>
<tr>
<td>PM</td>
<td>Powder Metallurgy</td>
</tr>
<tr>
<td>SAE</td>
<td>Society of Automotive Engineers</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress Corrosion Cracking</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SKPFM</td>
<td>Scanning Kelvin Probe Force Microscopy</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steel</td>
</tr>
<tr>
<td>SSs</td>
<td>Stainless Steels</td>
</tr>
<tr>
<td>UNS</td>
<td>Unified Numbering System</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>VAR</td>
<td>Vacuum Arc Refining</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
# Table of contents

## Chapter 1

1.1 Introduction

1.2 Problem description

1.3 Research objectives

1.4 Overall research questions

1.5 Technical approach adopted

## Chapter 2 Background

2.1 Introduction to tool steels

2.2 Classification of tool steels

2.2.1 Mold steels

2.3 Manufacturing process / Process flow

2.3.1 Chemical metallurgy stage

2.3.1.1 Melting

2.3.1.2 Ladle Treatment

2.3.1.3 Vacuum Degassing

2.3.1.4 Casting

2.3.1.5 Homogenizing treatment

2.3.1.6 Electro slag refining (ESR) process

2.3.1.7 Powder metallurgy route

2.3.1.7.1 Gas atomization

2.3.1.7.2 Hot iso-static processing (HIP)

2.3.2 Thermo-mechanical stage

2.3.3 Heat treatment stage

2.3.3.1 Step annealing

2.3.3.2 Normalizing

2.3.3.3 Soft annealing

2.3.3.4 Hardening
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.3.5</td>
<td>Tempering</td>
<td>14</td>
</tr>
<tr>
<td>2.4</td>
<td>Microstructure</td>
<td>15</td>
</tr>
<tr>
<td>2.5</td>
<td>Effect of alloying elements</td>
<td>16</td>
</tr>
<tr>
<td>2.6</td>
<td>Residual stress</td>
<td>16</td>
</tr>
<tr>
<td>2.6.1</td>
<td>Generation of residual stress due to thermal gradient</td>
<td>16</td>
</tr>
<tr>
<td>2.6.2</td>
<td>Generation of residual stress due to phase transformation</td>
<td>17</td>
</tr>
<tr>
<td>2.6.3</td>
<td>Generation of residual stress due to both thermal gradient and phase transformation</td>
<td>17</td>
</tr>
<tr>
<td>2.7</td>
<td>Corrosion</td>
<td>18</td>
</tr>
<tr>
<td>2.7.1</td>
<td>Principle of corrosion – electrochemistry</td>
<td>19</td>
</tr>
<tr>
<td>2.7.2</td>
<td>Electrode potential difference</td>
<td>20</td>
</tr>
<tr>
<td>2.7.2.1</td>
<td>Electrolyte</td>
<td>21</td>
</tr>
<tr>
<td>2.7.2.2</td>
<td>Potential</td>
<td>21</td>
</tr>
<tr>
<td>2.7.2.3</td>
<td>Outer potential</td>
<td>21</td>
</tr>
<tr>
<td>2.7.2.4</td>
<td>Outer potential difference</td>
<td>22</td>
</tr>
<tr>
<td>2.7.2.5</td>
<td>Surface potential</td>
<td>22</td>
</tr>
<tr>
<td>2.7.2.6</td>
<td>Surface potential difference</td>
<td>22</td>
</tr>
<tr>
<td>2.7.2.7</td>
<td>Inner potential</td>
<td>23</td>
</tr>
<tr>
<td>2.7.2.8</td>
<td>Absolute electrode-electrolyte potential difference</td>
<td>23</td>
</tr>
<tr>
<td>2.7.2.9</td>
<td>Chemical potential</td>
<td>24</td>
</tr>
<tr>
<td>2.7.2.10</td>
<td>Electrochemical potential</td>
<td>24</td>
</tr>
<tr>
<td>2.7.2.11</td>
<td>Electrochemical equilibrium</td>
<td>24</td>
</tr>
<tr>
<td>2.7.2.12</td>
<td>Work function</td>
<td>24</td>
</tr>
<tr>
<td>2.7.3</td>
<td>Electrode kinetics</td>
<td>24</td>
</tr>
<tr>
<td>2.7.4</td>
<td>Surface film on iron/steel</td>
<td>26</td>
</tr>
<tr>
<td>2.7.4.1</td>
<td>Surface films on stainless-steels</td>
<td>28</td>
</tr>
<tr>
<td>2.7.5</td>
<td>Pitting</td>
<td>28</td>
</tr>
<tr>
<td>2.7.6</td>
<td>Stress corrosion cracking</td>
<td>30</td>
</tr>
<tr>
<td>2.7.6.1</td>
<td>Active path dissolution</td>
<td>31</td>
</tr>
<tr>
<td>2.7.6.2</td>
<td>Hydrogen based mechanisms</td>
<td>31</td>
</tr>
</tbody>
</table>
Chapter 3 Experimental: Theory and Practice

Part 1

3.1.1 Studied material and the samples----------------------------- 33
3.1.2 Heat treatments performed------------------------------------ 33
3.1.3 Dilatometry--------------------------------------------------- 34
3.1.4 Phase prediction using Thermo-Calc-------------------------- 34
3.1.5 Mechanical testing--------------------------------------------- 35
3.1.5.1 Hardness measurement--------------------------------------- 35
3.1.5.2 Tensile testing---------------------------------------------- 35
3.1.5.3 Impact testing----------------------------------------------- 36
3.1.6 Microstructural observation----------------------------------- 36
3.1.6.1 Sample preparation------------------------------------------- 36
3.1.6.2 Light optical microscopy------------------------------------- 36
3.1.6.3 Scanning electron microscopy------------------------------- 38
3.1.6.4 Atomic force microscopy------------------------------------- 40
3.1.7 X-ray diffraction--------------------------------------------- 42
3.1.7.1 Phase identification----------------------------------------- 43
3.1.7.2 Determination of volume fraction of retained austenite---- 44
3.1.7.3 Determination of macro residual stress-------------------- 46

Part 2

3.2.1 Salt spray test--------------------------------------------- 49
3.2.2 Electrochemical measurements------------------------------- 50
3.2.2.1 Open circuit potential------------------------------------- 50
3.2.2.2 Cyclic potentiodynamic polarization------------------------ 51
3.2.3 Scanning Kelvin probe force microscopy-------------------- 52
3.2.4 In-situ AFM----------------------------------------------- 54

Part 3

3.3.1 A new method to study the stress relieving due to tempering - experimental procedure---------------------------------- 55
3.3.2 Constant load corrosion cracking setup and the experimental procedure--------------------------------- 56
## Chapter 4  Role of microstructure on the corrosion behavior of MSS

4.1 Prediction of equilibrium phases ........................................ 59
4.2 Phase transformation (Dilatometry) ...................................... 59
4.3 Microstructure .............................................................. 60
4.4 Salt spray test ............................................................... 66
4.5 Corrosion tendency of phases ............................................. 67
4.6 Open circuit potentials ..................................................... 68
4.7 Cyclic potentiodynamic polarization ..................................... 70
4.8 In-situ observation of localized corrosion behavior ................. 72
4.8.1 Fast quench (3°C/s) 250°C temper ................................. 72
4.8.2 Fast quench (3°C/s) 500°C temper ................................. 74
4.9 Post polarization SEM analysis .......................................... 76
4.10 Discussion ................................................................. 77
4.10.1 Microstructure evolution ............................................. 77
4.10.1.1 Hardening ............................................................ 77
4.10.1.2 Quenching ........................................................... 78
4.10.1.3 Tempering at 250°C ............................................... 79
4.10.1.4 Tempering at 500°C ............................................... 80
4.10.2 Effect of phases on the corrosion behavior ...................... 80
4.10.3 Effect of heat treatment on the corrosion behavior ............. 83
4.11 Summary ................................................................. 84

## Chapter 5  Role of stress on the environment-assisted cracking behavior of MSS

5.1 Mechanical behavior ....................................................... 85
5.2 Stress relaxation ........................................................... 85
5.3 EAC behavior .............................................................. 86
5.3.1 Fast quench condition .................................................. 86
5.3.2 Slow quench condition ................................................ 87
5.4 Characterization of surface corrosion attack .......................... 88
5.4.1 Fast quench condition .................................................. 88
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1.4.4</td>
<td>EAC behavior of slow quenched condition</td>
<td>107</td>
</tr>
<tr>
<td>6.1.4.5</td>
<td>Stress and strain evolution around a corrosion pit</td>
<td>108</td>
</tr>
<tr>
<td>6.2</td>
<td>Future work</td>
<td>108</td>
</tr>
<tr>
<td>6.2.1</td>
<td>Future exploration related to the microstructure</td>
<td>108</td>
</tr>
<tr>
<td>6.2.2</td>
<td>Future exploration related to the corrosion behavior</td>
<td>108</td>
</tr>
<tr>
<td>6.2.3</td>
<td>Future exploration related to mechanical behavior and stress relaxation associated with tempering</td>
<td>109</td>
</tr>
<tr>
<td>6.2.4</td>
<td>Future exploration related to the effect of stress on the localized corrosion behavior</td>
<td>109</td>
</tr>
<tr>
<td>6.2.5</td>
<td>Future exploration related to the effect of stress on the environment-assisted cracking behavior</td>
<td>110</td>
</tr>
<tr>
<td>6.2.6</td>
<td>Future exploration based on industrial relevance</td>
<td>110</td>
</tr>
</tbody>
</table>

Acknowledgements                                                                 111

Bibliography                                                                 115
Physical and economic well-being has been the unifying aspiration of diverse individuals since the dawn of human civilization. This has been primarily materialized with the help of technology. When an assemblage or a single component performs an intended activity, it can be termed as technology [1]. As the demand for technological advancement increases, consumption of all the products which are a part of a technology also increases, which in turn increases the consumption of resources used for manufacturing those products. Hence to encourage the evolution of technology in spite of the finite available natural resources, human beings need to opt for a sustainable model for producing and consuming goods so as to have a better and exciting tomorrow.

The U.S. Department of Commerce has defined sustainable manufacturing as “the creation of manufactured products that use processes that are non-polluting, conserve energy and natural resources, economically sound, and safe for employees, communities and consumers” [2]. These sustainably produced products should further possess the desired quality and recyclability [2]. Sustainability can further be ensured by enhancing the longevity (by avoiding/delaying the failure) of a product in service, which reduces the production of a new product, thereby lowering the energy and raw material consumption.

In order to minimize failure, first, we need to understand what a Failure is. One can define failure as a condition where the product is in a state of nonperformance. Failure can be categorized under four broad topics namely wear, distortion, fracture and corrosion [3]. The cause/s of failure can be due to individual, simultaneous and/or sequential attack/s of the categories mentioned above. By analyzing the root causes and by taking corrective actions, its reoccurrence can be minimized/avoided.

Wear is a failure in which the surface of a product is altered by its relative interaction with a solid surface or liquid medium or gas. Wear from a mechanistic point of view, is broadly classified into four types namely abrasive or cutting, adhesive or galling, surface fatigue and corrosive wear [4, 5]. Wear failures can eventually lead to fracture [6].

Distortion failure is a process in which the geometry of a product is altered (plastically deformed) due to the service/residual loading resulting in dysfunction. Distortion failures can be prevented by adopting a modified geometry or by adopting a high strength material [7].

Fracture is a condition in which a product splits into pieces leading towards dysfunction. It comprises of 3 progressive stages, such as crack initiation, crack growth, and final fracture stage (catastrophic stage) [7, 8]. A crack from a fracture point of view is only a
partial failure [9]. But depending upon the application and location of a crack, it may or may not be considered as a failure.

Corrosion is an electrochemical process in which the product reacts with its environment eventually leading towards dysfunction. Corrosion failure can also eventually lead to fracture [6]. The annual cost of corrosion globally is estimated to be 1.8 trillion US dollars which translates into 3 to 4% of GDP of industrialized countries [10]. In this thesis, this failure mode (corrosion) has been the subject of study.

1.2 Problem Description

For progressing towards a sustainable future, the environmental protection agency (EPA), USA has set a target of 54.5 miles/gallon (23 km/L) for the automotive industries by the year 2025 [11]. To meet this demand, automobile industries are opting for a lighter vehicle design where the usage of plastics and polymer composite [11] materials can have an increased share. Generally, plastic components are molded into their required shape with the help of steel molds [12] which in turn should possess properties such as corrosion resistance, wear resistance, machinability, polishability, dimension stability, compressive strength, and toughness [12-17]. As martensitic stainless steels (MSSs) fulfill the multitude of property requirements mentioned above, they are generally used as the tooling material for plastic molding applications [17, 18]. As the demand for plastic components are expected to increase, a need for a relatively enduring molding material is also expected. Currently, molds are designed with cooling channels to reduce the solidification time of molten plastic within the mold with an intent to improve the productivity. As water is generally used as the cooling medium, corrosion and sometimes even cracking leading towards the dysfunction of mold occurs, which has increased the downtime. Typically failed molds are shown in Figure 1.1.

![Figure 1.1: Failed plastic injection molds (a) Cross-section view of a cooling channel from which cracks had initiated, (b) Cracks had initiated from the groves on the outer diameter which was functioning as cooling channels. Courtesy: Uddeholms AB.](image)
1.3 Research objectives

The aim of this thesis is to study the corrosion behavior of martensitic stainless steel (MSS) from a material and microstructure point of view in order to improve the current understanding. The findings from this thesis will be horizontally deployed to further optimize the existing alloy/s as well as be used in the design and development of new steel grades. In this thesis, the commercial name of the tool steel investigated was Stavax ESR which is a MSS (AISI 420 modified) produced by Uddeholms AB at Hagfors, Sweden, for plastic molding applications.

1.4 Overall Research Questions

1. To investigate and understand the role of microstructure on the corrosion behavior of MSS

2. To investigate and understand the role of stress on the environment-assisted cracking behavior of MSS

1.5 Technical approach adopted

To execute the above-said objectives, a systematic technical approach was adopted which involved modifying the heat treatment parameters, characterizing the mechanical properties, analyzing the microstructure, characterizing and analyzing the localized corrosion behavior, and characterizing and analyzing the effect of stress on the environment-assisted cracking behavior. The technical approaches adopted for exploring the mentioned research questions are schematically shown in Figure 1.2 and Figure 1.3 respectively.
Figure 1.2: Technical approaches adopted for addressing the first research question.

Figure 1.3: Technical approach adopted for addressing the second research question.
CHAPTER 2 - Background

2.1 Introduction to tool steels

From an economic perspective, manufacturing/production means adding value to a material by either processing and/or by assembly operations, and this is achieved by using machinery, tooling and people [1]. So, tools are aids that assist manufacturing and/or assembly of products which are in general aimed at enabling people’s life either directly or indirectly. There are different types of tooling and based on the manufacturing and/or assembly processes, a specific type is used. The general classification of tools is schematically shown in Figure 2.1.

![Figure 2.1: Schematic classification of tools.](image)

Forming, shearing, and cutting tools are used to achieve the desired geometry by shaping the work material, parting the work material under the action of shearing, and removing the undesired portion of work material respectively [19], whereas the assembly tools are used to assist assembly operations. When steels are used as raw materials for tools, they are broadly termed as ‘tool steels’. The cutting tools are generally known as cutters or inserts whereas names such as punches, dies, core rods, back plates, molds, etc., generally specify the forming tools. A typical plastic mold which is made from a tool steel is shown in Figure 2.2.

Tool steels are generally alloyed with carbon and with carbide forming elements like chromium, molybdenum, vanadium, tungsten and titanium. Carbon content in tool steels are slightly more than in structural steels [20], but there are some tool steels with a low carbon content as well - like maraging steels (precipitation hardened). The final
properties of a tool steel are determined by the alloying elements along with processing treatments.

![Image](image.png)

**Figure 2.2**: Plastic mold (made from tool steel) along with molded products. Courtesy: Uddeholms AB.

### 2.2 Classification of tool steels

Country (American, German, Japanese, British, French, Swedish and others) specific standards are generally used in classifying tool steels [21] and here, only American based classification will be described. There are two ways by which tool steels are classified under that system, and they are American Iron and Steel Institute (AISI) and Unified Numbering System for metals and alloys (UNS). The later was established by the Society of Automotive Engineers (SAE) and American Society for Testing and Materials (ASTM). Under AISI, tool steels are classified based on the major alloying element, heat treatment performed or application. Table 2.1 shows the classification of tool steels based on AISI system. The chemical composition of the mentioned steel grades can be found elsewhere [21].

**Table 2.1. Classification of tool steels based on AISI system [21]**

<table>
<thead>
<tr>
<th>Group</th>
<th>AISI symbol</th>
<th>Specific steel within a group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-hardening tool steels</td>
<td>W</td>
<td>1, 2, 5</td>
</tr>
<tr>
<td>Shock-resisting tool steels</td>
<td>S</td>
<td>1, 2, 5, 6, 7</td>
</tr>
<tr>
<td>Oil-hardening cold-work tool steels</td>
<td>O</td>
<td>1, 2, 6, 7</td>
</tr>
<tr>
<td>Air-hardening, medium-alloy cold-work tool steels</td>
<td>A</td>
<td>2, 3, 4, 6, 7, 8, 9, 10</td>
</tr>
<tr>
<td>High carbon, high chromium cold-work tool steels</td>
<td>D</td>
<td>2, 3, 4, 5, 7</td>
</tr>
<tr>
<td>Low-alloy special purpose tool steels</td>
<td>L</td>
<td>2, 6</td>
</tr>
<tr>
<td>Mold steels</td>
<td>P</td>
<td>2, 3, 4, 5, 6, 20, 21</td>
</tr>
<tr>
<td>Chromium hot-work tool steels</td>
<td>H</td>
<td>10, 11, 12, 13, 14, 19</td>
</tr>
<tr>
<td>Tungsten hot-work tool steels</td>
<td></td>
<td>21, 22, 23, 24, 25, 26</td>
</tr>
<tr>
<td>Molybdenum hot-work tool steels</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>Tungsten high-speed tool steels</td>
<td>T</td>
<td>1, 2, 4, 5, 6, 8, 15</td>
</tr>
<tr>
<td>Molybdenum high-speed tool steels</td>
<td>M</td>
<td>1, 2, 3, 4, 6, 7, 10, 30, 33, 34, 36</td>
</tr>
<tr>
<td>Ultra-high-speed tool steels</td>
<td></td>
<td>41, 42, 43, 44, 46, 47</td>
</tr>
</tbody>
</table>
In this thesis, a specific type of mold steel was studied and hence a brief description of the same is discussed below.

2.2.1 Mold steels

Tool steels used for plastic molding application are called mold steels. They come under the group AISI P steels and their chemical composition can be found elsewhere [22]. Their general characteristic requirements are ease of hubbability, machinability, polishability, wear resistance, high surface hardness, high core strength, toughness, minimum dimensional change on hardening, resistance to corrosion and resistance to hardness loss on tempering [22]. Further, based on specific molding application and by that to satisfy their characteristic requirements, a specific tool steel is selected.

Other than the P grades, martensitic stainless steels (MSSs) are also used as mold steels when the application demands for a relatively higher corrosion resistance. As MSS come under the classification of stainless steels (SSs) they are designated based on the AISI classification of SS and not based on tool steels. AISI classification of SS constitutes 200, 300 (Austenitic SS) and 400 (Ferritic and MSS) series, wherein the latter demarcation between ferritic and MSS are based on the alloy addition [23] and is given by the following relations:

\[
\%\text{Cr} - (17 \times \%\text{C}) < 12.5\% \iff \text{MSS} \tag{2.1}
\]

\[
\%\text{Cr} - (17 \times \%\text{C}) \geq 12.5\% \iff \text{Ferritic SS} \tag{2.2}
\]

As hardening heat treatment forms the basis behind the transformation from austenite to martensite, MSSs are also called hardenable SSs [24].

Molds steels are generally divided into three groups: hubbing grades, machined cavity grades and corrosion-resistant grades [22]. Hubbing grades are low carbon (> 0.12 wt.%) grades where the required cavity is hubbed in the annealed condition and the final required hardness is achieved by surface hardening treatments (P2, P3, P4, P5, P6) [22]. Machined cavity grades are high carbon grades (P20 and P21) where the required cavity is generally machined post hardening, but sometimes carburization and hardening can be done after machining as well (P20) [22]. Corrosion resistant grades are MSS where the required cavity is either machined on a pre-hardened condition, or in a soft-annealed condition where the final hardness is achieved by the post-hardening and tempering treatments.

2.3 Manufacturing process / Process flow

Steel can be produced either from an ore based route or a scrap based route [25]. In the former, extracted iron ores are reduced under blast furnace to form pig iron which will have ca. 4 wt.% C and to remove the excess C it is further processed under a basic oxygen furnace (BOF) under highly oxidizing condition where the carbon oxidizes along
with Fe and other impurities. After removing the oxidized products, molten metal is refined for its temperature and alloy contents under a ladle treatment furnace. Then if needed degassing is performed on the liquid melt before teeming (pouring) the steel into either a continuous caster or into permanent molds (ingot molds). In the scrap-based steel making, selected steel scraps are melted in an electric arc furnace (EAF) followed by all the subsequent steps as mentioned above after BOF operation. At Uddeholms AB, scrap-based steel making is used for producing tool steel ingots.

Manufacturing processes of steels can be broadly classified into five sequential stages namely chemical metallurgical (process metallurgical), thermo-mechanical, heat treatment, finish machining and inspection stages. At Uddeholms AB, tool steels of different grades are manufactured in the stages mentioned above.

### 2.3.1 Chemical metallurgy stage

Processes from melting to casting come under this stage. List of processes and variants within this stage is shown in Figure 2.3.

![Chemical metallurgy stage at Uddeholms AB.](image)

#### 2.3.1.1 Melting

Electric furnaces use electrical energy to heat the charge, and there are five distinct types namely indirect arc furnace, direct arc furnace, direct arc furnace with conducting hearth, low frequency core type induction furnace and high frequency coreless induction furnace [26]. In the above-mentioned types, only direct arc and coreless induction furnaces are widely used [26]. In direct arc furnaces, the charge is also a part of an
electrical circuit and so the generated arc passes through the charge causing it to melt effectively. In direct electric arc furnaces (EAF), both alternating current (AC-EAF) and direct current (DC-EAF) are used, and in the former, graphite electrodes (three in number because of three electrical phases) are used as cathodes (-), and the charge as anodes (+).

After melting, refining is also performed by purging oxygen into the melt which reacts with elements like Al, Si, Mn, P, C (if present in the melt) and with Fe [27], forming slag. Primarily refining in EAF is aimed at adjusting carbon content in the melt.

At Uddeholms AB, selected steel scraps along with slag formers are charged in an AC-EAF and melted to the desired superheat temperature. The capacity of EAF ranges from 35 to 65 tons. Along with melting and alloying, phosphorus and carbon refining are also done.

2.3.1.2 Ladle Treatment

After refining treatment at EAF, the slag is removed and the heat (melt) is tapped (transferred) into a ladle vessel which then is covered on top by a retractable lid with electrodes. The ladle vessel with the melt along with the lid is called ladle treatment furnace (an electric arc furnace) where refining such as de-oxidation, de-sulfurization, de-phosphorization, inclusion modification, alloy adjustments, and temperature adjustments are generally done [28]. To homogenize the chemical composition and temperature throughout the bath, stirring of the melt by argon gas bubbling is generally performed.

At Uddeholms AB, the melt is processed in an either 35 or 65 tonne ASEA-SKF ladle furnace. After removing the EAF slag, Al bars or wires are added to the melt to kill the oxygen in the melt. Then alloying elements are added to adjust the chemical composition of the melt according to the specific grade. To protect the melt from re-oxidation, synthetic slag formers are added to the melt. The temperature of melt is maintained at around 1580°C to 1650°C and induction stirring is used for homogenizing the melt.

2.3.1.3 Vacuum Degassing

After refining and temperature adjustment, the ladle vessel is transported to the degassing station where removal of dissolved gases takes place. Dissolved gases like H₂, N₂, and O₂ are called simple gases because they dissolve in their atomic form (H, N, and O) whereas dissolved gases like CO₂, CO, H₂O, and SO₂ are called complex gases which are formed due to reaction among elements present in the melt [29]. Formation of the complex gases can be avoided/minimized by effective de-oxidation [29]. The equilibrium solubility of dissolved gases in a melt at a particular temperature is given by Sievert’s law which states that the quantity of dissolved gases present in a melt is
proportional to the square root of the partial pressure of that gas above the melt [29], hence by placing the ladle under a low-pressure environment, will lower the solubility of dissolved gases (hydrogen and nitrogen) in a melt at that temperature by diffusing out the excess amount. The effectiveness of the mentioned process can be further enhanced by inert gas purging (Ar) into the melt which will create effective mixing (turbulence) thereby enabling quicker out-fluxing of dissolved gases.

At Uddeholms AB, the melt is processed in a degasser (ladle vessel covered on top by a retractable lid) at a very low pressure. Argon gas is purged from the bottom of the ladle vessel using two porous plugs for specified duration to refine/remove entrapped gases and inclusions from the steel.

### 2.3.1.4 Casting

In this process, molten steel is teemed into mold/s of required shape/s and dimension where it solidifies. Generally, two types of practices are widely used for casting steels, and they are ingot and continuous casting. At Uddeholms AB, ingot casting is used for solidifying the molten metal and hence a brief description of the same is discussed further. The ingot casting process is further classified into downhill and uphill casting process. In the former, molten steel is directly teemed into a mold through its top opening, whereas in the later it is teemed through holloware assembly [30] into the mold through its bottom opening. In uphill casting, multiple molds can be assembled in a holloware set-up where through the central runner refectory, molten steel is conveyed to the assembled molds via center pot and end pot refractories. As the molten steel is changing its direction from vertical to horizontal and again to vertical during filling, splashing and rippling are minimized (as the melt slows down while filling), which in-turn yield a better surface quality than the downhill casting process [31]. Molds are generally manufactured from cast iron with a taper to enable easy retraction of the solidified ingot and they can be positioned in the holloware setup with their narrow-end-up or wide-end-up [32].

At Uddeholms AB downhill casting is practiced where the mold is positioned in the holloware setup with their wide-end-up.

### 2.3.1.5 Homogenizing Treatment

In the solidified ingot, the concentration of alloying elements within a phase will vary due to the non-equilibrium cooling rate of the molten steel due to insufficient time available for readjustment of the alloying elements during cooling. This phenomenon is called micro-segregation and its severity is reduced by a treatment called homogenization where the ingots are heated to a temperature above \( A_3 \) or \( A_{cm} \) (Figure 2.4) and soaked at that temperature followed by slow cooling (furnace cooling) [33]. At high temperatures with appropriate soaking time, diffusion of alloying elements is
enabled which will even-out the concentration gradients within a phase and will homogenize the microstructure.

At Uddeholms AB, if the ingots are not further processed through electro-slag refining (ESR), they are homogenized by heating up to high temperatures (varies based on grades).

2.3.1.6 Electro-Slag Refining (ESR) Process

Solidified ingots that require further purification based on the application requirements are generally refined further by either ESR or vacuum arc refining (VAR) process. At Uddeholms AB, ESR process is used on specific grades and hence a brief description of the same is discussed further. There are three main constituents in the ESR process and they are the metal to be refined, the mold, and the slag. The mold is open at the top to accommodate the entry of un-refined ingots/slabs and closed at the bottom with a base plate where the refined metal solidifies and starts building up. In the beginning, the ingot/slab is lowered into the mold until the slag, which is placed on the base plate of the mold. Alternating current is made to pass through the ingot/slab and the base plate of the mold via slag which acts as a resistor in the circuit (slag resistance > metal resistance [31]). The heat generated in this process is by the resistance and not by arc [34]. As slag gets heated, ingot that is in contact with the slag surface also melts locally forming a film of molten metal. As the slag density is lower than the melt, the melt passes through the slag and gets collected in the mold (bottom side of the slag), leaving the inclusions to the slag. This particular stage is called as the refining stage in the ESR process. The refined metal pool solidifies at the bottom portion of the mold, as it is water cooled, leading to build up of the refined ingot/slab. By carefully matching the melting rate and solidification rate, high-quality ingots can be obtained [35].

At Uddeholms AB, ingots of varying sizes are refined under ESR units.

2.3.1.7 Powder Metallurgy route

Two operations are involved in manufacturing steels through this route, and they are gas atomization and hot isostatic pressing. In the former, as steel powders are produced instead of ingots, segregation is to a greater extent minimized/avoided. Also, high alloyed grades can be manufactured without cracking during hot working [36].

2.3.1.7.1 Gas atomization

After refining, molten steel is transferred to the tundish, which channelizes the same into an atomizing chamber at a desired rate. Inside the atomizing chamber, the molten steel is disintegrated into particles by direct impact with gas. The free-falling melt solidifies and gets collected in the bottom of the chamber.
2.3.1.7.2 Hot Isostatic Processing (HIP)

The collected powder is then filled in a capsule followed by subjecting them to a high pressure and temperature [37], which yields a densified solid ingot. As capsule material also gets consolidated with the powdered material, the former is removed by post-HIP machining.

2.3.2 Thermo-mechanical stage

In order to eliminate the prior dendritic structure, ingots (both from the conventional and PM route) are plastically deformed under hot working (forging or rolling) operations. During plastic deformation, the material strain hardens (i.e., the stress required to strain the material increases), and if the working temperature is above the recrystallization temperature it generates new stress-free gains that will enable further reduction. The amount of plastic deformation that can be imparted in hot working depends on the working temperature (directly proportional) and straining rate (inversely proportional) [39]. At Uddeholms AB, after homogenizing at specified temperature for the prescribed amount of time, the conventional steel ingots are directly transferred to the rolling/forging station, while ESR based grades are heated to the required temperature first and then transferred to the rolling/forging station. High percentage reduction of ingots are employed, to meet the dimensional and microstructural requirements.

2.3.3 Heat treatment stage

The final performance of a steel product is generally determined by its mechanical properties which is related to its microstructure, which in turn is determined by the type of processing to which the steel is subjected to and its alloying elements [40]. Heat treatment (annealing, normalizing, hardening, tempering, etc.,) is one such processing where the microstructure is tailored to suit either the next operation or the final property requirements. In the context of steel manufacturing at Uddeholms AB, after hot working, step annealing, normalizing, and soft annealing are sequentially performed to get the desired microstructure. After soft annealing, based on the delivery condition, hardening and tempering heat treatments are also performed.

2.3.3.1 Step annealing

This treatment is also called isothermal annealing. Purpose of this treatment is twofold: to avoid martensitic transformation while cooling after hot working thereby avoiding the possibility of cracking; and to relieve entrapped hydrogen if any. While cooling, when the ingot temperature drops below the A1 temperature (Figure 2.4), they are placed in an annealing furnace and held at that temperature (ca. 700°C) according to their dimension [38], followed by cooling at a faster rate to room temperature. At the soaking temperature (below A1 – Figure 2.4), austenite will transform to ferrite + pearlite for
hypo-eutectoid and cementite + pearlite for hyper-eutectoid steels. If ingots are subjected to hydrogen treatment as well, then they are soaked for a longer time at the temperature mentioned above.

2.3.3.2 Normalizing

This heat treatment is done for specific grades of steels only. The purpose of this treatment is to refine the grains [33] and thereby enhance the toughness of the material. In the context of steel manufacturing, its purpose is to normalize the microstructure (making it predictable) so as to relatively ease the following soft annealing treatment. Ingots are austenitized by heating above $A_3$ (Figure 2.4) temperature and soaked at that temperature for a short time to avoid excessive grain growth and then cooled in still air, resulting in ferrite + pearlite phases with finer grains for hypo-eutectoid steels. Carbide networks if present in the incoming microstructure will dissolve at normalizing temperature, but can re-precipitate during cooling if the rate of cooling is insufficient, and hence relatively faster cooling is generally followed for dissolving carbide networks which in turn will yield a martensitic microstructure [38].

![Fe-C phase diagram](image)

**Figure 2.4:** Fe-C phase diagram [41].

2.3.3.3 Soft annealing

The purpose of this treatment is to transform the prior microstructure to enhance machinability. Generally, complex profiles are machined/formed on tools in the soft annealed condition as they are relatively soft, and then hardening and tempering treatments are performed to impart the necessary hardness. Tool steels are generally soft annealed by heating between the inter critical temperature range ($A_1 - A_3/A_{cm}$ – Figure 2.4) [42] and soaking at that temperature for the required amount of time
followed by slow cooling. During heating, carbides start to partly dissolve and spheroidize [42]. At the annealing temperature, the matrix transforms to austenite plus further spheroidization and coarsening of the carbides take place, and finally during cooling the austenite transforms to ferrite and further spheroidization of carbides takes place along with new precipitation of carbides [42]. As spherical shape will have the lowest interfacial energy/unit volume, carbide particles during soft annealing will tend to transform their morphology into a spherical shape (hence this process is also known as spheroidize annealing) [42]. The soft annealing temperature ranges from ca. 800°C to 900°C.

2.3.3.4 Hardening

Purpose of this treatment is to transform the prior microstructure to a martensitic structure. In hardening, the process of heating to a temperature which is above \( A_\text{3} \) or \( A_\text{cm} \) (Figure 2.4) and soaking at that temperature is called austenitization, and the following cooling is called quenching. Purpose of austenitization is to transform the soft annealed microstructure to a fully austenitic or austenite + carbides microstructure. During quenching (fast cooling) austenite transforms by a diffusionless-displacive transformation to a metastable phase called martensite, which starts to form and finishes at martensite start (\( M_s \)) and finish temperature (\( M_f \)) respectively. Instead of martensite, phases like pearlite, ferrite, cementite and bainite can form if the steel undergoes a relatively slow cooling from its austenitization temperature, and the minimum cooling rate with which martensite can be formed is determined by a parameter called hardenability. The higher the hardenability, the lower will be the cooling rate required to form martensite. By increasing the austenitization temperature, dissolution of carbides (relatively more) is enabled leading to more solutionizing of alloying elements in the matrix, which in turn increases the hardenability and volume fraction of martensite post quenching. But this leads to lowering of \( M_s \) temperature thereby retaining the austenite at room temperature. At higher austenitization temperature, grain growth can be expected, which will lower the toughness of the steel.

2.3.3.5 Tempering

This is generally done after hardening treatment and its purpose is to induce a relatively ductile microstructure primarily by reducing hardness, and relaxing stresses. In the tempering process, steels are heated anywhere below the \( A_\text{1} \) temperature (Figure 2.4), soaked and cooled at a required rate [41]. Generally, there are four stages in tempering of steels: precipitation of \( \varepsilon \) carbides in the temperature range 100°C to 200°C, decomposition of retained austenite in the temperature range 200°C to 300°C, precipitation of \( M_\text{s} \)C in the temperature range 250°C to 700°C, and precipitation of alloy carbides in the temperature range 500°C to 600°C (secondary hardening) [43].
At low temperature, redistribution of carbon in the martensitic matrix takes place, and upon further heating, ε carbide (Fe$_{2.3}$C) precipitates, which then transforms to Fe$_3$C (cementite) precipitates upon further increase in temperature [43]. Cementite precipitates grow upon further heating, and as hardness is directly related to the fineness of the precipitates in the matrix, hardness drops as the precipitates coarsen [43]. Generally, as the tempering temperature increases, hardness drops, and ductility increases. However, if the steels are alloyed with carbide and nitride forming elements, then at around 500°C, secondary carbides, and nitrides precipitate contributing to an increase in hardness. This is called secondary hardening [43]. These fine secondary carbides and nitrides replace the coarsened Fe$_3$C precipitates, and thereby increase the hardness of steel. Upon further increasing the tempering temperature, the secondary carbides coarsen and again the hardness drops. For the entrapped austenite (in between the transformed martensite) to transform to martensite during quenching, the latter has to deform, but as the latter being volumetrically bigger and harder than the former, the former gets retained even after the completion of quenching. Hence transformation of austenite to martensite during quenching is incomplete sometimes. During tempering as martensite relaxes, the untransformed austenite will transform to bainite (during holding time at tempering temperature) [44], or martensite (during cooling from the tempering temperature [45]), or ferrite + cementite (as per the phase diagram) [41]. If the retained austenite transforms to martensite then one more similar tempering operation is performed to convert the newly transformed untempered martensite into tempered martensite [46], which is called double tempering.

2.4 Microstructure

Only martensite phase is briefly described here as it is the primary phase related to the microstructure studied in this work. In steels, martensite is a metastable phase which forms by diffusionless - displacive transformation from the parent (austenite) phase upon rapid cooling [47]. Therefore there will be no compositional difference between the parent phase and product phase. The stable phase upon cooling from FCC is BCC iron, but because of non-equilibrium (rapid) cooling, carbon atoms get supersaturated in the octahedral sites and prevents BCC formation, leading to BCT crystal structure formation [47]. During tempering, carbon atom diffuses out of the octahedral sites because of thermal activation leading to the relaxation of BCT crystal structure [47]. The above-mentioned is not the full description of the crystallographic changes that happens during martensitic transformation [48]. Based on the observed experimental evidence, the mechanism of martensite formation was established and it is known as the phenomenological theory of martensite crystallography [48]. The morphologies of ferrous martensite changes with increasing carbon content and they are lath (up to 0.6 wt.%C), mixed (0.6 to 1.0 wt.%C) and plate (>1.0 wt.%C) martensite [47].
2.5 Effect of alloying elements

The role of alloying elements like Si, Mn, Cr, and V are briefly discussed below as they are the primary alloying elements other than Fe and C in the steel investigated in this thesis.

Silicon (Si): It does not tend to form carbides, it slightly increases the $A_t$ temperature [49], moderately increases the hardenability, and retards carbide precipitation thereby retaining the carbon in the martensite which in turn promotes strength [50].

Manganese (Mn): It is an austenite stabilizer [20] i.e., it lowers the $A_t$ temperature [49]. Mn has a slight tendency to form carbides, more than Fe but less than Cr, moderately increases the hardenability, and it combines with sulfur in liquid steel and forms MnS inclusions which are removed as slags [50].

Chromium (Cr): Cr is a ferrite stabilizer [20], it has a strong tendency to form carbides, more than Mn but less than W, increases the hardenability, increases corrosion resistance and retards softening during tempering by enabling secondary carbide precipitation [50].

Vanadium (V): It is a ferrite stabilizer [20] i.e., it increases the $A_t$ temperature [49]. V has a strong tendency to form carbides, less than Ti and Nb, significantly increases the hardenability, and retards softening during tempering by enabling secondary carbide precipitation [50].

2.6 Residual stress

Residual stresses are self-equilibrating stresses (resultant force and the moment is zero) in a structure, present in the absence of external loading [51] and their origins can be due to mechanical (bolting of two parts), plastic deformation (non-uniform deformation within a part or assembly), thermal gradients (differential cooling/heating within in a part), and phase transformations (volumetric difference among phases) [52]. In other words, residual stresses arise due to a misfit between different parts in an assembly, different phases within the same part, or different regions within the same part [53]. Here, a brief description of residual stress generation during quenching is discussed and it is based on the literature references [54, 55]. During quenching residual stresses arise due to thermal gradient as well as phase transformations.

2.6.1 Generation of residual stress due to thermal gradient

During quenching, the surface will always experience a faster cooling (relatively) than the core. Due to thermal coefficient of contraction, the surface tends to shrink more than the core and this differential contraction will restrict complete contraction of the surface inducing a residual tensile stress on the surface and a compressive stress on the core.
But this is only temporary and as the cooling continues, the core that has cooled relatively over a broader range of temperature will shrink more than the surface. This, in turn, will induce a tensile stress on the core because the surface will not allow the core to completely shrink, and a compressive stress on the surface.

### 2.6.2 Generation of residual stress due to phase transformation

When a part is quenched from its austenitization temperature, its surface reaches the martensite start temperature ($M_s$) relatively faster than the core. As martensite is volumetrically bigger than austenite, there will be an expansion in the surface inducing a compressive residual stress on the surface. When the core starts to transform, it expands and makes the surface to elastically stretch causing a stress state reversal, resulting in tensile residual stresses on the surface and compressive residual stresses on the core.

### 2.6.3 Generation of residual stress due to both thermal gradient and phase transformation

When both thermal gradient and phase transformation effects are considered together, a double reversal of the state of stress on the surface and core happens. As mentioned above, during the initial stages of quenching, the surface tends to shrink more than the core, and this will induce a tensile residual stress on the surface and a compressive residual stress on the core until the surface reaches the $M_s$ temperature. This is schematically shown from region $t_0$ to $t_1$ in Figure 2.5. After that, as the martensite starts to form on the surface there will be an expansion in the surface which will induce a compressive residual stress on the surface and a residual tensile stress on the core until the core reaches the $M_s$ temperature. This is schematically shown from region $t_1$ to $t_2$ in Figure 2.5 and it is the first stress reversal. After that, as the martensite starts to form on the core there will be an expansion in the core which will induce a tensile residual stress on the surface and a compressive residual stress on the core which is schematically shown from region $t_2$ to $t_3$ in Figure 2.5 and it is the second stress reversal. At the completion of cooling, the phase transformation induced tensile residual stress dominates over the thermally induced compressive residual stresses on the surface. This is only true when the phase transformation in the surface precedes the core. If the core transforms before the surface (poor hardenable steels), then there will be a compressive residual stress on the surface and a tensile residual stress on the core.
Figure 2.5: Evolution of residual stress upon quenching from austenitization temperature. Contribution from thermal contraction and phase transformation are included [54, 55].

2.7 Corrosion

Other than some metals like Au, Ag, and Pt, most of the metals do not occur in nature in their native/elemental form, instead they occur in the combined form such as oxides, sulphides, sulphates, carbonates, etc. [56]. These combined forms with other impurities (gangue) are collectively known as ores. After cleaning the impurities, the ores are subjected to extraction process (via pyrometallurgy or hydrometallurgy or electrometallurgy route) to obtain pure metals, which are further processed to become a desired raw material for products that go out to shape the world and even outer space lately.

One of the life-determining factors for these engineering products is corrosion resistance against its subjective environments. Corrosion, from a thermodynamic standpoint can be viewed as a process of metal trying to go back to its natural stable
form (oxides) [57]. For example, under standard conditions \((T = 298.15 \text{ K}, p = 100\text{kPa})\), the chemical potential of \(\text{Fe}_2\text{O}_3\) and \(\text{Fe}_3\text{O}_4\) are -741.04 kJ/mol and -1017.48kJ/mol respectively, which indicates that Fe would spontaneously combine with oxygen to form Fe-oxides [58]. Therefore, the main aim of the corrosion scientist/engineers is to delay the corrosion process so as to enhance the longevity of a product in the given environment.

In a broader perspective, corrosion can be classified as wet (aqueous) and dry corrosion, and they both are electrochemical processes [57]. Wet corrosion is a process where the metal interacts with a liquid environment (electrolyte) either at room or elevated temperature and deteriorates. Dry corrosion is a process where the metal interacts with an oxidizing gas (oxygen, carbon dioxide, sulphur, etc.) either at room or elevated temperature and deteriorates.

Before proceeding to the description of the electrochemical nature of corrosion, the difference between a chemical reaction and an electrochemical reaction is stated for clarity. In the former, there is no change in the valence electrons in reactants and products involved, whereas, in the latter, there is a change in valence electrons [59]. For example, a chemical reaction and an electrochemical reaction are shown below [59],

No change in valence electrons: \(\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2\)  
Change in valence electrons: \(\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-\)

\[2.3\]
\[2.4\]

2.7.1 Principle of corrosion – electrochemistry

As mentioned above, corrosion is an electrochemical process involving redox reactions (sum of oxidation and reduction half-cell reactions), dissolution/oxidation happens at one portion of the metal, and deposition/reduction happens at other portion. The portion where the metal loss happens (increase in oxidation number/loss of electrons) is called an anode and where the reduction happens (decrease in oxidation number/gain of electrons) is called a cathode.

The metal dissolution half-cell reaction can be written as [60],

\[\text{M} \rightarrow \text{M}^{n+} + \text{n}\text{e}^-\]

And the most commonly occurring reduction half-cell reaction can be written as [60],

**Hydrogen reduction**  
\[2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\]

**Water reduction**  
\[2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-\]

**Oxygen reduction in alkaline environment**  
\[\text{O}_2 + 4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-\]

**Oxygen reduction in acidic**  
\[\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}\]
environment

Metal ion reduction \[ M^{3+} + e^- \rightarrow M^{2+} \] [2.10]

The locations of anode and cathode are generally on the same metal surface at different points which are in contact with an electrolyte and they arise due to the difference in electrochemical potential locally. This potential difference can be due to the heterogeneous microstructure of the metal surface and/or due to the variation in the electrolyte. So for corrosion to initiate/progress, there must be an anode (where dissolution happens), a cathode (where reduction of ionic species happens), electrolyte (for ionic conduction) and an electrical path between anode and cathode for electronic conduction [61].

2.7.2 Electrode potential difference

When a metal is immersed in an electrolyte, due to charge separation a potential difference between the metal and electrolyte is induced which is called the electrode potential difference. As it is impossible to measure the absolute value of the mentioned potential difference, only a relative electrode potential difference is measured as a compromise with respect to a common reference electrode potential difference. This common reference electrode potential difference is the standard hydrogen electrode potential difference which is assumed as 0V.

\[ E_M = \varphi_{H_2} - \varphi_M \] [2.11]

where,
- \( E_M \) is the relative electrode potential difference
- \( \varphi_{H_2} \) is the absolute electrode potential difference of hydrogen electrode
- \( \varphi_M \) is the absolute electrode potential difference of metal electrode

Based on the above definition, a standard electrode reduction potential table is generated for different metals, from which their tendency to corrode can be predicted. The electrode potential difference indicates the driving force for a metal to corrode in the standard environment condition (298K, 1atm, 1mol/lit of the same dissolved species) [63]. The above relation is valid only when the \( \varphi_{H_2} \) and \( \varphi_M \) are at standard condition, and for non-standard conditions, Nernst equation is used which is given by the following relations [62]:

For a single electrode \[ E = E^0 - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]} \] [2.12]

For double electrodes \[ \Delta E = \Delta E^0 - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]} \] [2.13]

where,
E is the electrode potential difference at non-standard condition
E° is the electrode potential difference at standard condition
R is the gas constant (8.314 J/mol. K)
F is the Faraday’s constant (96500 C/mol)
T is the temperature in K

Using the Nernst equation, Porbaix [63] constructed plots of potential vs. pH for different metals, which can be used to predict the stability of a metal in water. There are three distinct regions such as immune, corroding and passive region in the potential vs. pH plots. Based on the pH and potential values, the state of the metal under investigation can be predicted.

In the following, a brief description of the potentials that are related to the electrode-electrolyte interface is given.

2.7.2.1 Electrolyte

Under the equilibrium condition, there is no net directed electric field present in the bulk of the electrolyte [64], and there will be a balance between the number of positive ions and negative ions. But at the interface, the condition is not the same as the bulk, there will be an orientation of ions surrounded by a hydration shell near the electrode surface in the electrolyte. That is, in a narrow boundary region within the electrolyte, electroneutrality is lost [64]. The electrified boundary region of the electrolyte induces an equal and opposite net charge on the electrode side of the boundary region. If the electrode is a metal, then the free electrons rearrange themselves in the boundary/interface region to establish the local electroneutrality. This induced charge separation at the interface, leads to a potential difference between the electrolyte and electrode. The electrified interface is called the electrical double layer or double layer [65].

2.7.2.2 Potential

It is the work done to move a unit charge (electrons or ions) from an arbitrary starting point to an ending point. Its unit is Volt (Nm/C).

2.7.2.3 Outer potential (Ψ)

This is also known as Volta potential. The work done to move a unit charge from an infinite distance in vacuum/insulator towards a charged conductor (electrode or electrolyte) until a plane where the influence of image force due to the conductor is zero is called the outer potential [64]. Ψ_M is the outer potential of the electrode and Ψ_S is the outer potential of the electrolyte. This is schematically shown in Figure 2.6a. The outer potentials of electrode and electrolyte are described independently, and it is based on a thought experiment to understand that there exists a potential just outside their corresponding phases.
2.7.2.4 Outer potential difference ($M\Delta S\Psi$)

This is also known as contact potential difference or Volta potential difference. It is the difference in outer potentials of electrode and electrolyte at the interface [64]. This is due to the presence of charge separation [64].

$$M\Delta S\Psi = \Psi_M - \Psi_S$$  \hspace{1cm} 2.14

2.7.2.5 Surface potential ($\chi$)

This is also known as dipole potential [64]. The description of this potential is also based on a thought experiment. In an electrolyte, ions along with the solvent dipoles rearrange themselves and electrify the interface. If the charge is removed and only the reorganized solvent dipoles are retained, then the work done to move a unit charge from an infinite distance in vacuum/insulator towards the electrolyte interface is called the surface potential of the electrolyte ($\chi_S$) [64]. This is schematically shown in Figure 2.6b. Even in metal electrodes, there will be a dipole layer formation due to the electron jumping the potential wells leaving behind a positively charged surface, then the work done to move a unit charge from an infinite distance in vacuum/insulator towards the metal electrode across the interface is called the surface potential of the metal electrode ($\chi_M$) [64].

2.7.2.6 Surface potential difference ($M\Delta S\chi$)

It is the difference in surface potentials of electrode and electrolyte at the interface [64]. This is due to the presence of a dipole layer [64].

$$M\Delta S\chi = \chi_M - \chi_S$$  \hspace{1cm} 2.15
2.7.2.7 Inner potential (φ)

This is also known as Galvani potential. The two sequential work done to move a unit charge from an infinite distance in vacuum/insulator to inside of the charged conductor (electrode or electrolyte) is called the inner potential [64]. This is the sum of outer potential and surface potential [64].

\[ \phi = \Psi + \chi \]  \hspace{1cm} 2.16

2.7.2.8 Absolute electrode-electrolyte potential difference (Δφ)

This is also known as Galvani potential difference [64]. Both outer potential difference (\( M\Delta^S\Psi \)) and surface potential difference (\( M\Delta^S\chi \)) contributes to the total electric potential difference across the electrode-electrolyte interface [64]. The sum of \( M\Delta^S\Psi \) and \( M\Delta^S\chi \) is called the total or absolute electric potential across an electrode-electrolyte interface [64].
Δφ = ΔΨ + Δχ

2.7.2.9 Chemical potential (µ)

The interaction of the unit charge described above was until it reaches just inside the conductor surface and its interaction within the conductor was not described. In the case of an electrolyte, the unit charge has to encounters the ion-solvent, ion-ion, and solvent-solvent interactions [64]. The description of this potential is also based on a thought experiment. The work done to move a test charge from an infinite distance in vacuum/insulator to inside the electrolyte in the absence of the Galvani potential is called the chemical potential of the electrolyte (µe) [64]. Likewise, µm is the chemical potential of the electrode.

2.7.2.10 Electrochemical potential (µe)

This is the sum of electrical potential and chemical potential. The total work done to move a unit charge from an infinite distance in vacuum/insulator to inside the electrolyte in the presence of the Galvani potential is called the electrochemical potential of the electrolyte (µes) [64]. Likewise, µem is the electrochemical chemical potential of the electrode.

2.7.2.11 Electrochemical equilibrium

The electrochemical potential across an interface is equal at electrochemical equilibrium [65]. This does not mean that the electrical and chemical potential across the interface becomes the same, instead, the opposing difference in electrical and chemical potential are in balance [65].

2.7.2.12 Work function (Φ)

The work necessary to move an electron from the metal to a position just outside the insulator/vacuum (until a plane where the influence of image force, refer Figure 2.6a) is called the work function of the material [64]. Each phase will have its own work function. It is the sum of chemical potential and surface potential but with a negative sign as per the convention [64].

$$\Phi^M = -\mu^M - ZF\chi^M$$

As the unit charge considered here is electron, the work function relation becomes,

$$\Phi^M = -\mu^M + F\chi^M$$

2.7.3 Electrode kinetics

Kinetics sheds light on the rate of corrosion. Faraday’s first law of electrolysis states that the amount of metal dissolving/depositing is directly proportional to the amount of
current passed through that electrode [62]. From this, the rate of metal dissolution per unit time per unit area is given by the following relation [66]:

$$\frac{dw}{A \times dt} = \frac{i \times a_m}{n \times F}$$

where,

dw/A x dt is the mass of metal dissolved / unit time / unit area (g/s/unit area)
i is the current density involved in the corrosion process (A/ unit area)
am is the atomic weight of the metal dissolving (g/mol)
n is the valence
F is the Faraday’s constant (96500 C/mol)

Corrosion rates are generally measured in mdd ($\frac{\text{milligrams}}{\text{decimeter}^2 \times \text{day}}$) or mpy ($\frac{\text{milli inch}}{\text{year}}$) [61].

The corrosion rate of a metal can be estimated from the corrosion current density ($i_{corr}$), which can be determined by polarizing the metal from the corrosion potential ($E_{corr}$) in both anodic and cathodic directions. Polarization in the context of corrosion means a deviation of metal-electrode potential from its $E_{corr}$ value by passage of current [57]. The magnitude of polarization is called the overpotential ($\eta$) [63]. Electrode potential of a metal in an electrolyte can be polarized anodically and cathodically by activation and/or concentration polarization. Activation polarization is based on altering the charge transfer reactions happening at the electrode-electrolyte interface and the concentration polarization is based on altering the concentration of ions in the electrolyte available at the interface for reaction.

For a reversible reaction in equilibrium ($M \leftrightarrow M^{n+}+ne^{-}$), the rate of forward reaction is equal to the rate of reverse reaction, i.e., the current densities of the forward and backward reactions are equal, and it is called the exchange current density ($i_0$) [63]. At equilibrium condition, there is no net transfer of charge, i.e., the dissolution rate is equal to the deposition rate. Polarization of an iron electrode from its equilibrium potential, vs. the current density is schematically shown in Figure 2.7a. In a system where multiple redox reactions happen simultaneously, in order to maintain charge conservation, the overall rate of oxidation reactions will be equal to the overall rate of reduction reactions [67]. At this condition, the metal-electrode becomes the mixed electrode and the potential at which the overall rate of oxidation reactions and overall rate of reduction reactions are equal is called the mixed potential or corrosion potential ($E_{corr}$), and the corresponding current density is called corrosion current density ($i_{corr}$) [67]. This is schematically shown in Figure 2.7b for an iron-hydrogen system.

Corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$) can be estimated from actual polarization curves by Tafel extrapolation analysis. By extrapolation of the linear region in the anodic and cathodic portion of the curve (Figure 3.7b), the corresponding
potential and current density at the intersection point are estimated as $E_{corr}$ and $i_{corr}$ respectively. The slopes of the linear region are called Tafel slopes ($\beta_{anodic}$, $\beta_{cathodic}$) and their values shed light on what is the overpotential (activation energy required for charge transfer reaction at the electrode interface) required for the system to move from the equilibrium potential for anodic and cathodic reactions towards the corrosion potential, i.e., when $\beta_{anodic} > \beta_{cathodic}$, the system is said to be in anodic control indicating that the $E_{corr}$ is close to the equilibrium potential of the cathode and vice versa [67].

![Figure 2.7](image)

**Figure 2.7:** (a) Polarized Fe electrode, (b) Electrode kinetics of Fe and H electrodes [68].

### 2.7.4 Surface film on iron/steel

When iron/steel interacts with an aqueous electrolyte or air, a protective (non-porous) or non-protective (porous) surface film forms. The protective surface film is also known as a passive film, as it reduces the substrate’s activity with the environment [69]. The mechanism of a passive film formation is different from a non-protective surface film formation. In the former, the surface film forms by a direct growth due to the metal-environment interaction, whereas in the latter it forms by a deposition process which in the first place happened due to dissolution of the metal surface [69]. The non-protective surface film on iron/steel is known as rust [70]. When iron/steel interacts with weakly acidic, neutral, or alkaline environment they have a tendency to passivate with the passive layer being different for different conditions, but if they are not spontaneous then the iron/steel will rust which in turn implies that a substantial amount of corrosion product will be required for slowing down the corrosion of underneath substrate [69].

The general corrosion products that are formed when iron/steel interacts with an electrolyte layer containing oxygen are ferric oxyhydroxides ($\alpha$-, $\beta$-, $\gamma$-FeOOH),
magnetite (Fe₃O₄) and amorphous ferric oxyhydroxides (FeOₓ (OH)₃₋₂ₓ) [71, 72]. Their formations can be represented by the following reactions [60, 70]:

Anodic reaction  
4Fe → 4Fe²⁺ + 8e⁻  \[2.21\]

Cathodic reaction  
2O₂ + 4H₂O + 8e⁻ → 8OH⁻  \[2.22\]

Redox reaction  
4Fe + 2O₂ + 4H₂O → 4Fe²⁺ + 8OH⁻  \[2.23\]

The ferrous ion further oxidizes to ferric ions [60, 70]:

Anodic reaction  
4Fe²⁺ → 4Fe³⁺ + 4e⁻  \[2.24\]

Cathodic reaction  
O₂ + 2H₂O + 4e⁻ → 4OH⁻  \[2.8\]

Redox reaction  
4Fe²⁺ + O₂ + 2H₂O → 4Fe³⁺ + 4OH⁻  \[2.25\]

The ferric ions react with hydroxyl ions and forms oxyhydroxides [70]:

4Fe³⁺ + 12OH⁻ → 4(FeOOH) + 4H₂O  \[2.26\]

Also, the ferrous ions can react with hydroxyl ions and form ferrous hydroxide, which can react further with oxygen and water to form iron (III) oxide-hydroxide [60]. The iron (III) oxide-hydroxide is the hydrated form of oxyhydroxide (FeOOH). These reactions are shown below [60],

Fe²⁺ + 2OH⁻ → Fe(OH)₂  \[2.27\]

2Fe(OH)₂ + O₂ + 2H₂O → 4Fe(OH)₃  \[2.28\]

The oxyhydroxide reacts with ferrous ions and forms magnetite [73],

2γFeOOH + Fe²⁺ → Fe₃O₄ + 2H⁺  \[2.29\]

The spontaneity of passive film formation depends upon the potential of the metal-electrolyte system, which can be explained by potential vs. current density plot (Figure 2.8a). In portion a-b, metal dissolves and the rate of dissolution increases exponentially with the potential. In portion b-c the dissolution rate decreases with increasing potential indicating the formation of passive film. In portion c-d, the dissolution is maintained at a constant rate indicating the presence of a passive film. In the passive region, the dissolution of metal remains constant even with increasing potential. In portion d-e, the dissolution again increases indicating the breakdown of the passive film. The terminologies other than E₀ and i₀ associated with this type of behavior are:

E_pp – primary passive potential
i_c – critical anodic current density for passivation
E_pit – pitting potential or breakdown potential
i_p – passive current density
If the $E_{corr}$ for a metal-electrolyte system is established in such a way that the cathodic reaction intersects the passive region of the metal, then the metal will spontaneously form a passive film. This is shown in Figure 2.8b.

![Diagram](image)

**Figure 2.8:** (a) Active - passive anodic polarization of a metal, (b) Passive corrosion behavior of a metal due to the polarized cathodic reaction [68].

### 2.7.4.1 Surface films on stainless-steels

Steels containing a minimum of ca.10.5 wt.% chromium as one of their alloying elements can be called stainless steels, and when they interact with an electrolyte, they form an oxide-hydroxide surface film (primarily composed of chromium oxide along with iron and molybdenum oxides) with a thickness of ca.1-3 nm which helps them in hindering the dissolution of the underlying substrate [74].

### 2.7.5 Pitting

As mentioned above, passive film forms on the metal surface at higher over potential. When the passive film breaks/damages locally, the driving force available for corrosion at that location becomes higher, thus leading to pitting corrosion which is a form of localized corrosion. There are three consecutive stages in the process of pitting: (1) passive film destruction (mechanical/chemical) leading to pit nucleation, (2) metastable pitting, and (3) stable pitting (pit propagation) [75]. As the name suggests, metastable pits may heal themselves, and the reason for the metastable pitting is the formation of a porous pit cover that acts as a barrier (ohmic [76], diffusion [75]) between the pit and outside electrolyte, and when the pit cover breaks, pits repassivates [76]. They generally have a lifetime ca. less than 5 s [77] and whichever survives longer will transform into a
stable pit. The transition from metastable pitting to stable pitting at high potentials may happen by a metal salt layer formation, which will be one to several microns thick based on the polarization potential [77]. The reason for the metal salt layer formation is described by the following [78]:

Metal dissolution – inside the pit
\[ M \rightarrow M^{n+} + n e^- \] 2.5

Oxygen reduction – outside the pit in aerated medium
\[ O_2 + 4H_2O + 4e^- \rightarrow 4OH^- \] 2.8

The dissolved metal cations will attract anions such as Cl⁻ ions into the pit to maintain charge neutrality [78], forming metal salts (M⁺Cl⁻) inside the pit. OH⁻ ions will also be attracted but they are relatively less mobile compared to Cl⁻ ions and hence their migration towards the pit is slow [78]. After reaching the saturation limit, the concentration of M⁺ cations and Cl⁻ anions in the pit electrolyte will be determined by the saturation limit of the metal salt, and for further dissolution to happen the M⁺ cations have to move out of the pit electrolyte [77]. This outward movement of M⁺ cations can happen due to the presence of a concentration gradient (diffusion) and/or potential gradient (electro-migration), however, the former is more predominant [77] which is independent of the pitting potential.

The metal cations also undergo hydrolysis as described below:

The metal dissolution half-cell reaction inside the pit can be written as [79],
\[ M \rightarrow M^{n+} + n e^- \] 2.5

The dissolved M⁺ in the pit electrolyte will hydrolyze and the reactions can be written as [79],

Stage 1 cationic hydrolysis
\[ M^{n+} + H_2O \rightarrow M(OH)^{(n-1)+} + H^+ \] 2.30

Stage 2 cationic hydrolysis
\[ M(OH)^{(n-1)+} + H_2O \rightarrow M(OH)_2^{(n-2)+} + H^+ \] 2.31

The number of stages of hydrolysis depends upon the valence of dissolving ion [79]. As we see from the product side of the above hydrolysis reactions, H⁺ ions are generated inside the pit making the pit electrolyte acidic. This makes the hydrogen reduction as the dominant cathodic reaction inside the pit. This is given by the following reaction [79]:
\[ 2H^+ + 2e^- \rightarrow H_2 \] 2.6

This acidic environment inside the pit supports continued pit propagation.

Critical factors (rate controlling) that are responsible for stable pitting concern two perspectives: (1) stable pitting will form only when the passive film fails, (2) the pit will only be stabilized under specific critical condition even when the passive film has failed.
Hence, in describing the mechanism of pitting for a particular metal electrode–electrolyte system, the appropriate one will be the rate limiting perspective [80].

**2.7.6 Stress corrosion cracking**

Stress corrosion cracking (SCC) is a cracking phenomenon and hence it should not be associated with the defect generation phase such as corrosion pits, machining defects, polishing defects, etc., which acts as precursors to cracking. SCC is an environmentally induced cracking process, in which the material fails well below its permissible strength due to the simultaneous interaction of stress, environment and the susceptible material (Figure 2.9). The term SCC does not indicate the mechanism by which the material fails and hence it is only a macro phenomenological term [81].

A crack can grow due to SCC in a stable manner with a crack velocity less than one third the speed of sound in the material [81], and when the crack dimensions reaches a critical value, i.e., when the fracture toughness of the material is exceeded, crack grows at a faster rate (one third the speed of the sound in the material [81]) eventually leading to fracturing of the structure. Since the final fast fracture (catastrophic growth phase) is delayed by the preceding stable crack growth phase (due to SCC), the failure mode is sometimes referred as delayed fracture/delayed failure [81]. The term sub-critical crack growth is also used for mentioning the stable crack growth phase (due to SCC) by the fracture mechanics community to elucidate that the stress intensity near the crack tip is less than the critical value (fracture toughness) to cause the initiation of final fracture phase [81].

SCC cracks can be divided into small cracks and long cracks. Crack length < 1mm can be considered as small cracks, and greater than that can be considered as long cracks [82]. For small cracks, fracture mechanics similitude breaks down [82] and hence damage tolerant approach cannot be used for predicting the failure rate.

Several mechanisms have been proposed for SCC crack growth, but here only active path dissolution and hydrogen-related mechanisms are described since they are more prominent in high strength steel failures [83-85].
2.7.6.1 *Active path dissolution*

This mechanism is also called slip-dissolution, film-rupture, and anodic-dissolution mechanisms [87]. In this mechanism, sub-critical crack growth generally starts from a favorable point where the loading is maximum and perpendicular within a preexisting defect and as they propagate, a plastic zone around them (crack tip) inside the material forms [88], causing the grown crack tip to blunt [89]. Further propagation happens by localized corrosion of new/fresh surface which gets exposed to the corrosant by the preceding cracking, followed by the mechanical reason as mentioned above. Cracking will only proceed when the repassivation rate of the crack tip is slower than the corrosion rate, if not it will stop proceeding [90]. The specific path of dissolution depends upon the microstructure of the material. Both corrosion and the stress act synergistically during the sub-critical crack growth.

2.7.6.2 *Hydrogen based mechanisms*

There are many proposed mechanisms for the role of hydrogen in the embrittlement of metals, such as adsorption induced dislocation emission (AIDE), hydrogen enhanced localized plasticity (HELP), and hydrogen enhanced de-cohesion (HEDE). In AIDE, the adsorbed hydrogen diffuses into the metal ahead of the crack and weakens the interatomic bond causing dislocation emission or de-cohesion [87]. The hydrogen at the crack tip along with the diffused hydrogen inside the metal, ahead of the crack tip, are collectively known as adsorbed hydrogen [87]. In HELP, the hydrogen atoms diffuse into the metal and interact with the dislocations in the plastic zone which is ahead of the crack causing the mobility of dislocation to increase, which in turn causes a localized ductile fracture (slip/micro-void coalescence) [87]. In HEDE, the cracking happens similar to AIDE by de-cohesion of the interatomic bonds, except here the interface is for a greater depth ahead of the crack tip [87].

---

**Figure 2.9:** Conditions required for stress corrosion cracking to occur [86].
CHAPTER 3 – Experimental: Theory and Practice

This chapter consists of three parts. The first part focuses on metallurgical investigations, the second part focuses on corrosion-related investigations, and the third part focuses on a method development for characterizing the stress relief due to tempering and the experimental procedure followed in testing the environment-assisted cracking behavior of the MSS.

Part 1

3.1.1 Studied Material and the samples

The typical chemical composition of the steel investigated in this work in wt.% is given in Table 3.1.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>V</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.37</td>
<td>0.96</td>
<td>0.47</td>
<td>13.8</td>
<td>0.3</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 3.1. The typical chemical composition of AISI 420 MSS studied in wt.%.

Samples of different sizes were cut along the rolling direction from a slab of 4000 mm x 350 mm x 40 mm dimensions in the soft annealed condition, and machined to the required dimensions.

3.1.2 Heat treatments performed

From the soft annealed condition, samples were hardened in a vacuum furnace followed by tempering in a muffle furnace. Hardening comprises of austenitizing and quenching processes and the detailed industrial procedure followed can be found elsewhere [91]. The samples were austenitized at 1020°C for 30 min followed by quenching in nitrogen gas at two different cooling rates to simulate fast quenching, \( t_{800-500} = 105s \) (3°C/s) and slow quenching, \( t_{800-500} = 526s \) (0.6°C/s). Then the samples were tempered at 250°C for 2 hours twice followed by air cooling. The heat treatment cycle is schematically shown in Figure 3.1.
Figure 3.1: Schematic illustration of the heat treatment cycle. The quenching rate was $X^\circ C/s = 3^\circ C/s$ and $0.6^\circ C/s$ and the tempering temperature was $Y^\circ C = 250^\circ C, 500^\circ C$, respectively.

### 3.1.3 Dilatometry

Heat treatment cycles, thermo-mechanical cycles, and thermal expansion/compression measurements can be performed in a dilatometer. An induction furnace and a cooling system are the primary units of a basic dilatometer, in which a gas (nitrogen, helium, and argon) quenching is generally employed [92, 93]. Cylindrical samples are generally used and its change in length during the cycles/measurements are recorded. The results are then plotted in the form of a graph with dilatation % (change in length / original length) on the y-axis and temperature on the x-axis [92]. Volumetric changes during heating and cooling in metallic materials can be due to the change in its thermal coefficient of expansion/compression, and also due to phase transformations. Hence, by using the dilatometer, phase transformations for different heat treatment cycles can be predicted. It is also used to generate time-temperature-transformation (TTT) diagrams that are also known as isothermal transformation diagrams.

In this work, to identify the phase transformations during hardening treatment, measurements were done on Ø3.0 x 10.0 mm, soft annealed samples using dilatometer DIL 805 from TA instrument with a resolution ($\Delta l/\circ C$) of $0.05\mu m/0.05^\circ C$. The sample was heated from $25^\circ C$ to $1020^\circ C$ at the rate of $199^\circ C/min$ and held at that temperature for 30 min, followed by quenching at a cooling rate of $T_{800-500} = 105s$ ($3^\circ C/s$), and $T_{800-500} = 526s$ ($0.6^\circ C/s$), respectively, using helium gas. The volumetric changes of the sample were collected, and the data was plotted as change in length vs. temperature.

### 3.1.4 Phase prediction using Thermo-Calc

Simulation was done for the chemical composition given in Table 3.1 using Thermo-Calc software TCFE7 steels/Fe-alloys database to obtain equilibrium phases and their volume fractions for the austenitization process.
3.1.5 Mechanical testing

3.1.5.1 Hardness measurement

Hardness is the measure of resistance to permanent deformation from a design engineer point of view [94]. There are many hardness scales among which Rockwell C (hardened and tempered condition), Vickers (hardened and tempered condition) and Brinell (soft annealed condition) scales are used for tool steels [37]. In Rockwell C hardness measurement, an indenter (diamond cone indenter with 120°) is made to penetrate the sample surface by applying an initial load (10 kg) for positioning the sample followed by a major load (150 kg), and the corresponding depth of penetration is measured and the hardness values are reported as arbitrary numbers ranging from 20 HRC to 70 HRC [95]. There is no unit for Rockwell hardness number, whereas Vickers hardness are measured in kgf/mm² or N/mm² [94]. In Vickers hardness measurement an indenter (diamond pyramid) is made to penetrate the sample surface by applying a load, and the surface area of indentation is measured optically by the diagonals of the square indent from which the hardness values are calculated from the following expression [94]:

\[
HV = \frac{1.854 \times P}{L^2}
\]

where,

- \( P \) – applied load in kg
- \( L \) – average length of the diagonals in mm

In this work, prior to hardness measurement, samples were first wet ground and then polished using 1 μm diamond suspension, followed by ultrasonically cleaning in ethanol for 10 min and drying in air. Rockwell C hardness was measured on polished samples at five locations on the surface using a Zwick/Roell ZHR hardness tester and the average values were reported.

3.1.5.2 Tensile testing

From the stress vs. strain plot of a material, a set of behavioral indicators like yield strength (N/mm²), Young's modulus (N/mm²), ultimate tensile strength (N/mm²), percentage elongation (measure of ductility), percentage area reduction (measure of ductility) can be obtained.

In this work, cylindrical tensile specimens with 35 mm gauge length and 5 mm gauge diameter were polished along the gauge length using 220 grit SiC paper. The tests were performed in an MTS hydraulic testing machine with a strain rate of 0.00025 s⁻¹ till yield point and 2.1 mm/min as the cross head speed thereafter. Three samples per heat treated conditions were tested and the average value was reported.
3.1.5.3 Impact testing

The ability of a material to absorb energy during fracture under high strain rate is called the impact toughness [96]. To determine the impact toughness, a heavy pendulum is released from a known height and made to strike on a specimen, and after breaking, the final height reached by the pendulum is measured. From the initial and final heights, potential energies are calculated and their difference is reported as the impact toughness [96]. Either a notched or un-notched specimen can be used. The impact toughness of an un-notched and notched specimens indicates the resistance of the material to crack initiation and crack propagation respectively [37]. The former is also a measure of ductility [37].

In this work, un-notched impact toughness of fast quenched and slow quenched samples tempered at 250°C, and 500°C, respectively, were determined using a ROELL AMSLER impact tester. The dimensions of un-notched specimen were 7 mm x 10 mm (cross-section) x 55 mm. Three samples per heat treated conditions were tested and the average value was reported.

3.1.6 Microstructural observation

3.1.6.1 Sample preparation

Overview of the steps taken in preparing the samples for microstructural observation, XRD analysis, SKPFM measurements, in-situ AFM measurements, and electrochemical measurements are listed in Table 3.2.

**Table 3.2: Sample preparation steps used in this work.**

<table>
<thead>
<tr>
<th>Steps</th>
<th>Preparation</th>
<th>Using</th>
<th>Time (ca.)</th>
<th>Composition</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rough grinding</td>
<td>120 grit SiC grinding stone</td>
<td>1 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Fine grinding</td>
<td>9μm diamond suspension</td>
<td>5 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Polishing</td>
<td>3μm diamond suspension</td>
<td>5 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Polishing</td>
<td>1μm diamond suspension</td>
<td>1.5 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Polishing</td>
<td>14μm diamond suspension</td>
<td>1 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Cleaning</td>
<td>In ethanol under sonication</td>
<td>10 min</td>
<td>5 cc HCl + 2 gr picric acid + 100 cc ethyl alcohol [x]</td>
<td>RT</td>
</tr>
<tr>
<td>7</td>
<td>Cleaning</td>
<td>In ethanol</td>
<td>10 s</td>
<td>0.7 ml ethanol + 0.1 ml ethylene glycol + 0.12 ml water + 0.08 ml perchloric acid</td>
<td>35V, RT</td>
</tr>
<tr>
<td>8</td>
<td>Drying</td>
<td>In air</td>
<td>10 s</td>
<td>95 vol. % ethanol + 5 vol. % perchloric acid</td>
<td>35V, 0°C</td>
</tr>
<tr>
<td>9</td>
<td>Chemical etching</td>
<td>Vilela’s reagent</td>
<td>106 - 208s</td>
<td>5 cc HCl + 2 gr picric acid + 100 cc ethyl alcohol [x]</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Electro polishing</td>
<td>Disa electrolyte</td>
<td>10 s</td>
<td>0.7 ml ethanol + 0.1 ml ethylene glycol + 0.12 ml water + 0.08 ml perchloric acid</td>
<td>35V, RT</td>
</tr>
<tr>
<td>11</td>
<td>Electro polishing</td>
<td>Electrolyte</td>
<td>10 s</td>
<td>95 vol. % ethanol + 5 vol. % perchloric acid</td>
<td>35V, 0°C</td>
</tr>
</tbody>
</table>

3.1.6.2 Light optical microscopy (LOM)

There are four essential components which constitute basic LOM: (a) a light source, (b) condenser lens, (c) objective lenses and (d) ocular lenses (eyepiece) [97]. First, the light illuminates the object (to be scoped) through condenser lenses, then the reflected light from the object is made to pass through the objective lenses to ocular lenses where the
image of the object is viewed by the observer [98]. Ernst Karl Abbe enunciated the theory of image formation in LOM, according to which there are three basic actions through which images are formed: (a) diffraction of the incoming light at the sample surface, (b) collection of those diffracted beams by the objective lenses, and (c) interference of collected diffracted and non-diffracted beams (which is un-deviated even after passing through the objective lens) in the image plane [99]. Actually, each point in the image has a distribution of intensity of light and not a single intensity value, which is schematically shown in Figure 3.2a [100], i.e., a point in the image is a diffraction pattern that is formed due to an interference of the diffracted beams. Hence by capturing more diffracted beams by the objective lens, more interference among them happens which in turn will form a better image. The ability of the objective lens to capture more diffracted beams is gauged by a parameter called numerical aperture (NA) which is given by the relation [100],

\[ NA = n \sin \theta \]  

where,

- \( n \) – refractive index of the medium between the sample surface and the objective lens
- \( \theta \) – half angle of the cone of light from the specimen that is accepted by the objective.

From the above relation it can be seen that by increasing the refractive index and/or the half angle, the numerical aperture can be increased. This, in turn, will increase the capacity of the objective lens to capture more diffracted beams. The ability to spatially resolve two diffraction patterns in an image (i.e. two points in an image) is given by Rayleigh criterion [99] according to the following relation:

\[ d = \frac{1.22 \lambda}{2 \text{NA}} = \frac{0.61 \lambda}{\text{NA}} \]  

where,

- \( d \) – minimum distance in \( \mu \text{m} \) that is resolved
- \( \lambda \) – wavelength in \( \mu \text{m} \) of the illuminating source
- \( \text{NA} \) – numerical aperture of the objective

Rayleigh criterion for spatial resolution states that two successive points in an image are resolved when the center of the central peak of a diffraction pattern is coinciding with the first minimum of the successive diffraction pattern [100] as shown in Figure 3.2b.

If we take the wavelength of light as 0.5 \( \mu \text{m} \), the refractive index as 1 (for air), and the maximum angle of angular aperture, which is 90° [100], then the features that are \( \geq 0.305 \mu \text{m} \) can be resolved. By lowering the wavelength and or by increasing the NA, spatial resolution can be further improved.
Figure 3.2: (a) Diffraction pattern of a single spot in an image, (b) diffraction pattern of two adjacent spots in an image that are just resolved [100].

In this work, prior to imaging, samples of either 15 mm x 20 mm x 5 mm or 42 mm x 42 mm x 15 mm dimensions were prepared in the step sequence 1-4, 6, 8, 9, cleaning in water and 8 (Table 3.2). To identify the grain size, grain boundary carbides, and for an overview of the microstructure, the prepared samples were examined using Zeiss Axiophot LOM.

3.1.6.3 Scanning electron microscopy

SEM comprises of three basic assembly units. They are a column (which houses electron gun assembly, condenser lenses, scan coils, and objective lenses), specimen chamber (which houses stage and detectors) and a computer control/processing unit (which comprises of a computer and its accessories to control, record and process the image). Electron gun assembly is classified into three types based on the principle behind electron generation, namely field emission (FE), Schottky, and thermionic gun [101]. Electron gun generates an electron beam which is directed towards the sample positioned in the stage, which is positively charged, through condenser and objective electromagnetic lenses, and scanned along the x, y-direction with the help of scan coils. The entire housing is maintained at low pressure (vacuum), with the column being maintained in a high vacuum compared to specimen chamber to avoid collision of the electron beam with air molecule, which will slow down/prevent the former from reaching the sample surface. Electron beam is used as the probing medium in SEM for its lower wavelength as the resolving power increases with decreasing wavelength. The relation for the motion of stream of electrons is given by the following relation [97]:

\[
\lambda = \frac{h}{mv}
\]

where,
\(\lambda\) – wavelength of the radiation
h – Planck’s constant
mv – momentum of the electrons

From the above relation, it can be seen that the $\lambda$ is inversely proportional to the velocity (v) of the electron beam. The latter is directly proportional to the applied voltage (V) (to the electron gun), which is related to the wavelength of the electron beam by the following approximate relation [97]:

$$\lambda = \sqrt{\frac{150}{V}}$$

where,
$\lambda$ – wavelength of the electron beam in Å
V – applied voltage in V

Due to the interaction between incoming electron beam and sample, the former scatters both elastically and inelastically within the sample leading to the generation of various signals as shown in Figure 3.3, and by choosing a particular mode, corresponding information about the sample can be obtained. The elastic scattering (energy is not lost) and inelastic scattering (energy is lost) of the incoming electron beam occur due to its interaction with the negatively charged electrons in the atoms of the sample and leaves the sample contributing to backscattered electrons [102]. In-elastic scattering of the incoming electron beam generates phonons, plasmons, secondary electrons, continuous X-rays, and characteristic X-rays [103]. The backscattered electrons produced by elastic scattering and inelastic scattering are from immediate sub-surface and deep inside of the sample respectively [104]. The ratio between backscattered electrons generated to incident electrons is called the backscatter coefficient ($\eta$), which increases with increasing atomic number of the elements present in the sample, and this, in turn, contributes to a contrast in the backscattered image called atomic number (Z) contrast [102]. As the secondary electrons (sample’s electrons) possess lower energy (< 50 eV), only those from immediate sub-surface leave the sample surface [102]. Secondary electrons produced by the incoming electron beam is called SE1 and from the exiting electron beam (in-elasctically backscattered electrons) is called SE2 [102], and they both constitute secondary electrons. When the inner shell electrons are bombarded by the incoming electron beam, the outer shell electrons fill in the inner shell and as a consequence, the excess energy is emitted as X-ray photons, which are unique to specific elements, hence the name characteristic X-rays [104]. When the incident electron beam changes its direction it loses some of its energy which is given out as continuous X-rays (also referred to as white X-rays / Brems-Strahlung), and since these are not specific to elements present in the sample they are regarded as the background noise [104].
In this work, prepared samples (same samples used for LOM imaging) were examined using FEI Quanta 600F with field emission gun SEM-EDS. SEM analyses were carried out in the secondary electron (SE) and backscatter electron (BSE) imaging modes at accelerating voltages between 10-20 kV. The size, shape and distribution of the undissolved carbides were characterized. To identify the chemical species present, EDX analysis were performed with X-max SDD 50 mm$^2$ from Oxford Instruments, operated with Aztec V3.3 software.

### 3.1.6.4 Atomic force microscopy

AFM is a characterizing tool that provides information of a surface at high resolution. There are three essential units that constitute a basic AFM: (a) a scanner (which houses a piezoelectric transducer, laser unit, a nose assembly to position the probe and a photodiode), (b) feedback unit and (c) a computer control unit. This is shown in Figure 3.4a. In order to image a surface under AFM, three sequential steps are to be followed, and they are alignment, approach and scanning. A brief description of these steps are given in the following [105]. In the alignment step, the probe is first positioned in the scanner, then the laser beam is aligned in such a way that the incident laser beam reflects off the cantilever and hits the photodiode at the center. In the approach step, the probe is made to approach the sample surface and stopped at a particular limit (which will move the laser spot from the center in the photodiode) based on the mode of operation. In the scanning step, the probe is scanned across the surface, which in turn will move the laser spot from the set point value in the photodiode to a new value based on the tip-sample interaction, and the deviation from the set point (if any) will be fed to the feedback which then will communicate with the piezoelectric transducer and adjusts the position of the scanner accordingly. This correction is further rendered as the image of the sample surface.

![Diagram of SEM signals](image)

**Figure 3.3:** Type of signals generated due to incident electrons in an SEM setup.
AFM is based on the forces that act between the surface of a sample and the probe. The nature of the interactive force can be understood from the force vs. distance of separation curve shown in Figure 3.4b. A brief description of the force vs. separation distance are given in the following [106]. At position 1, the distance between the probe and the surface is quite considerable and hence there will be no interaction between the two. At position 2, the distance is within the interaction regime and hence there will be an attraction and it will continue to be attractive until position 3. At position 4, even though the interaction is repulsive, the net interaction is still attractive, and this will continue to be attractive until position 5. At position 6, the distance between the tip and sample is very close and the interaction will be repulsive in nature.

There are three basic modes of operation such as contact mode, non-contact mode and the intermittent contact mode. A brief description of the AFM modes are given in the following [107]. In contact mode imaging, the tip touches the sample surface and it is scanned across the surface in the repulsive regime of the force-distance curve (Figure 3.4b). Here the deflection of the cantilever is set constant (constant force mode) and its deviation based on the topography is corrected in the piezo through the feedback unit. In the non-contact mode, after the alignment step, the probe is oscillated at its resonance frequency and it is approached towards the sample surface, and the imaging is done in the attractive regime of the force-distance curve (Figure 3.4b). Here the vibration amplitude of the cantilever is set constant and its deviation based on the topography is corrected in the piezo through the feedback unit. In the intermittent contact mode, after the alignment step, the probe is oscillated at its resonance frequency and it is approached towards the sample surface, and the imaging is done in the attractive-repulsive regime of the force-distance curve (Figure 3.4b). As the probe taps the surface, its oscillation gets trimmed on one side and the percentage trimmed
amplitude of the cantilever is set constant (constant force mode) and its deviation based on the topography is corrected in the piezo through the feedback unit.

In this work, to identify the tempering carbides present in the microstructure (paper 2), samples of 15 mm x 20 mm x 5 mm dimensions were prepared in the step sequence 1-4, 7, 8, 11, cleaning in water and 8 (Table 3.2). Prepared samples were examined using Agilent 5500 scanning probe microscope with MAC III controller. The type of probes used was SCM-PIT, and it was purchased from Bruker. The material of the probes was 0.010 – 0.025 Ω-cm Antimony (n) doped Si. The dimensions of the cantilever used were T (thickness) = 2.5 – 3.5µm, L (length) = 200 - 250µm and W (width) = 23 - 33µm. The resonance frequency of the cantilever was 60 – 100 kHz and the spring constant of the cantilever was 1 – 5 N/m. The cantilever was coated with 20nm thick PtIr on both front and back sides. The scanning speed was set at 0.5 lines/second and points/line was set at 512 for all the scan sizes. All the images were post-processed using Gwyddion-2.38 software. The sequential steps for processing the obtained images were: a) level data by mean plane subtraction, b) correct lines by matching height median, c) correct horizontal scars (strokes), d) shift minimum data value to zero.

3.1.7 X-ray diffraction

XRD is a characterizing tool which provides structural information of a crystalline material. The essential units of a basic XRD are: a diffractometer (which houses an X-ray source, sample stage, and a counter which detects the diffracted X-rays) and a computer interface. X-rays (in the X-ray source unit) generated by bombarding a specific target material (Cu, Mo, or Cr) with an incoming electron beam, are collimated and made to fall on the sample surface which is positioned in a stage. The incoming X-rays interact with the sample and get diffracted from the sample surface which are then collected by a counter. When a monochromatic wavelength strikes the sample at a particular diffracted angle satisfying the Bragg’s law, a peak in intensity is generated, which corresponds to the sample’s structural identity. Bragg’s law is given by the following relation [108]:

\[ 2d \sin \theta = n \lambda \] 3.6

where,
- \(d\) - interplanar spacing
- \(\theta\) – diffracted angle
- \(n\) – order of reflection
- \(\lambda\) – wavelength of the X-ray

Continuous measurement of diffracted X-rays can be obtained by either moving the sample with respect to a stationary X-ray source, or vice versa. This technique is used to characterize the crystal structure, lattice parameters, volume fraction of retained
austenite, macro residual stresses, micro residual stresses, etc. In this work, phase identification, determination of volume fraction of retained austenite and macro stress measurements were made.

### 3.1.7.1 Phase identification

In this work, phase identification was done primarily to identify the type of carbides. Samples of 15 mm x 20 mm x 5 mm dimensions were prepared following the step sequence 1-4, 7, 8, 11, cleaning in water and 8 (Table 3.2) for paper 2 and 1-4, 7, 8, 10, cleaning in water and 8 (Table 3.2) for paper 3. Table 3.3 below shows the measurement details.

#### Table 3.3. XRD experimental parameters for phase identification used in this work.

<table>
<thead>
<tr>
<th>Make - Diffractometer</th>
<th>X-ray source</th>
<th>Source voltage</th>
<th>Source current</th>
<th>Scan range</th>
<th>Step size</th>
<th>Scan rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seifert 3000 PTS</td>
<td>Cr</td>
<td>40 kV</td>
<td>35 mA</td>
<td>35° - 160°</td>
<td>0.01°</td>
<td>5 s/step</td>
<td>paper 2</td>
</tr>
<tr>
<td>Bruker Discover D8</td>
<td>Co</td>
<td>35 kV</td>
<td>40 mA</td>
<td>20° - 120°</td>
<td></td>
<td>6 s/step</td>
<td>paper 3</td>
</tr>
<tr>
<td>Bruker Discover D8</td>
<td>Cu</td>
<td>40 kV</td>
<td></td>
<td>10° - 110°</td>
<td></td>
<td>4 s/step</td>
<td>paper 3</td>
</tr>
</tbody>
</table>

Indexing of the XRD peaks was carried out by a manual search-match procedure of all diffraction peaks using the AutoCAD 2017 software (paper 2 and paper 3). Powder diffraction file (PDF) cards of all possible phases in AISI 420 MSS were obtained from the International Center for Diffraction Data (ICDD), as listed in Table 3.4, and used for phase identification. Peak positions of index data were compared with those obtained from standard powder diffraction file (PDF) cards. For identification of secondary carbides in steel tempered at 500°C (paper 3), the steel was immersed in a beaker with 400 ml of 1 M FeCl₃·6H₂O solution at room temperature for 5 days, which enabled chemical dissolution of the matrix material leaving insoluble particles in the solution. Then, the solution was centrifuged at 20000 rpm using the Beckman Optima L-90K Ultra centrifuge for 2 hours, yielding ca. 500 mg of powder. The XRD analysis was performed on the collected precipitates to increase the intensity-to-noise ratio allowing detection of small-sized phases and/or phases in low fractions.
### Table 3.4. PDF card numbers used for phase identification.

<table>
<thead>
<tr>
<th>Phases</th>
<th>PDF Card number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_{23}$C$_6$</td>
<td>00-035-0783</td>
</tr>
<tr>
<td>Cr$_7$C$_3$</td>
<td>00-036-1482</td>
</tr>
<tr>
<td>Cr$_3$C$_2$</td>
<td>00-035-0804</td>
</tr>
<tr>
<td>Cr$_2$C</td>
<td>01-081-8932</td>
</tr>
<tr>
<td>CrC</td>
<td>04-004-4288</td>
</tr>
<tr>
<td>Cr$_3$C</td>
<td>04-003-4577</td>
</tr>
<tr>
<td>Fe$_3$C</td>
<td>00-034-0001</td>
</tr>
<tr>
<td>VC</td>
<td>04-005-9701</td>
</tr>
<tr>
<td>AlN</td>
<td>00-008-0262</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>00-001-1059</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>00-001-1053</td>
</tr>
<tr>
<td>α-FeO(OH)</td>
<td>29-713</td>
</tr>
<tr>
<td>Fe(OH)$_2$</td>
<td>01-073-6991</td>
</tr>
</tbody>
</table>

### 3.1.7.2 Determination of volume fraction of retained austenite

The volume fraction of retained austenite is determined by assuming that the material (hardened steel) contains only martensite and austenite phases [109, 110], i.e.,

\[
c_{\gamma} + c_{\alpha} = 1
\]

Where \( c_\gamma \) and \( c_\alpha \) are the volume fractions of austenite and martensite phase respectively.

The intensity of martensite and austenite phases for a particular hkl plane are given by the following relations,

\[
I_{\gamma(hkl)} = \frac{K R_{\gamma(hkl)} c_{\gamma}}{2\mu_m}
\]

\[
I_{\alpha(hkl)} = \frac{K R_{\alpha(hkl)} c_{\alpha}}{2\mu_m}
\]

where,

- \( I \) – integrated intensity of a particular hkl plane
- \( K \) – constant independent of the kind and amount of the diffracting phase/substance
- \( R_{(hkl)} \) – depends on \( \theta \), hkl and the kind of substance
µm – linear absorption coefficient

\[
R = \frac{1}{v^2} \left| F \right|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) (e^{-2\mu m})
\]

3.10

where,

v – volume of the unit cell

F – structure factor (diffraction taking place from a single unit cell)

p – multiplicity factor

\((1 + \cos^2 2\theta / \sin^2 \theta \cos \theta)\) – Lorentz polarization factor

\((e^{-2\mu m})\) – temperature factor

R-value for a specific hkl plane can be either calculated or found in the literature.

By taking the ratio of integrated intensities of austenite and martensite, the K term and \(2\mu m\) term will cancel out, and the ratio will look like,

\[
\frac{I_{Y(hkl)}}{I_{a(hkl)}} = \frac{R_{Y(hkl)}}{R_{a(hkl)}} \frac{c_Y}{c_a}
\]

3.11

Thus, from the I (measured) and R (calculated) values for austenite and martensite, the volume fraction ratio between austenite and martensite for a specific pair of hkl planes can be obtained. Then by substituting the ratio in relation 3.7, the volume fraction of austenite for a specific hkl plane can be determined. Likewise, by comparing the intensities and their respective R values for many pairs of austenite and martensite planes, several values of volume fraction of austenite can be determined. The average values are reported as the volume fraction of retained austenite in the material.

In this work, the same sample dimensions used for phase identification were prepared in the step sequence 1-4, 7, 8, 10, 7 and 8 (Table 3.2). The volume fraction of retained austenite was calculated based on the assumption that only austenite and martensite phases were present [111]. The volume fraction of both phases was obtained by comparing the integrated intensities of (111), (200), (220) diffracting planes of austenite and (110), (200), (220) diffracting planes of martensite [110]. Post-processing of the data was done and a pseudo-Voigt fitting was used to determine the volume fraction of the retained austenite. The range of the retained austenite value was calculated with a 95% confidence interval. Table 3.5 below shows the measurement details.

**Table 3.5.** XRD experimental parameters for determination of volume fraction of retained austenite used in this work.

<table>
<thead>
<tr>
<th>Make - Diffractometer</th>
<th>X-ray source</th>
<th>Source voltage</th>
<th>Source current</th>
<th>Scan range</th>
<th>Step size</th>
<th>Scan rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seifert 3003 PTS</td>
<td>Cr Kα</td>
<td>40 kV</td>
<td>35 mA</td>
<td>50° - 165°</td>
<td>0.1°</td>
<td>1 s/step</td>
<td>paper 1</td>
</tr>
</tbody>
</table>
3.1.7.3 Determination of macro residual stress

Using XRD, elastic straining of the lattice due to either applied or residual stresses can be measured non-destructively. The general definition of strain is given by the following relation [112]:

\[
\varepsilon = \frac{\text{strained lattice spacing} - \text{unstrained lattice spacing}}{\text{unstrained lattice spacing}}
\]

Before proceeding to the description of stress measurement using XRD, a brief description of the relationships between stresses and strains are given here [113]. According to Hooke’s law, in a triaxial system, strain along any principal direction is the sum of strain caused by the stress acting along that specific direction plus the strain induced due to Poisson’s effect. The relationship between stress and strain is given by the following relations where the shear stresses are assumed to be zero:

\[
\epsilon_1 = \frac{1}{E} \left[ \sigma_1 - \vartheta (\sigma_2 + \sigma_3) \right]
\]

\[
\epsilon_2 = \frac{1}{E} \left[ \sigma_2 - \vartheta (\sigma_3 + \sigma_1) \right]
\]

\[
\epsilon_3 = \frac{1}{E} \left[ \sigma_3 - \vartheta (\sigma_1 + \sigma_2) \right]
\]

where, 
\(\epsilon_{1, 2, 3}\) – strains along principal axes
\(\sigma_{1, 2, 3}\) – stresses along principal axes
\(\vartheta\) – Poisson’s ratio
\(E\) – Young’s modulus

For arriving at the stress-strain relations, an infinitesimal spherical element as shown in Figure 3.5a, from a stressed body is considered. The strain acting along an oblique plane in the spherical element as shown in Figure 3.5a can be resolved along the principal axes and is given by the following:

\[
\epsilon_{\phi \psi} = \epsilon_1 \alpha_1^2 + \epsilon_2 \alpha_2^2 + \epsilon_3 \alpha_3^2
\]

\[
\sigma_{\phi \psi} = \sigma_1 \alpha_1^2 + \sigma_2 \alpha_2^2 + \sigma_3 \alpha_3^2
\]

where,
\(\epsilon_{\phi \psi}\) – strain along the oblique axis
\(\sigma_{\phi \psi}\) – stress along the oblique axis
\(\epsilon_{1, 2, 3}\) – strains along principal axes
\(\sigma_{1, 2, 3}\) – stresses along principal axes
\(\alpha_{1, 2, 3}\) – direction cosines with respect to principal strain and stress axes.
\(\alpha_1 = \cos \phi \sin \psi\)
\[ \alpha_2 = \sin \varphi \sin \psi \]
\[ \alpha_3 = \cos \psi = (1 - \sin^2 \psi)^{1/2} \]

At the surface, \( \sigma_3 \) becomes zero and \( \psi \) becomes 90°. Then the relation 3.17 becomes:

\[ \sigma_\psi = \sigma_1 \cos^2 \varphi + \sigma_2 \sin^2 \varphi \]

3.18

By combining relations 3.13, 3.14, 3.15 and 3.16, we get the general strain equation which is given by the following:

\[ \epsilon_{\varphi \psi} = \frac{1 + \vartheta}{E} (\sigma_1 \alpha_1^2 + \sigma_2 \alpha_2^2 + \sigma_3 \alpha_3^2) - \frac{\vartheta}{E} (\sigma_1 + \sigma_2 + \sigma_3) \]

3.19

Figure 3.5: (a) Spherical element showing all the stresses and strains acting along the axis and also along an oblique direction, (b) stresses/strains acting along the surface of the specimen, (c) \( \epsilon_{\varphi \psi} \) vs. \( \sin^2 \psi \) plot [113].

A brief description of X-ray stress analysis is given here [112, 113]. Figure 3.5b shows the surface of a stressed body. Let \( \sigma_1, \sigma_2, \sigma_3 \) and \( \varepsilon_1, \varepsilon_2, \varepsilon_3 \) be the principal stresses and strains, respectively, acting on the surface of a stressed body. The component of stress acting perpendicular to the surface of the body at the surface will be zero (\( \sigma_3 = 0 \)), but as mentioned above, \( \varepsilon_3 \) will not be equal to zero as it is given by the following relation:

\[ \varepsilon_3 = -\vartheta (\varepsilon_1 + \varepsilon_2) = -\frac{\vartheta}{E} (\sigma_1 + \sigma_2) \]

3.20

\[ \varepsilon_3 = \frac{d_\perp - d_0}{d_0} \]

3.21

\[ \frac{d_\perp - d_0}{d_0} = -\frac{\vartheta}{E} (\sigma_1 + \sigma_2) \]

3.22

where,
\( \vartheta \) – Poisson’s ratio
\( E \) – Young’s modulus
\(d_\perp\) – interplanar spacing of planes perpendicular to the incident X-rays

\(d_0\) – interplanar spacing of the same planes in the unstrained condition

To find \(\varepsilon_3\), \(d_0\) value should be known, but it is difficult to obtain the unstrained lattice spacing non-destructively. So two measurements, one perpendicular to the surface of the body and one along a specific oblique direction, are used to obtain the amount of strain and thereby the surface stress in the material. The strain acting along an oblique plane \(\varepsilon_{\phi\psi}\) in Figure 3.5b is given by the following, which is based on the relation 3.19 where the \(\sigma_3\) term is made zero because of plane strain condition:

\[
\varepsilon_{\phi\psi} = \frac{1 + \frac{\vartheta}{E}}{(\sigma_1\alpha_1^2 + \sigma_2\alpha_2^2)} - \frac{\vartheta}{E} (\sigma_1 + \sigma_2) 
\tag{3.23}
\]

Substituting the values of \(\alpha_1 = \cos \phi \sin \psi\) and \(\alpha_2 = \sin \phi \sin \psi\) in the above relation:

\[
\varepsilon_{\phi\psi} = \frac{1 + \frac{\vartheta}{E}}{(\sigma_1\cos^2 \varphi + \sigma_2\sin^2 \varphi)\sin^2 \psi} - \frac{\vartheta}{E} (\sigma_1 + \sigma_2) 
\tag{3.24}
\]

By substituting relation 3.18 in the above relation 3.24, the basic relationship between strain and surface stresses is obtained, which is the basis for stress measurement using XRD:

\[
\varepsilon_{\phi\psi} = \frac{1 + \frac{\vartheta}{E}}{\sigma_{\phi\psi}\sin^2 \psi} - \frac{\vartheta}{E} (\sigma_1 + \sigma_2) 
\tag{3.25}
\]

Also,

\[
\varepsilon_{\phi\psi} = \frac{d_{\phi\psi} - d_0}{d_0} 
\tag{3.26}
\]

where,

\(d_{\phi\psi}\) – interplanar spacing of planes perpendicular to the incident X-rays

\(d_0\) – interplanar spacing of the same planes in the unstrained condition

Substituting relations 3.22 and 3.26 in relation 3.25,

\[
\frac{d_{\phi\psi} - d_0}{d_0} = \frac{1 + \frac{\vartheta}{E}}{\sigma_{\phi\psi}\sin^2 \psi} + \frac{d_\perp - d_0}{d_0} 
\tag{3.27}
\]

\[
\frac{d_{\phi\psi} - d_0}{d_0} = \frac{1 + \frac{\vartheta}{E}}{\sigma_{\phi\psi}\sin^2 \psi} 
\tag{3.28}
\]

By approximating \(d_0 = d_\perp\) or \(d_{\phi\psi}\),

\[
\varepsilon_{\phi\psi} \approx \frac{d_{\phi\psi} - d_\perp}{d_\perp} = \frac{1 + \frac{\vartheta}{E}}{\sigma_{\phi\psi}\sin^2 \psi} 
\tag{3.29}
\]
In the sin²ψ method, many measurements of strains at different ψ angles for a particular φ angle is measured and the results are plotted with strain values (εφψ) on y-axis and sin²ψ on x-axis, which is schematically shown in Figure 3.5(c), where the surface stress can be obtained by calculating the slope which is given by the following:

\[ m = \frac{1 + \vartheta}{E} \sigma_\phi \quad \text{(3.30)} \]

Knowing the Poisson’s ratio and Young’s modulus, the surface stress \( \sigma_\phi \) can be obtained.

In this work samples of 5 mm x 5 mm (cross-section) x 65 mm dimensions in the bent condition were prepared for stress measurement as per step sequence 10, cleaning in water and 8 (Table 3.2). In order to restrict the polishing area to the center of the sample (concave region of the bent sample), a new masking plate was designed and manufactured to accommodate the bend radius, as shown in Figure 3.6.

![Figure 3.6](image)

**Figure 3.6:** Masking plate used for electropolishing of bent samples.

Macro stresses (type 1) were determined according to the \( \sin^2 \Psi \)-method using the Seifert 3000 PTS X-ray diffractometer with Cr-Kα radiation, operated at 40 kV and 35 mA, with an aperture size of 2 mm. Nine psi (Ψ) angles (0.0, ±20.7, ±30.0, ±37.8, and ±45.0) on the (211) martensite plane with a 2-Theta scan range between 145–165° was chosen for stress determination. Standard X-ray elastic constant (\( 1/2 \ S_2 = 5.81 \times 10^{-6} \) 1/MPa) was used for stress calculations.

**Part – 2**

### 3.2.1 Salt spray test

A salt spray test was performed to investigate the general corrosion behavior of the material. For the salt spray test, the samples of 42 x 42 x 15 mm dimensions were prepared in the step sequence 1-4, 6, and 8 (Table 3.2). Then they were placed inside an Ascott salt spray chamber in equidistance. This was so that they would each receive uniform exposure to the salt spray at room temperature for 6 hours with 0.1M NaCl solution. The exposed samples were compared visually and ranked.
3.2.2 Electrochemical measurements

There are many techniques that can be used for measuring the electrochemical behavior of a metal-electrolyte interface, and the choice depends upon the data needed/availability. The techniques used in this study are briefly described below.

An electrochemical cell with three electrodes was used in this study. The three electrodes are working electrode (sample), reference electrode (saturated Ag/AgCl) and auxiliary/counter electrode (Pt mesh or graphite). All the electrodes were connected to a potentiostat, which in turn was connected to a computer interface. The entire setup is schematically shown in Figure 3.7a.

In this work, prior to electrochemical measurements, samples of either 15 mm x 20 mm x 5 mm or 42 x 42 x 15 mm dimensions were either prepared in the step sequence 1-4, 6, and 8 (Table 3.2) or ground sequentially from 500 grit till 1200 grit SiC paper followed by steps 6 and 8 (Table 3.2).

![Figure 3.7: (a) Electrochemical setup, (b) Cyclic potentiodynamic polarization curve.](image)

**Figure 3.7:** (a) Electrochemical setup, (b) Cyclic potentiodynamic polarization curve.

3.2.2.1 Open circuit potential (OCP)

It is also known as the mixed potential, free corroding potential, or rest potential [67]. The mixed potential is briefly described in section 2.7.3 of chapter 2. The OCP of the working electrode (sample) - electrolyte interface is measured against a reference electrode, which is a non-polarizable electrode meaning that the potential difference across its own interface, i.e., so-called potential of the reference electrode, cannot be changed easily by the passage of current [114]. As mentioned in section 2.7.3 of chapter 2, at OCP the overall rate of anodic reactions will be equal to the overall rate of cathodic
reactions in the system [67]. Generally, OCP of a metal in an electrolyte is measured over time, and the steady-state value gives an indication of the metal’s propensity to anodically dissolve. For example, a positive OCP value indicates a passive behavior of the metal, implying lesser propensity to dissolve, and a negative OCP indicates an active behavior. The internal circuit in the potentiostat between the working electrode and reference electrode should have a high impedance to avoid/prevent the current flow due to measurement, which if allowed will polarize the interface and alter the measured potential [115].

In this work, OCP was measured at room temperature for varying times on samples tempered at different tempering temperatures, as shown in Table 3.6. The results were displayed in a potential (y-axis) vs. time (x-axis) plot.

Table 3.6: Parameters used for monitoring OCP of the samples.

<table>
<thead>
<tr>
<th>Measurement time (h)</th>
<th>Acquisition rate</th>
<th>Electrolyte</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 data points/s</td>
<td>0.1M NaCl</td>
<td>paper 1</td>
</tr>
<tr>
<td>1</td>
<td>5 data points/s</td>
<td>0.1M NaCl</td>
<td>paper 2</td>
</tr>
<tr>
<td>1</td>
<td>5 data points/s</td>
<td>0.01M NaCl</td>
<td>paper 3</td>
</tr>
<tr>
<td>72</td>
<td>1 data point/s</td>
<td>0.01M NaCl</td>
<td>paper 3</td>
</tr>
<tr>
<td>6</td>
<td>1 data point/s</td>
<td>0.3M NaCl</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>6</td>
<td>1 data point/s</td>
<td>0.3M NaCl</td>
<td>paper 5</td>
</tr>
</tbody>
</table>

3.2.2.2 Cyclic potentiodynamic polarization (CPP)

By polarizing the metal a given environment in cathodic and anodic directions, many insights can be gained regarding the interface, such as the dissolution/corrosion rate, tendency to passivate, tendency to re-passivate after pitting, and whether the interface is activation controlled or concentration controlled, etc. In potentiodynamic polarization experiments, the working electrode’s potential is swept from $E_{corr}$ value to desired values at a particular rate. In cyclic polarization measurements, the potential sweep is reversed in order to gain additional information about, pitting propagation and repassivation tendency. The polarization curve is generally plotted with potential on y-axis and current density on x-axis in log scale (Figure 3.7b), and from that values like free corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) can be derived based on electrochemical kinetic theory. Also, values like pitting potential ($E_{pit}$), re-passivation potential ($E_{rp}$), and limiting current density ($i_{lim}$) can be estimated.

Anodic polarization of the working electrode from its $E_{corr}$ value is done by changing the potential to higher values (positive direction) using the potentiostat. In order to compensate for the excess positive charge, the working electrode will generate electrons by the process of dissolution [63]. But if the net charge is positive on the working electrode then it is said to be anodically polarized. Similarly, cathodic polarization of the working electrode from its $E_{corr}$ value is done by changing the potential to lower values
(negative direction) using the potentiostat. In order to compensate the excess negative charge, the positive ions in the solution are attracted towards the working electrode [63]. If the net charge is negative on the working electrode then it is said to be cathodically polarized. Polarization of the working electrode is performed by the electronic circuit in potentiostat which is connected between the working electrode and auxiliary/counter electrode. The required potential difference across the working electrode interface is obtained by passing the necessary current between the working electrode and the counter/auxiliary electrode [115]. The magnitude of the polarization (overpotential) of the working electrode is then obtained by comparing the applied polarization potential with the OCP.

All CPP measurements were performed on samples (exposed to 0.01M, 0.1M, 0.3M NaCl solutions) after the OCP measurement for 1 hour. The starting polarization potential was set to -200mV vs. OCP, i.e., a cathodic polarization of the sample. This was followed by a potential scan toward positive direction vs. OCP, i.e., an anodic polarization which was further followed by a scan reversal. For the start of reversed scan, two limiting conditions were pre-set. The first limit was when the potential reaches 1200 mV vs. OCP, and the second limit was when the anodic current density reaches 100 µA/cm². The reversed scan starts when either of the above-mentioned criteria was satisfied. The purpose of reversed scan is to determine the re-passivation potential, if any. Termination of the scan was set when the anodic potential of the sample after reversal reaches the OCP. The scan rate used was 10 mV/min according to ASTM G61–86 [116]. Scan results were displayed in a potential (y-axis) vs. log io (x-axis) plot. Electrochemical parameters like $E_{corr}$, $i_{corr}$, were obtained by Tafel extrapolation using Corrview2 software. $E_{pit}$ and $E_{rp}$ were obtained from the polarization curves.

### 3.2.3 Scanning Kelvin probe force microscopy

The electrostatic force mode of AFM is briefly described in the following [117, 118]. In conductors, localized valence band electrons occupy the lower energy levels and non-localized conduction band electrons occupy the higher energy levels. There is an intrinsic energy level below which most of the energy levels are occupied and above which most of the levels are unoccupied. This threshold energy level is called the Fermi level, which is the highest occupied energy level (by electrons). Because of an energy barrier called the work function as described in section 2.7.2.12, the conduction band electrons (free electrons) stay intact in the material in spite of their repelling nature due to interactions with neighboring electrons. Each conductor has their own Fermi energy and hence unique work function. When two different metals are connected, electrons will flow from a metal that binds electrons weakly to the one that binds electrons strongly until their Fermi levels are equilibrated. This charging develops a potential difference between the two metals, which is called the contact potential difference and it is equal to the difference in work function between the two metals. One way to measure
this contact potential difference is by using an atomic force microscopy (AFM) where an equal and opposite bias potential is applied between the tip and sample to null the generated contact potential between them.

The contact potential of the substrate is denoted as $V_s(x, y)$.

The voltage applied between the tip and sample to null the generated contact potential is given by the following relation:

$$ V = V_{dc} + V_0 \sin(\omega_1 t) \quad 3.31 $$

where,

$V_{dc}$ – dc voltage applied
$V_0 \sin (\omega t)$ – ac voltage applied.

Both dc and ac voltages are applied simultaneously.

The bias voltage that needs to be applied to null the contact potential difference is given by the electrostatic force between the tip and the sample. The following relation shows the electrostatic force between the tip and sample:

$$ F = -\frac{1}{2} \frac{dc}{dz} (\Delta V)^2 \quad 3.32 $$

where,

$F$ – electrostatic force between the tip and the sample
$\frac{1}{2}$ - force exerted by the sample on tip only
$dc/dz$ – change in capacitance with respect to change in distance between the tip and the sample.
$\Delta V$ – contact potential difference between the tip and the sample.

Then by substituting the contact potential and the bias potential in the electrostatic force relation 3.32, we get,

$$ F = -\frac{1}{2} \frac{dc}{dz} [V_s(x, y) - (V_{dc} + V_0 \sin(\omega_1 t))]^2 \quad 3.33 $$

$$ F = -\frac{1}{2} \frac{dc}{dz} [(V_s(x, y) - V_{dc})^2 + V_0^2 \sin^2(\omega_1 t) - 2 (V_s(x, y) - V_{dc}) V_0 \sin(\omega_1 t)] \quad 3.34 $$

The last term in relation 3.34 is called the $\omega_1$ term and it is the electrostatic force between the tip and the sample at frequency $\omega_1$.

$$ F = \frac{dc}{dz} [(V_s(x, y) - V_{dc}) V_0 \sin(\omega_1 t)] \quad 3.35 $$

When $V_{dc}$ (applied) is made equal to $V_s(x, y)$, the electrostatic force between the tip and the sample at frequency $\omega_1$ will be zero. Hence, in scanning Kelvin probe microscopy
(SKPM) measurement, by applying a bias dc voltage to the tip, the electrostatic force at frequency $\omega_1$ is made zero and in this way the contact potential difference between the tip and the sample at a particular point is determined. By adjusting the bias voltage, to make the electrostatic force between the tip and the sample equal to zero at all points in the sample surface, the contact potential difference between the tip and the sample is mapped across the sample surface. For this purpose, an additional lock-in amplifier is used other than the standard lock-in amplifier used for topography imaging. There are two modes of operation, namely dual pass and single pass mode. In dual pass mode, the topography (intermittent contact mode or tapping mode) and contact potential difference between the tip and the sample are mapped separately in sequence, whereas in a single pass mode they are mapped simultaneously.

In this work, samples of 15 mm x 20 mm x 5 mm dimensions were prepared in the step sequence 1-6, 8, 9 (slightly), 7 and 8 (Table 3.2). Step 9 was performed to identify the phases in the topography. Bruker Icon AFM was used in the double-pass mode, which measures first the topography and then the local Volta potential difference. The mapping was done on areas of 20 x 20 µm² and 4 x 4 µm², with a tip velocity of 3 µm/s and a pixel resolution of 512 points/line, and the tip lift height was 50 nm. Potential acquisition was performed in PeakForce Tapping mode, in ambient air. A DC voltage of 6000 mV was applied to the tip, and the sample was ground. Nanoscope Analysis V1.5 software was used for analysis of the data. Heightmaps were flattened using 0th or 1st order flattening. Potential maps were not flattened, and no filter was applied to any map to smooth the data. The Volta potential roughness ($R_a$ mV), as earlier introduced by Örnek et al. [119], was measured. Here, higher positive Volta potential differences mean lower absolute Volta potentials, indicating lower electrochemical nobilities.

3.2.4 In-situ AFM

In this work, in-situ AFM samples (4.5 mm x 3.0 mm x 4.0 mm dimensions – paper 2 and 5.0 mm x 5.0 mm x 5.0 mm – paper 3) were prepared by placing them on top of a brass cylinder (Ø8.0 mm x 4.0 mm dimensions), then seating them together inside a Teflon cup (counterbore Ø of 8.1 mm, counterbore depth of 8.0 mm and the wall thickness of 2 mm), followed by cold molding using Via Fix Powder/Liquid from Stuers and curing for ~ 12 hr. The exposed sample area on top of the sample assembly was (4.5 mm x 3.0 mm – paper 2 and 5.0 mm x 5.0 mm – paper 3) further prepared as per the step sequence 1-4, 6, 8, 9 (slightly), 7 and 8 for paper 2 and 1-6, 8, 12, 7 and 8 for paper 3 (Table 3.2). To electropolish the sample surface (step 12), a new masking plate was designed and manufactured to accommodate the small sample which is shown in Figure 3.8a.

Then the prepared sample assembly was made to sit on top of an O-ring and fastened to the Teflon cell through a M3 bolt. The Teflon cell has a step on its outer diameter and it was assembled to a steel disc that holds the cell and connects it to AFM. The diameter of
the counterbore in the Teflon cell was Ø 26 mm and the depth of counterbore was 10 mm. Then a small volume of NaCl electrolyte (0.1 M in paper 2 and 0.01 M in paper 3) was added into the cell. The entire set up is as shown in Figure 3.8b.

Topographical changes over time (at OCP condition) at room temperature were monitored using an Agilent 5500 scanning probe microscope. Sequential imaging was done in contact mode using ContAl-G type probes (Si tip, Al reflex) with a tip apex of 8nm, purchased from Budget sensors. The dimensions of the cantilever used were thickness = 2.0 µm, length = 450 µm and width = 50 µm. The resonance frequency of the cantilever used was 13.0 kHz and the spring constant was 0.2 N/m. The scanning area was 10 x 10 µm²; the speed was set at 0.5 lines/s and points/line was set at 512 for all the scans. All the images were post-processed and analyzed as mentioned in section 3.1.6.4. For detailed analysis, line profiles were extracted from the images at chosen locations.

![Figure 3.8](image)

**Figure 3.8:** (a) Masking plate used for electropolishing AFM samples, (b) In-situ AFM setup used in this study.

**Part - 3**

**3.3.1 A new method to study the stress relieving due to tempering - experimental procedure**

This was performed to quantify the effect of tempering on macro stress relaxation. In order to induce a tensile stress on the hardened samples, four-point bending was performed (as against three-point bending) using a Zwick Z250 Retroline testing machine with a cross head speed of 1 mm/min, to have the maximum tensile stress over an area (between two inner rollers) [120] to facilitate ease in residual stress.
measurement (XRD). Nine rod specimens of 5 mm x 5 mm (cross section) x 65 mm dimensions were used for this purpose. Three specimens were bent until fracture to determine the maximum deflection at the onset of fracture. The remaining six specimens were bent until the maximum possible deformation just before the onset of failure, followed by unloading. Generally, when the specimens are bent under four-point bending fixture, tensile stresses are expected to be on the bottom face of the sample and compressive stresses to be on the top face, but after unloading, stress reversal on the bent sample surface was observed in this work. This is due to the spring back effect of the residual elastic regions in the sample [112], and hence the tensile stress measurement was performed on the top face in the electropolished area, as shown in Figure 3.9. Then among the six specimens, three were tempered at 250°C for 2 hours, and the remaining three at 500°C for 2 hours, followed by cooling in air. Again, on the same location in the same orientation, residual stress measurements were repeated, and the average values were calculated. The stress relief was quantified from the difference between the stresses before and after tempering. This method is schematically shown in Figure 3.9.

![Figure 3.9: Schematic illustration of the stress relieving measurement.](image)

### 3.3.2 Constant load environment-assisted cracking test and the experimental procedure

The experimental setup and geometry of the cylindrical tensile samples used are shown in Figure 3.10. Twenty-four samples were hardened, out which twelve were fast quenched (3°C/s) and the reaming twelve were slow quenched (0.6°C/s). Then, six fast quenched samples and six slow quenched samples were tempered at 250°C, and likewise, six fast quenched samples and six slow quenched samples were tempered at 500°C. The detailed heat treatment procedures were described in section 3.1.2. All the heat treated samples were polished along their gauge length using 600 grit SiC paper.

After fixing the bottom connection plate within the gauge length, a rubber stopper was attached to the sample, followed by the cell. The top connection plate was attached to the top shank section of the sample, and then the sample with the assembly was fastened to the test rig. Samples in the rig were tested in 0.3M NaCl solution under
uniaxial tension, applied by dead weights via levers. The severity of the solution was chosen to shorten the testing duration. Through an external flask where 1600 ml was maintained throughout the test, the meniscus of the solution in the cell was constantly maintained below the top radius portion of the sample. After loading the rig, linear variable displacement transducers (LVDT) from Denison Mayers Group (DMG) LTD. were fastened to the connection plates as shown in the Figure 3.10. Two LVDTs per sample were used to record the change in displacement along either side of the sample. After fastening, the LVDTs were first independently set to zero and then the average value of readings was recorded as output. Using the LabVIEW™ Signal Express software (National Instruments), version 2.5 the variation of the potential over time was recorded continuously. In order to correlate the potential values (mV) recorded through the LVDTs to change in displacement (mm), LVDTs were calibrated so that 2.0 V signal was equal to 1.0 mm, and the relationship was linear with an error equal to 1.0%. The collected data were plotted as change in displacement vs. time. For continuous recording, LVDTs were connected to a computer through an NI BNC 2120 shielded connector block from National Instruments. The overall time to failure was obtained from an hour meter, which was connected to a proximity switch positioned underneath the elevated weights as shown in Figure 3.10. Four rigs were operated in parallel to reduce the overall testing duration.

The loading procedure followed for an effective comparison of the EAC behavior of 250°C and 500°C tempers is mentioned below:

1) First, the yield strengths of both the tempers in fast- and slow-quenched conditions were determined.
2) Two levels of residual stresses were assumed in the as-quenched conditions – 30%σ0.2 and 90%σ0.2.
3) Based on the stress relaxation (refer section 3.3.1), 30%σ0.2 and 90%σ0.2 were altered accordingly for 250°C, and 500°C tempering in both fast- and slow-quenched conditions, respectively.
4) Based on the computed stress values (point 3), tempers were loaded.
Figure 3.10: Environment assisted cracking testing setup and sample details (Paper 4).
CHAPTER 4 – Role of microstructure on the corrosion behavior of MSS

Alloying elements added and heat treatment (if hardenable) performed will determine the microstructure, which, in turn, will have a direct influence on the corrosion behavior of the steel in a given environment. In this chapter, the influence of microstructure on the corrosion behavior of an AISI 420 modified MSS (Uddeholm Stavax ESR) in chloride environments is reported. The microstructure was varied by quenching and tempering treatments.

4.1 Prediction of equilibrium phases

Figure 4.1 shows the calculated phase diagram in the temperature range 800-1150°C, for the MSS investigated. At austenitization temperature (1020°C), the stable phases are M₇C₃ (Cr rich carbide) and austenite. Carbides that are stable at the austenitization temperature are called undissolved carbides. The volume fraction of austenite and M₇C₃ carbides were predicted to be 98.4% and 1.6% respectively. Furthermore, the dissolved Cr content in the austenite and M₇C₃ carbide were predicted to be 13.1 wt.% and 63.2 wt.% respectively.

Figure 4.1: Thermo-Calc simulation showing the equilibrium phases and corresponding phase fractions at the austenitization temperature (1020°C) (Paper 2).

4.2 Phase transformation (Dilatometry)

Heat treatments performed in industrial scale furnaces were reproduced in the dilatometer to identify the phase transformations. Figure 4.2 shows the variation in length vs. temperature for heating as well as for two quenching rates (3°C/s and
0.6°C/s) employed in this work. A linear expansion was observed with increase in temperature until ca. 910°C, followed by an immediate onset of shrinkage indicating the starting of phase transformation from ferrite (α) to austenite (γ). The shrinkage lasted until ca. 951°C indicating the completion of the phase transformation reaction $\alpha \rightarrow \gamma$ (A3 in Figure 4.2a-b). A further increase in length, until 1020°C, was observed due to thermal expansion of the austenitic lattice and the dissolution of carbide precipitates. The material was then cooled to room temperature at two different quenching rates (3°C/s and 0.6°C/s). In the fast quench (3°C/s), a linear behavior of the material length vs. temperature was seen, occurring until ca. 283°C at which rapid material expansion was observed indicating the onset of martensitic transformation ($\alpha'$), $M_s$ in Figure 4.2a. The change in length increased linearly with temperature until ca. 140°C, and then a bowing of the curve was seen indicating no further formation of martensite but cooling of the material. In the slow quench (0.6°C/s), a linear behavior of the material length vs. temperature was seen, occurring until ca. 320°C at which rapid material expansion was observed, indicating the onset of martensitic transformation ($\alpha'$), $M_s$ in Figure 4.2b. The change in length increased linearly with temperature until ca. 161°C, and then a bowing of the curve was seen indicating no further formation of martensite, simply cooling of the material to room temperature.

**Figure 4.2:** Dilatometry results showing the phase transformations for (a) fast quenched (3°C/s) (Paper 2) and (b) slow quenched (0.6°C/s) conditions. $A_1$, $A_3$, and $M_s$ temperatures are marked.

### 4.3 Microstructure

The LOM micrographs of heat treated samples are shown in Figure 4.3. A martensitic structure was observed in samples subjected to both quenching rates (3°C/s, 0.6°C/s) and tempering temperatures (250°C, 500°C). Also, for both quenching rates the martensitic structure was more pronounced in the 250°C tempered samples than in the
500°C tempered samples. More prior austenite grain boundary regions were observed in the slow quenched samples compared to the fast quenched samples. Few pearlitic regions were observed in the slow quenched samples subjected to 250°C, 500°C tempering. The grain size was observed to be 18±1 µm.

**Figure 4.3:** Light optical microscope images showing the microstructure of fast quenched (3°C/s) and slow quenched (0.6°C/s) samples, tempered at 250°C, and 500°C, respectively. Etched using Villella’s reagent. (Paper 1).

Figure 4.4 shows the SEM micrographs of heat treated samples. In both the tempers, in hierarchic lath martensitic matrix, undissolved carbides (number density 7 - 8/100 µm², maximum size 4.5 µm) with spherical and rod-like morphology were observed both in grain boundary and intragrain boundary regions. A hierarchy in tempered lath microstructure starts with prior austenite grain boundaries, which are divided into packets that are further divided into blocks, and then sub-blocks, and then laths [48, 121]. Some of the mentioned substructures were not clearly seen in the microstructure due to the typical chemical etching that has been employed. However, different orientations of the laths in Figure 4.4 give an indication of this hierarchic structure. Also few island of pearlitic phase was observed in the slow quenched samples subjected to 250°C, and 500°C tempering.

The morphology of tempering carbides can be seen from Figure 4.5. In 250°C temper, lenticular shaped precipitates were present along the lath boundary and also in the intra
lath region orthogonal to the lath (ca. 297 nm in length and ca. 87±40 nm in width). Lath boundaries were partially covered by films/precipitates.

EDX mapping over an area with undissolved carbides showed enrichment in chromium and carbon and depletion in iron, indicating chromium-rich carbides (Figure 4.6).

**Figure 4.4:** SEM images showing the microstructure of fast quench (FQ) (3°C/s) and tempered at (a) 250°C (Paper 2), (b) 500°C (Paper 3); slow quench (SQ) (0.6°C/s) and tempered at (c) 250°C, (d) 500°C; SQ and tempered at (e) 250°C and (f) 500°C with yellow circles indicating pearlitic regions. Etched using Villella’s reagent.

**Figure 4.5:** AFM images showing the microstructure of fast quench (3°C/s) and tempered at 250°C. Electropolished at 0°C using electrolyte with 95 vol. % ethanol and 5 vol. % perchloric acid.
The measured volume fraction of retained austenite for the heat treated samples is given in Table 4.1. Retained austenite volume fraction was similar among the fast quenched samples tempered at 250°C and 500°C, with slightly higher values observed in the former. Whereas, a significant difference was observed in slow quenched samples tempered at 250°C and 500°C, with a difference of 6.2 vol. % among the tempers. After tempering at 500°C, the retained austenite volume fraction for fast and slow quenched samples was similar.

![Image](https://example.com/image.png)

**Figure 4.6:** Backscattered electron SEM image and EDX maps of C, Cr, and Fe, showing Cr-rich undissolved carbides in the fast quench (3°C/s) and 500°C temper (Paper 3).

<table>
<thead>
<tr>
<th></th>
<th>Fast quenched</th>
<th>Slow quenched</th>
</tr>
</thead>
<tbody>
<tr>
<td>250°C Tempered</td>
<td>7.9 ± 2.0</td>
<td>12.6 ± 2.0</td>
</tr>
<tr>
<td>500°C Tempered</td>
<td>7.1 ± 2.0</td>
<td>6.4 ± 2.0</td>
</tr>
</tbody>
</table>

**Table 4.1:** Retained austenite in volume % (Paper 1).

Figure 4.7 and Figure 4.8 summarize the phase identification using XRD. Martensite ($\alpha'$), retained austenite ($\gamma$), and carbides were detected. Peaks confirmed the presence of the mentioned phases in the microstructure, while the intensity and number of peaks gave an indication of their fraction. Strong diffraction signals of $\alpha'$ were obtained from (110), (200), and (211) planes. Signals from (111), (200), and (220) planes of $\gamma$ were also obtained. The intensity of peak no. 7 and the left shoulder on peak no. 5 (Figure 4.8) seem to be slightly higher for the 250°C temper than the 500 °C temper, indicating a slight increase in retained austenite in the former. Other small peaks (visible in the inserts) in Figure 4.7 and Figure 4.8 indicate the presence of multiple phases, which could correspond to different types carbides such as Cr$_7$C$_3$, Cr$_{23}$C$_6$, Fe$_3$C, Cr$_3$C$_2$, Cr$_2$C and VC and their respective planes are mentioned in Table 4.2. Peaks marked as “?” in Figure 4.7 and Figure 4.8 do not correspond to any relevant phases. Hence, further work is needed to identify, from which phase/s these signals originate.
Figure 4.7: XRD spectra of fast quench 250°C temper, showing the presence of martensite, retained austenite and carbides (Paper 2).

Figure 4.8: XRD spectra of fast quench 250°C and 500°C temper, showing the presence of martensite, retained austenite and carbides (Paper 3).
Table 4.2: Probable planes closer to the peak positions (Paper 2).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr7C3</td>
<td>(002), (040), (051), (161)</td>
</tr>
<tr>
<td>Cr23C6</td>
<td>(420), (422), (440), (531)</td>
</tr>
<tr>
<td>Cr3C2</td>
<td>(230), (131), (221), (051), (250), (181), (332)</td>
</tr>
<tr>
<td>Cr2C</td>
<td>(101), (201)</td>
</tr>
<tr>
<td>VC</td>
<td>(200)</td>
</tr>
<tr>
<td>Fe3C</td>
<td>(201), (211), (102), (131)</td>
</tr>
</tbody>
</table>

As the identification of phases corresponding to small peaks was difficult because of their low intensity, the matrix of the sample was dissolved and powder XRD measurement was performed on the extracted particles (done only for the 500°C tempered sample).

Diffraction signals with a much higher intensity-to-noise ratio were obtained from the extracted powder. More peaks were seen than those obtained from the bulk XRD spectra (Figure 4.8). Only clear and unambiguous peaks are marked in the diffractogram (Figure 4.9). Five peaks correspond to Cr23C6, two peaks to Cr7C3, three peaks to Cr3C2, five peaks to Cr3C, two peaks to Cr2C, and one peak to CrC. These peaks are unique for each phase and do not show an overlap with any other phase, hence, confirming the presence of Cr23C6, Cr7C3, Cr3C2, Cr3C, Cr2C, and CrC. There were more peaks for the carbides in Figure 4.9, but these are ambiguous and are not satisfactory for phase identification. Further, peaks for FeCl3, Fe2O3, FeO (OH), and Fe (OH)2 were also seen but disregarded in this work. These were formed during the dissolution of the metal and are both corrosion products and remnants from the electrolyte. Therefore, clear and unique peaks are considered as evidence for the phases to be present in the microstructure. The XRD results are summarized in Table 4.3 where only distinctive peaks are listed. Both Cr23C6 and Cr7C3 yielded the highest intensities in contrast to the other carbides. Therefore, they are the major (significant) carbides in the microstructure and are thus the undissolved and secondary carbides.

Table 4.3: Peak positions and corresponding possible phases for fast quench 500°C temper (Paper 3).

<table>
<thead>
<tr>
<th>Phases</th>
<th>Peak Position (°)</th>
<th>Corresponding planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr23C6</td>
<td>27.94, 29.13, 33.68, 41.66, 92.00</td>
<td>(311), (222), (400), (422), (711)</td>
</tr>
<tr>
<td>Cr7C3</td>
<td>42.13, 56.89</td>
<td>(051), (312)</td>
</tr>
<tr>
<td>Cr3C2</td>
<td>45.66, 83.72, 93.43</td>
<td>(240), (242), (470)</td>
</tr>
<tr>
<td>Cr3C</td>
<td>73.65, 88.46, 102.33, 103.33, 105.84</td>
<td>(213), (114), (511), (403), (352)</td>
</tr>
<tr>
<td>Cr2C</td>
<td>102.95, 104.00</td>
<td>(210), (104)</td>
</tr>
<tr>
<td>CrC</td>
<td>38.69</td>
<td>(111)</td>
</tr>
</tbody>
</table>
4.4 Salt spray test

Figure 4.10 shows visual appearance of the samples after the salt spray test. Along with 250°C and 500°C tempers, 400°C temper was also included for comparison. A similar numbers of stain marks were observed on the 500°C temper in both fast and slow quenched conditions, and they were more in numbers compared to 250°C and 400°C tempers. In slow quenched condition, relatively more numbers of stain marks were observed on the 400°C temper compared to 250°C temper, and in fast quenched condition, no stain marks were observed on the 250°C temper and 400°C temper. The slow quenched samples exhibited relatively poor corrosion resistance as compared to the fast quenched samples when tempered at 250°C and 400°C.
4.5 Corrosion tendency of phases

Volta potential difference between the tip and carbide particles of different shapes, and between the tip and tempered martensitic matrix are shown in Figure 4.11. Potential variations of up to 60 mV were measured across martensitic regions with higher gradients measured at lath boundaries, shown in Figure 4.11b. The average Volta potential difference measured over the martensite matrix was $110 \pm 30$ mV with a potential roughness (Ra_mV) of $8 \pm 2$ mV. Undissolved carbide particles showed an average Volta potential difference of $70 \pm 10$ mV with a Ra_mV of $2 \pm 1$ mV. There is a Volta potential difference of ca. 40 mV between the martensite and the precipitates, indicating galvanic coupling. The potential difference measured over the carbides was less than that over the matrix, indicating higher electrochemical nobility of the carbides than $\alpha'$. High resolution Volta potential differences maps showed potential differences of up to 260 mV measured between the microstructure constituents, with large potential difference measured adjacent to carbides, as shown in Figure 4.11d. The corresponding topography map (Figure 4.11c) showed that this region corresponds to a depression, which could be associated with a precipitate/inclusion that was not outstanding from the surface. Such features were observed only in a few regions but, always next to the carbides.

Figure 4.11: SKPFM maps (a, c) topography, (b, d) Volta potential difference map (Paper 2).
4.6 Open circuit potentials

The measured OCP values for fast quenched and slow quenched samples tempered at 250°C and 500°C in 0.1 M NaCl solution, and for fast quenched samples tempered at 250°C and 500°C in 0.01 M NaCl solution are shown in Figure 4.12 and Figure 4.13, respectively. Potential variations with time and fluctuations were observed for all samples in both the environments, indicating general corrosion tendency and metastable local corrosion events [76, 122]. In 0.1 M NaCl solution, a higher frequency of potential fluctuations was observed on 250°C tempered samples (both fast and slow quenched conditions), with a slightly increasing trend towards the noble direction. Whereas for samples tempered at 500°C (both fast and slow quenched conditions), a decreasing trend were observed indicating a greater corrosion propensity. In 0.01 M NaCl solution, the trend was similar, with a lower OCP for 500°C tempered samples indicating a greater corrosion propensity. The average OCP values after 1h of exposure obtained from parallel samples are given in Table 4.4.

Figure 4.12: OCP vs. time plots measured on fast quenched (3°C/s) and slow quenched (0.6°C/s) samples tempered at 250°C, and 500°C, respectively, in 0.1M NaCl solution at room temperature. (a-d) shows the comparison among quenching rates and tempering temperatures (Papers 1, 2).
Figure 4.13: OCP vs. time plots measured on fast quenched (3°C/s) samples tempered at 250°C and 500°C in 0.01 M NaCl solution at room temperature. (a) short-term and (b) long-term variations of the OCP (Paper 3).

Table 4.4: Measured OCP values for fast quenched and slow quenched samples tempered at 250°C and 500°C after 1 h in a chloride-containing environment. The values are obtained from a minimum of three experiments (Papers 1, 2, 3).

<table>
<thead>
<tr>
<th>Condition</th>
<th>Tempering temp.</th>
<th>Duration</th>
<th>Solution</th>
<th>OCP (mV&lt;sub&gt;Ag/AgCl&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast quench (3°C/s)</td>
<td>250°C</td>
<td>1h</td>
<td>0.1 M NaCl</td>
<td>-110 ± 14</td>
</tr>
<tr>
<td></td>
<td>500°C</td>
<td></td>
<td></td>
<td>-326 ± 13</td>
</tr>
<tr>
<td>Slow quench (0.6°C/s)</td>
<td>250°C</td>
<td></td>
<td>0.01 M NaCl</td>
<td>-216 ± 13</td>
</tr>
<tr>
<td></td>
<td>500°C</td>
<td></td>
<td></td>
<td>-331 ± 3</td>
</tr>
<tr>
<td>Fast quench (3°C/s)</td>
<td>250°C</td>
<td></td>
<td>0.01 M NaCl</td>
<td>-34 ± 26</td>
</tr>
<tr>
<td></td>
<td>500°C</td>
<td></td>
<td></td>
<td>-154 ± 73</td>
</tr>
</tbody>
</table>

The environmental effect (severity of chloride solution) can also be inferred from Table 4.4. By comparing the fast quenched samples tempered at 250°C exposed to 0.1 M and 0.01 M NaCl solution, an OCP difference of ca. 76 mV was observed. Similarly, by comparing the fast quenched samples tempered at 500°C exposed to 0.1 M and 0.01 M NaCl solution, an OCP difference of ca. 172 mV was observed.

The long-term OCP variations recorded for both tempers (one sample each) in 0.01 M NaCl solution are shown in Figure 4.13b. The OCP of the 250°C tempered sample maintained an increasing trend for a certain period (tens of hours) before a large drop occurred, and then it continued to raise again, indicating a tendency to passivate in the solution. The OCP of 500°C tempered sample, in contrast, showed large drops in the initial period and continuous fluctuations around a low level during the entire measurement time, suggesting active corrosion tendency in the solution. The potential
fluctuations were probably caused by localized corrosion events related to the heterogeneous microstructure of the sample.

### 4.7 Cyclic potentiodynamic polarization

The cyclic polarization curves for fast and slow quenched samples tempered at 250°C and 500°C, in 0.1 M NaCl solution are shown in Figure 4.14, and in 0.01 M NaCl solution are shown in Figure 4.15. The extracted electrochemical parameters are summarized in Table 4.5.

**Figure 4.14:** Electrode potential vs. current density plots obtained for fast quenched (3°C/s) and slow quenched (0.6°C/s) samples tempered at 250°C and 500°C, in 0.1 M NaCl solution at room temperature. (a-d) shows the comparison among quenching rates and tempering temperatures (Papers 1, 2).

Among the fast quenched samples exposed to 0.1 M NaCl solution, an $E_{corr}$ difference of ca. 218 mV and $i_{corr}$ difference of ca. $544 \times 10^{-8}$ A/cm² was observed between 250°C and 500°C temps, respectively. Similarly, among the fast quenched samples exposed to 0.01 M NaCl solution, an $E_{corr}$ difference of ca. 117 mV and $i_{corr}$ difference of ca. $270 \times 10^{-8}$ A/cm² was observed between 250°C and 500°C temps, respectively.
A/cm² was observed between 250°C and 500°C tempers, respectively. Among the slow quenched samples exposed to 0.1 M NaCl solution, an $E_{corr}$ difference of ca. 115 mV and $i_{corr}$ difference of ca. 300 x 10⁻⁸ A/cm² was observed between 250°C and 500°C tempers, respectively.

The effect of quenching rate can also be inferred from Table 4.5. By comparing the fast quenched and slow quenched samples tempered at 250°C exposed to 0.1 M NaCl solution, an $E_{corr}$ difference of ca. 91 mV and $i_{corr}$ difference of ca. 121 x 10⁻⁸ A/cm² was observed. Similarly, by comparing the fast quenched and slow quenched samples tempered at 500°C exposed to 0.1 M NaCl solution, an $E_{corr}$ difference of ca. 12 mV and $i_{corr}$ difference of ca. 123 x 10⁻⁸ A/cm² was observed.

**Table 4.5:** Electrochemical data from cyclic polarization measurements giving average values obtained from a minimum of three experiments. All potential values are given in mV vs. Ag/AgCl (Papers 1, 2, 3).

<table>
<thead>
<tr>
<th>Condition</th>
<th>Tempering temp.</th>
<th>Solution</th>
<th>$E_{corr}$</th>
<th>$i_{corr}$ (A/cm²)</th>
<th>$E_{pit}$</th>
<th>$E_{rp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast quench (3°C/s)</td>
<td>250°C</td>
<td>0.1 M NaCl</td>
<td>-131 ± 10</td>
<td>(13.5 ± 4.2) x 10⁻⁸</td>
<td>77 ± 35</td>
<td>-</td>
</tr>
<tr>
<td>500°C</td>
<td></td>
<td></td>
<td>-349 ± 15</td>
<td>(557.3 ± 181.3) x 10⁻⁸</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Slow quench (0.6°C/s)</td>
<td>250°C</td>
<td></td>
<td>-222 ± 20</td>
<td>(134.6 ± 100.1) x 10⁻⁸</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>500°C</td>
<td></td>
<td></td>
<td>-337 ± 24</td>
<td>(434.4 ± 188.9) x 10⁻⁸</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fast quench (3°C/s)</td>
<td>250°C</td>
<td>0.01 M NaCl</td>
<td>-47 ± 22</td>
<td>(30 ± 20) x 10⁻⁸</td>
<td>295 ± 19</td>
<td>52 ± 10</td>
</tr>
<tr>
<td>500°C</td>
<td></td>
<td></td>
<td>-164 ± 72</td>
<td>(300 ± 400) x 10⁻⁸</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The environmental effect (severity of chloride solution) can also be inferred from Table 4.5. By comparing the fast quenched samples tempered at 250°C exposed to 0.1 M and 0.01 M NaCl solution, an $E_{corr}$ difference of ca. 84 mV and $i_{corr}$ difference of ca. 17 x 10⁻⁸ A/cm² was observed. Similarly, by comparing the fast quenched samples tempered at 500°C exposed to 0.1 M and 0.01 M NaCl solutions, an $E_{corr}$ difference of ca. 185 mV and $i_{corr}$ difference of ca. 257 x 10⁻⁸ A/cm² was observed.

Judged from these electrochemical measurements, the fast quenched samples tempered at 250°C exhibited a passive potential range where the current density increased slightly with increasing potential in both 0.1 M and 0.01 M NaCl solution. In the latter, passivity range was relatively well defined. Passivity breakdown occurred around 77 mV in 0.1 M NaCl solution and 295 mV in 0.01 M NaCl solution. Also, a re-passivation potential ($E_{rp}$) of 52 mV in 0.01 M NaCl solution was observed on fast quenched samples tempered at 250°C, indicating a repassivation tendency of material. The large loop in the cyclic polarization curve suggests a weak tendency to re-passivate i.e., localized corrosion will propagate substantially once stable pitting has initiated. Both in the fast quenched and slow quenched conditions, 500°C tempered samples showed an increasing anodic
current density with increasing potential with no clear passive range seen on the polarization curves in both 0.1 M and 0.01 M NaCl solution. Moreover, the anodic current remained high when the potential was decreased upon reverse scan and no defined $E_{rp}$ was observed, indicating weak repassivation tendency.

Figure 4.15: Electrode potential vs. current density plots obtained for fast quenched (3°C/s) samples tempered at 250°C and 500°C, in 0.01 M NaCl solution at room temperature (Paper 3).

4.8 In-situ observation of localized corrosion behavior

4.8.1 Fast quench (3°C/s) 250°C temper

Sequential AFM images of the sample surface on the same area were obtained, which revealed the minute topographic changes indicating the corrosion process at OCP condition in 0.1 M NaCl solution at room temperature. Figure 4.16 summarizes the in-situ AFM measurements over a period of 24 hours. The first image (Figure 4.16a) was acquired after ca. 30 min of exposure, as it was needed for assembling the cell, engaging the probe, selecting the suitable area to be scanned and fine-tuning for a better quality image. The microstructural features of the steel can be clearly seen from the image. The image became progressively unclear with increasing exposure time. Nevertheless, the sequential AFM images revealed detailed corrosion-induced changes of the carbide boundary regions as well as inter lath regions.

Evaluation of the local dissolution was done by comparing the images obtained at the beginning (Figure 4.16a) and end (Figure 4.16c) of the exposure, by extracting line profiles across individual microstructural features. There was a positive height change with an average of 9 nm ± 0.7 nm measured between the apex of carbides and the martensitic matrix, indicating preferential dissolution occurring on the martensitic
matrix. Pronounced localized corrosion attack was observed on adjacent sites of some precipitates, with a maximum local dissolution depth of 5 nm. Localized corrosion was seen to occur in certain regions only (Figure 4.16(a, c)). A predominant attack was observed on lath boundaries. No clear change in height was measured for the particle, whereas a decrease in height and width between inter-lath regions was observed (Figure 4.16(e, f)). The carbide particle size appeared to be larger and the distance between the carbide particles was smaller at the end of the exposure, again, indicating preferential dissolution of the matrix adjacent to carbide particles. Furthermore, the roughness of martensite changed from $R_a = 6.9 \pm 1.3$ nm to $4.5 \pm 0.7$ nm during 24 hours of exposure.

Figure 4.16: In-situ AFM topography maps showing corrosion events occurring on adjacent sites of precipitates: (a, b) initial condition, and (c, d) after 24 hours of exposure to 0.1 M NaCl
at room temperature; (e, f) height profiles for line 1 and 2 in (a, c) showing topographical changes occurred (Paper 2).

4.8.2 Fast quench (3°C/s) 500°C temper

The topography maps of the same region obtained on the 500°C temper during immersion in 0.01 M NaCl at OCP are shown in Figure 4.17. Numerous nanometer-sized secondary carbides with sizes between 20-170 nm were seen at the beginning of the experiment (Figure 4.17a), having a density of 6000 particles per 100 µm². The larger undissolved carbides were distinctive and less in number than the secondary carbides. The number of secondary carbides became noticeably reduced after 2 h 38 min of exposure (Figure 4.17b), which resulted in a reduction of the local roughness (Ra) from 10.3 nm to 9.5 nm. A further reduction of the number of secondary carbides was observed after 4 h 6 min (Figure 4.17c) with a reduction of Ra to 9 nm. Most of the secondary carbides seemed to have vanished from the surface after 11 h 26 min, with a further decrease of Ra to 8.2 nm (Figure 4.17d). Then, some localized attack was seen occurring on regions adjacent to undissolved carbides, indicating sensitization in these regions. After 52 h 32 min, the undissolved carbides became more distinctive (Figure 4.17e). Corrosion seemed to have progressed along the contour of the undissolved carbides. In the end, the undissolved carbides appeared to be more protruding from the surface and the height difference between the top surface of the carbide and the adjacent neighboring matrix was seen to increase (Figure 4.18(a-b)). The height difference varied between 1-10 nm, indicating localized dissolution of the matrix. The overall Ra further decreased to 6.1 nm. The map obtained after 52 h 32 min (Figure 4.17e) shows enhanced microstructural contrast because of a smaller Z-scale.
Figure 4.17: In-situ AFM maps of the 500°C tempered sample in 0.01M NaCl solution at room temperature showing localized corrosion processes of an area containing secondary and undissolved carbides: (a) after 20 min, (b) 2 h 38 min, (c) 4 h 6 min, (d) 11 h 26 min, (e) 52 h 32 min of exposure. Measurement area was 10 µm x 10 µm. Pixel resolution is 20 nm (Paper 3).
4.9 Post polarization SEM analysis

Figure 4.19 shows the backscattered SEM image obtained on fast quenched samples tempered at 250°C after the cyclic polarization measurement in 0.1 M NaCl solution. It can be seen that the preferential dissolution occurred along some of the carbide interphase regions, but not along all the carbide boundaries, whereas the periphery of most of the small particles seemed to have been not affected. In Figure 4.19b, some dissolved areas resemble the morphologies of undissolved carbides. This is probably due to an extended dissolution of the matrix, which could have occurred along the boundary region of the carbide eventually causing the particle to fall off from the surface.

Figure 4.20 shows the backscattered SEM image obtained on fast quenched samples tempered at 250°C and 500°C after the cyclic polarization measurement in 0.01 M NaCl solution. On the 250°C tempered sample (Figure 4.20(a-c)), fewer and smaller pits were observed with sizes ranging from 0.6 to 6 µm, and with similar shape of the undissolved carbides. On the 500°C tempered sample (Figure 4.20(d-f)), more and large pits were observed with different shapes and sizes ranging from 0.25-130 µm (Feret diameter –
longest dimension of the pit mouth). The images show selective dissolution occurred at interphase regions between undissolved carbides and the matrix, which was more pronounced on the 500°C tempered microstructure.

Figure 4.20: BSE-SEM images showing localized corrosion events occurred after the cyclic polarization measurement in 0.01 M NaCl solution on fast quenched samples tempered at 250°C (a, b, c) and 500°C (d, e, f) (Paper 3).

4.10 Discussion

4.10.1 Microstructure evolution

4.10.1.1 Hardening

The soft annealed microstructure that is the precursor to hardened and tempered microstructure is shown in Figure 4.21. It comprises of a ferritic matrix decorated primarily with Cr-rich carbides of M₇C₃ and/or M₂₃C₆ types depending on the processing condition [123]. Generally, during austenitizing the material is heated to a suitable austenitization temperature at which the ferritic matrix transforms into austenite [124]. This was observed in our dilatometer study in terms of volumetric compression (Figure 4.2). In order to dissolve all the carbides, higher austenitization temperature has to be employed, but this will lead to undesirable grain growth and lowering of Mₛ temperature which, in turn, will lead to retention of austenite [125]. The carbides that survive the austenitization treatment are called undissolved carbides. From Figure 4.3 and Figure 4.4, it can be inferred that the austenitization process employed in this work was not sufficient to dissolve all the carbides, which is in agreement with the Thermo-Calc simulation (Figure 4.1). From Figure 4.6, it can be
inferred that the undissolved carbides are rich in Cr. Thermo-Calc simulation (Figure 4.1) also predicted the undissolved carbides to be M\textsubscript{7}C\textsubscript{3} type, but some literatures [125] suggested that the undissolved carbides can be M\textsubscript{7}C\textsubscript{3} and M\textsubscript{23}C\textsubscript{6}. XRD examination confirmed the presence of both M\textsubscript{7}C\textsubscript{3} and M\textsubscript{23}C\textsubscript{6} (Figure 4.7, Figure 4.8, and Figure 4.9). However, as the XRD signals are from both undissolved and tempering carbides, electron diffraction is required for confirming the carbide type.

Figure 4.21: Light optical microscope image showing the soft annealed microstructure of the alloy studied. Etched using Villella’s reagent. Carbides in a ferritic matrix. Courtesy of Per-Olof Carlsson, Uddeholms AB.

4.10.1.2 Quenching

Generally, during quenching, the material is cooled at a suitable rate to transform the austenite into martensite [124]. This was observed in our dilatometer study (Figure 4.2). A ca. 37°C difference in M\textsubscript{s} temperature was observed between the fast quenched and slow quenched conditions. The higher M\textsubscript{s} temperature observed on slow quenched condition can be attributed to the compositional leaning of the austenite [47] due to pearlite formation at ca. 700°C (the CCT diagram [126]). The pearlite phase was observed in the micrograph (Figure 4.4(e, f)), but not in the dilatometer investigation (Figure 4.2 b), which could be due to a low volume fraction of pearlitic phase in the matrix. This is typical when the cooling rates are closer to the nose of C curve. The martensite transformation finish temperature (M\textsubscript{f}) also depends on the dissolved C content in the austenite [47, 125]. Generally, it is difficult to find the M\textsubscript{f} temperature, and for steels with C content ranging from 0.3 to 0.4 wt.%, a retained austenite content of 2 to 4 vol. % is measured [47]. The volume fraction of martensite transformed for Fe-C alloys with carbon content ranging from 0.37 to 1.1 wt.% is given by the Koistinen and Marburger relation [47],

\[ f = 1 - e^{- (1.10 + 0.01 \cdot DT)} \]
where,
f – volume fraction of martensite transformed
\( \Delta T \) – undercooling below \( M_s \) in °C

From the above relation, the volume fraction of martensite was calculated to be 94 vol.
% and 96 vol. % for fast (3°C/s) and slow (0.6°C/s) quenched conditions, respectively.
This is consistent with higher \( M_s \) temperature observed for the slow quenched condition. But, higher volume fraction of retained austenite was observed on the slow quenched condition than fast quenched condition (Table 4.1, compare the 250°C tempered among the quenching rates). This could be due to segregation of C to the potential nucleating sites in the untransformed austenite while slow cooling, thereby increasing the shear resistance of austenite leading to stabilization of austenite [47]. However, further investigation is required for confirming this hypothesis. In the slow quenched samples tempered at 250°C and 500°C, a semi-lamellar (not fully non-
lamellar or lamellar) morphology of the pearlitic phase was observed (Figure 4.4(e, f)).
Non-lamellar pearlitic morphology is generally observed when the cooling rate is low
[127], however, further investigation is required for confirming the type of morphology.

4.10.1.3 Tempering at 250°C

After hardening, a set of fast (3°C/s) and slow (0.6°C/s) quenched samples were
tempered at 250°C for 2hours, twice, followed by air-cooling to room temperature to
convert the metastable martensitic microstructure to a relative ductile microstructure.
As carbon is supersaturated in the martensite phase due to the non-equilibrium cooling,
during tempering, thermal activation enables diffusion of carbon atoms leading to
precipitation of carbides [43]. As carbon diffuses out of the martensitic structure, the
tetragonality reduces and eventually the martensite decompose to form stable ferrite (\( \alpha \))
and \( M_2C \) (\( Fe_3C \)) carbides depending on the tempering temperature and time [43]. Since
the tempering was done at 250°C, which is the third stage of tempering, \( M_2C \)
precipitates are expected [128, 129]. The morphology of tempering carbides in Figure
4.5 and the \( M_2C \) (\( Fe_3C \)) peaks identified in the XRD result (Figure 4.7) confirm the
presence of \( M_2C \) precipitates. After 250°C tempering, presence of retained austenite is
also confirmed by the XRD results (Figure 4.7, Figure 4.8). Generally, in lath martensitic
microstructure, retained austenite appears like film along the lath boundary regions
[130], and a similar morphology was observed in this work (Figure 4.5). However,
further characterization is required to confirm the elevated lath boundary films as
retained austenite. The tempering temperature was not high enough to decompose the
martensitic structure to ferritic structure as can be seen from Figure 4.4. More grain
boundary regions were observed on slow quench compared to fast quench samples
(Figure 4.3), which could be due to the presence of grain boundary carbides that
depletes the Cr content along the grain boundaries leading to more etching.
Precipitation of Cr-rich carbides may have occurred during rapid cooling (known as
quenching carbides), and they usually precipitate along grain boundary regions during quenching [131]. From the CCT diagram of the steel [126], it can be inferred that more precipitation can be expected in the slow quench conditions. However, further in-situ TEM investigation is required for confirmation.

4.10.1.4 Tempering at 500°C

Tempering at 500°C generally causes softening of a martensitic structure due to coarsening of M₃C precipitates and also due to recovery and recrystallization of the matrix [43]. But when the steel is alloyed with carbide forming elements, alloy carbides precipitate at ca. 500°C due to the enablement of substitutional atom diffusion leading to further hardening called secondary hardening [43]. In Cr alloyed steels, the carbide precipitation sequence is M₃C – M₇C₃ – M₂₃C₆ [44], where the coarse M₃C carbides are replaced by Cr-rich carbides. The precipitated alloy carbides are generally coherent with the matrix and they usually precipitate at the dislocations [43]. The hardening comes because the dislocations must overcome the coherency strains and has to spend the necessary energy for shearing the precipitates while moving [132]. High-resolution XRD analysis of the 500°C tempered sample confirms the Cr-rich carbides as Cr₂₃C₆, Cr₇C₃, Cr₅C, Cr₂C, CrC, and Cr₃C₂ (Figure 4.8 and 4.9). The detected signals are from both undissolved carbides and secondary carbides. The presence of these carbides indicates that the sequence of carbide formation mentioned above for Cr alloyed steels has not been completed, and some of them are possibly non-equilibrium carbides. The presence of Cr₃C can be attributed to Cr substitution of Fe in Fe₃C at high temperatures [133]. As the nucleation of secondary carbides is heterogeneous, there will always be a size distribution of them, usually in the nanometer range. The small carbides shown in the AFM maps (Figure 4.17) have sizes between 20-170 nm. These are clearly distinguishable from the larger undissolved carbides, indicating that the majority of them are secondary carbides.

4.10.2 Effect of phases on the corrosion behavior

Multi-phase microstructure can lead to either heterogeneous passive film or homogeneous passive film formation [134]. When a passive film fails at some sites, it will expose the underlying metal surface to the electrolyte causing localized corrosion. In fast quenched and tempered samples, undissolved Cr-rich carbides, tempering carbides, and retained austenite phases are all present in a martensitic matrix (Figure 4.4 - Figure 4.9, and Table 4.1). Additionally, the pearlite phase is also present in the slow quenched and tempered samples (Figure 4.4(e, d)).

The type/s of Cr rich undissolved carbides will be the same in all the microstructure variants studied in this work because of the same alloying elements, and heat treatments performed prior to hardening and austenitization treatment.
The SKPFM measurements across the microstructure (Figure 4.11) indicate that the martensitic regions next to the undissolved carbide regions is electrochemically less noble, which suggests that the carbide/matrix interphase regions could be more susceptible to corrosion during exposure to corrosive electrolytes. Large potential differences among microstructure constituents indicate galvanic coupling between them [119, 135, 136], and also in a tool alloy, the hard phases were shown to have a relative higher nobility compared to the surrounding matrix [137]. Hence, the martensitic matrix next to undissolved carbides would be expected to act as the local anode and the undissolved carbides as the local cathode, in a corroding system.

The investigated steel has a Cr content of 13.8 wt.%, which is slightly above the threshold level for a steel to be categorized as stainless steel [74]. As the C content in this steel is 0.38 wt.%, Cr-rich carbides will precipitate during solidification and upon further heat treatments, which could lead to local Cr depletion (sensitization) and consequently to a non-uniform passive film formation. Hence, regions around the carbide boundaries and grain boundary carbides are more susceptible to initiation of localized corrosion. Generally, the extent of sensitization increases with the size of carbides, leading to increased susceptibility to localized corrosion. However, during austenitization treatment (1020°C, 30min), the depleted zones, to some extent, can heal due to diffusion of the Cr atoms from higher concentration zones to low concentration zones (depleted zones). This can reduce and even fully recover the depletion of Cr depletion next to undissolved carbides. But, even in the healed condition, there can be a potential difference between a Cr-rich carbide and its surrounding matrix that may lead to the initiation of localized corrosion, similar to Zn-Cu alloys where Zn preferentially corrodes with respect to Cu [138] due to micro-galvanic coupling. Hence, the observed potential difference between the undissolved carbides and martensitic matrix can be due to depletion zones surrounding the undissolved carbides and/or due to the potential difference between a Cr-rich carbide and its surrounding healed matrix. By correlating the micro-galvanic activity observed in Figure 4.11 and the selective dissolution in Figure 4.19 and Figure 4.20, it can be inferred that sensitized zones were still present and had led to the micro-galvanic activity between neighboring regions causing localized corrosion on the sensitized zones. It seems that during austenitization, the healing of Cr depleted zones around undissolved carbides of different shapes and sizes (Figure 4.4) were not complete, as the Cr content of the surrounding matrix can vary depending on the type and geometry of the carbide [139].

As mentioned, based on the tempering temperature, the type of tempering carbides changes [43]. In this work, a direct evidence was provided for the effect of secondary carbides (that form during 500°C tempering) on the corrosion behavior (Figure 4.17 and 4.18). The effect of tempering carbides, that form during 250°C and 400°C tempering, on the corrosion behavior was investigated by cyclic polarization measurements (Figure 4.22). Also, their effect can be seen from the salt spray results (Figure 4.10). From
Figure 4.22 it can be inferred that the corrosion resistance of 250°C temper was superior to 400°C temper for both fast and slow quenched conditions, which could be due to the replacement of M in M₃C carbides from Fe-rich to Cr-rich, causing Cr depletion zones around the tempering carbides [133]. However, in-situ corrosion measurements with a focus on 250°C and 400°C tempering carbides needs to be done to prove this hypothesis. It has been reported that corrosion resistance of 13Cr super MSS increases with the presence of retained austenite [140], and hence, this could also be a reason for the observed inferior corrosion resistance trend with increasing tempering temperature.

The in-situ AFM study on the 500°C temper in 0.01 M NaCl solution showed that the localized corrosion begins at interphase boundary regions adjacent to nanometer-sized secondary carbides leading to their fallout from the matrix, followed by preferential dissolution of interphase boundary regions next to undissolved carbides (Figure 4.17). This was in line with the post-polarization observations (Figure 4.20) that showed bigger pits formation, and in some cases, enhanced dissolution along undissolved carbides on 500°C tempered samples. On the other hand, a lower extent of corrosion attacks was observed on the 250°C temper. This demonstrates the effect of secondary hardening, implying that sensitization is more pronounced in 500°C temper than in 250°C temper. Based on the in-situ AFM measurements, which showed a sequence of localized corrosion (Figure 4.17), it can be inferred that the sensitized regions are more in 500°C temper due to the secondary carbides in spite of their smaller sizes than the undissolved carbides.

**Figure 4.22**: Electrode potential vs. current density plots measured on fast quenched (a) (3°C/s) and (b) slow quenched (0.6°C/s) samples tempered at 250°C, 400°C and 500°C, respectively, in 0.1 M NaCl solution at room temperature.
4.10.3 Effect of heat treatment on the corrosion behavior

Distinct evolution of the OCP with time for the fast (3°C/s) and slow (0.6°C/s) quenched samples tempered at 250°C and 500°C, respectively, in both 0.1 M and 0.01 M NaCl solutions show different corrosion behavior (Figure 4.12 and Figure 4.13). The results indicate that the slow quenched condition is more active in corrosion than the fast quenched condition, and high temperature tempering is more active in corrosion than the low temperature tempering. More potential fluctuations were observed in fast and slow quenched samples tempered at 250°C than tempered at 500°C (Figure 4.12) in 0.1 M NaCl solution. Such fluctuations are typically associated with metastable pitting events. However, both SKPFM (Figure 4.11) and in-situ corrosion analyses (Figure 4.16) on fast quenched samples tempered at 250°C suggest that these were more likely due to localized corrosion attack related to the microstructure. Preferential dissolution on the sites adjacent to undissolved carbides and inter-lath regions were observed in the in-situ corrosion analyses (Figure 4.16), which is in good agreement with the SKPFM observations (Figure 4.11). Severe localized corrosion attacks were seen mostly on sensitized regions, indicating the highest anodic activity on the undissolved carbide boundary regions, whereas less severe corrosion attacks were observed on lath boundary regions. Intra-lath regions were observed to nobler as compared to the lath boundary regions. This observed anodic behavior of lath boundary regions could be due to their high stored energies [141] and/or due to strain localization [119, 135]. The material was still in its passive state since metastable localized corrosion events did not develop into stable pitting, at least within 24 hours of exposure, as can be seen from the in-situ AFM images (Figure 4.16).

The salt spray test results (Figure 4.10) and OCP results (Figure 4.12, Figure 4.13) show that the localized corrosion on fast and slow quenched samples tempered at 500°C may occur already under OCP conditions. Although the OCP results for slow quenched samples tempered at 250°C were relatively nobler than 500°C tempering, slight localized attacks were observed (Figure 4.10) on the former, indicating that the material may pit already under OCP condition. Localized corrosion attacks at can have a direct influence on the susceptibility to environment-assisted cracking (total time to failure), which will be discussed in the next chapter.

Like OCP measurements, the cyclic polarization measurements indicate a similar trend when comparing the fast and slow quenched samples tempered at 250°C and 500°C (Figure 4.14, Figure 4.15). Corrosion current densities measured on the samples were in agreement with the corrosion attacks observed in the salt spray test results (Figure 4.10). The cyclic polarization measurements on both fast and slow quenched samples tempered at 500°C, indicate a weaker tendency to passivate, and is more susceptible to corrosion than the 250°C temper in both 0.1 M and 0.01 M NaCl solutions (Figure 4.14 and Figure 4.15). These results suggest a clear effect of secondary hardening on the
corrosion behavior of the 500°C tempered samples. Moreover, the cyclic polarization measurements of the 250°C temper 0.1 M NaCl solution (Figure 4.14) show that the slow quenched samples had a weaker passivating tendency as compared to fast quenched samples. These results indicate an effect of pearlite phase formation during slow cooling on the corrosion behavior, since pearlite is known to have a poor corrosion resistance [142]. The dominating role of pearlite phase (decreases corrosion resistance) over the austenite phase (increases corrosion resistance) on the corrosion behavior can be observed by comparing the fast quench 250°C temper with slow quench 250°C temper (Figure 4.14 c). Also, the passivating tendency of fast quenched samples tempered at 250°C was observed to deteriorate with an increasing chloride concentration. Judged from the current-potential response (large hysteresis loop) of fast quenched samples tempered at 250°C, there will be a greater tendency for pits to propagate deeper after stable initiation [143, 144]. These observations are in line with those of Taji et al. [145], who also observed similar polarization behavior of AISI 403, tempered at 300°C, in 3.5 wt.% NaCl solution, and concluded susceptibility of the material to localized corrosion under the free natural corrosion potential.

Tempering at 500°C has resulted in the formation of different types of secondary Cr-rich carbides (Figure 4.9), leading to Cr-depletion (sensitization) of different extents in the microstructure. As a result, a discontinuous protective passive film could have formed on the surface of 500°C temper. This was reflected in the cyclic polarization results (Figure 4.14, Figure 4.15), which showed an active corrosion behavior indicating the absence of a continuous protective passive film in both 0.1 M and 0.01 M NaCl solutions. Moreover, the fallout of secondary Cr-rich carbides, as observed by in-situ AFM measurement (Figure 4.17) at open-circuit condition, clearly shows the effect of sensitization, which is apparently higher for secondary carbides despite their smaller sizes. In contrast, the 250°C temper exhibited a passive behavior and a lower susceptibility to localized corrosion.

4.11 Summary

In summary, samples tempered at 250°C exhibited higher corrosion resistance than samples tempered at 500°C in both fast quenched and slow quenched conditions. Fast quenched samples exhibited higher corrosion resistance with an ability to passivate than slow quenched samples when tempered at 250°C. However, when tempered at 500°C, the corrosion resistance was poor for both fast quenched and slow quenched samples. These observed differences clearly indicate the strong influence of microstructure on the corrosion behavior of the material. There are preferential active sites in the microstructure, which dictate the sequence of corrosion events. Secondary Cr-rich carbides formed during 500°C tempering apparently deteriorate the corrosion resistance in spite of their smaller sizes as compared to undissolved Cr-rich carbides.
CHAPTER 5 – Role of stress on the environment-assisted cracking behavior of MSS

The effect of tempering treatment is also associated with stress relieving and hence when comparing the environment assisted cracking (EAC) behavior among tempers, the initial loading conditions need to be altered accordingly for effective comparison. In this chapter, firstly, a new method devised to quantify the stress relieving associated with tempering at 250°C and 500°C is described. Secondly, the approach adopted to alter the initial loading in the EAC tests, based on the quantified stress relaxation values is described. Then the EAC behavior of fast (3°C/s) and slow quenched (0.6°C/s) AISI 420 modified MSS (Uddeholm Stavax ESR) tempered at 250°C, and 500°C, respectively, in a chloride environment are reported.

5.1 Mechanical behavior

Mechanical properties of both fast and slow quenched samples tempered at 250°C and 500°C are summarized in Table 5.1. In the fast quenched condition, 250°C temper showed higher yield, lower tensile stress, and higher ductility than the 500°C temper. Whereas in slow quenched condition, similar yield and ultimate tensile stress values were observed among 250°C and 500°C tempers, however, the former showed higher ductility than the latter. The impact toughness values also indicate higher ductility for 250°C temper compared to 500°C temper in both fast and slow quenched conditions.

<table>
<thead>
<tr>
<th>Tempering temperature (°C)</th>
<th>Yield stress (MPa)</th>
<th>UTS (MPa)</th>
<th>% Elongation (A5)</th>
<th>% Reduction in area</th>
<th>Impact toughness (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast quench (3°C/s) condition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>1375 ± 2</td>
<td>1779 ± 3</td>
<td>8</td>
<td>21</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>500</td>
<td>1321 ± 11</td>
<td>1830 ± 7</td>
<td>6</td>
<td>8</td>
<td>16 ± 1</td>
</tr>
<tr>
<td>Slow quench (0.6°C/s) condition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>1266 ± 9</td>
<td>1611 ± 13</td>
<td>4</td>
<td>4</td>
<td>28 ± 3</td>
</tr>
<tr>
<td>500</td>
<td>1257 ± 12</td>
<td>1622 ± 35</td>
<td>2</td>
<td>1</td>
<td>16 ± 4</td>
</tr>
</tbody>
</table>

5.2 Stress relaxation

The measured macro residual stresses and the computed percentage stress relaxed due to tempering at 250°C and 500°C for both fast and slow quench conditions were summarized in Table 5.2. Except for the fast quenched and 250°C tempered condition,
stress relaxation due to tempering was observed on all other conditions. In both fast and slow quench conditions, more stress relaxation was observed on 500°C temper. Compared to fast quench condition, more percentage stress relaxation was observed on slow quench condition for both the tempers.

**Table 5.2:** % Stress relaxation due to tempering at 250°C and 500°C.

<table>
<thead>
<tr>
<th>Macro Stress (MPa)</th>
<th>Tempering temperature</th>
<th>Macro Stress (MPa)</th>
<th>% Stress relaxation</th>
</tr>
</thead>
<tbody>
<tr>
<td>After bending and before tempering</td>
<td>After tempering</td>
<td>After tempering</td>
<td>% Stress relaxation</td>
</tr>
<tr>
<td>Fast quench (3°C/s) condition</td>
<td>656 ± 47</td>
<td>250°C</td>
<td>671 ± 33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500°C</td>
<td>504 ± 26</td>
</tr>
<tr>
<td>Slow quench (0.6°C/s) condition</td>
<td>695 ± 46</td>
<td>250°C</td>
<td>592 ± 35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500°C</td>
<td>343 ± 23</td>
</tr>
</tbody>
</table>

5.3 EAC Behavior

The computed loading values based on the stress relaxation associated with tempering are summarized in Table 5.3.

**Table 5.3:** Loading values used in EAC tests, based on the stress relaxation associated with tempering.

<table>
<thead>
<tr>
<th>Assumed residual stress in the as quenched condition</th>
<th>250°C Tempering</th>
<th>500°C Tempering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast quench (3°C/s) condition</td>
<td>30%σ_{o.2} = 413 MPa</td>
<td>30%σ_{o.2} = 396 MPa</td>
</tr>
<tr>
<td>% Retained stress after tempering</td>
<td>100%</td>
<td>76%</td>
</tr>
<tr>
<td>Retained stress after tempering</td>
<td>30%σ_{o.2} = 413 MPa</td>
<td>23%σ_{o.2} = 304 MPa</td>
</tr>
<tr>
<td></td>
<td>90%σ_{o.2} = 1238 MPa</td>
<td>68%σ_{o.2} = 898 MPa</td>
</tr>
<tr>
<td>Slow quench (0.6°C/s) condition</td>
<td>30%σ_{o.2} = 380 MPa</td>
<td>30%σ_{o.2} = 377 MPa</td>
</tr>
<tr>
<td>Assumed residual stress in the as quenched condition</td>
<td>90%σ_{o.2} = 1139 MPa</td>
<td>90%σ_{o.2} = 1131 MPa</td>
</tr>
<tr>
<td>% Retained stress after tempering</td>
<td>86%</td>
<td>49%</td>
</tr>
<tr>
<td>Retained stress after tempering</td>
<td>26%σ_{o.2} = 327 MPa</td>
<td>15%σ_{o.2} = 185 MPa</td>
</tr>
<tr>
<td></td>
<td>77%σ_{o.2} = 980 MPa</td>
<td>44%σ_{o.2} = 554 MPa</td>
</tr>
</tbody>
</table>

The values of retained stress after tempering were used in the EAC tests for effective comparison between tempers.

5.3.1 Fast quench condition

The EAC results are summarized in Figure 5.1a. No failure was observed on the 250°C tempered samples. Post-exposure SEM examinations did not show any noticeable corrosion attack on the exposed surface of the tensile specimens. These samples were
further tested for residual tensile strength, and no significant change in yield stress and ultimate tensile strength was observed in comparison to non-exposed specimens. In contrast, the 500°C tempered samples loaded to 23%σ₀.2 failed after 37 h, and those loaded to 68%σ₀.2 failed after 3 h. Figure 5.1b shows the displacement measured by the extensometer throughout the experiments for all tested conditions. For the 500°C-tempered samples, the overall slope of the displacement change per unit time was 350 µm/year at lower (23%σ₀.2) and 17170 µm/year at higher (68%σ₀.2) loads, respectively, which is a measure of the rate of failure and approximately also the crack growth rate.

**Figure 5.1:** (a) Time to failure of the fast quenched (3°C/s) MSS tempered at 250°C and 500°C temper vs. applied tensile stress, (b) change of sample’s gauge length (given in displacement) measured with the extensometer over time.

### 5.3.2 Slow quench condition

The EAC results are summarized in Figure 5.2a. The 250°C temper loaded to 26%σ₀.2 failed after 86 ± 26 h, and those loaded to 77%σ₀.2 failed after 7 ± 2 h, whereas the 500°C temper loaded to 15%σ₀.2 failed after 146 ± 53 h, and those loaded to 44%σ₀.2 failed after 21 ± 2 h. Figure 5.2b shows the displacement measured by the extensometer over time for all tested conditions. For the 250°C tempered samples, the overall slope of the displacement change per unit time was 228 ± 140 µm/year at lower (26%σ₀.2) and 1349 µm/year at higher (77%σ₀.2) loads respectively, whereas for the 500°C tempered samples, it was 237 ± 150 µm/year at lower (15%σ₀.2) and 1507 ± 387 µm/year at higher (44%σ₀.2) loads respectively, indicating the overall rate of failure.
Figure 5.2: (a) Time to failure of the slow quenched (0.6°C/s) MSS tempered at 250°C and 500°C temper vs. applied tensile stress, (b) change of sample’s gauge length (given in displacement) measured with the extensometer over time.

5.4 Characterization of surface corrosion attacks

5.4.1 Fast quench condition

The exposed surface of the 500°C temper-tensile specimens showed several corrosion pits, indicating enhanced susceptibility to localized corrosion (Figure 5.3). Pits in sizes of 50-200 µm of diameter (Feret diameter - longest distance of pit mouth opening) were observed on the samples loaded to 23%σ₀.₂, nucleated next to each other and being interconnected, whereas those loaded to 68%σ₀.₂ showed more discrete pits distributed over the surface (Figure 5.3(a, b)).

Figure 5.3: SEM micrographs revealing localized corrosion on the exposed area of the samples tempered at 500°C, loaded to: (a) 23%σ₀.₂ showing numerous corrosion sites next to each other, (b) 68%σ₀.₂ showing two corrosion pits.
5.4.2 Slow quench condition

Various corrosion morphologies were observed on the 250°C and 500°C tempers subjected to low and high loads (Figure 5.4), indicating their susceptibility to localized corrosion under the OCP condition. Both discrete pits (Figure 5.4(d, h)) and constellations of pits (Figure 5.4(a, g)) were observed on the samples. A crack-like corrosion morphology with a wide crack width (Figure 5.4c) and a resolvable crack emanating from a pit mouth (Figure 5.4b) grown ca.50° to the loading direction were observed on 250°C temper subjected to 26%σ₀.2. A laterally leaner, long pit (Figure 5.4f) grown ca.40° to the loading direction was observed on 500°C temper subjected to 15%σ₀.2. No cracks were observed to be emanating from pit mouth on 500°C temper subjected to 15%σ₀.2 and 44%σ₀.2.

![Figure 5.4.](image)

**Figure 5.4.** SEM micrographs revealing localized corrosion on the exposed area of samples tempered at 250°C, loaded to: (a, b, c) 26%σ₀.2 showing constellation of pits, crack emanating from pit mouth and a crack like corrosion morphology, and (d) 77%σ₀.2 showing discrete pits; and samples tempered at 500°C and loaded to: (e, f, g) 15%σ₀.2 showing constellation of pits, and (h) 44%σ₀.2 showing discrete pits.

Pit density of 22 cm⁻² (corresponding to 51 pits) and 9 cm⁻² (corresponding to 20 pits) were observed on the 250°C temper subjected to 26%σ₀.2 and 77%σ₀.2 respectively, whereas a pit density of 132 cm⁻² (corresponding to 305 pits) and 49 cm⁻² (corresponding to 112 pits) were observed on the 500°C temper subjected to 15%σ₀.2 and 44%σ₀.2 respectively (Figure 5.5a). Pitting development rates (number of pits developed/h) were calculated to be 0.6 pits/h and 0.9 pits/h for 250°C temper subjected to 26%σ₀.2 and 77%σ₀.2 respectively, and 2 pits/h, and 5 pits/h for 500°C temper subjected to 15%σ₀.2 and 44%σ₀.2 respectively (Figure 5.5c). The distribution of pit size for both the tempers is shown in Figure 5.6, which indicates the proportion of pits in their respective size interval. An overall decreasing proportion with increasing size...
interval, with a maximum proportion of pits in the smaller size interval, was observed for both the tempers subjected to low and high loads. The proportion of pits were observed to be greater for samples subjected to low loads than for samples subjected to high loads in most of the size intervals (ca. 70%). The maximum size of pits (Feret diameter) was observed to be 285 µm and 267 µm on 250°C temper subjected to 26%σ₀.₂ and 77%σ₀.₂ respectively, and 545 µm and 412 µm on 500°C temper subjected to 15%σ₀.₂ and 44%σ₀.₂ respectively. Relatively deeper pits were observed on 500°C temper than on 250°C temper subjected to low and high loads (Figure 5.5b). The maximum pit depth measured on 250°C temper subjected to 26%σ₀.₂ and 77%σ₀.₂ was similar, ca. 49 µm, whereas pit depth of 117 µm and 72 µm were measured on 500°C temper subjected to 15%σ₀.₂ and 44%σ₀.₂ respectively (Figure 5.5b).

Figure 5.5. (a) Pit density of 250°C and 500°C temper vs. applied tensile stress, (b) Maximum pit depth of 250°C and 500°C temper vs. applied tensile stress, (c) Pit development rate (number of pits developed/h) of 250°C and 500°C temper vs. applied tensile stress.

Figure 5.6. Pit size (Feret diameter) for 250°C and 500°C tempers indicating the proportion of pits in their respective size interval.
5.5 Fractography

5.5.1 Fast quench condition

Fractography was examined for 500°C tempered condition since failure was observed only on this material. An overview of the fracture surface of 500°C tempered specimen loaded to 23%σ₀.₂ and 68%σ₀.₂ is given in the stereomicroscopic images in Figure 5.7. The gauge cross-section area of the tensile specimen did not change after a catastrophic failure, indicating no noticeable yielding occurred during EAC testing. Large corrosion pits in sizes of up to 640 µm in width and 430 µm in depth were seen on the specimen loaded to 23%σ₀.₂. The specimen loaded to 68%σ₀.₂, in contrast, showed shallow pits with maximum depths of 160 µm. The fracture surface was quite even, with the lower loaded specimens showing a cliff-like morphology in the center of the fracture surface, indicating some ductile rupture prior to catastrophic failure.

![Figure 5.7: Stereomicroscopic images showing the fracture surface of the specimens tempered at 500°C, loaded to 23%σ₀.₂ and 68%σ₀.₂, respectively. The arrows show corrosion pits formed on the exposed surface of the specimen from where EAC cracks initiated.](image)

More detailed SEM analysis of the fracture surface of the specimen loaded to 23%σ₀.₂ revealed intergranular fracture morphology (Figure 5.8a), striation facets (Figure 5.8c), and some quasi-cleavage (Figure 5.8d) with some dimple rupture (Figure 5.8e). In contrast, the higher loaded (68%σ₀.₂) specimens showed no clear signs of dimple rupture but some quasi-cleavage features (Figure 5.8g) with some wide step marks (Figure 5.8h), and also some visible cracks at grain boundaries (Figure 5.8l).

Cross-sectional examinations along the longitudinal axis of the failed specimens revealed corrosion networks with multiple cracking events developed within the interior of the bulk microstructure (Figure 5.9). Cracks were observed to be perpendicular to the loading direction, emanating from corrosion pits and being of transgranular (Figure
5.9b) as well as intergranular (Figure 5.9c) nature. Some cracks were seen to have circumvented undissolved carbides.

Figure 5.8: SEM images showing the fracture surface of the specimen tempered at 500°C, loaded to 23%σ₀.₂: (a,b) grain facets indicating intergranular corrosion/SCC, (c) striation facets indicating hydrogen-assisted cracking, (d) cleavage features indicating brittle behavior, (e,f) dimple rupture and intergranular cracks; loaded to 68%σ₀.₂: (g,h) cleavage features indicating brittle behavior, (i) cleavage and intergranular features, (j-k) grain facets with striation marks indicating both intergranular and hydrogen-assisted SCC, (l) intergranular cracks.
Figure 5.9: SEM cross-section micrographs showing localized corrosion sites and EAC cracks formed in the sample tempered at 500°C and loaded to 23%σ₀.2: (a) numerous discrete localized corrosion sites and cracks initiated at the bottom of the corrosion site, (b) transgranular cracking, (c) branched intergranular cracks which circumvented carbides, (d) multiple corrosion sites and both trans- and intergranular EAC cracks.

5.5.2 Slow quench condition

No macroscopic yielding on the failed faces of both the tempers subjected to low and high loads were observed (Figure 5.10(a, f) and Figure 5.11(a, f)), indicating the embrittling action of the environment. On a macroscopic level, the fractured faces were observed to be primarily in-plane fracture except for a step mark on 500°C temper subjected to 44%σ₀.2 (Figure 5.11f). Micro-fractographic features of both the temper subjected to low and high loads were shown in Figure 5.10(b, c, d, g h, i) and Figure 5.11(b, c, d, g h, i), respectively. Mixed mode fracture morphology consisting of three distinct features such as intergranular with unattacked grain facets, intergranular with attacked grain facets and dimple rupture were observed on 250°C temper subjected to 26%σ₀.2 and 77%σ₀.2. Similarly, three distinct features such as intergranular with unattacked grain facets, intergranular with attacked grain facets and quasi-cleavage were observed on 500°C temper subjected to 14%σ₀.2 and 44%σ₀.2. Even though similar fractographic features were observed, there could be a difference in their area fraction among the samples subjected to low and high loads on a particular temper. Quantifying the fractographic fractions was beyond the scope of this work, however, efforts at Uddeholms AB are made in that direction. Secondary cracks were observed on both the tempers subjected to low and high loads (Figure 5.10(e, j), and Figure 5.11(e, j)). Cracks along the intergranular boundaries with attacked grain facets (Figure 5.11e), across a grain (transgranular cracking) (Figure 5.10e) and along intergranular boundaries (Figure 5.10j and Figure 5.11j) were also observed.
Figure 5.10. SEM images showing the fracture surface of the specimen tempered at 250°C and loaded to 26%σ₀.₂ (a, b, c, d, e) and 77%σ₀.₂ (f, g, h, i, j). (a, f) macroscopic brittle failure, (b, g) intergranular features, (c, f) transgranular features, (d, i) dimple rupture features, (e, j) transgranular and intergranular cracks.

Figure 5.11. SEM images showing the fracture surface of the specimen tempered at 500°C and loaded to 15%σ₀.₂ (a, b, c, d, e) and 44%σ₀.₂ (f, g, h, i, j). (a, f) macroscopic brittle failure, (b, g) intergranular features, (c, f) transgranular features, (d, i) quasi-cleavage features, (e, j) intergranular cracks.

5.6 Simulation

5.6.1 Method

To assist clarification on the effect of stress/strain on the initiation of EAC associated with corrosion pits, FEM modeling was performed using ABAQUS™ 2017 software, to simulate stress and strain evolution around a model pit in a tensile sample, as schematically illustrated in Figure 5.12. The dimensions of the pits, however, were taken from the pit sizes (Feret diameters) measured on the fast quenched 500°C temper. The simulations were performed only for the mentioned condition. The strain and stress
development on a spherical segment, shallow and deep corresponding to pit geometries, were computed using a quarter cylinder volume in order to reduce the computational time. Meshes of tetrahedral elements were created with sufficiently small elements close to the pit. Simulations were performed with models subjected to 23% $\sigma_{0.2}$ and 68% $\sigma_{0.2}$, assuming Young’s modulus of 210 GPa and Poisson’s ratio of 0.3. Plastic properties of the material were taken from the data obtained from tensile tests. The FEM simulation in this work considers real corrosion pits observed during the tests, which are more relevant than fictive cavities often used for simulations. The depth and width are measured values from real pits observed on the samples, whereas the radius (R) is calculated from depth (a) and width (b) values assuming a spherical pit shape \[ R = \left(\frac{a}{2}\right) + \left(\frac{b^2}{8a}\right) \].

![Figure 5.12](image)

**Figure 5.12**: (a) Cylindrical geometry with a model pit used for FEM simulation with the sectioning planes, (b) quarter volume of a spherical model pit, (c) shallow pit model (low depth-to-radius ratio), (d) deep pit model (high depth-to-radius ratio).

### 5.6.2 Stress and strain evolution around a corrosion pit

FEM simulations showed different level of strain and stress developments around deep and shallow corrosion pits. The classification of pits as deep and shallow in this study is based on the depth-to-radius ratio (a/R), where the deeper pits are the ones with relatively higher a/R ratio than the shallower pits. When loaded to 23$\%\sigma_{0.2}$, on the deep pit with a/R of 1.6, the strain and stress localization appeared at the mouth of the pit, whereas on a shallow pit with a/R = 0.7, the strain and stress development was seen to be distributed at the pit surface/walls. Both the pits showed only elastic deformations (Figure 5.13). Varying amount of strain and stress intensities were seen to develop, with maxima at the pit mouth for deep pits having a/R > 1, whereas maxima at the pit surface/wall for shallow pits with a/R < 1 was seen (Figure 5.13 and Table 5.4). In general, deep pits showed approximately double the amount of strain and stress than shallow pits.

When loaded to 68$\%\sigma_{0.2}$, larger strain and stress intensities were seen on similar shallow pits (a/R < 1), with the strain and stress affected volume becoming 2-3-times larger than those seen on the pits loaded to 23$\%\sigma_{0.2}$ (Figure 5.13). Strain and stress localization was seen over the entire pit surface, with the stress values reaching up to
1460 MPa, indicating the onset of plastic deformation. Pits with $a/R < 0.7$ were not observed on these specimens and therefore no modelling was done. However, a pit with similar aspect ratios ($a/R = 0.8$), but significantly smaller size (see Table 5.4), showed slightly larger strain and stress, suggesting larger strain and stress development for smaller pits.

**Table 5.4**: Simulation results of computed* maximum principal strain and stress around pits with varying sizes.

<table>
<thead>
<tr>
<th>Load (fraction of $\sigma_{0.2}$)</th>
<th>Pit depth - $a$ (µm)</th>
<th>Pit width - $b$ (µm)</th>
<th>Pit radius - $R$ (µm)</th>
<th>Depth/radius ($a/R$) ratio</th>
<th>Max. stress (MPa)</th>
<th>Max. strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>23%</td>
<td>70</td>
<td>70</td>
<td>44</td>
<td>1.6</td>
<td>911</td>
<td>0.0043</td>
</tr>
<tr>
<td>23%</td>
<td>430</td>
<td>640</td>
<td>334</td>
<td>1.3</td>
<td>797</td>
<td>0.0038</td>
</tr>
<tr>
<td>23%</td>
<td>20</td>
<td>50</td>
<td>26</td>
<td>0.8</td>
<td>608</td>
<td>0.0028</td>
</tr>
<tr>
<td>23%</td>
<td>160</td>
<td>450</td>
<td>238</td>
<td>0.7</td>
<td>598</td>
<td>0.0028</td>
</tr>
<tr>
<td>68%</td>
<td>20</td>
<td>50</td>
<td>26</td>
<td>0.8</td>
<td>1496</td>
<td>0.0091</td>
</tr>
<tr>
<td>68%</td>
<td>160</td>
<td>450</td>
<td>238</td>
<td>0.7</td>
<td>1460</td>
<td>0.0089</td>
</tr>
</tbody>
</table>

*The depth and width are measured values from real pits observed on the samples. Whereas the radius ($R$) is calculated from depth ($a$) and width ($b$) values assuming a spherical pit shape $R = \frac{a}{2} + \frac{b^2}{8a}$. 

![Simulation results of computed* maximum principal strain and stress around pits with varying sizes.](image)
Figure 5.13: FEM simulation showing the evolution of principal strain and stress adjacent to a deep pit and a shallow pit in the specimens as shown in Figure 5.7 (Fast quench 500°C temper) when loaded to $23\%\sigma_{0.2}$ and $68\%\sigma_{0.2}$.

5.7 Electrochemical Behavior

The long-term OCP trend over time for both fast and slow quenched samples tempered at 250°C and 500°C, respectively, are shown in Figure 5.14. The overall trend for fast quenched 250°C temper showed a slight increasing trend, whereas the fast quenched 500°C temper showed a decreasing trend, indicating an increased dissolution behavior for the latter. Whereas in slow quenched condition, both 250°C and 500°C tempers showed a decreasing trend indicating a similar corrosion behavior, with the latter being more active than the former. The average OCP of three parallel samples after 6 hours of exposure for both fast and slow quenched samples tempered at 250°C and 500°C, respectively, are summarized in Table 5.5.

Table 5.5: Average OCP (vs. Ag/AgCl) of three parallel samples after 6 hours of exposure in 0.3 M NaCl.

<table>
<thead>
<tr>
<th>Quenching rate</th>
<th>Tempering temperature</th>
<th>OCP after 6h of exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast quench (3°C/s)</td>
<td>250°C</td>
<td>-69 ± 36 mV</td>
</tr>
<tr>
<td></td>
<td>500°C</td>
<td>-350 ± 5 mV</td>
</tr>
<tr>
<td>Slow quench (0.6°C/s)</td>
<td>250°C</td>
<td>-294 ± 10 mV</td>
</tr>
<tr>
<td></td>
<td>500°C</td>
<td>-330 ± 9 mV</td>
</tr>
</tbody>
</table>

Figure 5.14: OCP variation over time for both (a) fast and (b) slow quenched samples, tempered at 250°C and 500°C, measured in 0.3 M NaCl solution at room temperature for 6 h (without any applied stress).
5.8 Discussion

5.8.1 Mechanical behavior

The difference between the yield stress and ultimate tensile stress is a measure of the degree of strain hardening (an increase in resistance to localized plastic deformation [39]) [146]. From Table 5.1 it can be inferred that the strain hardening was higher for 500°C temper compared to 250°C temper in both fast and slow quenched conditions. This could be the reason for the observed drop in percentage elongation (measure of ductility) for 500°C temper (Table 5.1). The lower yield stress observed on 500°C temper compared to 250°C temper in both fast and slow quenched conditions could be due to the availability of unpinned dislocations that are free to move under the action of applied stresses [146]. The reason for the availability of unpinned dislocations could be due to the precipitation of secondary carbides at 500°C that removes the carbon, pining the dislocations in the martensitic matrix [146]. Because of the presence of secondary carbides, the dislocation mean free path in the plastic deformation regime is shortened, i.e., the dislocations can move freely only to a shorter distance due to the presence of secondary carbides, which could be the reason for the observed higher ultimate tensile stress on 500°C temper compared to 250°C temper in both fast and slow quenched conditions [146]. It can also be inferred from literature that the total elongation decreases with increasing carbon content at a particular tempering temperature [146].

As the dissolved carbon in the martensitic matrix could be more in the 250°C temper compared to 500°C temper in both fast and slow quenched conditions due to the precipitation of secondary carbides in the later, percentage elongation (a measure of ductility) should be lower for the former than the latter, but the contrary was observed in the measurement. Further investigations are needed to clarify the reason/s for the observations.

5.8.2 Stress relaxation

As seen in Table 5.2, the magnitude of residual stresses after bending and before tempering was more in the slow quenched condition than in the fast quenched condition, i.e., slow quenched samples were bent more than the fast quenched samples due to a greater maximum permissible deformation. A possible reason could be due to the presence of pearlite phase in the slow quenched condition. One of the main sources for residual stress generation in MSS's is the quenching process, and depending on the size of the steel quenched, the magnitude of residual stress changes [55]. During tempering, the magnitude of residual stresses drops with increasing temperature typically due to the enablement of the recovery process [42]. Also, diffusion is enhanced at higher temperatures and therefore tempering at higher temperatures will have a larger effect on solute atom diffusion, which reduces the defect densities in the martensitic matrix and contributes to stress relaxation [147]. However, the secondary
precipitates that form during high temperature tempering can hinder the dislocation recovery due to the presence of carbide coherency strains, thereby increasing the microstrains in the microstructure [148]. Further investigation is needed to comprehensively understand the role of individual phenomena to elucidate the formation/relaxation mechanism of residual stresses at a particular stage of the tempering process. The microstructure has partially recovered after tempering at 250°C and 500°C, seemingly more when tempered at 500°C. Moreover, the magnitude of stress relaxation was more in the slow quenched condition than in the fast quenched condition (Table 5.2). This could be due to a martensitic matrix with a leaner carbon content in the slow quenched condition due to the pearlite phase transformation during cooling. Since the dissolved carbon content is lower in the matrix, the pinning of dislocation could also be lower [146], which could have enabled enhanced recovery during tempering. As tensile stresses are detrimental in EAC from a crack propagation point of view [86], 500°C temper should outlive 250°C temper in both fast and slow quenched condition. This was indeed observed in slow quenched samples tempered at 250°C and 500°C, whereas the contrary was observed in fast quenched samples tempered at 250°C and 500°C, indicating other dominant factors in the failure.

5.8.3 Effect of material

In this study, different microstructures were obtained among samples, by varying the process parameters of heat treatment, without varying the alloying elements. From literature it can be inferred that different microstructures can have different kinetic behavior in the delayed fracture [84]. Also, alloying elements can play a significant role in the kinetics of delayed fractures of martensitic steels (heat treated to a same tensile strength) in distilled water environment; with low alloyed steels exhibiting relatively shorter life [84, 149]. Generally, the EAC susceptibility increases with increasing yield strength of the material [150], but the contrary was observed for fast quenched 250°C temper (Table 5.1 and Figure 5.1), indicating the role of microstructure on the passive film formation. The slow quenched 250°C temper did fail, indicating the role of residual stress on the EAC behavior (total time to failure).

5.8.4 Localized corrosion behavior

The OCP measurements (Figure 5.14, Figure 4.12 and Figure 4.13) suggest that, in both fast and slow quenched conditions, 250°C temper possess better corrosion resistance compared to 500°C temper. The difference in corrosion behavior between fast and slow quenched conditions is due to the different microstructural features such as pearlite and retained austenite. Hence, from a corrosion initiation point of view, 250°C temper should outlive 500°C temper in the EAC test, which was indeed observed in fast quenched condition, whereas the contrary was observed in slow quenched condition, indicating different dominating factors in the environment-assisted failure, in the latter.
5.8.5 EAC behavior

In this study, total time to failure was the criterion used to compare the effect of tempering on the EAC behavior of both fast and slow quenched samples tempered at 250°C, and 500°C, respectively. The 250°C temper did not fail in the fast quenched condition, thus indicating its resistance to localized corrosion. The results showed that in fast quenched condition at two different loading conditions, 500°C temper failed earlier than the 250°C temper (Figure 5.1a) in spite of lower applied stress (Table 5.3), whereas in the slow quenched condition, 250°C temper failed earlier than the 500°C temper (Figure 5.2a) in spite of having a relatively superior resistance to corrosion (Figure 5.13). It is known that the total time to failure in EAC comprises of time to pit, induction time needed for a pit to transform into a crack, time for small cracks to grow and time for long cracks to grow before the catastrophic failure stage [151]. Quantifying the above-mentioned time periods individually is beyond the scope of this work. However, from the pit data analysis (Figure 5.5, and Figure 5.7), failure times (Figure 5.1a, Figure 5.2a), failure rates (Figure 5.1b, Figure 5.2b) and from fractography (Figure 5.8, Figure 5.10 and Figure 5.11), a qualitative assessment can be made regarding the pit growth rate and the cracking rate among the tempers.

On fast quenched, 500°C temper samples, as well as in slow quenched, 250°C, and 500°C tempered samples, higher pit density was found in the low loading condition than in the high loading condition (Figure 5.3 and Figure 5.5a), but on the contrary, higher pit development rate (number of pits developed/unit time) was observed (Figure 5.3 and Figure 5.5c) in the high loading condition than in the low loading condition for both fast and slow quenched condition. From this, it can be inferred that increasing the magnitude of applied stresses on both the tempers increases the pitting susceptibility. Similar behavior regarding the effect of applied stress on the pitting susceptibility of 12%Cr steel was reported in the literature [152], in agreement with our observation.

Both from the overall rate of failure (Figure 5.1b) and survival time data (Figure 5.1a) for fast quenched, 500°C tempered samples, loaded to 304 MPa and 898 MPa, it can be inferred that, most likely the crack growth rate was faster in the latter than in the former.

In the slow quenched condition, as the pit development rate is faster in 500°C temper compared to 250°C temper, the crack growth rate could be slower in the former than in the latter since they both have a similar overall rate of failure in all the loading scenarios (327 MPa (250°C temper) = 228 ± 140 µm/year, 980 MPa (250°C temper) = 1349 µm/year, 185 MPa (500°C temper) = 237 ± 150 µm/year and 554 MPa (500°C temper) = 1507 ± 387 µm/year). Similarly, judged from the survival time data (Figure 5.2a), crack growth rate could be slower in 500°C temper as the survival time is longer for 500°C temper compared to 250°C temper, in all the loading scenarios, in spite of a lower impact toughness (250°C temper = 28J, 500°C temper = 16J). This indicates the
dominant role of applied stress in the failure of slow quenched 250°C temper. However, further work is needed to decouple the crack growth rate from the overall failure rate.

5.8.6 Probable location of crack initiation (pit to crack transition)

This analysis was done only for the fast quenched condition tempered at 500°C. FEM simulation on shallower and deeper pits subjected to 304 MPa revealed elastic strain evolution at the pit surface/wall and mouth, respectively, whereas the simulation on shallower pits subjected to 898 MPa showed a development of plastic deformation around the pit surface/wall (Figure 5.13). This suggests the advancement of pit-to-crack transition (faster crack growth kinetics) for the high loaded specimen (fast quenched, 500°C temper). The simulation also showed that, depending on the aspect ratio (a/R) of the pit, strain and stress localization shifted from pit surface/wall towards pit mouth, when loaded to 304 MPa. Maximum strain and stress was seen to develop near the mouth for deep pits with aspect ratios of ~1.6. In contrast, the strain and stress reached a maximum at the pit surface/wall for shallow pits with aspect ratios of ~0.7. These simulation results are in line with the work of D. A. Horner et al. who simulated pit-to-crack transition in steels [153].

Moreover, the FEM simulation showed that only elastic strains were developed at the pit walls when loaded to 304 MPa. Furthermore, the experimental results suggest that those pits could have evolved into cracks since the samples failed in this loading condition. But from literature it can be inferred that, plastic deformation is needed for a crack to initiate [167], and hence the difference in prediction and experimental observation indicates that, other contributing factors like microstructural effects, which were not considered in the modelling, could have enabled plastic deformation leading to cracking. However, based on Figure 5.3 and Figure 5.13, most likely the crack could have initiated from pit mouth in samples loaded to 23%σ₀.₂. The threshold depth of a pit needed for transition to cracking in a similar steel with comparable loads was shown to be around 50 μm for stresses below the yield point [154], which is in-line with the observations in this study.

5.8.7 Criteria for cracking

Cracking, if due to corrosion, requires a pit or pit-like cavity with a critical size and crack-supporting electrochemistry at the crack tip for a stable crack growth [153, 155-158]. The pit can act as a stress concentrator, which may lead to cracking. The pit depth must be greater than a threshold depth for a crack to initiate from its bottom, which corresponds to a threshold stress intensity, and the pit must actively grow [153, 157]. Cracking is only possible if the crack growth rate equals or exceeds the pit growth rate [155, 156]. At the point of transition from a pit to a crack, the crack may be considered to
have the same depth as the source pit [153, 155] for cases where the crack initiates from
the bottom of the pit.

5.8.8 Mechanism

The observed increasing failure rates (Figure 5.1b, Figure 5.2b) with increasing applied
stresses for both the tempers indicate that the crack tip straining has played an
important role in the cracking process. From literature it can be inferred that the strain
rate and repassivation rate at the crack tip determines the crack increment [159]. If the
former is greater than the latter, arresting of the crack will happen, and if the former is
lesser than the latter, crack advancement will happen, and hence the role of crack tip
straining is to fracture the passive film on the crack tip [159]. Based on the applied
stress, strain rate at the crack tip of fast quenched 500°C temper loaded to 898 MPa is
expected to be higher than the fast quenched 500°C temper loaded to 304 MPa, and the
strain rate at the crack tip of slow quenched 250°C temper is expected to be higher than
the 500°C temper at both loading scenarios. This could have been the reason for the
observed shorter survival time for the above-mentioned samples (Figure 5.1a, Figure
5.2a), as the higher strain rate at the crack tip would have accelerated the successive
events in the failure process [159]. The crack growth in the samples could be due to
active path dissolution and/or hydrogen embrittlement (HE), as these two mechanisms
are predominant in high strength steels [83, 84].

In the active path dissolution mechanism, cracking happens along a susceptible path
[84, 159], and in HE, hydrogen diffuses into the material and causes de-cohesive
rupture [84, 160]. In this study, the experiments were performed under free corrosion
conditions, implying both anodic and cathodic reactions happened on the sample
surface causing anodic dissolution along the active path, which most-likely resulted in
intergranular corrosion and/or intergranular SCC. Hydrogen produced by the cathodic
reaction most-likely diffused into the steel and had led to transgranular cracking [161].
Hence, a combination of the two mentioned mechanisms could have operated during
the failure, in varying magnitude in respective scenarios.

Considering the severity of cracking (total time to failure, Figure 5.1, Figure 5.2) on the
samples with high applied stress, i.e., loaded to 898 MPa (fast quenched, 500°C
temper), 980 MPa (slow quenched, 250°C temper) and 554 MPa (slow quenched, 500°C
temper) (high applied stress samples), active path dissolution alone cannot be the root
cause for cracking. This suggests that hydrogen-assisted cracking in the form of HE was
also involved in the cracking, supporting the SCC process. The hydrogen generated from
the cathodic reaction can be easily absorbed into the microstructure and can rapidly
diffuse (170 µm/s [162]) towards and ahead of the crack tip, accelerating crack growth
[163]. Hydrogen also reduces the capability of stainless steel to passivate and changes
the nature of the surface oxide film [164]. One of the preferential sites for hydrogen
absorption is the stress fields that prevail near the growing crack tip, and as the applied stresses were more in the above-mentioned samples compared to the samples with low applied stresses, it can be inferred that HE could have been the dominating mechanism in the samples with high applied stresses.

Considering the cracking based on the total time to failure (Figure 5.1, Figure 5.2) on the samples with low applied stresses, i.e., loaded to 304 MPa (fast quenched, 500°C temper), 327 MPa (slow quenched 250°C temper) and 185 MPa (slow quenched 500°C temper), active path dissolution could have been the dominating cracking mechanism. The active path for dissolution in these samples would be the Cr-depleted regions along the grain boundaries and also along the boundary of aggregation of grains, which can be observed from the intergranular fractographic features (Figure 5.8, Figure 5.10 and Figure 5.11). But from literature it can be inferred that hydrogen attack can also occur along grain boundaries in high strength steels [163]. The rate of electrochemical hydrogen evolution inside pits and crack tips/walls is directly proportional to the corroding tendency of the material [159], and hence more hydrogen would have been generated in the samples with high applied stresses compared to the samples with low applied stresses (Figure 5.3, Figure 5.5 c). So, active path dissolution mechanism could have been the dominating failure mechanism in the samples with low applied stresses.

By comparing the 500°C temper and 250°C temper in the slow quenched condition, it can be inferred that active path dissolution could have been the dominating mechanism in the later due to its relatively superior corrosion resistance (Figure 5.14). This is also supported by the measured volume fraction of retained austenite (Table 4.1), as the diffusion of hydrogen is slower in the austenite [166]. Probably more fresh surfaces (active path regions) in the slow quenched, 250°C temper became exposed to the corrosive environment due to greater crack tip straining (based on applied stress) leading to shorter survival time (Figure 5.2a) compared to the slow quenched 500°C temper. Whereas, HE could be the dominating mechanism in the slow quenched 500°C temper due to its relatively inferior corrosion resistance (Figure 5.14). The observed longer survival time in the slow quenched 500°C temper could be due to the presence of coherency strains around tempering carbides which act as a trap for hydrogen [165] thus delaying the failure.

5.9 Summary

In summary, stress relaxation increased with increasing tempering temperature. In the fast quenched condition, 250°C temper exhibited superior EAC resistance than 500°C temper in both loading scenarios, indicating the dominant role of corrosion resistance in delaying the failure. Whereas in slow quenched condition, 500°C temper exhibited superior EAC resistance than 250°C temper in both loading scenarios, indicating the dominant role of applied stress in delaying the failure. The pitting susceptibility
increased with increasing applied stress on both fast and slow quenched conditions. The fractographic features suggest that the mechanism of failure was mixed mode involving both active path dissolution and hydrogen embrittlement, which could have been operative during the failure in varying magnitude in respective scenarios.
This study was instituted to gain better understanding of the localized corrosion and environment-assisted cracking behavior of AISI 420 martensitic stainless steel. Many interesting findings were obtained in the process of this study along with new interesting questions. The former is summarized below while the latter is mentioned in the future work section.

**6.1 Conclusions**

**6.1.1 Objective 1**

To understand the role of microstructure on the corrosion behavior of MSS.

**6.1.2. Outcome**

Different microstructures of the steel were obtained by varying the quenching rates and tempering temperatures, without varying the alloying elements of the steel.

**6.1.2.1 Evolution of microstructure**

- Fast quenched (3°C/s) samples, tempered at 250°C consisted of undissolved carbides and nano-sized tempering carbides of the type Cr$_7$C$_3$, Cr$_{23}$C$_6$ and Fe$_3$C, and retained austenite in a martensitic matrix.

- Fast quenched (3°C/s) samples, tempered at 500°C consisted of undissolved carbides and secondary carbides of the type Cr$_{23}$C$_6$, Cr$_7$C$_3$, Cr$_3$C, CrC, Cr$_3$C$_2$ and Cr$_2$C carbides, and retained austenite in a martensitic matrix.

- Slow quenched (0.6°C/s) samples, also consisted of pearlite phase in addition to the above-mentioned phases.

- In both fast quenched (3°C/s) and slow quenched (0.6°C/s) conditions, the volume fraction of the retained austenite was higher for 250°C temper than 500°C temper. The amount of retained austenite was highest in the slow quench 250°C temper.

**6.1.2.2 Role of microstructure on the corrosion behavior**

- Open circuit potential and cyclic potentiodynamic polarization measurements in 0.1 M NaCl solution showed that corrosion resistance of 250°C temper was higher than 500°C temper in both fast and slow quenched conditions.

- Corrosion resistance in 0.1 M NaCl solution for fast quenched 250°C temper was higher than the slow quenched 250°C temper.
Corrosion resistance in 0.1 M NaCl solution was similar for fast and slow quenched samples tempered at 500°C.

Open circuit potential and cyclic potentiodynamic polarization measurements showed metastable local corrosion events on fast quenched 250°C temper, which could develop into stable pitting in 0.1 M NaCl solution.

Fast quenched 250°C temper exhibited a passivating tendency in both 0.1 M and 0.01 M NaCl solutions, and re-passivation of metastable corrosion sites. A weak tendency for re-passivation upon pitting indicated a risk for localized corrosion in 0.1 M NaCl solution.

Fast quenched 500°C temper exhibited an active corrosion behavior indicating no or weak passivating tendency in both 0.1 M and 0.01M NaCl solution.

In fast quenched corrosion, for both 250°C and 500°C tempers, the corrosion potential ($E_{corr}$) decreased and corrosion rate ($i_{corr}$) increased, with increasing chloride concentration. The 500°C temper exhibited a higher susceptibility to localized corrosion.

SKPFM mapping of Volta potential and in-situ AFM measurements showed higher nobility of undissolved carbides than the martensitic matrix in fast quenched 250°C temper.

In fast quenched 250°C temper, regions in the microstructure with the highest susceptibility to localized corrosion were regions adjacent to undissolved carbides, followed by inter-lath regions.

In-situ AFM measurements on fast quenched 250°C temper in 0.1 M NaCl solution revealed metastable localized corrosion events that did not develop into stable pitting.

In-situ AFM measurements in 0.01 M NaCl solution revealed a sequence of localized corrosion for the 500°C tempered condition: first preferential dissolution in the neighboring matrix adjacent to secondary carbides occurs, and then the neighboring matrix next to undissolved carbide dissolves, causing particle fallout from the matrix.

6.1.3 Objective 2

To understand the role of stress on the environment-assisted cracking behavior of MSS.

6.1.4 Outcome

A new method was devised to quantify the stress relieving associated with tempering at 250°C, and 500°C, respectively. Then the quantified values were factorized accordingly
in the initial loading to investigate the EAC behavior of 250°C and 500°C temper in chloride environment.

6.1.4.1 Stress relaxation associated with tempering

➢ Stress relaxation increased with increasing tempering temperature.

➢ In fast quenched condition, surface residual stresses reduced by 24% after tempering at 500°C, whereas no noticeable change after tempering at 250°C was measured.

➢ In slow quenched condition, surface residual stresses reduced by 14%, and 51% after tempering at 250°C, and 500°C, respectively.

6.1.4.2 Loading scheme based on stress relaxation

➢ Two loading scenarios, 30%σ<sub>0.2</sub> and 90%σ<sub>0.2</sub>, were chosen for the EAC testing for both fast quenched and slow quenched conditions.

➢ Based on stress relaxation, fast quenched 250°C temper was loaded to 30%σ<sub>0.2</sub> and 90%σ<sub>0.2</sub>, whereas fast quenched 500°C temper was loaded to 23%σ<sub>0.2</sub> and 68%σ<sub>0.2</sub>, respectively.

➢ Based on stress relaxation, slow quenched 250°C temper was loaded to 26%σ<sub>0.2</sub> and 77%σ<sub>0.2</sub>, whereas slow quenched 500°C temper was loaded to 15%σ<sub>0.2</sub> and 44%σ<sub>0.2</sub>, respectively.

6.1.4.3 EAC behavior of fast quenched condition

➢ The 250°C temper did neither corrode nor crack, thus exhibiting superior resistance to EAC as compared to 500°C temper.

➢ The observed increase in failure rate with increase in applied stress for 500°C temper, indicate the important role played by crack tip straining in the cracking process.

➢ Fractographic observations suggested mixed mode fracture, indicating involvement of both active path dissolution and HE mechanisms.

➢ The total time to failure and the overall failure rate suggest that HE plays an important role in 500°C temper loaded to 68%σ<sub>0.2</sub> compared to 500°C temper loaded to 23%σ<sub>0.2</sub>.

6.1.4.4 EAC behavior of slow quenched condition

➢ The 500°C temper had a longer survival time (superior resistance to EAC) than the 250°C temper in spite of its inferior corrosion behavior, due to the lower amount of applied stresses.
Pitting occurred on both the tempers with pit density decreasing with increasing applied stresses. Pit development rate (number of pits developed over time) increased with increase in applied stress, indicating the enhanced pitting susceptibility.

The pit development rate was faster in 500°C temper compared to 250°C temper, indicating that the crack growth rate could be slower in the former than in the latter as they both have a similar overall rate of failure in both loading scenarios.

The observed increase in failure rate with increase in applied stress for both the tempers, indicate that the crack tip straining has played an important role in the cracking process.

Fractographic observations suggested mixed mode fracture, indicating involvement of both active path dissolution and HE mechanisms for both the tempers.

The total time to failure and the overall failure rate suggest that HE plays a less important role in the EAC behavior in 250°C and 500°C temper loaded to 26%σ₀.2 and 15%σ₀.2 respectively, compared to 250°C and 500°C temper loaded to 77%σ₀.2 and 44%σ₀.2 respectively.

On comparing the corrosion behavior of both the tempers, it can be inferred that HE plays a less important role in the EAC behavior in 250°C temper compared to 500°C temper.

6.1.4.5 Stress and strain evolution around a corrosion pit

FEM simulation showed development of only elastic strains at the pit mouth for deep pits with depth-to-radius (a/R) ratios of ~1.6 for low loads (23%σ₀.2), whereas plastic strains were developed at the pit surface/wall for shallow pits with a/R ratios of ~0.7 for higher loads (68%σ₀.2).

FEM simulation suggested crack formation at the pit mouth for deeper pits, while at the pit surface/wall for shallow corroding sites.

6.2 Future work

The proposals for future work mentioned here are primarily based on the questions that arose during the analysis of results, which are categorized into evidence generation and newer ideas.
6.2.1 Further exploration related to the microstructure

- To support/strengthen the bulk XRD measurements performed, electron diffraction of the undissolved, 250°C, and 500°C tempering carbides needs to be carried out.
- It will be interesting to investigate the reason/s for the observed higher amount of retained austenite in slow quenched condition in spite of higher $M_s$ temperature, and to investigate the reason for the observed morphology of the pearlite phase.

6.2.2 Further exploration related to the corrosion behavior

It will be interesting to,

- Investigate the effect of retained austenite on the corrosion behavior by magnetic force microscopy and scanning Kelvin probe force microscopy.
- Study the effect of austenitizing time on the associated healing (curing of the Cr depletion) effect around the undissolved carbides.
- Perform an in-situ AFM measurement to follow the corrosion process with a focus on 250°C and 400°C tempering carbides. Also exploring the corrosion process of the island pearlite phase observed in the martensitic matrix, will be interesting.
- Study the passive films formed on different tempers by surface sensitive techniques such as X-ray photo electron spectroscopy (XPS), synchrotron-based ambient-pressure XPS (AP-XPS) (high lateral resolution) and photoemission electron microscopy (PEEM).

6.2.3 Further exploration related to mechanical behavior and stress relaxation associated with tempering

It will be interesting to,

- Investigate the reason for the observed lower elongation% on 500°C in spite of having a leaner dissolved carbon content in the martensitic matrix compared to 250°C temper.
- Investigate the mechanism of stress relaxation due to tempering at different temperatures, and to see whether changing the initial applied stress prior to tempering changes the stress relaxation associated with tempering.

6.2.4 Further exploration related to the effect of stress on the localized corrosion behavior

It will be interesting to,
Investigate the effect of applied stress on the localized corrosion behavior of different tempers, which can be used to model the system.

Map the corrosion tendency related to the microstructure under stressed conditions by scanning Kelvin probe force microscopy.

6.2.5 Further exploration related to the effect of stress on the environment-assisted cracking behavior

It will be interesting to,

- Test other loading levels on the tempers, which can be used to model the system.
- Investigate the crack growth of 250°C and 500°C tempers using Kic samples.
- Investigate the failure of tempers from a mechanistic point of view to further support the observation made in this work.

6.2.6 Further exploration based on industrial relevance

- Knowing the exact cooling water chemistry from mold users will enable to customize further studies and tailor the recommendations for users.
- It will be interesting to derive the size (categorized as small and big sized molds) of the molds based on the cooling rate difference between the core and the surface.
Acknowledgements

In this journey of learning and un-learning, I was not only the passenger but also the driver, which has been extremely challenging. This would not have been possible without the support of many people.

Uddeholms AB is gratefully acknowledged for financing this PhD project, which has not only enabled me to explore the questions and answers related to corrosion but also about my own capabilities to handle dynamic situations. Thanks for giving me an opportunity to be a certified researcher.

I would like to thank KTH Royal institute of Technology for partial financing, and giving me a very satisfying and memorable experience during my PhD. The erudite atmosphere is gratefully acknowledged.

I would like to express my heartfelt gratitude to my academic supervisor Professor Jinshan Pan for his kind and able guidance throughout my thesis work. Your crucial support in the beginning of this PhD project is highly acknowledged. Your scientific guidance in the form of critical comments, constructive criticism and open discussions throughout my PhD work are highly acknowledged. I would like to maintain the association with you Sir for future collaboration.

I would like to thank my industrial supervisors for their kind and able guidance throughout this project. Dr. Johnny Sjöström - your engagement was highly motivating and gave me confidence to go beyond my comfort zone. Your critical comments and constructive criticism are highly acknowledged; Dr. Anna Medvedeva - your kind support during the rough contours of this project, your critical comments, your focus on the main issue and timeline are highly acknowledged; Sebastian Ejnermark - metallurgical discussions we had were amazing and thought provoking. Sharing of your metallurgical wisdom and your openness to technical discussion are highly acknowledged. All of your faith, interests and inputs are highly acknowledged.

I would like to thank Dr. Jörgen Andersson for having given me the opportunity (selecting) to do my PhD.

I would like to thank Dr. Cem Örnek for his scientific contribution and genuine help. The loud discussions we had were amazing and thought provoking. Your swiftness in reading my manuscript and giving me the required feedback is highly appreciated. Special thanks goes to Dr. Fan Zhang, Dr. Mattias Forslund, and Dr. Majid Sababi in Professor Jinshan Pan’s group for acclimatizing me to the electrochemical lab, tutoring me how to operate the AFM and for all the technical discussions.

At the Division of Surface and Corrosion Science, KTH Royal institute of Technology, I would like to thank Emeritus Professor Christofer Leygraf, Professor Per Martin
Claesson, Professor Inger Odnevall Wallinder, Professor Mark Rutland, Adjunct Professor Bruce Lyne, Associate Professor Eva Blomberg, Associate Professor Magnus Johnson, Associate Professor Eric Tyrode, Docent Andra Dedinaite, Docent Yolanda Hedberg, Researcher Gunilla Herting PhD, Researcher Jonas Hedberg PhD, Researcher Peter Szakalos PhD, past colleagues - Dr. Akanksha Raj, Dr. Golrokh Heydari, Dr. Hui Huang, Dr. Jesper Ejenstam, Dr. Jing Li, Dr. Junxue An, Dr. Min Wang, Dr. Neda Mazinanian, Dr. Nicklas Hjalmarsson, Dr. Rubén Álvarez-Asencio, Licentiate Sulena Pradhan, Dr. Xian Zhang, Dr. Xiaoyan Liu, Dr. Xin Wang, Dr. Yousef Alipour, present colleagues - Dr. Anna Oleshkevych, Dr. Georgia Pilkington, Dr. Illia Dobbyden, Dr. Jie Cheng, Dr. Patricia Pedraz Carrasco, Dr. Sanghamitra Sengupta, Dr. Seiya Watanabe, Adrien Sthoer, Erik Bergendal, Gen Li, Marie Långberg, Min Liu, Nanxuan Mei, Peter Dömstedt, Tingru Chang, Weijie Zhao, Xuying Wang, Yunjuan He, Zheng Wei for enlightening me by their amazing talks during the Tuesday seminars, and also for listening to my talk, giving me feedback and suggestions. I enjoyed the wonderful fikas, lunch time discussions, and barbecues.

I would like to thank Rolf Helg at AlbaNova mechanical workshop for understanding my drawings and manufacturing the contraptions I designed.

At Uddeholms AB, I would like to thank Dr. Anders Thuvander for his constant support and his involvement in this project. I thoroughly enjoyed our discussions. I would also like to thank Magnus Tidesten, Lars Ekman, Lars Göran Nordh, Lars Jönsson, Jan Johansson, Per-Erik Skogholt, Johan Jensen, Ruslan Sevastopolev, Amanda Forsberg, Anders Johansson, Annica Thörne, Åsa Nilsson, and Per-Olof Carlsson for their excellent support and discussions. I would like to thank the Machining department, Workshop, Customer service department and Chemical analysis lab for rendering excellent support.

I would like to thank Dr. Seshendra Karamchedu for letting me stay in his apartment during my visits to Hagfors. I thoroughly enjoyed the discussions we had about my work as well as on many other tangential topics. I would like to thank Dr. Christos Oikonomou and Sebastian Sivertsen for the free car rides from Hagfors to Karlstad. I would like to thank Dr. Giulio Maistro, and Aydin Selte for the movie nights in Hagfors. I would like to thank Arbab Rehan for the good discussions we had related to the retained austenite and its transformation during tempering. Also I thoroughly enjoyed other discussions and our trips together.

NPTEL (India), MIT OpenCourseWare, nanoHUB and Professor Harry Bhadeshia’s YouTube channel – bhadeshia 123 are thanked for their FREE video lectures.

Abigail Rebecca Oliver is thanked for proofreading the thesis.
I would like to thank my parents for their unconditional love and letting me do what I wanted to do when I showed no sign of progress in what I was doing. I hope now it is pay day for your courage/faith and tremendous patience.

I would like to thank my in-laws for their kind support.

I would like to thank my elder brother and his family for their kind support and affection.

Finally, I would like to thank my female self (my wife) Ramaa for her support during this PhD project. Your amazing adaptability to new situations has enabled me to frequently shuttle between Stockholm and Hagfors without any prior notice. Your patience in reading my manuscripts, and suggestions are highly acknowledged. I believe serenity at home and lip-smacking curry for lunch and dinner has enabled me to explore this PhD-labyrinth without any hesitation.

Krishnan Hariramabadran Anantha
Hagfors, Sweden.
Bibliography


[54] B. Hildenwall, Prediction of the residual stresses created during quenching, PhD thesis, Department of mechanical engineering, Linkoping University, Linkoping, Sweden, 1979, p. 6 - 16.


