Phase Transformation in Advanced High Strength Steels during Austenite Decomposition at Low Temperatures

Fasetransformatie in geavanceerde hoogsterktestaalsoorten gedurende austenietdecompositie bij lage temperaturen

Elisabete Pinto da Silva

Promotoren: prof. dr. ir. R. Petrov, prof. dr. ir. J. Sietsma
Proefschrift ingediend tot het behalen van de graad van Doctor in de Ingenieurswetenschappen: Materiaalkunde

Vakgroep Toegepaste Materiaalwetenschappen
Voorzitter: prof. dr. ir. J. Degrieck
Faculteit Ingenieurswetenschappen en Architectuur
Academiejaar 2015 - 2016
ACKNOWLEDGMENT

I would like to take a moment to express my gratitude for having the opportunity to accomplish this study and to all great people who have been involved and contributed to it. As such, I would like to mention some of them in particular.

First and foremost, I would like to acknowledge my promoters, Prof. Dr. Ir. Roumen Petrov and Prof. Dr. Ir. Jilt Sietsma for all their commitment, patience and motivating talks. I also thank Prof. Dr. Ir. Yvan Houbaert, for his interest, discussions and support in this project. I am honored and pleased to have worked under their guidance.

I would like to thank ArcelorMittal Global R&D Gent for the financial and experimental support to the research project. Also, my supervisor of OCAS, Wei Xu, for sharing his knowledge, advices and industrial input.

I gratefully acknowledge the examination board members for their valuable comments to this thesis contributing to the closing of this study.

My gratitude to Prof. Dr. Ir. Telmo R. Strohaecker, who gave me the opportunity and support to start my studies in the Metallurgy field. Besides, the Physical Metallurgy Laboratory (LAMEF) which was my second house for many years and the “velha-guarda” (Mariane, Neiva, Susi, Etiene, Fabiano, Osvaldo…) who was my second family and good friends.

I would also like to thank Dr. Vitaliy Bliznuk, who has helped me with TEM experiments. Furthermore, Dr. Irene Diego de Calderón for her guidance and assistance for nanoindentation testing; Athina for Dutch translations; Tuan for his help with crystallography issues and Alfonso, the P.hD. student from TUDelft for helping me with modeling.

Thanks to the technicians of the Materials Science Department and OCAS, for their assistance when needed.

I would like to extend my acknowledge to my colleagues from the Materials Science Department for the pleasant moments within and outside work. Particularly, Hadi, Edgar and Jurij, thanks for helping me in topics related to EBSD and for all the nice events organized. Moreover, my dear girls: An Verdiere, Athina Puype, Aurélie Laureys, Dorien De Knijf, Evelien De Wilde, and Irene Diego de Calderón for their friendship.
I could not forget to mention mijn vrienden Maggie and Rebecca; my chicas, Laura and Eva; mon ami Philippe; os amigos Henrique e Juliana; e as malas Cinthia, Camila e Daiane for all their caring.

Many thanks to Marin and his family, for believing and encouraging me during this path.

My special gratitude to my lovely parents and family for trusting and supporting me on my priorities.

This study was only possible thanks to all of you!

Elisabete

Ghent, 15th April 2016
The demand of industrial applications for better mechanical properties of steels has resulted in the development of new steel grades, especially in the past two decades. Improved mechanical properties can be obtained by processing and/or alloying. It is well established that optimum strength and ductility are attained in steels with multiphase microstructures that consist of at least two different products of austenite decomposition. In recent years, significant progress has been made in the development of multiphase steels containing ferrite and/or martensite, bainite, and retained austenite. This trend has been driven mainly by the automotive industry’s needs for vehicle weight reduction, fuel consumption reduction, and enhanced crash performance. Earlier, these requirements were aimed at the development of conventional high strength steels (HSS) and one example is the high strength low alloy (HSLA) steels. However, the balance between strength and ductility limited the performance and the manufacturability of HSLA steels. To fulfill the requirements for increasing strength without compromising ductility and formability, advanced high strength steels (AHSS) have been developed.

AHSS are classified in three generations. The first generation of AHSS consists of microstructures based on bcc phases, including dual-phase (DP) steel, martensitic steel (MS), complex-phase (CP) steel and transformation-induced plasticity (TRIP) steel. Although the strength level for this generation of AHSS is considered satisfactory, the ductility remains a problem.

The second generation of AHSS is based upon an austenitic microstructure, such as the Twinning-induced plasticity (TWIP) steel. This generation of steels exhibits better formability (due to the ductile austenite matrix), but their application is limited, considering that they are highly alloyed steels, resulting in a significant cost increase.

As such, the development of the third generation of AHSS is intended to produce steels with a better combination of strength and ductility than the first generation and at a lower cost than the second generation. The design and control of the microstructure become essential for the third generation. One of the most promising routes is the “Quenching and Partitioning” (Q&P) process, proposed by J. Speer. Besides initial martensite formation, this process causes retention of austenite in the microstructure, resulting in excellent combinations of strength and ductility. During Q&P processing, the steel is annealed to form a fully austenitic microstructure or
austenite–ferrite two-phase structure, and subsequently quenched to a temperature below the martensite start (M_s) temperature. Afterwards, a partitioning treatment is applied (at or above the quenching temperature) and diffusion of carbon from the supersaturated martensite to the untransformed austenite (carbon partitioning) occurs. Austenite is thus stabilized to be retained after quenching to room temperature (RT).

Competing reactions during the partitioning step, such as carbide precipitation or decomposition of austenite, have been reported by several studies. However, the nature of these isothermal transformations still raises the discussion concerning issues like isothermal formation of martensite and bainite. Knowledge of the transformation products and mechanisms that can occur during the isothermal decomposition of austenite at temperatures below M_s is essential to reach the desired microstructure and mechanical properties of a final product.

The understanding of transformation mechanisms and microstructural characteristics formed during the one-step Q&P treatment (in which the partitioning temperature is the same as the quenching temperature) with a longer partitioning time, can be applied to other important processes, such as Quenching and Coiling (Q&C). In this case, the steel is rapidly cooled from the austenitic temperature to a selected coiling temperature. The coil will cool very slowly, and various phase transformation mechanisms may occur, such as: (i) bainite formation, (ii) martensitic transformation, (iii) carbon partitioning from martensite to austenite, (iv) carbide precipitation in bainite and/or martensite, (v) tempering of martensite, etc.

The present study aims to distinguish between the different phase transformations and mechanisms that occur during and govern, respectively, the isothermal and non-isothermal decomposition of austenite at relatively low temperatures.

In this work, two Advanced High Strength Steels (AHSS) were studied: low-silicon (L_Si) steel (0.16C-1.6Mn-0.4Si-0.8Cr-0.3Mo, in wt. %) and high-silicon (H_Si) steel (0.3C-3.0Mn-1.5Si, in wt. %).

The transformation experiments were performed in a dilatometer. The phase transformations in AHSS were investigated during the isothermal decomposition of austenite, with or without initial martensite formation. Rapid cooling to various temperatures above or below \( M_s \) was carried out in a dilatometer with the intention to form controlled volume fractions of initial martensite and austenite, followed by isothermal holding. In a second series of experiments,
non-isothermal decomposition of austenite was studied, cooling to the same temperatures as in the isothermal experiments, simulating coiling by very slow cooling to RT.

According to the results from dilatometry (Chapter V), in the case of the H_Si steel, the isothermal transformation starts after a longer time compared to the same transformation in the L_Si steel. Bainite forms more rapidly in the latter case at isothermal temperatures above $M_s$. The influence of initial martensite on bainite formation is clearly revealed when the isothermal holding is below $M_s$, in the case of the H_Si steel. The results obtained from the coiling experiments (Chapter VIII), exhibit the same trends as those obtained from the isothermal experiments in the L_Si steel. However, in the case of the H_Si steel, the trends associated with the decomposition of austenite during coiling differ from those observed in the case of the isothermal experiments. An important difference is that this decomposition is accompanied by continuous formation of martensite during slow cooling.

The microstructural evolution was characterized by optical microscopy (OM), scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) describing the morphology features of the microstructural constituents. The microstructures obtained after coiling are similar to those obtained from the isothermal treatments in the L_Si steel. These microstructures are formed by different fractions of lower bainite and tempered martensite (or auto-tempered martensite) at temperatures below $M_s$. In the case of temperatures above $M_s$, fresh martensite and retained austenite are also found. On the other hand, in the case of the H_Si steel, the microstructures obtained in isothermal treatments and after coiling differ. The microstructures from isothermal treatments follow the same trend as in L_Si, but after coiling they are mainly formed by martensite.

The phases and volume fractions of retained austenite were analysed by X-ray diffraction (XRD). The retained austenite fraction was found to be relatively independent on the isothermal and/or coiling temperatures, mainly in the H_Si steel. However, austenite is stabilized in lower fractions during the slow cooling than in isothermal experiments when the steel is highly alloyed in silicon. In addition, fresh martensite was formed only at high isothermal and/or coiling temperatures (above $M_s$) because of partial stabilisation of austenite.

Transmission electron microscopy (TEM) and differential scanning calorimetry (DSC) were used for carbide identification (Chapter VI). It was observed that, in the L_Si steel, carbide precipitated in both isothermal and coiling experiments, in lower bainite and tempered (or auto-tempered) martensite. In the H_Si steel, carbides were found predominantly in lower bainite; however, features of tempered martensite accompanied by carbides were also found.
Summary

Vickers hardness was measured to acquire the overall hardness of final microstructures. The results reveal that the mainly bainitic microstructures formed at high temperatures (above \( M_S \)) in isothermal holding and coiling result in softening of the L_Si steel. In addition, a decrease of the experimental temperatures results in hardening of the L_Si steel, owing to the increase of the martensite fraction. This trend is also observed in the case of the H_Si steel in isothermal holding experiments. However, the hardness values are similar for all coiling temperatures in the H_Si steel, i.e., the \( M_S \) temperature does not influence the hardness at the coiling experiments.

Nanoindentation measurements were performed after EBSD scans (Chapter VII) to specify the hardness of individual microstructural constituents formed in the isothermal experiments. A relationship with image quality (IQ) parameter from EBSD and nanohardness is made. These analyses indicated that lower bainite (high-IQ) is the softest phase and fresh martensite (low-IQ) is the hardest microstructural constituent.

The kinetics of isothermal bainite formation was well described by a nucleation-based transformation model, above and below the \( M_S \) temperature. However, the kinetics of non-isothermal decomposition of austenite is not applicable for modeling. It is probably due to the fact that martensite continues to form during the slow cooling.

According to the results obtained from both experiments, a clear difference is observed on the decomposition of austenite in the H_Si steel, depending on the thermal condition it is subjected to. On the other hand, the L_Si steel presents similar transformations, independent of the nature of the experiments (isothermal or non-isothermal). The main findings can be summarized as follows:

- **Isothermal holding:** (i) above \( M_S \): austenite transforms to bainite with carbide precipitates (both steels), and (ii) below \( M_S \): initial martensite is present, which affects the isothermal transformation (bainite) mainly in the H_Si steel, and martensite undergoes tempering, or is auto-tempered in the case of the L_Si steel.
- **Coiling:** (i) above \( M_S \): initially no martensite, but it does form and tempers as soon as the \( M_S \) temperature is passed during slow cooling, and (ii) below \( M_S \): initial martensite is present from the beginning and undergoes tempering. Also in this case, more martensite is formed during slow cooling.
SAMENVATTING

De vraag naar betere mechanische eigenschappen van staal voor industriële toepassingen heeft geresulteerd in de ontwikkeling van nieuwe staalsoorten in de afgelopen 15 – 20 jaar. Verbeterde mechanische eigenschappen kunnen worden verkregen door aanpassingen in de processing en/of de samenstelling van het materiaal. Optimale sterkte en taaiheid worden bereikt in staalsoorten met meer-fasige microstructuren die bestaan uit ten minste twee verschillende fasen die vanuit austeniet gevormd worden. In de afgelopen jaren is aanzienlijke vooruitgang geboekt in de ontwikkeling van geavanceerde multi-fasen staalsoorten, bestaande uit ferriet en/of martensiet, bainiet en austeniet. Staalontwikkeling wordt gedreven door de noden van de automobilindustrie om voertuigen lichter te maken, brandstofverbruik te verlagen en om een verhoogde prestatie bij impact te verkrijgen. Deze vereisten waren eerder al de doeleinden voor de ontwikkeling van gebruikelijke hoge sterkte stalen (HSS) met als voorbeeld de hoge sterkte, laag gelegeerde (HSLA) stalen. Desalniettemin beperkte de balans tussen sterkte en taaiheid de prestatie van de HSLA stalen en de mogelijkheid deze op grote schaal te produceren. Om aan de huidige strengere vereisten te voldoen werden er geavanceerde staalsoorten ontwikkeld om de sterkte te verhogen, zonder afbreuk te doen aan de taaiheid en vervormbaarheid.

Geavanceerde hoge sterkte stalen (AHSS) zijn geclassificeerd volgens drie generaties. De eerste generatie AHSS zijn ferritisch gebaseerde microstructuren, inclusief Dual-Phase (DP) staal, martensitisch staal (MS), complex-phase (CP) staal en Transformation Induced Plasticity (TRIP) staal. Hoewel het sterkteniveau voor deze generatie staal acceptabel is, blijft de taaiheid een probleem.

De ontwikkeling van de tweede generatie AHSS is gebaseerd op een austeniet microstructuur, zoals Twinning induced plasticity TWIP staal. Deze generatie staal vertoont een betere taaiheid (te danken aan de ductiele austeniet matrix), maar ook hun toepassing is beperkt, rekening houdend met het feit dat deze staalsoorten hoog gelegeerd zijn, hetgeen resulteert in een sterke stijging in productiekosten.

Zodoende is de intentie van derde generatie AHSS staal om staal te produceren met een betere combinatie van sterkte en taaiheid in vergelijking met de eerste generatie en een lagere kost dan de tweede generatie van AHSS stalen. De ontwikkeling en controle van de microstructuur zijn van essentieel belang voor de derde generatie staalsoorten en kan bij voorbeeld gerealiseerd
worden door de Quenching & Partitioning methode, voorgesteld door J. Speer. Naast de initiële martensietvorming, veroorzaakt deze methode een behoud van austeniet in de microstructuur, hetgeen resulteert in een zeer goede combinatie van sterkte en taaiheid. Gedurende het afschrik-en partitionerings- (Q&P) proces wordt het staal afgeschrikt vanuit een volledig austenitische microstructuur of een austenitische-ferritische microstructuur bekomen door interkritisch gloeien naar een temperatuur lager dan de martensitische start ($M_S$) temperatuur. Nadien wordt er een partitioneringsbehandeling toegepast (op een temperatuur hoger of gelijk aan de afschriktemperatuur) waardoor er diffusie van koolstof uit de oververzadigde martensiet naar ongetransformeerde austeniet (partitie van koolstof) optreedt. Hierdoor wordt de austeniet gestabiliseerd na afschrikken tot kamertemperatuur.

Concurrerende reacties tijdens de partitioning stap, zoals carbideprecipitatie of transformatie van austeniet, zijn gevonden in verschillende studies. Echter, de aard van deze isotherme transformaties roept nog steeds discussie op over kwesties als isotherme vorming van martensiet en bainiet. Kennis van de omzettingsproducten en mechanismen die kunnen optreden tijdens de isotherme onttbinding van austeniet bij temperaturen onder $M_S$ is essentieel om de gewenste mechanische eigenschappen van een eindproduct te verkrijgen. Daarom is het begrip van transformatiemecanismen en karakteristieken tijdens de een-stap Q&P behandeling met een langere tijd partitioneren toegepast op andere belangrijke processen, zoals afschrikken en oprollen (Quenching & Coiling). In dit proces wordt het staal na een aanvankelijke snelle afkoeling naar aan gekozen temperatuur zeer langzaam gekoeld. Verscheidene fase transformatiemecanismes kunnen voorkomen, zoals (i) bainitische transformatie, (ii) isotherme martensitische transformatie, (iii) koolstofpartitie van martensiet naar austeniet, (iv) carbideprecipitatie in bainiet en/of martensiet en (v) ontlaten van martensiet.

De onderhavige studie beoogt onderscheid te maken tussen de verschillende faseovergangen en mechanismen die optreden en bepalend zijn tijdens de isotherme en niet-isotherme transformatie van austeniet bij relatief lage temperaturen.

In dit werk worden twee geavanceerde hoogsterkte stalen (AHSS) bestudeerd: laag-silicium ($L_{Si}$) staal (0.16C-1.6Mn-0.4Si-0.8Cr-0.3Mo in gew.%) en hoog-silicium ($H_{Si}$) staal (0.3C-3.0Mn-1.5Si in gew.%).

De transformatie-experimenten werden uitgevoerd in een dilatometer. De fase-transformaties in AHSS werden onderzocht tijdens de isotherme onttbinding van austeniet, na aanvankelijke martensietvorming. Proefstukken werden snel afgekoeld tot verschillende temperaturen boven of onder $M_S$ in een dilatometer, met de bedoeling om gecontroleerde volumefracties initiële
martensiet en austeniet te bewerkstelligen. Deze quenching stap werd gevolgd door isotherm gloeien. Bovendien werd niet-isotherme transformatie van austeniet bestudeerd door te koelen tot dezelfde temperatuur als in de isotherme experimenten en vervolgens een langzame afkoeling tot kamertemperatuur uit te voeren.

Data verkregen met de dilatometer (Hoofdstuk V) tonen aan dat de isotherme transformatie van H_Si staal later begint dan de gelijkwaardige transformatie in L_Si staal. Bainiet vormt namelijk sneller in L_Si staal bij isotherme temperaturen boven $M_S$. De invloed van primair gevormde martensiet op de bainietvorming is duidelijk te zien wanneer een isotherme temperatuur boven $M_S$ wordt aangehouden in het geval van H_Si staal. De resultaten verkregen met de niet-isotherme oprolexperimenten (Hoofdstuk VIII) vertonen dezelfde trends als verkregen met de isotherme experimenten in L_Si staal. Niettegenstaande, in het geval van het H_Si staal, verschillen de tendensen die geassocieerd werden met de decompositie van austeniet gedurende niet-isotherm oprollen van deze geobserveerd in het geval van isotherme experimenten. Een belangrijk verschil is dat de decompositie tot bainiet simultaan gebeurt met een continue vorming van martensiet tijdens traag afkoelen.

De microstructurele veranderingen werden waargenomen door optische microscopie (OM), scanning elektronenmicroscopie (SEM) en electron backscatter diffraction (EBSD) om de morfologische kenmerken van de microstructurele componenten te kunnen beschrijven. De microstructuren van L_Si staal verkregen met niet-isotherm oprollen zijn vergelijkbaar met degenen verkregen met isotherme behandelingen. In het algemeen werden de microstructuren gevormd door verschillende fracties lagere bainiet en ontlaten martensiet (of zelf-ontlaten martensiet). In sommige gevallen is er ook restausteniet en verse martensiet gevonden. Daar staat tegenover dat in het geval van H_Si staal, de microstructuren verkregen door isotherme behandelingen en door niet-isotherm oprollen, van elkaar verschillen. De microstructuren verkregen door de isotherme behandelingen volgen dezelfde tendensen als in L_Si staal, maar na niet-isotherm oprollen bestaan de microstructuren in H_Si staal voornamelijk uit martensiet.

De fasen en volumefracties van restausteniet werden geanalyseerd met X-stralen diffractie (XRD). De restaustenietfractie was relatief onafhankelijk van de isotherme en/of oprol temperaturen. Echter, verse martensiet werd enkel gevormd bij hoge isotherme en/of oprol temperaturen wegens onvoldoende (of gedeeltelijke) stabilisatie van de austeniet.

Transmissie elektronen microscopie (TEM) en differentiële scanning calorimetrie (DSC) werden gebruikt voor de identificatie van carbides. In L_Si staal precipiteren de carbides in laag bainiet en ontlaten (of zelf-ontlaten) martensiet, zowel in de isotherme als in de oprol
Samenvatting

experimenten. In H_Si staal werden de carbides vooral gevonden in laag bainiet, maar ook in het ontlaten martensiet.

Vickers hardheidsmetingen werden gebruikt om de hardheid van de uiteindelijke microstructuren te karakteriseren. De resultaten tonen aan dat de bainiet microstructuren, gevormd bij een hoge temperaturen (boven $M_s$) gedurende het isotherm aanhouden van de temperatuur en gedurende het niet-isotherm oprollen, resulteren in een verzachtning van L_Si staal. Additioneel resulteert een verlaging van de experimenteel gebruikte temperaturen in een verharding van L_Si staal, omwille van een verhoging van de martensietfractie. Deze tendens werd ook geobserveerd in het geval van H_Si staal tijdens de isotherme experimenten. De hardheidswaarden zijn vergelijkbaar voor alle oproltemperaturen in het H_Si staal; dit betekent dat de $M_s$ temperatuur geen invloed heeft op de hardheid bij de oprolexperimenten.

Nanoindentation werd uitgevoerd op met EBSD onderzochte samples (Hoofdstuk VII) om de hardheid van de afzonderlijke microstructurele componenten te specificeren. De correlatie tussen de kwaliteit van de indexatie van het diffractiepatroon in EBSD en de nanohardheid werd onderzocht. Daaruit bleek dat het laag bainiet (hoge indexatie kwaliteit) de zachtste microstructurele component is en vers martensiet (lage indexatiekwaliteit) de hardste.

De kinetiek van de isotherme bainietvorming wordt goed beschreven door een nucleatie-gebaseerd transformatie-model, voor temperaturen hoger en lager dan de $M_s$ temperatuur. Daar tegenover staat dat de kinetiek van niet isotherme ontbinding van austeniet naar bainiet niet kan worden gemodelleerd met bestaande modellen. Een mogelijke verklaring hiervoor is dat martensiet blijft gevormd tijdens het trage afkoelen.

Volgens de verkregen resultaten van beide experimenten is er een duidelijk verschil merkbaar tussen de decompositie van austeniet in H_Si staal afhankelijk van de thermische condities van de behandelingen. Aan de andere kant vertonen de transformaties in L_Si staal geen afhankelijkheid van de aard van de experimenten (isotherm of niet-isotherm). De voornaamste bevindingen kunnen samengevat worden als volgt:

- Isotherme experimenten: (i) boven $M_s$: austeniet transformeert naar bainiet met koolstofprecipitatben (dit resultaat geldt voor beide stalen). (ii) Onder $M_s$: primair gevormd martensiet is aanwezig in het staal. Deze martensiet beïnvloedt voornamelijk de isotherme transformatie (bainiet) in H_Si staal, waarbij de martensiet zelf ontlaten wordt of, in het geval van L_Si staal, auto-ontlaten wordt.

- Niet-isotherme oprolexperimenten: (i) oproltemperatuur boven $M_s$: initieel is er geen martensiet aanwezig, maar het wordt gevormd en ontlaten zodra de $M_s$ temperatuur
is bereikt gedurende het traag afkoelen. (ii) oprooltemperatuur onder $M_S$: primair gevormd martensiet is aanwezig en wordt ontlaaten. Tijdens de niet-isotherme oprolexperimenten zal er meer martensiet gevormd worden tijdens het traag afkoelen.
LIST OF PUBLICATIONS

**International Journals of the Science Citation Index (A1)**


**International Scientific Journal (A2)**


**International Journal of the Conference Proceedings Citation Index (P1)**


**To be submitted (A1)**

### List of Abbreviations and Symbols

- $a_c$: Projected contact area in the surface
- $Ac_1$: Start of austenite formation during heating
- $Ac_3$: End of austenite formation during heating
- $Ae_3$: End of austenite formation at equilibrium
- AFM: Atomic force microscopy
- AHSS: Advanced high strength steels
- Al$_2$O$_3$: Aluminium oxide
- B: Bain
- Bcc: Body-centered cubic
- Bct: Body-centered tetragonal
- BF: Bright field
- $Bs$: Bainite start temperature
- $c$: Radius of the plastic zone
- CCT: Continuous cooling transformation
- CI: Confidence index
- CP: Complex phase
- Cr$_7$C$_3$: Chromium carbide
- $D$: Diagonal of the indent
- DIC: Digital image correlation
- DP: Dual phase
- DSC: Differential scanning calorimetry
- $d^\gamma$: Austenite grain size
- $E$: Elastic modulus
- EBSD: Electron backscatter diffraction
- EDX: Energy dispersive X-ray
- $f$: Bainite volume fraction
- fcc: Face-centered cubic
- Fe-C: Iron-carbon
- FEG: Field emission gun
- FIB: Focused ion beam
- FM: Fresh martensite
$f_m$ Fraction of martensite

$F_{max}$ Applied force

gf Gram force

GPa Giga Pascal

$H$ Hardness

$\dot{h}$ Penetration rate

$h$ Penetration depth

$h_p$ Planck constant

$H_{Si}$ High-silicon

$h_c$ Contact depth

$h_f$ Final displacement

$h_{max}$ Displacement at the maximum load applied

HV Vickers hardness

IM Initial martensite

IPF Inverse pole figure

IPS Invariant plane strain

IQ Image quality

$k$ Boltzmann constant

$K_1$ Material constant

kgf Kilo-gram force

KJMA Kolmogorov–Johnson–Mehl–Avrami

K-M Koistinen-Marburger

K-S Kurdjumov-Sachs

kV Kilovolts

$L_{Si}$ Low-silicon

LB Lower bainite

LVDT Linear variable differential transformer

$M_f$ Martensite finish temperature

mm Millimeters

Mo$_2$C Molybdenum carbide

$M_s$ Martensite start temperature

$N$ Newton

nA NanoAmpers

ND Normal direction

$N_i$ Number density of potential nucleation sites
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>nm</td>
<td>Nanometers</td>
</tr>
<tr>
<td>N-W</td>
<td>Nishiyama-Wasserman</td>
</tr>
<tr>
<td>OM</td>
<td>Optical microscopy</td>
</tr>
<tr>
<td>OR</td>
<td>Orientation relationship</td>
</tr>
<tr>
<td>$P$</td>
<td>Load</td>
</tr>
<tr>
<td>PAG</td>
<td>Prior austenite grain</td>
</tr>
<tr>
<td>$P_{\text{max}}$</td>
<td>Maximum load applied</td>
</tr>
<tr>
<td>Q&amp;C</td>
<td>Quenching and coiling</td>
</tr>
<tr>
<td>Q&amp;P</td>
<td>Quenching and partitioning</td>
</tr>
<tr>
<td>Q&amp;T</td>
<td>Quenching and tempering</td>
</tr>
<tr>
<td>$Q^*$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>RA</td>
<td>Retained austenite</td>
</tr>
<tr>
<td>RD</td>
<td>Rolling direction</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotation per minute</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>$S$</td>
<td>Initial unloading contact stiffness</td>
</tr>
<tr>
<td>s</td>
<td>Seconds</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Modification of $T_0$</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Free energies of austenite and ferrite are equal</td>
</tr>
<tr>
<td>$T_{\text{coil}}$</td>
<td>Coiling temperature</td>
</tr>
<tr>
<td>$T_{\text{iso}}$</td>
<td>Isothermal temperature</td>
</tr>
<tr>
<td>TD</td>
<td>Transverse direction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>$T_f$</td>
<td>Finishing the transformation</td>
</tr>
<tr>
<td>$T_h$</td>
<td>Highest temperature for displacive transformation</td>
</tr>
<tr>
<td>TM</td>
<td>Tempered martensite</td>
</tr>
<tr>
<td>$T_P$</td>
<td>Partitioning temperature</td>
</tr>
<tr>
<td>$T_Q$</td>
<td>Quenching temperature</td>
</tr>
</tbody>
</table>
TRIP  Transformation Induced Plasticity
Ts  Starting the transformation
TTT  Temperature-time-transformation
TWIP  Twinning induced plasticity
Vb  Volume of bainitic sub-units
VC  Vanadium carbide
vol.  Volume
W2C  Tungsten carbide
wt.  Weight
XRD  X-ray diffraction
xαb  Carbon concentration in bainitic ferrite
xγret  Carbon concentration in remaining austenite
x  Carbon concentration
xi  Fraction of element i
xα  Ferrite composition in free energy
xγ  Austenite composition in free energy
Z  Geometrical factor
α  Ferrite
αb  Effectiveness of austenite grain boundaries for bainite nucleation
αm  Koistinen-Marburger rate parameter
γ  Austenite
δ  Effective thickness of the austenite grain boundary
ε  Transition carbide (epsilon)
εb  Constant for Berkovich indenter
η  Transition carbide (eta)
θ/Fe3C  Iron carbide (cementite)
κ  Rate parameter (Kappa)
λ  Autocatalytic nucleation
ν  Vibration frequency
χ  Chi carbide
Γ  Derivative of the maximum driving force
ΔGm  Maximum driving force
ε  Strain rate
°C  Temperature in degree celsius
µm  Micrometers
# TABLE OF CONTENTS

Acknowledgment........................................................................................................................................... i  
Summary.......................................................................................................................................................... iii  
Samenvatting.................................................................................................................................................. vii  
List of publications......................................................................................................................................... xiii  
List of abbreviations and symbols.................................................................................................................. xv  
Table of contents............................................................................................................................................ xix

Chapter I: Introduction ................................................................................................................................. 1  
I.1. SYNOPSIS.................................................................................................................................................. 1  
I.2. OBJECTIVE AND THESIS OUTLINE ..................................................................................................... 3  

Chapter II: Literature review .......................................................................................................................... 9  
II.1. INTRODUCTION ....................................................................................................................................... 9  
II.2. ADVANCED HIGH STRENGTH STEEL GRADES (AHSS) .......................................................................... 9  
II.3. AUSTENITE DECOMPOSITION PRODUCTS ............................................................................................ 10  
   II.3.1. BAINITE .............................................................................................................................................. 12  
   II.3.2. MARTENSITE .................................................................................................................................... 16  
   II.3.3. COMBINATION OF MARTENSITE AND BAINITE ............................................................................ 21  
II.4. HEAT TREATMENTS FOR AUSTENITE DECOMPOSITION .................................................................... 23  
   II.4.1. QUENCHING .................................................................................................................................... 23  
   II.4.2. QUENCHING AND TEMPERING ..................................................................................................... 23  
   II.4.3. QUENCHING AND PARTITIONING ................................................................................................. 25  
II.5. MODELING OF ISOTHERMAL TRANSFORMATIONS IN AHSS ................................................................. 28  
REFERENCES................................................................................................................................................... 32

Chapter III: Experimental procedure ............................................................................................................. 37  
III.1. INTRODUCTION ..................................................................................................................................... 37  
III.2. MATERIALS .......................................................................................................................................... 37  
III.3. TRANSFORMATION EXPERIMENTS ...................................................................................................... 38  
   III.3.1. DILATOMETRY .................................................................................................................................. 38  
III.4. MICROSTRUCTURAL CHARACTERIZATION ........................................................................................ 42  
   III.4.1. OPTICAL MICROSCOPY (OM) ......................................................................................................... 42  
   III.4.2. SCANNING ELECTRON MICROSCOPY (SEM) .............................................................................. 43  
   III.4.3. ELECTRON BACKSCATTER DIFFRACTION (EBSD) ...................................................................... 43  
   III.4.4. X-RAY DIFFRACTION (XRD) ........................................................................................................ 45  
   III.4.5. NANOINDENTATION ...................................................................................................................... 46
Chapter IV: Transformation behavior of advanced high strength steels during heating and cooling .............................................................. 53
IV.1. INTRODUCTION .................................................................. 53
IV.2. HEAT TREATMENTS ............................................................. 53
IV.3. CONTINUOUS COOLING TRANSFORMATION (CCT) DIAGRAMS ........................................................................... 58
IV.4. MICROSTRUCTURES ............................................................... 60
IV.5. DISCUSSION ....................................................................... 64
IV.6. CONCLUSIONS .................................................................. 64
REFERENCES ............................................................................ 65

Chapter V: Isothermal transformations in advanced high strength steels above and below the M$_t$ temperature ........................................... 67
V.1. INTRODUCTION .................................................................. 67
V.2. TRANSFORMATION EXPERIMENTS ....................................... 67
V.3. DILATOMETRY STUDY .......................................................... 69
V.3.1. L$_{SI}$ STEEL .................................................................. 69
V.3.2. H$_{SI}$ STEEL .................................................................. 71
V.4. MODELING OF ISOTHERMAL TRANSFORMATIONS ..................... 73
V.4.1. L$_{SI}$ STEEL .................................................................. 73
V.4.2. H$_{SI}$ STEEL .................................................................. 76
V.5. DISCUSSION ....................................................................... 78
V.6. CONCLUSIONS .................................................................. 79
REFERENCES ............................................................................ 81

Chapter VI: Microstructural evolution of advanced high strength steels under isothermal conditions ................................................................. 83
VI.1. INTRODUCTION .................................................................. 83
VI.2. L$_{SI}$ STEEL .................................................................. 83
VI.2.1. MICROSTRUCTURAL CHARACTERIZATION ..................... 83
VI.2.2. X-RAY DIFFRACTION (XRD) .................................................. 89
VI.2.3. CARBIDE IDENTIFICATION ................................................. 89
VI.2.4. QUANTITATIVE ANALYSES OF MICROSTRUCTURAL CONSTITUENTS .............................................................. 91
VI.3. H$_{SI}$ STEEL .................................................................. 92
VI.3.1. MICROSTRUCTURAL CHARACTERIZATION................................................................. 92
VI.3.2. X-RAY DIFFRACTION (XRD) .................................................................................. 96
VI.3.3. CARBIDE IDENTIFICATION .................................................................................... 97
VI.3.4. QUANTITATIVE ANALYSIS OF MICROSTRUCTURAL CONSTITUENTS............... 100
VI.4. DISCUSSION ............................................................................................................. 103
VI.5. CONCLUSIONS ....................................................................................................... 103
REFERENCES .................................................................................................................. 104

Chapter VII: Microstructural Characterization via EBSD and Nanoindentation......... 107
VII.1. INTRODUCTION ........................................................................................................ 107
VII.2. EXPERIMENTAL METHODS .................................................................................... 108
VII.2.1. MATERIALS AND HEAT TREATMENTS ................................................................. 108
VII.2.2. NANOINDENTATION MEASUREMENTS ............................................................... 108
VII.3. MICROSTRUCTURAL EVOLUTION ............................................................................. 111
VII.4. ELECTRON BACKSCATTER DIFFRACTION (EBSD) ............................................. 113
VII.5. NANOHARDNESS .................................................................................................. 113
VII.5.1. H_Si STEEL ........................................................................................................ 113
VII.5.2. L_Si STEEL ....................................................................................................... 118
VII.6. DISCUSSION ........................................................................................................... 121
VII.7. CONCLUSIONS ..................................................................................................... 122
REFERENCES .................................................................................................................. 123

Chapter VIII: Phase transformations in advanced high strength steels during coiling.. 127
VIII.1. INTRODUCTION ........................................................................................................ 127
VIII.2. EXPERIMENTAL METHODS .................................................................................. 127
VIII.2.1. MATERIALS AND HEAT TREATMENTS ............................................................... 127
VIII.3. RESULTS ................................................................................................................ 128
VIII.3.1. L_Si STEEL ....................................................................................................... 128
VIII.3.2. H_Si STEEL ....................................................................................................... 135
VIII.4. MODELING OF THE KINETICS OF MARTENSITE AND BAINITE FORMATION........ 141
VIII.5. DISCUSSION ........................................................................................................... 143
VIII.6. CONCLUSIONS ..................................................................................................... 144
REFERENCES .................................................................................................................. 145

Chapter IX: General discussion, conclusions and suggestion for future work .......... 147
IX.1. GENERAL DISCUSSION ............................................................................................. 147
IX.1.1. QUENCHING TO RT ............................................................................................ 147
IX.2. ISOTHERMAL EXPERIMENTS ................................................................................... 148
IX.3. COILING VS. ISOTHERMAL EXPERIMENTS ........................................................... 150
IX.2. CONCLUSIONS ........................................................................................................ 160
XI.3. SUGGESTIONS FOR FUTURE WORK ......................................................................... 162
REFERENCES .................................................................................................................. 163
I.1. Synopsis

In recent years, significant progress has been made in the development of multiphase steels, in response to the demands of industrial applications. Improvements have been achieved by adjusting the chemical composition and/or processing of the steels [1]. For example, the development of Advanced High Strength Steels (AHSS) was driven mainly by the automotive industry. These grades have been developed with the primary goal of achieving an excellent balance of low cost, low weight, and optimal mechanical properties (i.e., increase in strength without significant loss of ductility) [2, 3].

First-generation AHSS grades typically have multiphase microstructures that constitute mixtures of ferrite and martensite, ferrite and bainite with retained austenite or a complex mixture of martensite, bainite, and retained austenite. Steels with these microstructures are typically referred to as dual phase (DP), transformation induced plasticity (TRIP), and complex phase (CP) steels, respectively. However, second-generation AHSS, such as highly alloyed twinning induced plasticity (TWIP) steels, have mainly austenitic microstructures owing to the higher manganese content, and are hence significantly more expensive than their first-generation counterparts. Steels produced via “Quenching and Partitioning” (Q&P) processes are classified as third-generation AHSS and exhibit an excellent combination of strength and ductility [4, 5].

Q&P is a new processing concept, proposed by Speer et al. [6-8], for creating steel microstructures with martensite and retained austenite. This concept is based on a fundamental understanding of carbon partitioning between martensite and retained austenite. The Q&P process starts with either a fully austenitic microstructure or an austenite/ferrite microstructure in the case of intercritical annealing followed by rapid cooling to the quenching temperature \( T_Q \). In order to form a pre-determined fraction of martensite, a \( T_Q \) lower than the martensite start \( (M_s) \) temperature is used. This part of the heat treatment is referred to as the “quenching step”. In the subsequent “partitioning step”, an isothermal treatment is performed at the same or higher temperature in order to induce the diffusion of carbon from the supersaturated...
martensite to the residual austenite. The Q&P process is classified as (i) one-step: when the partitioning step occurs at $T_Q$ and (ii) two-step: when the partitioning step occurs at a higher temperature. During the final step, the steel is quenched to room temperature (RT) and the low-stability austenite may transform to martensite (referred to as “fresh martensite”), whereas the sufficiently carbon-enriched austenite is retained at RT.

Several studies [7, 9-13] have reported that time-dependent phase transformations occur during isothermal treatments below $M_S$ (after quenching and initial martensite formation). In the case of the Q&P process, competing reactions such as carbide precipitation, decomposition of austenite to bainite or martensite have been reported during short and long partitioning.

Van Bohemen et al. [12] confirmed, through experiments, that bainite forms below $M_S$ in a high-carbon steel (0.66 wt.% C). The transformation kinetics was determined from dilatometry curves and analyzed by using the Kolmogorov–Johnson–Mehl–Avrami model. Furthermore, a combination of dilatometry results and microstructural observations via scanning electron microscopy (SEM) revealed that bainite is formed during the decomposition of austenite below $M_S$.

In another study, Somani et al. [14] investigated different aspects of the decomposition of austenite in a low-carbon steel (0.2C-1.5Si-2.0Mn-0.6Cr in wt.%) during Q&P processing. Dilatometer experiments that consisted of cooling to a temperature below $M_S$, and partitioning for different times and at different temperatures, were performed. The resulting dilatation curves showed that the samples expanded gradually during partitioning, to an extent greater than the dilatation predicted for carbon partitioning. This volume increase was attributed to the isothermal formation of martensite at irregularly changing rates of volume expansion. Prolonged partitioning leads, however, to the transformation of some austenite islands to lower bainite (ferrite laths containing carbides aligned in the same direction). The time required for the initiation of bainite formation decreases with increasing partitioning temperature ($T_p$). At low temperatures (close to 200 °C), untempered, in some cases twinned, high-carbon martensite forms marked by inflexions in the dilatation curves.

In Ref. [15], one-step Q&P heat treatments were conducted on medium-carbon low-alloy steel, with partitioning times of 10, 100, and 1000 s. The sample partitioned for 100 s was the only one that contained, besides lath and plate martensite, thin-film like retained austenite (RA) in the final microstructure. Another observation was the presence of very fine transition carbides inside the thick plates of martensite. The martensite formed on initial quench was tempered
during partitioning step, as in conventional tempering process. Up to this stage (partitioning of 100 s), the carbide precipitation is slow rather than carbon enrichment of austenite is more active. However, on prolonged partitioning, the kinetics of transformation shift in such a way that carbon preferentially accumulate more in carbide instead of RA.

Recently [16], the commonly employed Q&P thermal profile was modified to evaluate the non-isothermal partitioning that might occur during cooling of a wound coil, using a steel with composition 0.19C-1.59Mn-1.63Si (wt. %). The results show that several microstructures could be obtained. Intercritically annealed samples, at the highest cooling temperatures (450 °C to 500 °C), exhibited microstructures containing pearlite with very fine interlamellar spacing as well as grain boundary carbides. At low cooling temperatures (175 °C to 250 °C), most of the austenite was likely stabilized by carbon partitioning from martensite. Samples coiled between 175 °C and 350 °C exhibited microstructural features typical of Q&P steels, i.e., martensite blocks with austenite adjacent to martensite as pools or between martensitic laths as thick films. In addition, some TRIP-like bainite features were also observed in these samples.

Debates persist, however, regarding the nature of these isothermal and non-isothermal transformations (such as, the isothermal formation of martensite and bainite). Nevertheless, knowledge of the transformation products and mechanisms governing the decomposition of austenite at temperatures below $M_S$ is essential to reach the desired microstructure and mechanical properties of the final product.

I.2. Objective and Thesis Outline

The aforementioned discussion reveals that further study of austenite decomposition below $M_S$ is required. The knowledge garnered about the microstructural constituents is essential for understanding the transformation mechanisms and hence the prediction of the kinetics.

Therefore, the aim of this study is to investigate and better understand the nature of the microstructural constituents that form in hot-rolled, coiled AHSS after coiling at low temperatures, i.e., around the $M_S$ temperature. It is known that microstructural processes may occur during the slow cooling after coiling, such as:

- Martensitic transformation;
- Bainitic transformation below $M_S$;
- Carbon partitioning from martensite to remaining austenite;
Introduction

- Carbide precipitation;
- Tempering of martensite.

In the present study, two AHSS grades will be studied, for which the concentration of carbon, silicon, manganese, chromium, and molybdenum constitutes the main difference. These steels are referred to in terms of their silicon concentration, i.e., as H_Si and L_Si, which correspond to high-silicon and low-silicon, respectively, and differing transformation kinetics is expected, based on these differences. The elements C and Mn are γ stabilizers that lower the γ/α phase transformation temperature and reduce the critical quench rate for martensite formation. In addition, alloying with Si increases the time for isothermal transformation; this time is therefore longer for the H_Si steel than for its L_Si counterpart.

As such, an investigation of the transformation kinetics and microstructural evolution in both steels during simulated coiling, supported by isothermal treatments, is aimed at determining:

1) The nature and sequence of the mechanisms that govern the transformations, which occur during the slow cooling of the coils;

2) Influence of the microstructure before the coiling/isothermal treatment (for example, influence of the quenching temperature and quenching rate);

3) The microstructural features (morphology, carbide precipitation, etc.) of the transformation products;

4) Effect on the mechanical properties;

5) Qualitative influence of the alloying effects.

This thesis describes the methods used for the aforementioned determination and the major findings of the study, and is structured as follows:

In Chapter II, a literature overview of the phase transformations occurring in the range of the martensitic transformation temperature is presented. The current literature consists of several studies on isothermal transformations below \( M_s \) and modeling approaches that can be applied to study these isothermal transformations.

The two studied AHSS, the transformation experiments, and the techniques used in this work to characterize the microstructures and the mechanical properties, are described in Chapter III.
The influence of different cooling rates on the final microstructures is described in Chapter IV. Dilatometry data are used to build the CCT diagrams from which the critical cooling rate to avoid ferrite/pearlite and bainite formation, is derived.

In Chapter V, the design of the isothermal transformation experiments and a study of the corresponding kinetics are presented. The characterization of the resulting microstructures is presented in Chapter VI.

The microstructures (and constituents thereof) formed during the isothermal experiments are presented, and a combination of nanoindentation and EBSD techniques is described in Chapter VII. This approach is used to distinguish between martensite and bainite. The grain-average Image Quality (IQ) parameter and the nanohardness data are used to differentiate among the microstructural constituents, based on the assumption that the IQ and nanohardness are both affected by the lattice imperfections.

Once the effect of the isothermal conditions on the phase transformations in AHSS is understood, the influence of a slow cooling (after coiling) on the decomposition of austenite in AHSS is determined. These results are presented in Chapter VIII and the transformation kinetics as well as the microstructural evolution are discussed.

The overall discussion in the final chapter (Chapter IX), focuses on the difference in the chemical composition of the steels and the temperatures applied during the isothermal and non-isothermal treatments. Therefore, the main conclusions drawn, relate the characteristics of the phase transformations (i.e., microstructural constituents and transformation mechanisms) in the two studied AHSS to temperatures in the vicinity of the Ms temperature.


II.1. Introduction

This chapter focuses on various aspects of austenite decomposition and modeling of isothermal transformations in the steel of interest. The most important section represents the state-of-the-art of methods used to characterize the austenite decomposition products and determine the transformation mechanisms. This knowledge constitutes the basis for the experimental procedure and furthers the understanding and interpretation of the obtained results.

II.2. Advanced High Strength Steel Grades (AHSS)

In the last few decades, significant research has focused on the development of advanced high strength steels (AHSS) in an attempt to respond to the demands of industrial applications. The main goal of developing these grades is to improve the balance of low cost, light weight, and excellent mechanical properties, i.e., increase in strength without significant loss of ductility \(^{[1-3]}\).

Several steel grades have been developed, including dual phase (DP), transformation induced plasticity (TRIP), complex phase (CP), and twinning induced plasticity (TWIP) steels; DP, TRIP, and CP steels are classified as 1\(^{\text{st}}\) generation AHSS whereas TWIP steels are referred to as 2\(^{\text{nd}}\) generation AHSS. An overview of representative mechanical properties, for different AHSS grades, is shown in Figure II-1.

The 1\(^{\text{st}}\) generation AHSS typically have multiphase microstructures consisting of mixtures of ferrite and martensite (DP-steels), ferrite and bainite with retained austenite (TRIP-steels) or complex mixtures of martensite, bainite and retained austenite (CP-steels). However, owing to the high manganese concentration, high-alloy 2\(^{\text{nd}}\) generation TWIP-steels have mainly austenitic microstructures, which are produced at exorbitant costs \(^{[4-6]}\).

Consequently, a 3\(^{\text{rd}}\) generation AHSS has been developed and one of the most promising and innovative heat treatments of this generation is the quenching and partitioning
Literature Review

(Q&P) process \cite{7,8}. The ideal microstructure of Q&P steels consists of martensite and retained austenite, and the desired mechanical properties are achieved by controlling the volume fraction of initial martensite and carbon enrichment of the austenite \cite{4-6}.

![Figure II-1: Overview of the mechanical properties of different classes of conventional and advanced high-strength steel (AHSS) grades \cite{5}.]

II.3. Austenite Decomposition Products

The design of the microstructure starts with the austenitization process, which is performed in accordance with parameters such as the heating rate, temperature, and duration of austenitization. Upon cooling, austenite may decompose into various transformation products, each of which forms via different mechanisms, thereby resulting in different types of microstructures. Several phase transformations occur concurrently, in general starting from the same parent phase (austenite). These transformations may occur at different rates. However, the resulting competition in terms of kinetics and the partitioning of the driving force between the precipitating phases, is essential for the development of many microstructures found in commercial alloys \cite{9,10}.

At high temperatures (below $Ae_3$) and low cooling rates, austenite first decomposes to ferrite. This transformation is driven by a reduction in the free energy, of the total system, that occurs when the lattice of austenite transforms to a relatively stable mixture of austenite and ferrite. The change in free energy change is illustrated in Figure II-2(a). As the schematic shows, the total free energy of the system is reduced when austenite having a carbon concentration of $\bar{x}$ at a temperature $T$, is transformed to ferrite that has a composition of $x^{\alpha\gamma}$; the remaining austenite has a composition of $x^{\gamma\alpha}$ \cite{11}.
Austenite is enriched via carbon partitioning during the growth of ferrite grains. Under equilibrium conditions, the composition of austenite follows the $A_{e3}$ line until the eutectoid temperature is reached. The molar fraction of carbon in the ferrite ($x^\alpha$) is in equilibrium with austenite of composition $x^\gamma$. When plotted, these compositions form the boundaries in the Fe-C phase diagram, as illustrated in Figure II-2(b).

Dubé classified the ferrite morphologies into four categories, namely: (i) ferrite as grain boundary allotriomorphs, (ii) Widmanstätten side plates or laths, (iii) intragranular idiomorphs and (iv) intragranular plates. Aaronson has made some additions to the Dubé classification.

Pearlite, i.e., a lamellar mixture of ferrite and cementite, forms when the temperature is lowered. Ideally, pearlite is nucleated as hemispherical nodules on austenite grain boundaries and inclusions, and grow gradually into the austenite grain. The spacing of the lamellae in pearlite varies with the transformation temperature and decreases with increasing degree of undercooling below the eutectoid temperature. Well-defined crystallographic orientation relationships are formed between the cementite and ferrite lamellae within the pearlite nodule, but neither of them has an orientation relationship with the austenite grain into which they grow. These types of decomposition, from austenite to ferrite and pearlite, occur by means of a “diffusional” transformation mechanism. In this case, the transformation occurs via the rearrangement of atoms and the new phase is formed through a diffusional process at the interphase boundary. No substantial strain energy is developed.

At temperatures ranging from 300 – 500 °C, austenite decomposes to bainite, which is considered one of the most complex products of austenite decomposition. Bainitic microstructures are typically described as non-lamellar aggregates of carbides and plate-shaped ferrite. The formation mechanism differs from the diffusional, cooperative, shared-growth
A bainitic ferrite is governed by diffusional or diffusionless (displacive) mechanisms.

Austenite transforms to martensite, i.e., a supersaturated solid solution of carbon in ferritic iron, when high cooling rates are applied (as in quenching) during processing. Martensite has a body-centered tetragonal structure, and for a certain composition, is first formed at the martensite start ($M_S$) temperature. This formation is an athermal process, that is governed by a “displacive” mechanism, and hence the transformation occurs without the diffusion of carbon\cite{11,13}. A schematic illustration of austenite decomposing to ferrite and martensite is shown in Figure II-3.

Bainite and martensite will be described in the following subsections in accordance with the focus of this study; here, the phase transformations resulting from the low-temperature decomposition of austenite are investigated in detail.

**Figure II-3:** Schematic illustration of the transformation mechanisms. IPS = invariant plane strain\cite{11}.

**II.3.1. Bainite**

Around 1940, the term bainite was first used in reference to a decomposition product of austenite that forms at temperatures between the martensite formation and pearlite.
transformation temperatures; this term was used in honor of the significant contribution of one of the researchers, (Bain [14]) who first identified this phase.

Bainite is considered one of the most complex products of austenite decomposition and some issues regarding its formation remain unresolved [15]. Several morphologies have been reported for this phase [16, 17].

**Morphology**

As known from continuous cooling transformation (CCT) diagrams, complex microstructures are formed at various cooling rates. They result from the growth of an acicular ferrite phase associated with a second constituent, which may consist of carbides, martensite, and/or austenite [16, 17]. In order to discuss the basic aspects of bainite, a description of the morphology of isothermally formed bainite will be presented here.

Bainitic microstructures are, in general, described as non-lamellar aggregates of carbides and plate-shaped ferrite. In fact, the morphologies of ferrite-cementite bainitic microstructures are typically classified into two major categories, namely upper and lower (temperature) bainite, in accordance with their formation temperatures (Figure II-4) [18]. The transition between these two morphologies is not always sharp and hence microstructures may contain elements of both.

![Figure II-4: Schematic illustration of the transition from upper to lower bainite](image)

**Upper bainite**

Upper bainite is usually formed at temperatures ranging from 550 °C – 400°C, and consists of clustered fine plates of bainitic ferrite, which are referred to as sheaves. These sheaves have the same crystallographic orientation, which is related to that of the parent austenite phase in which they grow.
The formation of upper bainite starts with the nucleation of ferrite plates at austenite grain boundaries. The growth of each plate is accompanied by a change in the shape of the transformed region and the resulting large strain, cannot be sustained by the austenite. These strains are relaxed by plastic deformation of the adjacent austenite. Consequently, the growth of the bainitic ferrite plate is interrupted, thereby resulting in sub-units that are significantly smaller than the austenite grain. The aforementioned shape change suggests that the growth of bainitic ferrite is governed by a displacive mechanism \[^{12}\].

During the formation of bainitic ferrite, the remaining carbon-enriched austenite, and carbides can precipitate in the regions between the ferritic sub-units. Cementite is the most commonly occurring carbide and as such, elongated cementite particles decorate the boundaries of the bainitic ferrite plates. The magnitude and continuity of the cementite layer varies with the carbon concentration of the steel. Therefore, if sufficient concentrations of alloying elements are present in the steel, then the precipitation of cementite can be suppressed \[^{18-20}\].

**Lower bainite**

Lower bainite forms over a lower range of transformation temperatures (400 °C – 250 °C), compared to upper bainite. In lower bainite, cementite precipitates from both the carbon-enriched austenite (which separates the bainitic ferrite plates), and the supersaturated ferrite (inside the plates of bainitic ferrite). As in the case of upper bainite, cementite constitutes only one of the many possible types of precipitate formed in lower bainite. Cementite precipitation can be suppressed in high-silicon steels (i.e., steels containing >1 wt.% silicon), and transition carbides, such as epsilon carbide, typically precipitate in the bainitic ferrite \[^{12}\]. In addition, cementite precipitates in a unique variant of the orientation relationship, i.e., these precipitates form in parallel arrays at an angle of ~60° to the axis of the bainitic plates.

**Transformation Mechanism**

Over the years there has been an extensive discussion regarding the nature of the bainitic transformation in steels. Although the microstructural or kinetic features of bainite have been repeatedly observed, a generally accepted definition of bainite remains elusive \[^{21}\]. There are two main schools of thought, namely the displacive school and the diffusional school. These schools consist of those who believe that bainite forms by means of a mechanism that is essentially martensitic in nature, and that bainite is a diffusional transformation product, respectively \[^{22}\].
According to the diffusional theory, bainite both nucleates and grows via a reconstructive mechanism with carbon diffusion. The growth rate is greater in the edgewise direction: lengthening of subunits dominates over thickening. This results in the formation and propagation of ledges; with carbide precipitation at the austenite/ferrite boundaries, is relatively similar to that of Widmanstätten ferrite \[21,24\].

The displacive theory \[15, 23, 24\], on the other hand, asserts that a sub-unit of bainitic ferrite nucleates and grows displacively until growth is halted by plastic deformation in the adjacent austenite. Carbon is then rejected from the supersaturated ferrite, via diffusion and precipitation, as carbides in the austenite (forming upper bainite) or precipitates within the sub-unit (forming lower bainite). In addition, new sub-units nucleate and grow on the tips of old ones, in a process referred to as “autocatalytic nucleation”. If carbide precipitation is suppressed, then the growth of bainite is limited by carbon concentration and temperature of the $T_o'$ line, thereby resulting in an incomplete transformation (Figure II-5); the $T_o'$ line represents a modification of $T_0$, which corresponds to the point at which the free energies of austenite and ferrite of the same composition are equal.

**Incomplete reaction**

The incomplete transformation phenomenon may be described as the formation of a significantly smaller fraction of ferrite than that possible under equilibrium conditions at a given isothermal temperature \[25\]. Bainite growth by means of a diffusionless mechanism occurs at temperatures below $T_0$, where the free energy (Figure II-5) of the bainitic ferrite is lower than that of austenite of the same composition. The $T_o'$ curve has a similar definition to $T_0$, except that the stored energy \[26\] (400 J mol$^{-1}$) of the ferrite owing to the displacive mechanism of transformation is taken into account. During isothermal transformation, the excess carbon in the bainite is partitioned into residual austenite, and hence the subsequent plate grows from carbon-enriched austenite. The process ends when the carbon content of austenite reaches the $T_o'$ value, leading to the so-called “incomplete reaction phenomenon” \[19, 27\].
II.3.2. Martensite

Upon cooling, the parent phase, austenite, undergoes a diffusionless transformation to martensite of exactly the same composition (for up to 2 wt.% C), depending on the alloy composition. The solubility of carbon in the bcc structure is exceeded with this transformation. Therefore, martensite assumes a body-centered tetragonal (bct) unit cell in which the \(c\) parameter is greater than the two \(a\) parameters. The higher carbon concentration of the martensite, compared to that of the bcc structure, results in the filling of a greater number of interstitial sites, and hence the tetragonality increases. The consequent lattice distortion and solid-solution hardening by the C atoms, lead to a high hardness of the Fe-C martensite.

The diffusionless, shear mechanism of martensitic transformation is indicative of the strict crystallographic coupling between the parent and product phases. This coupling is typically described by an orientation relationship, which specifies planes and directions of the parent phase and the planes and directions of the product martensite to which they are parallel. The Kurdjumov-Sachs (K-S) and Greninger and Troiano (also attributed to Nishiyama-Wasserman (N-W)) constitute two of the well-established orientation relationships (ORs) determined for ferrous alloy systems. These ORs are described below.

**Kurdjumow-Sachs:** The general form of the K-S lattice is given as:

\[
\{111\}_\gamma // \{101\}_\alpha \\
\langle110\rangle_\gamma // \langle111\rangle_\alpha \quad \text{Habit plane: } \{225\}_\gamma
\]
There are 24 possible variations of this relationship for any crystal and 12 twin pairs with the same habit plane.

**Nishiyama-Wasserman:** The N-W lattice correspondence is given as:

\[
\{111\}_\gamma // \{011\}_M
\]

\[
\langle 112 \rangle_\gamma // \langle 011 \rangle_\alpha
\]

Habit plane: \{259\}_{\gamma}

There are 12 possible variants of this relationship.

In the case of the bcc-phase, the K-S and N-W relationships differ by only 5.3°.

The habit plane is the other important crystallographic parameter that describes the relationship between the parent and product phases. In steels, the habit plane is the plane in the parent austenite on which the martensite forms and grows. When the martensitic transformation is complete, the habit plane corresponds (ideally) the planar interface between the retained austenite and the martensite crystals.

**Transformation Kinetics of Martensitic Transformation**

Austenite decomposes to martensite through an athermal (i.e., non-thermally activated) transformation that occurs mainly with decreasing temperature during uninterrupted cooling. Additional transformation, usually by means of the nucleation and rapid growth of new plates of martensite, is accomplished only by cooling to lower temperatures than those at which the original transformation occurs.

The temperature at which martensite starts to form in a given alloy is designated as the martensite start (\(M_S\)) temperature. The \(M_S\) varies significantly with the chemical composition, especially the carbon concentration, and is indicative of the thermodynamic driving force required to initiate the shear transformation of austenite to martensite.

Likewise, the martensite finish (\(M_F\)) temperature refers to the temperature at which the martensitic transformation is considered complete. However, fractions of untransformed austenite often persist at \(M_F\). Alloys containing more than ~0.3 wt.% C have \(M_F\) values lower than room temperature (RT) and therefore, at RT, significant fractions of untransformed austenite may coexist with martensite, especially in high-carbon steels.
Although martensitic transformations in heat-treatable carbon steels are governed primarily by athermal transformation kinetics, high-carbon, often hyper-eutectoid, or highly Ni-alloyed steels typically undergo isothermal martensitic transformations [30-32].

**Thermodynamics of Martensitic Transformation**

Athermal martensitic transformations must be initiated by some driving force. In other words, austenite decomposes to martensite (of the same composition) only if the free energy of the former is higher than that of the latter. The driving force is given as \( T_0 - M_S \), where \( T_0 \) is defined as the temperature at which strain-free austenite and martensite have the same free energy. The martensitic transformation is initiated with an undercooling and the corresponding driving force increases with decreasing temperature [12]. Therefore, the transformation of austenite to martensite starts at temperatures, which are sufficiently lower than \( T_0 \); at these temperatures, the free energy available from the transformation is able to compensate the strain energy that accompanies the transformation [33]. The schematic in Figure II-6 shows the free energy of austenite and martensite as a function of temperature.

![Schematic showing the free energy of austenite and martensite as a function of temperature](image)

*Figure II-6: Schematic showing the free energy of austenite and martensite as a function of temperature [34].*

**Morphology of Martensite**

Martensite occurs with two main morphologies, namely lath and plate, in heat-treatable carbon steels. Figure II-7 shows the \( M_S \) temperature as a function of carbon concentration. The aforementioned morphologies are formed in the indicated concentration ranges [28].
Chapter II

Figure II-7: Martensite start (\(M_s\)) temperature and morphologies of martensite as a function of the carbon concentration in Fe–C alloys\(^{[28]}\).

Low-carbon martensite (lath martensite): This type of morphology is found in plain-carbon and low-alloy steels with a carbon concentration up to 0.5 wt.% C. The laths are parallel, have approximately the same size (~0.5 μm wide), and they are grouped in packets with low angle boundaries between each lath.

Medium-carbon martensite (acicular martensite): This type of martensite occurs as lenticular plates, forms initially in steels with carbon concentration of ~0.5 wt.%, and for concentrations ranging from 0.5 – 1.0 wt.%, may occur concurrently with lath martensite.

High-carbon martensite (lenticular plate): This type of morphology differs from lath martensite, as evidenced by the non-parallel alignment of the plates. The first plates formed tend to span the parent austenite grains, thereby partitioning the austenite, and hence, the subsequently formed plates are extremely small. Despite this, however, these plates vary significantly in size and are heavily twinned.

Effect of Alloying elements

Most of the alloying elements in solid solution in austenite influence the transformation temperature of the steels, as qualitatively shown in Figure II-8. Increases in the alloying concentration shift the ferrite/pearlite transformation to the right and the bainite onset temperature downwards. With the exception of cobalt and aluminum, the alloying elements lower the \(M_s\) temperature \(^{[35]}\).
Several equations that relate the $M_S$ temperature to the composition of the steel [32,35,36] have been formulated. According to the most widely used equation, suggested in Ref. [37]:

$$M_S(°C) = 565 - (31x_{Mn} + 13x_{Si} + 10x_{Cr} + 18x_{Ni} + 12x_{Mo}) - 600(1 - \exp^{-0.96x_c})$$

the $M_S$ temperature varies exponentially with the carbon concentration. $x_i$ denotes the fraction of element $i$ in wt. % and $M_S$ is in °C.

Besides the alloying elements, carbon has various effects on the transformation. In fact, carbon:

- Lowers the $M_S$ temperature.
- Influences the fraction of retained austenite.
- Influences the morphology of martensite (transition from lath to plate martensite upon increasing carbon concentration).
- Changes the habit plane of martensite.

The $M_S$ temperature also depends on the austenite grain size, which in turn varies with the austenitization temperature [38]. This dependence has been attributed to a refinement of the (austenite) grain size that leads to Hall-Petch strengthening of the austenite; martensite is therefore more easily formed from coarse-grained austenite than from its fine-grained counterpart. In addition, solid-solution strengthening affects the nucleation of martensite and bainite by providing significant resistance to the motion of dislocations involved in the nucleation process.
The volume fraction of austenite and martensite at a selected quenching temperature can be estimated, if the Ms temperature is known. The extent of the athermal transformation of austenite to martensite depends on the undercooling below the Ms temperature and is calculated by using the Koistinen-Marburger relationship which is given as:

\[ f_m = 1 - \exp^{-\alpha(M_s-T_Q)} \]

Equation II-1

where \( f_m \), \( T_Q \), and \( \alpha \) are the fraction of austenite that transforms to martensite during quenching, quenching temperature, and rate parameter, which determines the temperature-dependence of martensite formation, respectively. A value of 0.011 K\(^{-1}\) is typically used for \( \alpha \). However, a composition dependence of this parameter has recently been proposed. This relationship is given as follows:

\[ \alpha(10^{-3}K^{-1}) = 27.2 - (0.14x_{Mn} + 0.21x_{Si} + 0.11x_{Cr} + 0.08x_{Ni} + 0.05x_{Mo}) - 19.8(1 - \exp^{-1.56x_C}) \]

Equation II-2

II.3.3. Combination of Martensite and Bainite

Several studies have reported that a time-dependent phase transformation can occur subsequent to the formation of initial martensite, i.e., after quenching, during the isothermal treatment below the Ms temperature.

This dependence was first observed in high-carbon, often hypereutectoid, or highly Ni-alloyed steels and more recently, low-carbon steels subjected to quenching and partitioning (Q&P) processes. However, questions regarding the nature of the isothermal formation of martensite and bainite, remain unresolved.

Van Bohemen et al. provided experimental evidence of bainite formation below Ms in a high-carbon steel (0.66 wt.% C). The transformation kinetics was investigated from dilatometry curves and analyzed using the Kolmogorov-Johnson-Mehl-Avrami (KJMA) model. The combination of microstructural observations by SEM and dilatometry results revealed that bainite was formed during austenite decomposition below Ms.

In another study, Somani et al. evaluated various aspects of austenite decomposition in a low-carbon steel (0.2C-1.5Si-2.0Mn-0.6Cr in wt.%) subjected to Q&P processing. The corresponding dilatometry experiments consisted of cooling to a temperature below Ms, and partitioning at various times and temperatures. The dilatation curves revealed a gradual
expansion during holding, which exceeded that predicted for carbon partitioning. The volume increase, and the irregular rate thereof, were attributed to the isothermal formation of martensite. A uniform distribution of martensite laths (throughout the microstructure) that thicken with decreasing quenching temperature \((T_Q)\) and fraction of austenite, is also assumed. In contrast, the interlath films are assumed to have approximately constant thickness and when \(T_Q\) is reached, untransformed islands or volumes of austenite transform to martensite. Some of these islands transformed to lower bainite (ferrite laths containing carbides aligned in the same direction) during prolonged partitioning. Moreover, the time required for the start of the bainite transformation decreased with increasing partitioning temperature \((T_P)\).

The influence of initial martensite on the formation of bainite has also been investigated. Kawata \textit{et al.}\cite{46} reported that pre-existing martensite accelerates the bainite transformation, owing to the increased density of nucleation sites at the martensite/austenite interfaces.

Santofimia \textit{et al.}\cite{47} evaluated the possibility of (carbide-free) bainite formation during the partitioning step (in the presence of initial martensite), from the viewpoint of austenite stabilization during the Q&P process. Carbon partitioning and the formation of bainite, both lead to significant carbon enrichment of the austenite. In fact, the change in carbon concentration of the austenite, owing to the formation of bainite, affects the balance between the carbon in the martensite and the carbon in the austenite. The rate at which austenite will attract carbon from the martensite is therefore also affected. Similarly, the increased carbon concentration of the austenite (owing to the carbon partitioning from martensite) would accelerate the rate at which the austenite reaches the maximum carbon content, at which bainite formation ceases.

Many features of the bainite transformation are consistent with those described in the phenomenological theory of martensitic transformations at low temperatures, and hence these transformations are considered similar. This is especially true for low-carbon “lath” martensite and low-carbon bainite, although similar habit planes and morphologies are sometimes observed for martensite and bainite in higher-carbon steels. In fact, if the behavior of substitutional atoms is examined in detail, then lower bainite appears extremely similar to lath martensite, except that the martensitic transformation occurs without the diffusion of carbon\cite{22}.
II.4. Heat Treatments for Austenite Decomposition

II.4.1. Quenching

During quenching, the steel is rapidly cooled to low temperatures (usually RT), at which nearly all of the austenite transforms to martensite. The corresponding critical quenching rate represents the minimum rate of quenching required to avoid the occurrence of other transformations at temperatures higher than RT. The resulting fully martensitic microstructure is quite hard but may be very brittle and has a low toughness.

In low-carbon steels, carbides often precipitate within the quenched martensite. This precipitation is related to the auto-tempering process, in which the martensite initially formed near $M_s$ is tempered during the remaining quenching time \[48\].

Carbon diffusion is typically negligible at the quenching temperatures, (normally RT, 150 – 250 °C in Q&P processing). However, some studies \[7, 8, 39, 40\] have indicated that carbon partitioning from martensite to austenite, manifested as thin interlath films, occurs during cooling to temperatures just below the $M_s$ temperature.

II.4.2. Quenching and Tempering

Quenching and tempering (Q&T) is a combined heat treatment process, which consists of quenching to RT and subsequent heating to a higher temperature. This process is commonly applied to martensitic structures, where tempering is performed in order to achieve optimum mechanical properties tailored for specific applications. The final properties of a quenched and tempered steel will depend on the microstructure that results from the Q&T process \[49\]. In general, the microstructure of a Q&T steel consists of tempered martensite with carbide precipitates, and depending on the temperature, the martensite decomposes as follows \[29\]:

- Martensite $\rightarrow \alpha + \eta/\epsilon$-carbide (Fe$_2$C/Fe$_{2,4}$C)
- Martensite $\rightarrow \alpha + \theta$-carbide (Fe$_3$C)

The density and size of the carbides increase, in general, with increasing tempering temperature. However, an investigation of high-frequency induction heat treatments revealed that this dependence is not always observed \[50\].
As briefly described in the following sections\textsuperscript{[28]}, parameters such as the temperature, time at temperature, cooling rate from the temperature, and composition of the steel, are essential for the tempering process.

**Tempering Temperature:** The tempering temperature influences the mechanical properties. For example, the ductility at ambient temperatures, as determined from either the elongation or the reduction in area, increases with tempering temperature, i.e., the elongation and reduction in area increase continuously with the temperature. The toughness of most steels (as determined by means of a notched-bar impact test) varies with the tempering temperature. At tempering temperatures ranging from 260 – 320 °C, the impact energy decreases to a value below that obtained at \( \sim 150 \) °C, and above 320 °C, increases again with increasing temperature. Plain-carbon and alloy steels both exhibit this type of tempering behavior.

**Tempering Time:** Steels are usually tempered for 1 – 2 h. Prolonged tempering is avoided, in order to prevent an excessive decrease in the hardness and possible temper embrittlement.

**Cooling Rate:** Some of the mechanical properties (for example, the toughness) are also affected by the cooling rate from the tempering temperature. The toughness decreases if the steel is cooled slowly through temperatures ranging from 375 – 575 °C. The elongation and reduction in area may also be affected.

**Steel Composition:** Alloaying elements typically slow the rate of softening, especially at high tempering temperatures. In fact, compared to carbon steels, alloy steels must be tempered at higher tempering temperatures in order to achieve a given hardness in a certain amount of time. Alloaying elements can be characterized as carbide forming or non-carbide forming. Carbide-forming elements (chromium, molybdenum, tungsten, vanadium, tantalum, niobium, and titanium) retard the softening process, owing to the formation of alloy carbides. In contrast, the non-carbide forming elements (nickel, silicon, aluminum, and manganese) remain in solution in the ferrite and have only a small effect on the hardness resulting from the tempering process. Strong carbide-forming elements (chromium, molybdenum, and vanadium) are the most effective in increasing the hardness, at temperatures higher than 205 °C.

Carbon has the most intense effect on steels during tempering. The carbon concentration influences the hardness of the as-quenched martensite, and changes the crystal orientation of the laths. In addition, the \( Ms \) temperature and the probability of auto-tempering decrease with increasing carbon concentration\textsuperscript{[12]}. 


The tempering of as-quenched martensite is based on Fe-C martensite, whose carbon concentration ranges from 0.1 – 2.0 wt.%. This tempering is divided into four distinct but overlapping stages, as described in the following

**Tempering Stages**

**First Stage:** The first stage of tempering occurs at temperatures ranging from 100 to 200 °C. Depending on the composition, plates or rods of epsilon (ε) carbide are formed at these temperatures. Surface relief accompanies the precipitation of these carbides, whose faulted substructure, indicates that the precipitation is diffusion-controlled.

**Second Stage:** The second stage of tempering occurs at temperatures ranging from 200 to 300 °C, where retained austenite decomposes into cementite and ferrite. In low-carbon steels, the retained austenite occurs as interlath films, and the cementite films formed during the decomposition play an important role in tempered martensite embrittlement. The stability of the films may be partly attributed to the redistribution of carbon to the interlath austenite films during quenching. In high-carbon steels, retained austenite is present as volumes trapped between the martensite plates and decomposition occurs via nucleation of the ferrite/carbide aggregates at the martensite-austenite interface.

**Third Stage:** The third stage of tempering occurs at temperatures ranging from 250 to 700 °C, and involves a number of competing processes. In the early part of this stage, χ carbides are formed (rather than ε carbides) and these are gradually replaced by cementite. Initially, cementite precipitates have a plate-like morphology, and are transformed into spheroidal particles with increasing tempering temperature and the occurrence of “Ostwald” ripening. The martensitic matrix may also undergo recrystallization, recovery, and grain growth.

**Fourth Stage:** The fourth stage of tempering occurs at temperatures ranging from 500 to 700 °C. If strong carbide-formers (such as chromium, molybdenum, tungsten, and vanadium) are present in the steels, cementite is replaced by more stable alloy carbides such as Cr7C3, Mo2C, W2C or VC, whose formation is controlled by the diffusion of substitutional elements.

**II.4.3. Quenching and Partitioning**

Quenching and Partitioning (Q&P) is a new processing concept, proposed by Speer et al. [7, 8] for creating steel microstructures that contain retained austenite. This concept is based on a fundamental understanding of carbon partitioning between martensite and retained austenite.
The Q&P process starts with a fully austenitic microstructure (or austenite/ferrite in the case of intercritical annealing), which is then rapidly cooled to the quenching temperature ($T_Q$). In order to form a pre-determined fraction of martensite, a $T_Q$ lower than the $M_S$ temperature is chosen. This part of the heat treatment is referred to as the “quenching step”. After the quenching step, an isothermal treatment is performed at the same or higher temperature in order to induce the diffusion of carbon from the supersaturated martensite to the residual austenite; this is referred to as the “partitioning step”. The Q&P process is described as either (i) one-step: when the partitioning step is performed at $T_Q$ or (ii) two-step: when the partitioning step is performed at a temperature higher than $T_Q$. After the partitioning step, the steel is quenched to RT during which the less stable austenite may transform to martensite (called “fresh martensite”), whereas the sufficiently carbon-enriched austenite is retained at RT. A schematic of the heat treatment process is shown in Figure II-9.

![Schematic of the Q&P process](image)

**Figure II-9: Schematic of the Q&P process**

### Resulting Microstructures

The microstructures resulting from Q&P process typically consist of martensite and retained austenite (when fully austenitized), or with ferrite (when intercritically annealed) \[^{51-53}\].

Two types of martensite can be formed:

(i) Initial martensite (IM): this type of martensite is formed during the first quench, has a lath-type morphology, and undergoes tempering during the partitioning step. The dislocation density decreases owing to recovery, and hence this transformation product is less hard and easier to etch than the other type of martensite.
(ii) Fresh martensite (FM): this type of martensite is formed during the final quench to RT from austenite that has a higher carbon concentration than the nominal concentration of the steel and the IM. Furthermore, FM is an untempered martensite and is therefore more difficult to etch than IM; the extremely high dislocation density of FM also results in brittleness of the material. The characterization of, and distinction between, IM and FM is difficult. After suitable etching of the materials, the volume fraction of these constituents can be quantified via dilatometry and SEM. Moreover, electron backscatter diffraction (EBSD) microscopy provides insight into the morphology, crystallography or internal structure of the constituents. The correspondence between image quality (IQ) of the crystal reflections and martensitic constituents can be used to distinguish between IM and FM. As previously mentioned, IM grains consist of fewer lattice imperfections and, accordingly, exhibit higher IQ than FM. However, the effect of grain boundary regions on the IQ measurements must be excluded, in order to accurately quantify the volume fraction of martensitic constituents, by using the IQ $^{[54]}$.

Retained austenite exhibits various morphologies, and can be stabilized as both interlath film and blocky retained austenite on the martensite packet boundaries or the parent austenite grain boundaries.

**Importance of the chemical composition design**

The chemical composition has a significant influence on the microstructures that are achievable via the Q&P process. The composition should fulfil the following requirements $^{[3, 7, 8]}$:

(i) Avoid possible formation of reconstructive phases, such as ferrite and/or pearlite, during the first quench. Furthermore, the elements present should retard the formation of bainite and reduce the bainite start temperature, in order to minimize the possible overlap between the carbon partitioning and the formation of bainite. This can be achieved by alloying additions of Mn, Ni or Cr, which will shift the nose of the TTT diagram to longer times, compared to those without the additions; at these longer times bainitic transformation during carbon partitioning can be avoided.

(ii) Suppression of carbide precipitation: carbide formation leads to carbon consumption, and the consumed carbon atoms are therefore no longer available to enrich the austenite. Understanding and controlling carbide precipitation processes that may occur during partitioning treatments associated with the Q&P process are therefore essential.
Cementite formation can be eliminated or suppressed through additions of Si or Al. The formation of cementite can therefore be prevented during the tempering of martensite. Moreover, the possible formation of transition carbides (ε or η carbides are present from early-stage tempering), can be delayed to later-stage tempering (where θ-Fe₃C can form) [43, 55].

II.5. Modeling of Isothermal Transformations in AHSS

The isothermal formation of bainite has been extensively investigated in recent years. As previously mentioned, there are two main theories that describe the kinetics of bainite formation, i.e., one that attributes the kinetics to diffusional mechanisms and the other to displacive mechanisms; the existing models for bainite formation are usually divided into these two categories [37, 56-58].

Santofimia et al. [59] conducted a thorough evaluation of displacive models for bainite transformation kinetics. Most models give a reasonable prediction of the kinetics for high-silicon steels. However, issues surrounding the potential nucleation sites in lean-silicon steels remain unresolved. In addition, it is not clear which fitting parameters are used in several papers.

Van Bohemen and Sietsma [60] developed a model for Fe-C alloys with low-silicon content. In that model, a dependence of the nucleation rate on the number density of potential nucleation sites ($N_i$), a factor accounting for autocatalytic nucleation ($\lambda$), and an activation energy ($Q^*$) for nucleation is assumed.

Bainite formation is considered to start with the nucleation of sub-units at the boundaries of austenite grains. The strains generated in the surrounding austenite lead to “autocatalytic nucleation” at the tip of these sub-units, which are assumed to grow rapidly. Nucleation, which proceeds more slowly than the growth of these sub-units, is, therefore, the rate-determining process.

The rate of bainite nucleation, is expressed as:

$$\frac{dN}{dt} = \frac{kT}{\hbar_p} (1 - f - f_M)N_i(1 + \lambda f) \exp\left(-\frac{Q^*}{RT}\right)$$

Equation II-3
where

\( k \) = Boltzmann constant.

\( h_P \) = Planck constant.

\( N_i \) = number density of potential nucleation sites initially present in the austenite.

\( \lambda \) = autocatalytic nucleation parameter.

\( Q^* \) = activation energy for nucleation.

\( R \) = gas constant.

\( f \) = bainite volume fraction.

\( f_M \) = martensite volume fraction.

\( T \) = temperature.

\( t \) = time.

\( Q^* \) is assumed to be constant during the course of isothermal bainite formation, when carbide precipitation prevents carbon enrichment of austenite. Moreover, bainite grows rapidly and the average volume of the bainitic sub-units (\( V_b \)) is assumed to be constant during the transformation. Therefore, the volume fraction of bainite varies with the nucleation rate as follows:

\[
\frac{df}{dt} = \frac{dN}{dt} V_b
\]

*Equation II-4*

Substituting Equation II-3 into Equation II-4 leads to a differential equation for the formation of bainite:

\[
\frac{df}{dt} = (1 - f - f_M)(1 + \lambda f)\kappa
\]

*Equation II-5*

where \( \kappa \) is a temperature-dependent rate parameter that is defined as:

\[
\kappa = \frac{kT}{h} \alpha^b (T_h - T) \exp \left(-\frac{Q^*}{kT}\right)
\]

*Equation II-6*

In Ref. [60], \( N_i \) is proposed as:

\[
N_i = \frac{\alpha^b}{V_b} (T_h - T)
\]

*Equation II-7*
Literature Review

where

\( T_h = \) highest temperature at which displacive transformations can occur.

\( \alpha^b = \) represents the effectiveness of austenite grain boundaries for the nucleation of bainite, and is determined from:

\[
\alpha^b = \frac{Z\delta}{d^\gamma} \alpha^m
\]

*Equation II-8*

\( Z, \delta, d^\gamma, \) and \( \alpha^m \) are a geometrical factor, the effective thickness of the austenite grain boundary, the austenite grain size, and the Koistinen-Marburger rate parameter for martensite formation, respectively. Equation II-8 shows that \( \alpha^b \) is inversely proportional to the austenite grain size.

\( T_h \) can be calculated considering the influence of the chemical composition using the empirical equation proposed by Van Bohemen \[37\]:

\[
T_h = 835 - 198x_c - 91x_{Mn} - 15x_{Si} - 73x_{Cr} - 36x_{Ni} - 87x_{Mo}
\]

*Equation II-9*

where the concentration \( x_i \) of element \( i \) is expressed in weight percent and \( T_h \) is in °C.

Equation II-5 corresponds to the time-dependent volume fraction of bainite in lean-silicon steels and contains only two fitting parameters, \( \lambda \) and \( \kappa \); these are determined from the best fit to the experimental isothermal transformation kinetics. In this model, \( Q^* \) decreases linearly with temperature. The influence of the austenitizing temperature is reflected in \( \lambda \), which increases with increasing austenite grain size.

The aforementioned model \[60\] can also be used to calculate the kinetics of bainite formation in high-silicon steels, with the addition of a procedure that accounts for the carbon enrichment of the remaining austenite \[37\]. The carbon concentration in the remaining austenite is determined from the volume fraction of bainitic ferrite and its effective carbon concentration. In this case, the rate parameter \( \kappa \) is given as:

\[
\kappa = \nu \ast \alpha^b \exp\left(-\frac{K_1 \Gamma}{R} \right) (T_h - T) \exp\left(- \frac{Q_b}{RT} \right)
\]

*Equation II-10*

where \( \nu \) is the oscillation frequency, \( K_1 \) is a material constant, \( \Gamma \) is the derivative of the maximum driving force \( \Delta G_m \) with respect to \( T \) and \( Q_b = Q_0 - K_1 \Gamma T_1 \).

*Equation II-11*
The rate parameter is both composition- and temperature-dependent and is affected by an increase in the carbon concentration of the austenite. Compared to a low-carbon concentration, a high concentration gives rise to a higher effective activation energy and hence a smaller undercooling. The carbon concentration leads therefore to a strong dependence of $\kappa$ on $Q_b$ and $T_b$ (see Equation II-10).
References


Chapter III: EXPERIMENTAL PROCEDURE

III.1. Introduction

This chapter presents a summary of the studied steels, the heat treatments employed to create various microstructures, and the material characterization techniques used in the present study. Additional experimental details are provided, where necessary, in the following chapters.

III.2. Materials

Table III-1 shows the chemical compositions of the two advanced high strength steels (AHSS) studied in this work. These steels are referred to in terms of their silicon concentration, i.e., as H_Si and L_Si, which correspond to high-silicon and low-silicon, respectively.

The studied steel compositions were selected based on previous studies by the industrial partner. The L_Si steel has addition of Cr and Mo in order to improve the hardenability. The H_Si steel, which was initially designed for the Q&P process, has a higher concentration of C and Mn than the L_Si steel to stabilize austenite, and the Si concentration was increased to suppress carbide precipitation.

Table III-1: Chemical compositions of the studied steels (wt. %).

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_Si</td>
<td>0.16</td>
<td>1.6</td>
<td>0.4</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>H_Si</td>
<td>0.3</td>
<td>3.0</td>
<td>1.5</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

A temperature-time-transformation (TTT) diagram (Figure III-1), which is based on a thermodynamic model \(^{[1]}\), was calculated for both chemical compositions. These diagrams indicate that there are differences between the transformation kinetics of the steels. In fact, owing to the high concentration of alloying elements (Mn and Si), H_Si exhibits slower transformation kinetics and lower transformation temperatures than its L_Si counterpart. The predicted bainite and martensite start temperatures \((B_S \text{ and } M_S)\) are 560 °C and 400 °C for the L_Si steel, and 340 °C and 300 °C, respectively, for the H_Si steel.
The $M_S$ temperatures were also determined from the chemical compositions, by using an empirical relationship that expresses the $M_S$ temperature dependence on the carbon concentration as follows [3]:

$$
M_S(°C) = 565 - (31x_{Mn} + 13x_{Si} + 10x_{Cr} + 18x_{Ni} + 12x_{Mo}) - 600(1 - \exp^{-0.96x_C})
$$

(Equation III-1)

where $x_i$ denotes the fraction of element $i$ in wt. % and $M_S$ is in °C.

Respective $M_S$ values of 416 °C and 302 °C were determined for the L_Si and H_Si steels.

III.3. Transformation Experiments

The heat treatment experiments were performed in argon atmosphere ($10^{-4}$ mbar) in a Bähr DIL 805A/D dilatometer, operated in quenching mode; these treatments were performed on flat 10 (RD) $\times$ 4 (TD) $\times$ 4 (ND) mm$^3$ samples (where RD, TD, and ND correspond to the rolling, transverse, and normal directions, respectively, of the rolled sheet).

III.3.1. Dilatometry

Dilatometry is a technique that is most commonly used to determine the phase transformation temperatures and transformation kinetics during cooling and heating as well as under isothermal conditions. This technique reveals changes in the specific volume of a sample that occur during a phase transformation [3]. A schematic illustration of a dilatometer is shown in Figure III-2. Dimensional variations of the samples are transmitted via an amorphous silica push-rod to a linear variable differential transformer (LVDT) sensor in the chamber (connected to a computer-controlled system [4]), where they are accurately measured. A type S thermocouple is
spot-welded to the middle, and used to monitor the temperature, of the samples. Moreover, the sample is heated by an induction coil and cooled by means of a helium flow blown directly onto the sample surface. The dilatometer may also be equipped with a deformation unit (load cell), which enables the tracking of transformations in deformed samples.

Both steels were subjected to various heat treatments, according to the three following schemes, which are described as follows (see Figure III-3):

(i) Heating at 20 °C/s to 900 °C and cooling to room temperature (RT) at different cooling rates, in order to determine the kinetics of formation of the various microstructural constituents.

(ii) Isothermal experiments after austenitization:
- fast cooling to a temperature above $M_s$ (in the bainite temperature range), isothermal holding at this temperature for 1 h, and subsequent quenching to RT, to investigate the formation of bainite,
- fast cooling to temperatures below $M_s$, 1 h isothermal holding at these temperatures, and subsequent quenching to RT, to evaluate the transformation products formed below $M_s$.

(iii) Coiling experiments (after austenitization):
- fast cooling to the same temperatures applied in the isothermal experiments and slow cooling (0.1 °C/s) to RT, to evaluate microstructural evolution of the steels under cooling conditions similar to those in the coil.

Cooling/quenching rates of 100 °C/s and 20 °C/s were used for L_Si and H_Si, respectively, in scheme (ii) and (iii). These cooling rates were considered high enough to prevent other diffusional or bainitic transformations, which may occur in accordance with scheme (i).
Experimental Procedure

Scheme (i), performed at respective cooling rates of 100 °C/s and 20 °C/s for the L_Si and H_Si steels, gave rise to martensitic microstructures in both cases. Together with the bainitic microstructure resulting from the heat treatment described in (ii), they were used as a reference in understanding the mixed microstructures obtained at temperatures below $M_S$.

Figure III-3: Schematic illustration of the heat treatments performed in the dilatometer and the microstructural constituents formed during (i) heating and cooling to RT, (ii) the isothermal experiments, and (iii) the coiling experiments; $\gamma$ = austenite, IM = initial martensite, $A_c_3$ = austenitization temperature, $M_S$ = martensite start temperature, RT = room temperature.
The dilatometry curves obtained during cooling (at 100 °C/s for L_Si and 20 °C/s for H_Si) to RT (considered direct quenching), revealed the progress of the martensite formation. The volume fractions of initial martensite formed during cooling, and austenite present at the beginning of isothermal holding, were determined via the lever-rule, as shown in Figure III-4. This rule is used to determine the length difference between the dilatation curve and extrapolations of the linear parts of the curve, before and after the transformation. The start of the γ→α transformation is defined as the temperature at which the thermal contraction first deviates from linearity; this deviation leads to significant curvature in the cooling curve. In order to minimize measurement errors, the transformation temperatures were determined after 5 % completion of the transformations.

![Lever-rule diagram](image)

**Figure III-4:** Schematic illustration of the lever-rule applied to a dilatation-temperature curve of the martensitic transformation during fast cooling.

As Figure III-5(a) shows, $M_S(5\%) = 420$ °C and 290 °C for the L_Si and H_Si steel, respectively. The corresponding fraction of martensite formed is derived from the kinetic curves shown in Figure III-5(b).

![Dilatometry curves](image)

**Figure III-5:** Dilatometry curves obtained during direct quenching (scheme (i)) showing the (a) $M_S$ temperatures and (b) kinetic curves of martensitic transformation.
Experimental Procedure

Based on the microstructures obtained after cooling (i.e., the fractions of initial martensite (IM) formed), the isothermal temperatures ($T_{iso}$) were defined as follows:

- In the case of the L$_{Si}$ steel, an isothermal holding temperature of $T_{iso} = 450 \, ^\circ C$ (bainite temperature range), was selected because IM does not form at this temperature; this temperature is 30 °C higher than the $M_s$ temperature of the steel. In addition, samples were isothermally held at temperatures ranging from $T_{iso} = 350 \, ^\circ C - 100 \, ^\circ C$, which are lower than $M_s$, in order to obtain different fractions of the IM.

- In the case of the H$_{Si}$ steel, isothermal holding was performed at temperatures below $M_s$; temperatures of $T_{iso} = 325 \, ^\circ C$ (i.e., in the bainite temperature range) and ranging from $T_{iso} = 280 \, ^\circ C - 200 \, ^\circ C$ (below $M_s$) were selected. These temperatures were used to determine the influence of the IM fraction on the isothermal transformations.

Additional transformation experiments were performed and they will be described in Chapter IV, as deemed necessary.

III.4. Microstructural Characterization

III.4.1. Optical Microscopy (OM)

Dilatometer samples designated for microstructural characterization were prepared by using the typical metallographic techniques. The samples were ground and polished, and the final step consisted of polishing with 1-$\mu$m diamond paste. The samples were then etched for 5 s in 4 vol.% HNO$_3$ in ethanol (Nital 4 %), in order to reveal the microstructures (Figure III-6(a)), which were subsequently examined via bright-field OM. Furthermore, color etchants were used to reveal specific phases in selected samples. For example, when LePera etchant [$^6$] is used, martensite and/or austenite appear in white (Figure III-6(b)), ferrite has (mainly) an orange-brown color, and bainite and/or pearlite appear as darkly shaded regions.

*Figure III-6: Microstructure of L$_{Si}$ steel, after cooling at 0.1 °C/s to RT, etched with (a) Nital 4 % and (b) LePera.*
III.4.2. Scanning Electron Microscopy (SEM)

In addition to OM, SEM analysis was performed by using a FEI Quanta™450-FEG (field emission gun). Images of the microstructures were acquired at accelerating voltages of 15 or 20 kV and a beam current corresponding to an FEI spot size of 5 nm.

Compared to OM, SEM provides a higher resolution view of, and additional details regarding, the morphology (Figure III-7) of the microstructural constituents.

![SEM image of a final microstructure of the H_Si steel, after isothermally held for 1 h above the M_S temperature and quenched to RT.](image)

**Figure III-7**: SEM image of a final microstructure of the H_Si steel, after isothermally held for 1 h above the M_S temperature and quenched to RT.

III.4.3. Electron Backscatter Diffraction (EBSD)

The characteristics of the microstructural constituents in some samples were examined in further detail by employing EBSD. In this case, the sample preparation procedure consisted of polishing steps additional to those required for OM. The last step in the procedure consisted of electrolytic polishing with Struers A2 electrolyte followed by mechanical polishing with a colloidal silica suspension (Struers OPS), containing 0.035-µm-sized particles; the deformed surface layer that results from grinding and polishing and gives rise to mis-indexed Kikuchi patterns, is almost completely removed by this electrolytic polishing. However, electrolytic polishing of multiphase steels results in strong surface relief, which leads to ambiguous diffraction patterns and hence unreliable indexation. In this work, surface relief was eliminated via prolonged (30 min) mechanical polishing with OPS, under a low pressure of ~5 N.

EBSD patterns were obtained using a FEI Quanta™ 450 FEG-SEM equipped with TSL OIM-Data Collection version 6.2® software. The patterns were collected under the following conditions: accelerating voltage of 20 or 25 kV, beam current of 2.3 nA (spot size of 5 nm),
Experimental Procedure

working distance of 16 mm, specimen tilt angle of 70°, and step size of scan varying from 40 to 60 nm on a hexagonal scan grid, depending on the aim of the analyses.

The EBSD data were post-processed and the raw data were subjected to a three-step clean up procedure that is described as follows: (i) a grain confidence index (CI) standardization was performed, where a grain tolerance angle and minimum grain size of 5° and 4 pixels, respectively, were selected. This clean-up algorithm changes the CI of each point in a grain to the maximum CI found among all of the points belonging to that grain; (ii) neighbor CI correlation in which only CI values higher than 0.1 are allowed. In other words, the orientation of a particular point whose CI is lower than 0.1, is replaced by the orientation of the neighboring pixel that has the highest CI, and (iii) if the majority of neighbors of a particular point (smaller than 4 pixels and has a grain tolerance angle of 5°) belong to the same grain, then the orientation of the particular point is changed to match that of the majority grain, i.e., grain dilation was applied.

The phases and microstructural constituents present in the steels were characterized primarily through the use of image quality (IQ) distribution maps, phase maps, and grain-average image quality maps.

The IQ indicates the sharpness of the diffraction bands in the EBSD patterns and is used to discriminate between perfect and defect-containing lattice regions in the samples. For example, the darker regions in Figure III-8(a) are indicative of grains that have lower IQ, and hence a higher density of lattice imperfections, such as dislocations, than those in the lightly colored regions. The phase map was used to differentiate the phases present in the microstructure. In the phase map shown in Figure III-8(b), retained austenite is highlighted in green, while the BCC constituents (martensite and bainite) are shaded in red. The grains are also characterized via the grain-average image quality parameter, i.e., once defined, each grain is shaded according to the average IQ of all the pixels inside that grain. As previously stated, a grain is defined as a region that exhibits an orientation spread of < 5° and contains a minimum of 4 pixels. Therefore, each grain in an average IQ color map is shaded in a color that corresponds to the average IQ the entire grain (Figure III-8(c)).
The grain-average IQ is especially useful for the characterization of multiphase structures. In fact, different phases (for example, martensite and ferrite in DP steels) that have the same type of crystal lattice can be well accurately differentiated by using this parameter. In other words, this parameter takes all of the pixels into consideration, thereby eliminating the problem of underestimation of the pixels in the vicinity of the grain boundaries \[^{10}\].

### III.4.4. X-Ray Diffraction (XRD)

XRD (Siemens D5000) measurements performed at 40 mA and 40 kV, using Mo-K\(\alpha\) radiation, were used to determine the phases present and the volume fraction of retained austenite at room temperature. The samples were scanned over 20 ranging from 10° – 100° (L\_Si) and 25° – 40° (H\_Si), using step sizes of 0.002° – 0.005°, a dwell-time of 2 s, and a rotation speed of 15 rpm. The data were post-processed by subtracting the background radiation and the K\(\alpha_2\) contribution. Furthermore, the volume fractions of austenite were determined from the equation

\[
V_Y = \frac{1}{4} \left( \frac{I_{Y220}^2}{1.42 + I_{\alpha 200}^2 + I_{Y220}^2} + \frac{I_{Y220}^2}{0.71 + I_{\alpha 211}^2 + I_{Y220}^2} + \frac{I_{Y311}^2}{1.62 + I_{\alpha 200}^2 + I_{Y311}^2} + \frac{I_{Y311}^2}{0.81 + I_{\alpha 211}^2 + I_{Y311}^2} \right)
\]

proposed by Cullity \[^{11}\], which incorporates the integrated intensity of the (220), (311) austenite, as well as the (200) and (211) peaks corresponding to ferrite. These peaks (Figure III-9) lie within the range of 20 values used during the measurements.
III.4.5. Nanoindentation

Although used primarily for the study of mechanical properties (hardness and elastic modulus) of nanoscale materials, the nanoindentation technique has also been used to characterize complex microstructures \cite{12-17}. Therefore, nanoindentation measurements were used in conjunction with EBSD observations, to determine the difference in hardness of the microstructural constituents \cite{13, 15, 16, 18}.

The measurements were performed using a Triboindenter TI 950 Nanoindenter in displacement control testing mode; the indents were made at a constant strain rate ($\dot{\varepsilon} = \dot{h} / h$) of 0.07 s$^{-1}$, where $h$ and $\dot{h}$ are the penetration depth and penetration rate, respectively, of the indenter \cite{15, 16}. Indentations were performed using a Berkovich type indenter \cite{15}. Due to the expected small size of the microstructural constituents, an imposed maximum depth of 100 nm was chosen in order to keep the plastic zone within the individual microstructural constituent. These indents were made in specific microstructural constituents, previously identified by EBSD (Figure III-10(Figure VII-12(a)), and as arrays (Figure III-10(b) in various regions. Moreover, selected indents were visualized (Figure III-10(a)–(b)) via topography scans performed using contact-mode atomic force microscopy (AFM; Park XE150, Park Systems Corp., Suwon, South Korea).

The measurement procedure will be described in further detail in Chapter VII.
III.5. Carbide Characterization

III.5.1. Transmission Electron Microscopy (TEM)

TEM experiments were performed by using a JEOL JEM-2200FS/Cs-FEG TEM instrument, operated at 200 kV, equipped with an in-column electron energy filter and dispersive X-ray spectrometer (EDX), for detection and analysis of carbides. The foils used for this analysis were prepared, by using SiC papers to grind the dilatometer samples to a thickness of 0.08 mm. Subsequently, 3 mm-diameter discs were punched from the thinned samples and electropolished until a small hole formed in the center of each disc; by means of a twin-jet method, electropolishing was performed at room temperature and a potential of 20 V, using a solution of 5% perchloric acid in acetic acid. Foils were also prepared from selected regions of specific samples, by using a focused ion beam (FIB).

The carbides were initially observed in bright field (Figure III-11(a)). Selected area electron diffraction (SAED) patterns (Figure III-11(b)) were collected \(^{19}\) and the presence of carbides was further confirmed via dark-field imaging (Figure III-11(c)). These patterns were indexed with the aid of the Java Electron Microscopy Software (JEMS) \(^{20}\) and ELDIST (searching for solutions, satisfying orientation relationship (OR)) \(^{21}\).
III.5.2. Differential Scanning Calorimetry (DSC)

DSC is a thermo-analytical technique in which the difference in heat flow is determined by measuring the heat flow difference of a defined thermal path between the sample and a reference. The basic principle of this technique is that, when the sample undergoes a physical transformation such as a phase transition, more (or less) heat must flow to the sample than to the reference; this requirement ensures that both are maintained at the same temperature. The amount of heat that flows to the sample depends on whether the process is exothermic or endothermic. There are two main types of differential scanning calorimeters: heat flux DSCs (sample and reference are placed in the same furnace) and power compensation DSCs (separate heaters are used for the sample and reference).

In this work, DSC measurements were used to investigate martensite tempering. These measurements reveal the correlation between heat flow in the sample from exothermic reactions during heating, and carbide precipitation. The measurements were performed using a Netzsch 404C apparatus, heat flux system (Figure III-12(a)), and Al₂O₃ pans (Figure III-12(b)) with diameter equal to 6.8 mm. An argon-gas flow was used to prevent oxidation. The baseline was determined by running the same program (that was used for the measurements) with two empty crucibles. Prior to the DSC experiments, entirely martensitic microstructures were obtained through full austenitization of the samples at 900 °C in the dilatometer and subsequent quenching in liquid nitrogen. These samples were then slowly cut with a water-cooled grinding disc, thereby yielding DSC samples, which each had a mass of ~100 mg. The parameters used for the DSC experiments will be mentioned when the data are discussed in Chapter VI.

Figure III-12: (a) Schematic illustration of a heat flux DSC and (b) Al₂O₃ pans containing the sample and reference.
III.6. Mechanical Characterization

III.6.1. Vickers hardness (HV)

The global hardness of the resulting microstructures was determined via the Vickers method. In this test, a small diamond indenter with pyramidal geometry is forced into the surface of the sample, as illustrated in Figure III-13(a). When the loads are very small (0.24, 0.49 or 0.98 N), the method is also referred to as micro-hardness testing. The resulting indent (Figure III-13(b)), is observed under a microscope, measured, and converted into a hardness number via the formula [21]:

\[
H_V = 1.854 \frac{F_{\text{max}}}{D^2}
\]

(Equation III-2)

where \(F_{\text{max}}\) and \(D\) are the applied force (N) and the diagonal (\(\mu\)m) of the indent, respectively.

The surface of the sample must be flat, smooth, and (ideally) perpendicular to the indenter in order to obtain a regular-shaped print; this regular shape is essential for obtaining reliable results [22, 23]. Therefore, the measurements were performed on samples subjected to a final polishing with 3-\(\mu\)m diamond paste. A load of 29 N was applied for 10 s and five indentations were made in each sample.

Figure III-13: (a) Shape of the indenter in side view and (b) top view of the indentation.


12. J. Wu, Development of a New Technique to Identify and Quantify Complex Austenite Decomposition Products, University of Pittsburgh, Editor (2005)


Chapter IV: TRANSFORMATION BEHAVIOR OF ADVANCED HIGH STRENGTH STEELS DURING HEATING AND COOLING

IV.1. Introduction

The H_Si and L_Si steels are subjected to continuous heating and cooling treatments. This chapter provides a description of the respective transformation temperatures and products resulting from these treatments. These data are then used to derive the respective continuous cooling transformation (CCT) diagrams, which describe the transformation of the steels during the treatments. CCT diagrams constitute a valuable tool for characterizing the heat-treatment-induced phase transformations in steel and are therefore used in this study, as a guide for defining the parameters of the main transformation experiments.

IV.2. Heat Treatments

Heat treatments consisting of continuous heating and cooling (cf. Figure IV-1) steps were performed in the dilatometer. Samples were heated at low rates of 10 °C/s – 20 °C/s (which are typically used in industry) to a temperature of 900 °C or 1000 °C. Thermodynamic calculations of the corresponding phase equilibria were performed by using the Thermo-Calc software\textsuperscript{1}. The results (Table IV-2) revealed that the applied temperatures are sufficient for completion of the austenitization process; the transformation temperatures for the start and completion of austenitization (\(A_{c1}\) and \(A_{c3}\), respectively) were also determined at this temperature. In addition, the samples were cooled to room temperature (RT) at various cooling rates (Table IV-1), in order to evaluate the non-isothermal decomposition of austenite at each rate. These data were then used to derive, experimentally, the continuous cooling transformation (CCT) diagram of each steel.

\textsuperscript{1} Thermo-Calc is a software used for thermodynamic calculations, including phase diagrams, transformation temperatures, driving forces for phase transformations, etc.
Table IV-1: Parameters used for the heat treatments.

<table>
<thead>
<tr>
<th>Steels</th>
<th>Heating rate (°C/s)</th>
<th>Austenitization temperature (°C)</th>
<th>Cooling rates (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_Si</td>
<td>10</td>
<td>1000</td>
<td>0.1, 1, 2, 5, 10, 30, 100, 300</td>
</tr>
<tr>
<td>H_Si</td>
<td>20</td>
<td>900</td>
<td>1, 2, 5, 10, 20, 50, 100</td>
</tr>
</tbody>
</table>

Figure IV-1: Schematic illustration of the heat treatments performed in the dilatometer; the resulting data were used to construct the CCT diagrams.

IV.2. Transformation Temperatures

As Figure IV-2 shows, the \( A_{c1} \) temperature is defined as the temperature at which the linear thermal expansion curve, first deviates from linearity. This deviation results from the volume contraction (which accompanies austenite formation) that opposes the thermal expansion stemming from an increase in the temperature of the steel. Similarly, the \( A_{c3} \) is determined when the plot of the dilatation vs. temperature becomes linear again and the \( \alpha \)-\( \gamma \) transformation is completed. The temperatures at which the deviations occur were obtained by extrapolating the linear portions of the thermal expansion curve before and after the transformation \(^{[2-4]}\). In addition, the lever rule\(^2\) was used to determine the transformation start and finish temperatures \(^{[5, 6]}\), as explained in Chapter III; the transformation temperatures were determined at 5 and 95 % completion of the transformations. Figure IV-2 shows a typical dilatometry curve obtained during the heating and cooling experiments. The change in length is plotted as a

\(^2\) As described in Chapter III – Experimental Procedure.
function of temperature, using the data obtained from an experiment in which the L_Si steel is cooled at a rate at 0.1 °C/s.

Figure IV-2: Dilatometry curve illustrating the determination of transformation temperatures in L_Si steel after cooling at 0.1 °C/s.

The transformation temperatures during cooling were determined by using the procedure illustrated in Figure IV-2. Analysis of the dilatation curves (Figure IV-2 and Figure IV-3(a)) revealed that two different transformations occurred during the slow cooling of the L_Si steel from the fully austenitic state. The first transformation starts at point $T_{S1}$. The portion of the curve at higher temperature corresponds to the thermal contraction of the specimen during the slow cooling of the steel in the austenitic phase. In addition, the transformation from austenite to ferrite starts at point $T_{S1(5\%)} = 725 °C$ and proceeds until the $T_{f1}$ (finishing temperature of the first transformation) is reached. At temperatures lower than $T_{f1(95\%)} = 640 °C$, linear contraction is followed by an austenite-to-bainite phase transformation that occurs at temperatures ranging from $T_{S2(5\%)} = 505 °C$ to $T_{f2} (95\%) = 410 °C$; a final contraction occurs over a subsequent temperature range. Austenite and ferrite co-exist at temperatures ranging from $T_{f1}$ to $T_{S2}$, whereas a mixture of ferrite and bainite occurs at temperatures lower than $T_{f2}$.

Figure IV-3(a)–(c) show that the phase transformations of austenite start at different temperatures, depending on the cooling rate. For example, at 10 °C/s, the first transformation of undercooled austenite starts at 550 °C, which lies in the bainite (rather than ferrite) transformation range (see the deviation of the dilatation curve from linearity). This temperature range (which starts at 550 °C) coincides with the second transformation range of the samples cooled at 0.1 °C/s (Figure IV-3(a)), which were considered to be bainitic. However, the dilatation curve associated with the bainitic transformation that occurs during cooling at 10 °C/s differs from the one obtained during cooling at 0.1 °C/s. Analysis of the dilatation curves
reveals that both bainitic and martensitic transformations (Figure IV-3(b)) occur during cooling at 10 °C/s; however, during cooling at 100 °C/s, austenite transforms to martensite only (Figure IV-3(c)).

Figure IV-3: Dilatation curves obtained for various cooling rates applied, after austenitization of the L_Si steel at 900 °C.

As expected, the H_Si steel behaved differently from its L_Si counterpart. The calculated TTT diagram (Figure III-1), and Thermo-Calc calculation indicated that phase transformations should occur at lower temperatures in the former than in the latter [7-10]. Analysis of the dilatation curves in Figure IV-4(a)–(d), reveals that the austenite-to-ferrite transformation does not occur even at low cooling rates (such as 1 °C/s). On the other hand, the slope of the thermal contraction changes (owing probably to the difference in the thermal expansion coefficients) at ~550 °C. This change in slope is observed for cooling rates ranging from 1 °C/s to 5 °C/s, and may be associated with bainite formation, followed by martensitic transformation, cf. Figure IV-4(a)–(b). At cooling rates higher than 5 °C/s, the steel transforms only to martensite (Figure IV-4(c)–(d)).
Figure IV-4: Dilatation curves obtained for various cooling rates applied, after austenitization of the H_Si steel at 900°C.

The $M_S$ temperatures are experimentally derived, as shown in Figure IV-5, after the H_Si and L_Si steels are quenched at rates of 20 °C/s and 100 °C/s, respectively.

Figure IV-5: Experimentally derived $M_S$ temperature of the studied steels.

The experimentally determined transformation temperatures of both steels (Table IV-2), are compared with those calculated by using Thermo-Calc and Andrews equation \[^11\]. These temperatures increase with the heating rate \[^12\] and therefore, the experimentally determined values are higher than those calculated by Thermo-Calc.
Table IV-2: Transformation temperatures (in °C) of both steels.

<table>
<thead>
<tr>
<th>Steels</th>
<th>Method</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$A_{c1}$</td>
<td>$A_{c3}$</td>
</tr>
<tr>
<td>$L_{Si}$</td>
<td>Thermo-calc</td>
<td>730</td>
<td>820</td>
</tr>
<tr>
<td></td>
<td>Andrews</td>
<td>735</td>
<td>808</td>
</tr>
<tr>
<td></td>
<td>Experiments</td>
<td>760 ± 3</td>
<td>825 ± 4</td>
</tr>
<tr>
<td>$H_{Si}$</td>
<td>Thermo-calc</td>
<td>700</td>
<td>775</td>
</tr>
<tr>
<td></td>
<td>Andrews</td>
<td>742</td>
<td>780</td>
</tr>
<tr>
<td></td>
<td>Experiments</td>
<td>750 ± 2</td>
<td>818 ± 3</td>
</tr>
</tbody>
</table>

* The $M_S$ temperature was defined as the temperature at which 5% martensite was formed.

IV.3. Continuous Cooling Transformation (CCT) Diagrams

As previously mentioned, the experimentally determined transformation temperatures were used to derive the CCT diagrams, which show the start and finish of phase transitions during continuous cooling.

At low cooling rates, such as 0.1 °C/s (Figure IV-3(a)), various phases form as products of the diffusional transformation at high temperatures. Figure IV-3(b)–(c) and Figure IV-4(a)–(d) show, however, that these diffusional transformations are suppressed at cooling rates higher than 0.1 °C/s. Therefore, austenite decomposes to displacive transformation products (bainite and/or martensite) at lower temperatures than those at which decomposition occurs, when the cooling rate is 0.1 °C/s.

However, the phase transformations in the $L_{Si}$ steel (cf. Figure IV-6) start at higher temperatures than those (Figure IV-7) in the $H_{Si}$. This stems mainly from the presence of austenite-stabilizing alloying elements; for example, at high-manganese concentration, the transformations are shifted to longer times and lower temperatures compared to those occurring at low concentration.

The critical cooling rate for martensite formation, i.e., the lowest cooling rate at which only martensite forms, can be determined from a CCT diagram. Critical cooling rates of 30 °C/s and 10 °C/s were determined for the $L_{Si}$ and $H_{Si}$ steels, respectively. Additionally, hardness results are given in the CCT diagrams.
Figure IV-6: Experimentally derived CCT diagram of the L_Si steel.

Figure IV-7: Experimentally derived CCT diagram of the H_Si steel.
IV.4. Microstructures

The microstructures resulting from the treatments were characterized via optical microscopy (OM) after sample preparation and etching with Nital 4%. The microstructures of selected samples were also examined via scanning electron microscopy (SEM).

These microstructures are used as a reference for the identification of microstructures formed during the isothermal holding experiments.

- $L_{Si}$

Figure IV-8(a)–(h) show the microstructural evolution for different cooling rates.
The microstructure formed after slow cooling at a rate of 0.1 °C/s (Figure IV-8(a)), consists of ferrite (white and equiaxed grains) and upper bainite (lath morphology). For high cooling rates, ferrite formation is gradually suppressed, and hence only a few ferrite grains are observed in the microstructures (Figure IV-8(b)–(c)) formed after cooling at 1 °C/s and 2 °C/s. This observation concurs with the CCT diagram, i.e., ferrite is not detected during the dilatometry measurements since its volume fraction is very low. Figure IV-8(b)–(e) show that the microstructure changes from ferrite and bainite to a mixture of bainite and martensite. However, the bainite in the microstructure cannot be clearly distinguished from the martensite via OM. In contrast, carbide precipitates, as indicated by the arrows in Figure IV-9(a)-(b), are clearly revealed via SEM examination. Figure IV-9(b) shows a microstructure formed after a cooling rate of 100 °C/s is applied. As previously mentioned, carbide precipitation occurs even during fast cooling (as evidenced by the presence of fine carbides in the quenched martensite). This precipitation results, in general, from the auto-tempering process that occurs at a relatively high $M_s$ temperature\(^\text{[14]}\). Therefore, similar-looking microstructures are obtained at cooling rates higher than 5 °C/s, since they consist of tempered martensite and bainite, which both contain carbide precipitates.

\(^3\) Auto-tempering: is a phenomenon in which the first-formed martensite near the $M_s$ is tempered during the remaining process of quenching or slow cooling.
Figure IV-9: SEM images of the microstructures formed after continuous cooling of the L_Si steel at rates of (a) 5 °C/s and (b) 100 °C/s. The carbides are indicated by the arrows.

- **H_Si**

The optical images in Figure IV-10(a)–(g) reveal that martensite laths are formed at all the cooling rates applied to the H_Si steel. Bainite is formed at low cooling rates, as indicated in the CCT diagram, but constitutes a very low (Figure IV-10(a)–(c)) fraction of the microstructure and therefore cannot be resolved by OM. However, bainite consisting of carbide precipitates is clearly revealed (Figure IV-11(a)) via SEM examination. The formation of fully martensitic microstructures (Figure IV-11(b)) at cooling rates higher than 5 °C/s [15], is consistent with the trends shown in the CCT diagram.
Figure IV-10: OM images of the microstructures formed after continuous cooling of the H_Si steel at rates (°C/s) of (a) 1, (c) 2, (d) 5, (e) 10, (f) 20, (g) 50 and (h) 100.

Figure IV-11: SEM images of the microstructures formed during continuous cooling of the H_Si steel at rates of (a) 1 °C/s and (b) 100 °C/s.
IV.5. Discussion

The two AHSS investigated in this work had differing silicon, carbon, manganese, chromium, and molybdenum concentrations; these steels were subjected to various heating and cooling treatments.

The chemical composition had an effect on the transformation temperatures and the range of transformation products formed. In other words, compared to those of the H_Si steel, the temperatures and range of products were higher and wider, respectively, in the steel with low-silicon concentration. In addition, significant carbide precipitation occurred in the L_Si steel. Carbide precipitates formed in bainite when low or medium cooling rates were used; fine carbides also formed within the quenched martensite. Furthermore, the microstructure resulting from the use of high cooling rates, confirmed that the auto-tempering process occurred, owing to the relatively high $M_S$ temperature ($T = 420 \degree C$).

On the other hand, the phase transformations were delayed and the cementite precipitation in martensite was inhibited, due to the high Mn and Si concentrations, respectively, of the H_Si steel [9,16]. A fully martensitic microstructure was therefore obtained for a wide range of cooling rates and the auto-tempering process was prevented, owing to this delay and inhibition.

IV.6. Conclusions

The transformation temperatures, critical cooling rates, and microstructural constituents of the studied AHSS were determined via dilatometry and microscopy. The results are summarized as follows:

- Owing to its higher C and Mn concentrations, the transformation temperatures and times of the H_Si steel are greater than those of its L_Si counterpart.
- The critical cooling rates for martensitic transformation are 30 °C/s and 10 °C/s in the case of the L_Si and H_Si steels, respectively.
- Carbide precipitation is significantly more pronounced in the L_Si steel than in the H_Si steel.
- Mixed microstructures consisting of ferrite, bainite, and martensite are formed in the L_Si steel, depending on the cooling rate used.
- In the case of the H_Si steel, a fully martensitic microstructure is formed for a wide range of cooling rates.
References


Chapter V: ISOTHERMAL TRANSFORMATIONS IN ADVANCED HIGH STRENGTH STEELS ABOVE AND BELOW THE $M_S$ TEMPERATURE

V.1. Introduction

The decomposition of austenite during isothermal holding of the studied steels above and below $M_S$, is described in this chapter\(^4\); this decomposition is investigated via dilatometry and analysis of the transformation kinetics. Isothermal holding treatments after rapid cooling to various temperatures (forming a controlled volume fraction of initial martensite below $M_S$) were performed in a dilatometer. The results show that the microstructures formed during isothermal holding below the $M_S$ temperature are mainly bainitic, mixed with tempered martensite and in some cases also retained austenite. The kinetics of isothermal bainite formation was described by a nucleation-based transformation model. The complex competition and interaction between the transformation mechanisms operating during the isothermal holding in different temperature regimes, are discussed. For the sake of clarity, the results of each steel are presented separately in most cases.

V.2. Transformation Experiments

The thermal profiles of the isothermal heat treatments were designed, based on the transformation temperatures determined in Chapter IV – Section IV.2.

Various experiments were performed; each experiment began with full austenitization and was continued as follows:

(i) Initial fast cooling to the bainite temperature range, 1 h isothermal holding at the respective temperatures, and subsequent quenching to room temperature (RT), in order to evaluate the formation of bainite.

\(^4\) This chapter is partially based on the published papers: “Phase Transformations during the Decomposition of Austenite below $M_S$ in a Low-carbon Steel” - Materials Characterization 95 (2014) 85 - 93 and “Isothermal Transformations in Advanced High Strength Steels below the Martensite Start Temperature” – Materials Science and Technology, Vol. 31 - N°. 7 (2014) 808 - 816.
Isothermal transformations in Advanced High Strength Steels above and below the $M_S$ temperature

(ii) Initial fast cooling to temperatures below $M_S$, 1 h isothermal holding at each temperature, and subsequent quenching to RT, in order to evaluate the isothermal transformations that occur below $M_S$.

The isothermal holding temperatures ($T_{iso}$), listed in Table V-1, were chosen by defining distinguishing criteria for the microstructures formed after the initial fast cooling. These criteria are listed as follows:

(i) there is no martensite formation above the $M_S$ temperature,

(ii) a certain fraction of initial martensite (IM) is present at temperatures below $M_S$.

Table V-1: Isothermal holding temperatures of each steel.

<table>
<thead>
<tr>
<th>AHSS</th>
<th>Above $M_S$</th>
<th>Below $M_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{Si}$</td>
<td>450</td>
<td>400, 350, 300, 250, 200, and 100</td>
</tr>
<tr>
<td>$H_{Si}$</td>
<td>325</td>
<td>280, 250, and 200</td>
</tr>
</tbody>
</table>

The dilatometry curves (Figure V-1(a)) obtained from direct quenching from the austenitic temperature to RT revealed the progress of the martensitic transformation. Therefore, the lever rule could be used to determine the fraction of IM formed during cooling (Figure V-1(b)) and hence, the fraction of untransformed austenite present at the beginning of isothermal holding.

The volume fraction (Figure V-1(b)) of IM was also calculated by using the Koistinen-Marburger (KM) relationship. Martensite formed relatively fast below $M_S$ and 0.1 – 0.7 (i.e., volume fractions) of IM formed in the $L_{Si}$ and $H_{Si}$ steels at temperatures ranging from 400 – 350 $^\circ$C and 300 – 200 $^\circ$C, respectively; the transformation occurs at lower rates outside this temperature range, as shown in Figure V-1(b).

Figure V-1: (a) Martensitic transformation and (b) volume fraction of initial martensite derived from the dilatation signal, as well as fits with the Koistinen-Marburger (KM).

---

5 The cooling experiments presented in Chapter IV are considered as “quenching” when cooling rates higher than the critical rate for martensite formation (for example, 100°C/s) are applied.
V.3. Dilatometry Study

This study focuses on the transformation products that result from the isothermal decomposition of austenite at temperatures in the range of the $M_S$ temperature. However, the influence of the other steps, on the transformations, must also be taken into account. As such, the athermal \cite{1, 2} and isothermal transformations \cite{3-7} will both be taken into account in the discussion of the dilatometry curves.

V.3.1. L$_{Si}$ Steel

The phase transformations can be identified via the temperature-dependent changes in length. For example, Figure V-2(a) shows the dilatation during the following steps: cooling to $T_{iso}$, isothermal holding at temperatures ranging from 450 – 100 °C, and quenching to RT. Some of the dilatation curves exhibit an initial deviation from the pre-set isothermal holding temperature (Figure V-2(a)). These deviations (± 10 °C) occur at the start of the isothermal holding step and lasts for a few seconds. Although part of the transformation takes place during this interval, the overall kinetics of the transformation is only slightly affected, and the character of the transformation remains the same.

In Figure V-2(b), the phase transformations are represented as time-dependent changes in length. The transition between the cooling and isothermal holding steps is clearly visualized by designating that $t = 0$ when $T = 650$ °C for all curves, thereby resulting in a downward shift of the curves.

The curve obtained at $T_{iso} = 450$ °C, corresponds to the isothermal decomposition of austenite to bainite. Furthermore, the dilatation increases rapidly (Figure V-2(b)) below the $M_s$, when initial martensite (IM) is formed during cooling to the temperatures of isothermal holding.

The results obtained at $T_{iso} = 450, 350$, and 100 °C will be discussed in further detail, since they exhibit the main features of the phase transformations that occur during the heat treatments indicated in Figure V-2.
Isothermal transformations in Advanced High Strength Steels above and below the $M_S$ temperature

Figure V-2: Dilatometry curves plotted as a function of the (a) temperature and (b) time; the curves are shifted along the vertical axis, in order to show the steps corresponding to (I) cooling to $T_{iso}$, (II) isothermal holding at $T_{iso}$, and (III) quenching to RT.

Analysis of the curve (Figure V-2(a)) corresponding to the sample isothermally held at $T_{iso} = 450 \, ^\circ C$, revealed that phase transformations did not occur during cooling. This was expected, since the employed cooling rate was high enough to suppress the formation of ferrite and bainite prior to reaching the isothermal holding temperature. In addition, IM formation is prevented with the interruption of cooling at temperatures higher than the $M_S$ temperature, and hence austenite decomposes to bainite during the isothermal step. This decomposition is manifested in the dilatometry curve (Figure V-2(a)), as an increase in the length of the sample [8]. Most of the transformation occurs in the first minute (shown in Figure V-2(b)) of the treatment and, compared to the kinetics during this time, the transformation continues with slower kinetics thereafter. Moreover, interruption of the bainitic transformation after 1 h (by quenching to RT) did not lead to a pronounced transformation during the final quench (cf. Figure V-2(a)).

The dilatometry curves corresponding to $T_{iso} = 350 \, ^\circ C$ and $T_{iso} = 100 \, ^\circ C$ (below $M_S$) reveal the typical martensitic transformation that occurs during cooling, prior to reaching the selected isothermal temperatures. The volume fraction of IM formed at these temperatures are 0.73 ± 0.08 and 0.98 ± 0.03, respectively. An initial length increase occurs during the subsequent isothermal holding at $T_{iso} = 350 \, ^\circ C$, where the transformation progresses rapidly in the first minute. This increase results mainly from the bainitic transformation [5, 8]. In addition, the IM is tempered during holding, thereby leading to contraction of the samples. The contraction of fully martensitic samples was evaluated. For this evaluation, dilatometry samples were fully austenitized at 900 °C, quenched to RT, and subsequently submerged in liquid nitrogen, in order to obtain a fully martensitic microstructure. The samples were then heated to
the same range (100 – 450 °C) of temperatures used in the isothermal transformation experiments, isothermally held for 1 h at each temperature, and finally quenched to RT (Figure V-3(b)). A fully martensitic sample tempered at 350 °C underwent a contraction of <1 µm in 1 h (Figure V-3(b)) and therefore, the effect of tempering on the change in length was deemed negligible. The volume fraction of bainite (Figure V-3(a)) after the isothermal treatments were determined from the length changes observed via dilatometry.

The curve corresponding to the lowest temperature ($T_{\text{iso}} = 100 ^\circ \text{C}$), exhibited only a slight transformation effect during the isothermal holding, after almost complete formation of martensite (cf. Figure V-2(b) and Figure V-3(a)). However, the bainitic transformation cannot be excluded entirely.

![Figure V-3: (a) Transformation fractions during isothermal holding and (b) dilatometry curves obtained during tempering of martensite in the samples quenched in liquid nitrogen.](image)

**V.3.2. H_Si Steel**

The dilatometry curve (Figure V-4(a)) obtained at $T_{\text{iso}} = 325 ^\circ \text{C}$, which is above $M_S$, shows that austenite decomposes to lower bainite, as evidenced by the expansion of the sample during the isothermal holding. In order to highlight the transition between the athermal and isothermal transformations, Figure V-4(a)–(b) show data obtained under isothermal conditions and during the cooling before isothermal holding. The time is plotted on the logarithmic scale and the time corresponding to $T = 340 ^\circ \text{C}$ is considered as $t = 0$; therefore, the curves are all shifted downward. The incubation time for the bainitic transformation is approximately 200 s, which concurs with the theoretical predictions based on TTT diagrams. Phase transformations did not occur during the other steps (cooling to $T_{\text{iso}}$ or quenching to RT). However, the bainitic transformation is incomplete at the interruption of holding (i.e., during expansion of the sample), and this results in a certain fraction of retained austenite at RT (cf. Figure V-4(b)–(c)).

---

6 TTT diagrams were calculated based on the chemical composition and are shown in Chapter III in Figure III-1.
Furthermore, the dilatation deviates slightly from linearity during quenching to RT (Figure V-4(a)), which could correspond to the decomposition of remaining austenite to fresh martensite.

![Dilatometry curves as a function of the (a) temperature and (b)-(c) time, showing stages corresponding to (I) cooling to \( T_{iso} \), (II) isothermal holding at \( T_{iso} \), and (III) quenching to RT.](image)

The typical martensitic transformation is observed (Figure V-4(a)) after fast cooling to temperatures of isothermal holding (\( T_{iso} \)) that are below \( M_s \) (i.e., at \( T_{iso} = 280 \) °C, 250 °C, and 200 °C). Cooling from these temperatures yielded IM fractions of 0.2, 0.6 and 0.85, respectively, as determined by applying the lever rule to the data obtained from dilatometry measurements. The dilatation of the samples increases rapidly below \( M_s \) due to the IM formation. During the subsequent isothermal holding, the dilatation continues to increase (cf. Figure V-4(b)). However, small isothermal dilatation is observed when high volume fractions of IM have been formed during cooling to the isothermal temperatures. Furthermore, analysis of the isothermal step of the treatment (Figure V-4(c)), excluding the IM formation (\( t = 0 \) when \( T_{iso} \) is reached), reveals that there is no incubation time for bainite formation below \( M_s \). These results cannot be solely attributed to microstructural changes of the martensite that occur, for example, during tempering of the martensite. As mentioned previously, tempering of the martensite leads to a slight decrease the length of the sample \([5, 8, 9]\), as shown in
Chapter V

73

This indicates that the volume expansion results from the decomposition of austenite to lower bainite, which is accelerated after cooling owing to the presence of IM. These results are consistent with those reported by Van Bohemen, Kawata, and Santofimia \[5, 7, 10\]. The kinetics of diffusionless bainite formation is governed by nucleation. Therefore, IM influences bainite formation by providing additional nucleation sites for bainite. In other words, IM can contribute, via autocatalytic nucleation, to changes in the transformation kinetics. The bainitic transformation is not finished even at the end of the isothermal holding (i.e., the sample length continues to increase with holding times of up to 12 h). When holding is interrupted, by quenching to RT, the dilatation deviates slightly from linearity, possibly resulting in fresh martensite (FM), besides retained austenite (RA).

Moreover, Figure V-4(a) shows that the final dilatation at RT decreases slightly with increasing \( T_{is} \). This behavior may be attributed to the tempering of martensite during the isothermal holding step; tempering is more pronounced at high temperatures, than at low ones, and leads to a decrease in the final length \[5\].

V.4. Modeling of Isothermal Transformations

The transformation is modeled based on the assumption that bainite is the isothermal product formed at temperatures above and below \( M_S \) in both AHSS studied; the corresponding kinetics is compared to the transformation kinetics determined via dilatometry. The model used in the present study assumes that bainite nucleation precedes displacive growth. This model was initially proposed by Van Bohemen \[11\] for lean-Si steels and was subsequently adapted for high-Si steels \[12\], as previously mentioned in Chapter II – Section II.5.

V.4.1. L_Si Steel

In the model proposed by Van Bohemen \[11\], the volume fraction of bainite is expressed as a function of time as follows:

\[
\frac{df}{dt} = (1 - f - f_M)(1 + \lambda f)\kappa
\]

*Equation V-1*

where \( f, \lambda, f_M, \text{ and } \kappa \) are the volume fraction of bainite, autocatalytic nucleation parameter, volume fraction of martensite, and the rate parameter, respectively; \( \kappa \) is determined from:
Isothermal transformations in Advanced High Strength Steels above and below the $M_s$ temperature

$$\kappa = \frac{kT}{h} \alpha^b (T_h - T) \exp \left( \frac{-Q^*}{kT} \right)$$

Equation V-2

where, $\alpha^b$ represents the effectiveness of austenite grain boundaries for the nucleation of bainite, $T_h$ is the highest temperature at which displacive transformations can occur and $Q^*$ is the activation energy for nucleation (see Chapter II – Section II.5).

$T_h$ varies with the chemical composition and is determined from the empirical equation [11]:

$$T_h(\degree C) = 835 - 198x_c - 91x_{Mn} - 15x_{Si} - 73x_{Cr} - 36x_{Ni} - 87x_{Mo}$$

Equation V-3

A $T_h$ of 567 °C was determined in this work. In addition, the fitting parameters ($\lambda$ and $\kappa$) were obtained from the best fit to the experimentally determined kinetics of the isothermal transformation. To account for the incomplete bainite transformation resulting from austenite at $T_{iso} = 450 \degree C$, the right-hand side of Equation V-1 was multiplied by the additional fitting parameter, $f_{max} = 0.85$. However, the determination of the model parameters is less accurate at low temperatures ($T_{iso} = 250 – 100 \degree C$) than at high ones, owing to the small fraction of bainite formed during the isothermal holding. Figure V-5(a)–(g) compare the experimental and fitted volume fraction curves obtained for various holding temperatures; the vertical axis of each plot represents the total volume fraction of decomposed austenite, i.e., the sum of initial martensite and bainite.
The kinetics of bainite formation in this temperature range is well-described when $\lambda = 0$, indicating that autocatalytic nucleation is insignificant at this stage. The autocatalytic parameter varies with the austenitization treatment \cite{13}. In the present study, the austenite grain size is the same for all heat treatments (austenitization at 900 °C), and a constant value of $\lambda$ is expected. For example, austenitization at this temperature yielded $\lambda$ values of 3 and 12 for steels with 0.46 and 0.66 wt.% C, and austenite grain sizes of 24 and 34 μm, respectively \cite{11}. The difference in the $\lambda$ values obtained here and those reported in Ref. \cite{11} stems possibly from the fact that autocatalytic nucleation varies with the carbon concentration of the steel. Other studies, for example, Ref. \cite{14}, showed that the chemical composition has an effect on the autocatalytic factor associated with upper bainite formation in high-silicon steels. Carbon ejection from the newly formed bainitic ferrite into austenite was assumed to be greater in high-carbon steels than in their low-carbon counterparts. The increase in the carbon concentration results in a local

---

**Figure V-5:** Fitting of the kinetics of bainite formation (dashed lines) to the experimentally determined data of the isothermal transformations (solid lines).
Isothermal transformations in Advanced High Strength Steels above and below the M_s temperature
decrease in the driving force for diffusionless transformation. This in turn leads to a smaller
autocatalytic effect in high-carbon steels compared to that occurring in their low-carbon
counterparts. However, in the case of low-silicon steels, the effect of carbon concentration on
the autocatalytic parameter may differ from that observed in high-silicon steels; further study
is required to validate this hypothesis.

Figure V-6(a) shows the temperature-dependence of the $\kappa$ extracted from the fitting shown in
Figure V-5(a)–(g). These data are adequately described by Equation V-2, when the linear
temperature-dependence of the activation energy $Q^*$ \cite{11} and the calculated values
$\alpha_b = 12.5 \times 10^{-6}$ K^{-1} \cite{11} and $T_h = 567$ °C, are used. Furthermore, $\kappa$ has a maximum value at
470 °C, owing to the balance between undercooling ($T_h - T$) and the absolute temperature that
influences the overall kinetics. As Figure V-6(b) shows, $Q^*$ decreases from ~170 J/mol at near-
$T_h$ temperatures, to ~100 J/mol at large undercooling.

![Figure V-6: (a) Temperature-dependence of the rate parameter $\kappa$ and (b) activation energy as a function
of the undercooling.](image)

V.4.2. H_Si Steel

As previously mentioned in Chapter II, the model developed by Van Bohemen \cite{11} was adapted
in order to describe the kinetics of bainite formation in high-Si steels \cite{15}; a procedure that
accounts for the carbon enrichment of the remaining austenite was added to the model. The
carbon concentration of the remaining austenite ($x_{\gamma_{\text{ret}}}$) was determined from the volume fraction
of the bainitic ferrite and its effective carbon concentration ($x_{\text{eff}}$). As such, the autocatalytic
factor and the carbon content of bainite were used as fitting parameters in Ref. \cite{15}. The rate
parameter ($\kappa$), which is both temperature- and composition-dependent, is affected by the carbon
enrichment of the austenite, being related to a high effective activation energy and a small
undercooling. In addition, a variable oscillation frequency ($v$) was assumed for this steel
composition; in the literature, the value of $v$ varies from $10^5$-$10^{13}$ s^{-1} \cite{16}. Therefore, $v$ was used
as an additional fitting parameter in this study. Figure V-7(a)–(d) compare the experimentally determined and fitted volume fraction-time curves obtained at each isothermal holding temperature.

Figure V-7: Fitting of the kinetics of bainite formation (dashed lines) and experimentally determined data of isothermal transformations (solid lines).

As Figure V-8(a) shows, a value of $14 \pm 1.2$ is obtained for $\lambda$ (the autocatalytic parameter), which leads to the S-shape of the fraction-time curve. The slight increase in $\lambda$ with decreasing $T_{iso}$, reflects the accelerated kinetics resulting from the previously formed martensite, cf. Figure V-8(a). However, the determination of the model parameters is less accurate at the lowest temperature ($T_{iso} = 200 ^\circ C$), than at high ones, owing to the high volume fraction of IM formed during cooling. The carbon concentration (Figure V-8(b) and Table V-2) in the austenite remaining ($x_{\gamma\text{ret}}$) at the end of the isothermal transformation was derived from the results of the fitting performed at each isothermal temperature. As shown, the modeled values for $x_{\gamma\text{ret}}$ decrease with decreasing isothermal temperature. Furthermore, it can be observed that the values of $x_{\gamma\text{ret}}$ are mostly lower than the experimentally ones obtained using XRD technique.
Isothermal transformations in Advanced High Strength Steels above and below the $M_S$ temperature

Figure V-8: (a) Fitting parameter $\lambda$ as a function of the initial fraction of martensite and (b) comparison of the carbon content of austenite calculated by the model at the end of the isothermal transformation (open symbols), and the values (solid squares) determined from XRD measurements.

The values of the carbon concentration in bainitic ferrite ($x_{\alpha b}$) obtained for the different isothermal transformations are given in Table V-2. Actually, $x_{\alpha b}$ reflects both the carbon in bainitic ferrite and the carbon in the carbides. If carbon is completely partitioned from bainitic ferrite into austenite during transformation, $x_{\alpha b}$ would be equal to 0. However, the value of $x_{\alpha b}$ would never actually reach zero due to the finite solubility of carbon in bainitic ferrite. As the degree of carbide precipitation increases, the value of $x_{\alpha b}$ also increases \[17\]. The model indicates that the $x_{\alpha b}$ value is lower than the bulk carbon concentration of the steel. Besides, it can be observed that the $x_{\alpha b}$ value increases with decreasing isothermal transformation temperature. This trend is due to the increase in the driving force for carbide precipitation as the temperature decreases. This suggests that the effect of silicon on carbide suppression decreases with decreasing transformation temperature.

Table V-2: Experimental results from dilatometry and XRD and fitting values obtained from the modeling.

<table>
<thead>
<tr>
<th>$T_{iso}$ (°C)</th>
<th>IM fraction (dilato.)</th>
<th>$\gamma_{ret}$ fraction (vol.%)</th>
<th>$x_{\gamma ret}$ XRD (wt.%)</th>
<th>$x_{\gamma ret}$ Model. (wt.%)</th>
<th>$x_{\alpha b}$ Model. (wt.%)</th>
<th>$v$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>0</td>
<td>11.4 ± 0.4</td>
<td>1.18</td>
<td>0.96</td>
<td>0.09</td>
<td>$1 \times 10^{13}$</td>
</tr>
<tr>
<td>280</td>
<td>19 ± 2.0</td>
<td>10.4 ± 1.0</td>
<td>1.27</td>
<td>0.77</td>
<td>0.22</td>
<td>$5 \times 10^{12}$</td>
</tr>
<tr>
<td>250</td>
<td>63 ± 1.7</td>
<td>13 ± 1.0</td>
<td>1.1</td>
<td>0.42</td>
<td>0.23</td>
<td>$3 \times 10^{12}$</td>
</tr>
<tr>
<td>200</td>
<td>84 ± 0.6</td>
<td>10.4 ± 0.9</td>
<td>0.87</td>
<td>0.47</td>
<td>0.001</td>
<td>$4 \times 10^{13}$</td>
</tr>
</tbody>
</table>

V.5. Discussion

There is a significant difference in the transformation kinetics of the AHSS studied, as indicated by the TTT diagrams. In the case of the L$_{Si}$ steel, the isothermal transformations progressed
rapidly, and were complete within the first few minutes of holding. On the other hand, the transformations in the H_Si steel began only after some incubation time that varied with the fraction of initial martensite. As such, the influence of initial martensite on the acceleration of bainite formation was clearly observed.

The isothermal bainitic transformations were adequately described by a nucleation-based model. Excellent agreement between the experimental and calculated results were obtained when the model was validated using dilatometry data derived for the L_Si and H_Si steel. However, in the case of the H_Si steel, an adjustment of the carbon concentration of the bainitic ferrite ($x_{\alpha_b}$) was necessary, in order to account for the carbon enrichment of the remaining austenite. $x_{\alpha_b}$ is an extremely important parameter that gives a measure of the carbon redistribution during the bainite formation. This carbon redistribution is seen to be more pronounced when decreasing the isothermal temperature. This can also explain the decrease of carbon content in austenite with decreasing isothermal temperatures, since the precipitation of carbides implies in an ineffective carbon enrichment of austenite.

V.6. Conclusions

The decomposition of austenite during isothermal treatments above and below $M_s$, was investigated in two AHSS after the formation of various fractions of initial martensite. The main conclusions of this study are summarized as follows:

**L_Si Steel:**

i. Austenite decomposes and rapidly transforms to bainite within the first minute of isothermal holding above and below $M_s$.

ii. After the formation of initial martensite, the transformation kinetics that describes the isothermal decomposition of austenite below $M_s$, coincides with that of the isothermal bainite transformation above $M_s$; modeling of the kinetics confirms that the remaining austenite decomposes to bainite. The model also shows that autocatalytic nucleation is not significant in the investigated material, under the conditions considered.

**H_Si Steel:**

i. The isothermal decomposition of austenite gives rise to lower bainite, at temperatures both above and below $M_s$.
ii. The transformation kinetics of bainite formed below $M_S$, depends on the temperature of isothermal holding and the fraction of initial martensite.

iii. Significant fraction of austenite is stabilized at the end of the heat treatment, irrespective of the holding temperature.

iv. When the carbon enrichment of the remaining austenite is taken into account, the model proposed by Van Bohemen provides an accurate description of the kinetics associated with the isothermal bainitic transformation; this is true for transformations both above and below $M_S$. Moreover, autocatalytic nucleation occurs in this material under the conditions considered.
References


<table>
<thead>
<tr>
<th></th>
<th>Authors</th>
<th>Title</th>
<th>Journal/Source</th>
</tr>
</thead>
</table>
Chapter VI: MICROSTRUCTURAL EVOLUTION OF ADVANCED HIGH STRENGTH STEELS UNDER ISOTHERMAL CONDITIONS

VI.1. Introduction

This chapter presents a detailed characterization of the microstructural evolution resulting from the transformation experiments performed (via dilatometry) on L_Si and H_Si steels; these experiments were described in Chapter V - Section V.2 and V.3.

The characterization was performed as follows: (i) microstructural features: Optical Microscopy (OIM) and scanning electron microscopy (SEM), (ii) identification and quantification of transformation products: Electron Backscatter Diffraction (EBSD), (iii) phase identification: X-ray diffraction (XRD) and (iv) carbide identification: Transmission Electron Microscopy (TEM) and differential scanning calorimetry (DSC).

VI.2. L_Si Steel

VI.2.1. Microstructural Characterization

The microstructures obtained after isothermal holding of the L_Si steel at various temperatures and direct quenching to RT are shown in Figure VI-1(a)-(h). As the figures shown, the microstructures change with decreasing isothermal temperature \( T_{\text{iso}} \). A mixture of bainite with carbide precipitates and other constituents that have a blocky morphology (Figure VI-1(a)), is transformed to a mixture of lath martensite and bainite with carbide precipitates, as shown in Figure VI-1(g)–(h). The isothermal temperatures \( T_{\text{iso}} = 450, 350 \) and \( 100 \) °C give rise to the main features of the resulting microstructures and hence will be discussed in detail.
Figure VI-1: Microstructures resulting from heat treatments at $T_{iso}$ (°C): (a) 450, (b) 400, (c) 350, (d) 300, (e) 250, (f) 200, (g) 100 and (h) quenching to room temperature.
Higher magnification micrographs (compared to those shown in Figure VI-1) of the directly quenched microstructure and those resulting from the three selected holding temperatures are shown in Figure VI-2. Lath martensite (Figure VI-2(d)) forms when the sample is directly quenched to room temperature (RT). Carbides resulting from the auto-tempering process \[^{[1, 2]}\] that occurs at relatively high $M_s$ temperatures, are distributed within the quenched martensite. Above the $M_s$ temperature, i.e., at $T_{iso} = 450 \, ^\circ\text{C}$, intragranular and intergranular carbides typical of lower bainite \[^{[3, 4]}\] are formed in addition to isothermal bainite (Figure VI-2(a)). Another transformation product, enclosed in the dashed line in (Figure VI-2(a)), is also formed. This product was analyzed in detail by EBSD and was found to be most probably fresh martensite (FM), as shown in Figure VI-3. When the isothermal holding is interrupted, a certain volume fraction of untransformed austenite remains, and is subsequently transformed (for the most part) to FM during the final quench. However, a relatively low fraction of retained austenite (RA) that has a blocky phase structure and smooth appearance after etching \[^{[5-7]}\] is locked within the FM, which is considered to be untempered martensite. This type of martensite is more difficult to etch than the carbide-containing phases.

Figure VI-2: Microstructures resulting from (a) $T_{iso} = 450 \, ^\circ\text{C}$, (b) $T_{iso} = 350 \, ^\circ\text{C}$, (c) $T_{iso} = 100 \, ^\circ\text{C}$, and (d) quenched to RT.
Figure VI-3(a)–(c) show an image quality (IQ) map of regions consisting of LB, FM and RA. The darker areas in Figure VI-3(a) correspond to low IQ regions, which have a higher density of lattice imperfections [8-10], than the less dark regions; these low-IQ regions are associated with FM. In the phase map (Figure VI-3(b)), the face centered cubic (FCC) RA and the body centered cubic (BCC) transformation products (martensite and bainitic ferrite) are shown in green and red, respectively. The RA enclosed in the rectangle (Figure VI-3(b)), and the phase boundaries (misorientations between 15° and 180°) between austenite and transformation products are shown in Figure VI-3(c). The misorientation between RA and bainite and martensite are usually described by an axis/angle correspondence. The most widely used orientation relations are the Kurdjumov-Sachs (K-S) <1 1 2>90°, Nishiyama-Wasserman (N-W) <3 6 2>95.3°, and Bain (B) correspondences <0 0 1>45° [10, 11]. In Figure VI-3(c), the K-S, N-W, B, and all the others boundaries are shown in blue, orange, yellow, and black, respectively. A tolerance of 2.5° was used in order to avoid an overlap of these boundaries. As Figure VI-3(c) shows, boundaries exhibiting N-W correspondence slightly outnumbered their K-S counterparts, whereas those satisfying the Bain correspondence were absent from the region of interest. In addition, these RA grains have an average diameter of only 0.17 µm.

The prior austenite grain size (PAGS) was determined from the EBSD data by plotting the grain boundary maps (Figure VI-4(b)) for the rotation angles between 21.1° and 47.1°, as suggested by Bernier et al. [12]. In addition, an alternative method, also based on grain boundary misorientations, was used for the parent phase reconstruction. This method [16] uses a graphical clustering algorithm to find groups of crystallographically related grains that originate from a single parent grain. The reconstructed prior austenite grains are shown through the use of the
unique grain color map, cf. Figure VI-4(c). In this map, each grain is assigned a color. The colors do not denote an orientation, the grains are simply colored to distinguish them from neighboring grains. An average PAGS of 7.2 ± 1.5 µm was determined by using the linear intercept method.

![Figure VI-4: T_{iso} = 350 °C (a) Image quality map and (b) grain boundary map showing boundaries with rotation angles between 21.1° and 47.1°, surrounding the prior austenite grains, and (c) prior austenite grain reconstruction using a graphical clustering technique, shown in the unique grain color map.](image)

Isothermal holding at $T_{iso} = 350$ °C gives rise to a microstructure (Figure VI-2(b)) that has a relatively large fraction of fine carbides, resulting (in part) from the tempering of initial martensite (IM). Although this process was not reflected in the dilatometer curve (presented in Chapter V - Section V.3.1), previous studies have reported that tempering occurs in this temperature range $^{[13,14]}$. Some regions consist of similar features to those of isothermal bainite (Figure VI-2(a)) formed at $T_{iso} = 450$ °C. Isothermal holding at $T_{iso} = 100$ °C gives rise to lath martensite, cf. Figure VI-2(c), which bears striking similarities to that (Figure VI-2(d)) obtained from direct quenching to RT. In addition, RA was absent from the microstructures obtained by directly quenching to RT, and also from those isothermally treated at temperatures below $M_s$. The EBSD maps, shown in Figure VI-5(a)–(d) confirm that FM and RA are both absent from the microstructures obtained at $T_{iso} = 350$ °C and $T_{iso} = 100$ °C. This indicates that the
transformations were completed during the isothermal holding stage, as evidenced by the dilatation curve in the dilatometry experiments.

Figure VI-5: IQ and phase maps from EBSD: (a)-(b) $T_{iso} = 350$ °C and (c)-(d) $T_{iso} = 100$ °C. Black lines in (b) and (d) illustrate the grain boundaries with misorientations between 15 and 180°.

Figure VI-6 shows the hardness as a function of the isothermal temperatures. As expected, processing at high temperatures leads to a relatively softer microstructure (since the microstructure is mainly bainitic) than those formed at low temperatures. On the other hand, owing to the higher IM fractions, lower isothermal temperatures lead to higher hardness values, compared to those obtained at higher temperatures. Microstructures consisting of a mixture of bainite and martensite (which are formed for example, at $T_{iso} = 350$ °C) have intermediate hardness values.

Figure VI-6: Vickers hardness (HV3) of the microstructures formed after isothermal holding at the indicated temperatures. The hardness value obtained after direct quenching to RT is indicated by the arrow.
VI.2.2. X-ray Diffraction (XRD)

The results of XRD analysis Figure VI-7(a) confirm the presence of BCC phases (ferrite, bainitic ferrite and martensite). However, these phases cannot be distinguished by using this technique. Moreover, RA (FCC phase) is absent from the spectrum and, owing to their low volume fraction and fine dispersion, the carbides cannot be identified by using this technique.

![Figure VI-7: XRD spectrum with peaks corresponding to the BCC phase.](image)

VI.2.3. Carbide Identification

Transmission Electron Microscopy (TEM)

The bright field (BF) TEM micrographs shown in Figure VI-8(a)–(d) reveal the rod-like morphology of the carbides in all of the samples [3]. These carbides are aligned within the ferrite platelets (cf. Figure VI-8(a)), in the case of the isothermal bainite formed at \( T_{iso} = 450 \, ^\circ C \). The occurrence of these carbides at \( T_{iso} = 350 \, ^\circ C \), confirmed the hypothesis for isothermal bainite formation (Figure VI-8(b)) at this temperature. As expected, multi-variant carbide precipitates (Figure VI-8(c)), originating from the tempered martensite [4, 15], are also observed at \( T_{iso} = 350 \, ^\circ C \). The sample treated at \( T_{iso} = 100 \, ^\circ C \) exhibits, however, only multi-variant carbide precipitation from tempered martensite. The selected area electron diffraction (SAED) pattern of the carbides and the possible solutions for the corresponding indexation are shown in the upper right-hand corner of the micrographs. The SAED patterns exhibit diffraction spots corresponding to orthorhombic cementite (Fe\(_3\)C). The formation of Fe\(_3\)C in this low-silicon steel is favored over that of other carbides. Moreover, the low isothermal temperatures result in insignificant diffusion of Cr or Mo (as further shown in the DSC experiments), and hence the formation of carbides, from the alloying elements, is not favored in the temperatures used.
Differential Scanning Calorimetry (DSC)

The DSC experiments were performed after austenitization and quenching to RT and liquid nitrogen (see Figure VI-9(a)). Three exothermic peaks were observed when the sample was heated at 10 °C/min. The first and second peaks occurred at temperatures ranging from 250 – 300 °C and 380 – 450 °C, which according to the literature records are typically associated with the formation of epsilon (ε) carbides and cementite, respectively. Furthermore, a third small peak that occurs at ~510 °C is attributed to alloy carbides. Figure VI-9(b)–(c) show the SEM images of the quenched dilatometer samples after simulating heating at 10 °C/min to 350 and 500 °C, respectively. The carbides, whose formation resulted in the first peak, are shown in Figure VI-9(b); Figure VI-9(c) shows a similar type of carbide that gave rise to the second peak.
VI.2.4. Quantitative Analyses of Microstructural Constituents

The EBSD results (low image quality for fresh martensite and highlighting RA in the phase maps) were combined with those (fractions of fcc microstructural constituents during initial cooling and isothermal holding) obtained from dilatometry. Table VI-1 shows the fractions of constituents in the microstructures, as determined by using this combination.

<table>
<thead>
<tr>
<th>$T_{iso}$ (°C)</th>
<th>IM</th>
<th>Bainite</th>
<th>FM + RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>-</td>
<td>0.85 ± 0.03</td>
<td>0.15 ± 0.03</td>
</tr>
<tr>
<td>350</td>
<td>0.73 ± 0.08</td>
<td>0.27 ± 0.08</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>0.98 ± 0.03</td>
<td>0.02 ± 0.03</td>
<td>-</td>
</tr>
</tbody>
</table>

*Table VI-1: Volume fractions of transformation products formed during the heat treatment.*
VI.3. H_Si Steel

VI.3.1. Microstructural Characterization

A fully martensitic microstructure with typical lath morphology (see Figure VI-10(a)) was formed when the sample was directly quenched to RT. Carbide precipitates and RA were both absent in this microstructure. Lower bainite was formed after an isothermal treatment within the bainite temperature range (see Figure VI-10(b)). The formation of lower bainite is accompanied by the precipitation of carbides, with rod-like morphology. As previously dilatometry curve\(^7\) showed, the bainite transformation was not finished during isothermal holding. Therefore, in addition to isothermal bainite, fresh martensite (enclosed by the dashed lines in Figure VI-10(b) is formed during the quench to RT; part of the austenite (enclosed within the solid lines in Figure VI-10(b)).

![Figure VI-10](image)

Figure VI-10: Scanning electron micrographs: (a) Quenched to RT, (b) \(T_{iso} = 325\) °C - 1 h. LB = lower bainite, RA = retained austenite, FM = fresh martensite.

The microstructure obtained after holding at \(T_{iso} = 325\) °C were analysed by EBSD, and the results are shown in Figure VI-11(a)–(d). In the combined IQ and phase map (Figure VI-11(a)), the dark regions represent low-IQ grains, which have a high density of lattice imperfections; these grains are associated with FM. In the phase map, the BCC transformation products (martensite and bainite) and RA are shown in red and green, respectively. Figure VI-11(b) shows a higher magnification view of the region enclosed in the rectangle in Figure VI-11(a), with only the phase boundaries (misorientations between 15 and 180°) between austenite and transformation products highlighted. The misorientation between RA and bainite and martensite is described by the K-S \(<1 1 2>90°, N-W <3 6 2>95.3°\) and Bain (B) \(<0 0 1>45°\) \[^{10, 11}\], as

\(^7\) Described in Chapter V.
Chapter VI

mentioned in Section VI.2.1. The K-S and N-W boundaries are shown in blue and orange, respectively, and the latter boundaries outnumber the former; boundaries described by the B correspondence (yellow) are absent from the region of interest. In addition, as Figure VI-11(c) shows, RA is stabilized with a blocky morphology (0.67 ± 0.13 µm) and as interlath regions in bainite (0.27 ± 0.12 µm).

![Microstructure](image)

*Figure VI-11: Microstructure obtained after treatment at $T_{\text{iso}} = 325 \, ^{\circ}\text{C}$: (a) IQ + phase map, (b) higher-magnification view of the retained austenite; grain boundaries corresponding to the N-W and K-S relations, tolerance of ± 2.5°, are highlighted, (c) IQ + IPF of austenite, and (d) grain-average IQ map. Grains were defined by setting the minimum number of pixels per grain and misorientation to 4 and 5°, respectively. LB = lower bainite, RA = retained austenite, FM = fresh martensite.*

Both types of austenite have the same crystallographic orientation (common origin), as indicated by the inverse pole figure (IPF) map combined with the corresponding IQ map (Figure VI-11(c)). The prior austenite grains had an average size of $5.8 \pm 1.6 \, \mu\text{m}$. 
Figure VI-11(d) shows the grain-average IQ color map of bcc phases. The white regions would correspond to RA (fcc phase), which were excluded from the partitioning. This map was obtained by first defining the grain, and then averaging the IQ of all pixels inside the grain. In Figure VI-11(d) each grain is shaded in a color corresponding to the average IQ of the entire grain. The blue and green colors correspond to low IQ (FM), whereas higher-IQ grains (i.e., bainite) are shaded in yellow, orange and red color.

The microstructural evolution that occurs at $T_{iso} = 280\, ^\circ C$, $250\, ^\circ C$, and $200\, ^\circ C$, i.e., at temperatures below the $M_S$ temperature, is shown in Figure VI-12(a)-(f). The microstructures shown in these figures have IM fractions of 0.2, 0.6, and 0.85, respectively. This martensite, which is formed during cooling, undergoes tempering during the 1-h isothermal hold, and is therefore referred to as tempered martensite (TM). The high-magnification image shown in Figure VI-12(b) reveals the blocky morphology and substructure of this TM. Carbide precipitates are absent from the blocks, owing possibly to the high silicon content and low tempering temperature. In addition to TM, the microstructure exhibits features typical of lower bainite and consists of rod-like carbides aligned in ferrite platelets (Figure VI-12(d)). These observations confirm that lower bainite is formed during the isothermal holding below $M_S$. 

![Microstructural Evolution of Advanced High Strength Steels under Isothermal Conditions](image-url)
Chapter VI

Figure VI-12: Scanning electron micrographs of the microstructures formed at: (a)-(b) $T_{iso} = 280 \, ^\circ C \cdot 1 \, h$, (c)-(d) $T_{iso} = 250 \, ^\circ C \cdot 1 \, h$, and (e)-(f) $T_{iso} = 200 \, ^\circ C \cdot 1 \, h$. LB = lower bainite, RA = retained austenite, TM = tempered martensite.

The micrographs (Figure VI-13(a)–(b)) obtained via scanning transmission electron microscopy (STEM) of disk foils, confirm the absence of carbide precipitates in the blocky morphology of TM. These precipitates occur, however, in the lower bainite formed in microstructures obtained at $T_{iso} = 250 \, ^\circ C$. Although absent from the TM with blocky morphology, carbide precipitates were observed (Figure VI-12(d)) in the lath-type TM.

Figure VI-13: Scanning transmission electron microscopy (STEM) images of the microstructure resulting from the $T_{iso} = 250 \, ^\circ C \cdot 1 \, h$ treatment.

The EBSD phase maps (cf. Figure VI-14(a)–(c)) indicate that in addition to the interlath lamellar austenite (highlighted in green), blocky grains were also stabilized at high $T_{iso}$.

Figure VI-14: Phase map with grain boundaries having misorientations between 15 and 180°, illustrating the morphology of retained austenite in microstructures obtained at: (a) $T_{iso} = 200 \, ^\circ C$, (b) $T_{iso} = 250 \, ^\circ C$, and (c) $T_{iso} = 280 \, ^\circ C$. 
Although the resolution of the EBSD technique is reasonably high, film-like austenite grains between the martensite/bainite laths are not reliably resolved. The RA fractions determined from XRD measurements are therefore deemed more reliable than those obtained via EBSD analysis. Figure VI-15 shows the hardness as a function of the isothermal temperatures. The hardness values decrease with increasing the processing temperature, i.e., the microstructures are mainly formed by bainite above $M_S$. On the other hand, owing to the higher IM fractions, lower isothermal temperatures lead to higher hardness values, compared to those obtained at higher temperatures. Microstructures consisting of a mixture of bainite and martensite (which are formed for example, at $T_{iso} = 250 \degree C$ and $280 \degree C$) have intermediate hardness values.

![Figure VI-15: Vickers hardness (HV$_3$) of the microstructures formed after isothermal holding at the indicated temperatures. The hardness value obtained after direct quenching to RT is indicated by the arrow.](image)

**VI.3.2. X-ray Diffraction (XRD)**

The fraction of RA was evaluated from at least two dilatometric samples that were subjected to identical heat treatments. In all of the isothermal experiments, austenite was retained (Figure VI-16) after quenching to RT, but was absent from the microstructure obtained via direct quenching to RT.

![Figure VI-16: XRD spectrum showing the peaks corresponding to retained austenite.](image)
Carbon partitioning from IM to the untransformed austenite leads to the retention of austenite. The austenite is stabilized with this carbon enrichment and as a result, persists in the final microstructure. As Figure VI-17 shows, an approximately constant fraction (between 10 and 13 %) of RA is obtained with varying isothermal temperature.

![Figure VI-17: Fraction of retained austenite, as determined from XRD measurements.](image)

**VI.3.3. Carbide Identification**

**Transmission Electron Microscopy (TEM)**

Figure VI-18(a)–(b) show bright field (BF) TEM micrographs of microstructures obtained after isothermal holding ($T_{iso} = 325 \, ^\circ C$) above the $M_S$ temperature. Silicon is known to inhibit formation of cementite at high tempering temperatures but has little or no effect in suppressing transition carbide precipitation at low tempering temperatures. However, rod-like carbides aligned within the ferrite platelets, whose occurrence is typical of isothermal bainite, are revealed in Figure VI-18(a)–(b). Local chemical analysis of the carbides (the yellow point in Figure VI-19(a)) and matrix (the purple point in Figure VI-19(a)) reveals that the alloying elements are not segregated in the carbides (cf. Figure VI-19(b)), indicating that these are an iron-carbide type of precipitate.

TEM micrographs showing the microstructures obtained from isothermal holding, ($T_{iso} = 250 \, ^\circ C$) below $M_S$ temperature, are shown in Figure VI-20(a)-(b). As the figures show, carbide precipitates are aligned inside the bainite ferritic laths, similar to the ones found in the microstructure obtained after $T_{iso} = 325 \, ^\circ C$. 

97
Figure VI-18: Transmission electron microscopy bright field (TEM BF) micrographs showing the carbide precipitation that occurs at $T_{iso} = 325 \, ^\circ\text{C}$.

Figure VI-19: $T_{iso} = 325 \, ^\circ\text{C}$: (a) TEM BF micrograph showing carbide and matrix points measured during EDX; EDX pattern from the (b) carbidies (the yellow point in Figure VI-19(a)) and (c) matrix (the purple point in Figure VI-19(a)).

The SAED pattern of the carbides and a possible solution for the corresponding indexation are illustrated in Figure VI-20(c). The SAED patterns exhibit diffraction spots that correspond to
orthorhombic cementite (Fe$_3$C). Carbides with different orientations, as the ones typically present in tempered martensite (Figure VI-12(d)), could not be found via TEM.

![Figure VI-20](image)

*Figure VI-20: $T_{\text{iso}} = 250$ °C: (a) TEM BF micrographs showing the carbide precipitates, (b) TEM DF image, and (c) diffraction from and SAED corresponding to the carbide.*

**Differential Scanning Calorimetry (DSC)**

The DSC experiments were performed after austenitization and quenching to RT, see Figure VI-21(a). The activation energy for carbide precipitation was determined by heating the sample at rates of 10 and 30 °C/min. The first exothermal peak occurred at temperatures ranging from 150 – 300 °C and corresponded to an activation energy of 99 kJ/mol., which is associated with the formation of epsilon (ε) carbides. The second peak, which occurred at temperatures...
ranging from 400 – 525 °C and an activation energy of 255 kJ/mol., is associated with cementite formation. Figure VI-21(b)–(c) show the SEM images of the quenched dilatometer samples after heating to 350 and 550°C, respectively. As the figures show, lath-type ε carbides and larger, globular cementite are associated with the respective first and second peaks.

**Figure VI-21:** (a) Differential scanning calorimetry curve exhibiting two exothermic peaks with activation energies of 99 and 255 kJ/mol. during reheating at 10 °C/min, after full austenitization and quenching to RT; SEM images of sample heated to (b) 350 °C and (c) 550 °C and quenched to RT.

### VI.3.4. Quantitative Analysis of Microstructural constituents

The fraction of bcc constituents was quantified via the method proposed by Wu et al. [8]. The microstructure corresponding to $T_{iso} = 250$ °C is used as an example of the results obtained by using this procedure. Figure VI-22(a)–(b) shows the IQ map and the corresponding asymmetrically shaped distribution of the normalized IQ, respectively.

The data were post-processed in order to exclude the effect of the grain-boundary regions. In the procedure, pixels that were contiguous to interfaces with a misorientation larger than 15° were removed. The experimental data of the IQ-distribution were fitted assuming a Gaussian distribution [8]. The peak corresponding to low-IQ (dash-dotted line) was associated to TM, whereas the peak corresponding to high-IQ (dotted line) was associated to lower bainite. Although the carbon concentration and lattice distortion of the IM decrease during the isothermal treatment (tempering), LB contains a lower density of lattice imperfections than TM.
and, accordingly, displays a higher IQ. Therefore, the volume fractions of TM and LB were derived from the areas beneath the low-IQ and the high-IQ distributions, respectively, and corrected with the fraction of retained austenite determined by XRD.

Low- and high-IQ grains were then selected in order to validate the results of the aforementioned procedure. Pixels having an IQ ≥ 45 are designated as LB. These pixels are then excluded and an IPF map is overlaid (Figure VI-22(c)), with the SEM image. The colors coincide with the low-IQ zones, consistent with the regions, which are considered TM.

![Figure VI-22: Microstructure formed at $T_{iso} = 250$ °C: (a) IQ map, (b) number of pixels belonging to bcc grains vs normalized IQ, (c) IPF overlaid with the SEM image, highlighting the low-IQ (TM) regions.](image)

An almost-symmetrical IQ distribution was obtained for the experiment performed at $T_{iso} = 200$ °C, owing to the high fraction of IM. In other words, LB constitutes only a low fraction of the microstructure and does not lead to a pronounced individual peak, as illustrated in Figure VI-23(d). In this case, the IQ distribution is not suitable to distinguish the microstructural constituents.

The phase fraction of each constituent in the microstructures formed below the $M_s$ temperature, may also be quantified based on the dilatation that occurs during transformations. After the IM and RA (from cooling to $T_{iso}$ and quenching to RT, respectively) fractions are determined, the
remaining dilatation is attributed to decomposition of the remaining austenite to LB during the isothermal holding. In other words, the phase fractions were determined through a combination of dilatometry, EBSD, and XRD measurements. The volume fractions of the microstructural constituents are shown in Table VI-2.

![Image](image_url)

**Figure VI-23:** Distribution of image quality for a $T_{iso}$ of (a) 325, (b) 280, (c) 250, and (d) 200 °C.

**Table VI-2:** Volume fraction (%) of phases formed during the heat treatment, as determined by using various methods.

<table>
<thead>
<tr>
<th>$T_{iso}$ (°C)</th>
<th>Dilatometer</th>
<th>EBSD</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TM</td>
<td>LB</td>
<td>FM</td>
</tr>
<tr>
<td>325</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>280</td>
<td>19 ± 2.0</td>
<td>70.6 ± 2.0</td>
<td>0</td>
</tr>
<tr>
<td>250</td>
<td>60 ± 1.7</td>
<td>30 ± 1.7</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>84 ± 0.6</td>
<td>6 ± 0.6</td>
<td>0</td>
</tr>
</tbody>
</table>
VI.4. Discussion

Isothermal bainite, accompanied by carbide precipitation, occurred in most of the microstructures of both steels. According to DSC experiments, tempering of martensite in H_Si steel resulted in the formation of ε carbides at low isothermal temperatures and cementite at high isothermal temperatures. Although some carbide precipitates in TM were observed in the microstructures via SEM, they were not observed via TEM. Carbide precipitation (cementite) is attributed to the formation of isothermal bainite, both above and below the $M_S$ temperature. On the other hand, owing to the low-silicon concentration and high $M_S$ of the L_Si steel, carbide precipitation occurred in both TM and isothermal bainite, as well as during quenching (auto-tempering).

Austenite is retained in all microstructures of the H_Si steel. However, the morphology of RA varies with the isothermal temperature and, at high temperatures, is stabilized mainly as blocky austenite, although interlath austenite with bainite and/or FM also occur; RA occurs mainly as interlath regions in bainite when the isothermal temperature is lowered. Moreover, RA constitutes a very low fraction of the microstructures of the L_Si steel and occurs only at temperatures above $M_S$.

VI.5. Conclusions

The final microstructures of two AHSS (mainly with different Si concentration) subjected to cooling and isothermal heat treatments by means of dilatometry, are evaluated.

The influence of the isothermal temperatures on the microstructures can be summarized as follows:

- Isothermal bainite accompanied by carbide precipitation occurs both above and below the $M_S$ temperature of both steels.
- In the case of the H_Si steel, carbide precipitation is not significant below the $M_S$ temperature where TM forms.
- Austenite of various morphologies is retained after all of the isothermal heat treatments.
- Lower volume fractions or absence of retained austenite are obtained in the L_Si steel than in its H_Si counterpart.
References


Chapter VI


Chapter VII: MICROSTRUCTURAL CHARACTERIZATION VIA EBSD AND NANOINDENTATION

VII.1. Introduction

Advanced high strength steels (AHSS) have complex multiphase microstructures that usually consist of nanometer-sized grains and complex-morphology grain boundaries, and hence, phase identification and quantification is often not straightforward. The accuracy of these tasks can be improved by using a combination of techniques. In fact, nanoindentation can be used to determine the hardness of distinct phases in the microstructure; this hardness can then be correlated with structural parameters, such as the defect density, at the location of interest. The hardness and defect density variation are usually associated with different types of austenite decomposition products. The variation in hardness and defect density results, in general, from different types of austenite decomposition products. For example, allotriomorphic ferrite and bainite typically have dislocation densities of $0.4 \times 10^{14} \text{ m}^{-2}$ and $2.5 \times 10^{14} \text{ m}^{-2}$ [1], respectively. The corresponding variations in hardness can therefore be used to identify zones corresponding to different microstructural constituents.

Some studies [2-8] have reported that the microstructural constituents of dual phase (DP) steel and TRansformation Induced Plasticity (TRIP) steels exhibit composition-dependent nanohardness. Nanohardness values ranging from 2.9 to 3.1 GPa and approximately 6.5 GPa have been reported for ferrite and tempered martensite, respectively, in DP steels [5, 7]. In TRIP steels, respective nanohardness of 3.4 to 4.8 GPa and ~ 7.0 to 7.5 GPa [2, 7, 8] have been reported for ferrite and bainite. Various values (5.5 to 11.5 GPa [5, 7] and ~16.7 GPa) have been reported for the initial martensite in DP and TRIP steel, respectively. Several values (ranging from 4.65 to 10 GPa) have also been reported for retained austenite [2, 8].

Furnemont et al. [2] used nanoindentation to measure the hardness of individual phases in the microstructures of two TRIP-assisted multiphase steels, with differing silicon concentration. They analyzed the method that was used to prepare the surface prior to the measurements and determined the influence of the silicon concentration on the hardness. The ferritic matrix and martensite had the lowest and highest hardness values, respectively, whereas bainite and austenite had intermediate values. Furthermore, owing to solid solution strengthening, the ferritic matrix in the high-silicon concentration steel had a higher hardness than its counterpart.
in the low-silicon steel. The authors concluded that electropolishing after mechanical polishing leads to more accurate nanohardness values than those obtained after mechanical polishing only or thermal etched samples.

Nanoindentation combined with in-situ mechanical testing and digital image correlation (DIC) analysis was recently \[^3\], used to study the micron-scale local mechanical properties and deformation behavior of the microstructure in multiphase materials. Furthermore, Wu et al. \[^4\] used the Image Quality (IQ) parameter obtained from Electron Backscatter Diffraction (EBSD) measurements to characterize the degree of lattice imperfection in complex microstructures (such as those typical of AHSS). The nanohardness is also affected by lattice imperfections, and hence the IQ values are related with the nanohardness. However, details of the microstructural evolution were not presented in that study. Therefore, in this chapter, an approach that employs nanoindentation combined with microstructural characterization via SEM and EBSD is used to distinguish between martensite and bainite. The grain-average IQ parameter and the nanohardness data are used to distinguish the microstructural constituents, based on the assumption that the IQ and nanohardness are both affected by the lattice imperfections.

VII.2. Experimental Methods

VII.2.1. Materials and Heat Treatments

The chemical compositions of the studied steels are listed in Table III-1 in Chapter III - Section III.2. The concentration of carbon, manganese, silicon, chromium and molybdenum constitutes the main difference between these compositions.

Two samples, heat treated according to the parameters given in Chapter V – Section V.2, were selected from each steel by using the following criteria: austenitized at 900 °C and cooled to a temperature: above MS (450 °C for L_Si and 325 °C for H_Si) and below MS (350 °C for L_Si and 280 °C for H_Si), held for 1 h and quenched to room temperature (RT).

VII.2.2. Nanoindentation Measurements

Nanoindentation is typically used for the study of mechanical properties, primarily the hardness \((H)\) and elastic modulus \((E)\), of nanoscale materials \[^9\]. However, as previously mentioned, the nanoindentation technique has also been used to characterize complex microstructures \[^3,4,10,11\].
During the experiments, load ($P$) and penetration depth ($h$) are recorded as the indenter tip is pressed into the surface of the material, in accordance with a prescribed loading and unloading profile. The load-displacement curve (often referred to as $P$-$h$ curve), which is schematically illustrated in Figure VII-1(a), constitutes the response of interest. As the indenter is pressed into the sample (loading part), elastic and plastic deformation occur, thereby resulting in the formation of a hardness impression that conforms to the shape of the indenter. During the withdrawal of the indenter (unloading part), only the elastic portion of the displacement is recovered \[^{12}\]. The schematic in Figure VII-1(b) shows the deformation pattern that forms during and after the indentation. In Figure VII-1(a)–(b), $h_{\text{max}}$, $h_c$, and $h_f$ represent the displacement at the maximum load applied ($P_{\text{max}}$), contact depth (depth of the indenter in contact with the sample under load), and final displacement of the material surface after unloading, respectively. Moreover, $S$ is the initial unloading contact stiffness and $a_c$ is the projected contact area in the surface. The shape of the $P$-$h$ curve depends on the material and reflects, in general, the mechanical properties of the material \[^2, 13, 14\].

*Figure VII-1: (a) Schematic load-displacement curve (P-h curve) and (b) deformation pattern formed during and after nanoindentation.*

In this study, the hardness ($H$), which is defined as the indentation load divided by the projected contact area of the indentation, constitutes the mechanical property of interest. The hardness is the mean pressure that a material can support under load \[^9\] and can be determined from the peak load of the load displacement curve, via the following equation:

$$H = \frac{P_{\text{max}}}{A_c}$$

*(Equation VII-1)*
where, $P_{\text{max}}$ is the maximum load and $A_c$ is the projected contact area of the indentation (indicated by $a_c$ in Figure VII-1(b)). $A_c$ varies with the contact depth and in the case of a Berkovich indenter, is given as:

$$A_c = 24.56 \ h_c^2$$

(Equation VII-2)

In addition, the contact depth can be estimated from the $P$-$h$ curve by using the following relation:

$$h_c = h_{\text{max}} - \varepsilon_B \ \frac{P_{\text{max}}}{s}$$

(Equation VII-3)

where $\varepsilon_B$ is a constant that varies with the type of indenter and is equal to 0.72 in the case of a Berkovich indenter [5, 9].

Nanoindentation measurements were performed as one means of determining the differences among the microstructural constituents in the steels studied in this work. As described in Chapter III - Section III.6.2, various regions of each microstructure, resulting from the treatments, were indented. The samples were initially analyzed via EBSD (Chapter III - Section III.4.3) and therefore, the surfaces designated for indentation exhibited very low roughness, which is essential for accurate measurements [12,9,14]. Prior to indentation, the regions previously scanned by EBSD were scanned with a Berkovich tip, using a scanning probe microscope (SPM) in contact mode, and specific microstructural constituents (identified via EBSD) were targeted.

Nanoindentation measurements were performed, at a constant strain rate ($\dot{\varepsilon} = \dot{h}/h$) of 0.07 s$^{-1}$, using a Triboindenter TI 950 Nanoindenter in displacement-control testing mode; $h$ and $\dot{h}$ are the penetration depth and the penetration rate of the indenter, respectively. Indentations were performed to a depth of 100 nm [3]. The diamond indenter tip used for the measurements has the same shape as a symmetric three-sided pyramid, and is referred to as a Berkovich indenter.

Arrays of 10 × 10 indentations were created in different regions of each sample. The indents were spaced 2 μm in both directions, in order to eliminate the potential effects of overlapping plastic zones. Furthermore, the indentations were considered successful and taken into account only when located strictly within a well-defined grain and (when) a reliable corresponding load-penetration depth curve was obtained. We eliminated data obtained from two or several constituents, by using this approach.

The indentations were visualized via topography scans performed by means of contact-mode atomic force microscopy (AFM). After nanoindentation measurements and AFM scans, the
samples were etched (as described in Chapter III - Section III.4.1) in order to reveal the microstructure and identify the indents via SEM. The IQ data, determined from the EBSD scans, were matched with the nanoindentation data by means of this SEM examination.

VII.3. Microstructural Evolution

The microstructures of both steels are described in Chapter VI - Section VI.2.1 and V.3.1. In order to obtain additional data, EBSD scans were performed and phase maps were used to distinguish among martensite, bainite, and retained austenite. Although retained austenite can be identified in a straightforward manner, tempered martensite and lower bainite, which both have bcc lattices, are not easily distinguished. The IQ was therefore used to distinguish between, and quantify the fraction of, martensite and bainite [15]. This parameter describes the quality of an EBSD pattern, which is affected primarily by the perfection of the crystal lattice in the diffracting volume [16]. In IQ maps, the minimum and maximum (IQ) values are denoted as black and white, respectively, and the other gray values are scaled linearly between these two extremes [17, 18]. The IQ is, however, a relative (rather than absolute) value, since it depends on additional factors such as the camera sensitivity, sample preparation, and grain orientation [19-22]. Moreover, IQ values can range from zero to very large numbers, and increase with increasing sharpness of the diffraction pattern. Defect-free crystal regions therefore have a high-IQ, whereas regions with a high defect density (e.g. adjacent to interfaces, severely deformed zones, inclusions, etc.) have a low-IQ [23]. The IQ parameter may be used for a qualitative description of the strain distribution in a microstructure. In fact, this parameter has been used to distinguish between ferrite (high-IQ) and martensite (low-IQ) in DP steels [10, 19] and fresh martensite (low-IQ) and tempered martensite (high-IQ) [24, 25] in Q&P steels. Fresh martensite has a higher density of lattice defects than tempered martensite or bainite, and therefore appears with a lower IQ in the EBSD maps [24].

The results presented in Chapter VI, are summarized as follows:

✓ **Formed in isothermal conditions above M_s** (see section VII.2.1. for description of the heat treatment): L_Si and H_Si consist of lower bainite (LB) with carbide precipitates, fresh martensite (FM) and retained austenite (RA). However, as shown in Figure VII-2(a)–(d), the L_Si steel has an extremely low fraction (i.e., <1 %) of RA.

✓ **Formed in isothermal conditions below M_s** (see section VII.2.1. for description of the heat treatment): Both steels consist of tempered martensite (TM) and LB with carbide
precipitates (cementite). In addition, the H_Si steel also contains about 10 % of RA, as shown in Figure VII-3(a)–(d).

Figure VII-2: Microstructures formed after isothermal holding above $M_S$: (a) SEM and (b) phase map + IQ map of the H_Si steel, (c) SEM image, and (d) phase map + IQ map of the L_Si steel.

Figure VII-3: Microstructures formed after isothermal holding below $M_S$: (a) SEM and (b) phase map + IQ map of H_Si steel, (c) SEM image, and (d) Phase map + IQ map of the L_Si steel.
VII.4. Electron Backscatter Diffraction (EBSD)

The IQ was used to distinguish between, and quantify, the microstructural constituents \[15\]. In addition, the method proposed by Wu et al. \[4, 10\] was used to reduce the effect of grain boundaries on the IQ indexation. The grain-average IQ is considered the most accurate method of correlating the IQ in the grain to the location of the indent. In other words, the use of a general IQ map and chart to determine the constituents imposes significant uncertainties, because the IQ changes gradually in the vicinity of the grain boundaries; therefore, the fraction of low-IQ phase is overestimated. The approach used by Wu et al. \[4, 10\] minimizes this inaccuracy to some extent, but does not allow the IQ-based selection of individual grains from the EBSD scan. As such, the grain-average IQ is used in this work, in order to overcome this limitation. Using this approach, the grains are first defined, and the IQ of all the pixels contained therein are subsequently averaged. Grains are defined as regions that contain a minimum of 4 pixels and exhibit a variation in orientation of <5°. In the grain-average IQ color map, each pixel is shaded in a color corresponding to the average IQ of the entire grain.

VII.5. Nanohardness

**VII.5.1. H_Si Steel**

An example of the nanoindentation measurements performed at an isothermal temperature of \(T_{iso} = 325 ^\circ C\) (i.e., above \(M_S\)) is shown in Figure VII-4(a)–(d). Figure VII-4(a) shows an EBSD map of the region that was subsequently nanoindented. In this image, the IQ map is superimposed with the phase map. Figure VII-4(b) shows the grain-average IQ color map, with high angle boundaries in the bcc phase. The white areas correspond to retained austenite (fcc phase), which is excluded from the partitioning. The color scale corresponds to the grain-average IQ values. Therefore, grains shaded in blue have the lowest IQ whereas those shaded in red have the highest IQ. Figure VII-4(c) shows a SEM image of residual indents on the pre-selected area (cf. Figure VII-4(a)–(b)). The corresponding microstructure in Figure VII-4(d), confirms the location of the indents (indicated by the yellow arrows) with respect to the microstructural constituents. Three indents, labelled 1, 2 and 3, were made in target microstructural constituents. Figure VII-4(a)-(d) reveal that:

(i) indent 1 was made in the red region that corresponds to the bcc phase shown in Figure VII-4(a). This phase appears as a yellow (i.e., intermediate IQ-value)
region in Figure VII-4(b). Carbide precipitates also occur in this region (cf. Figure VII-4(d));

(ii) as indicated by the blue shading (Figure VII-4(b)), indent 2 was made in a low-IQ region of the bcc phase (Figure VII-4(a)); this region has a blocky morphology (Figure VII-4(d));

(iii) indent 3 was made in RA, which is shaded in green in Figure VII-4(a).

Figure VII-4: $H_{Si,T_{iso}} = 325$ °C: (a) IQ + phase map of the selected area, where and represent retained austenite and ferrite, respectively, (b) grain-avg. IQ where the range of values is displayed in different colors, (c) nanohardness indentations, and (d) corresponding microstructure.

Images (Figure VII-5(a)), obtained from AFM of these indents, reveal a difference in their sizes. For example, indents 1 and 2 lie within high-IQ and low-IQ grains, respectively, and hence the former is larger and has a greater residual depth (0.71 μm vs. 0.55 μm) than the latter.

Load-displacement curves corresponding to the nanoindentation measurements are shown in Figure VII-5(b). Each microstructural constituent is characterized by a different load-displacement relationship. The loading part of the curve, which describes the plastic characteristics of the constituents, and the maximum load constitute the main differences in the relationships. Furthermore, the high-IQ (indent 1) zone is associated with the softest constituent (in this case, LB). Indent 2, in contrast, lies in a zone that has the lowest IQ and hence experiences the highest load; in other words, this indent lies therefore in the hardest constituent
(i.e., FM $^{[3]}$) of the microstructure. Compared to FM and LB, RA exhibits intermediate deformation resistance.

![Image](image.png)

Figure VII-5: $H_{Si,T_{iso}} = 325 ^\circ C$: (a) nanoindentations and AFM images from selected indents, (b) load-displacement curves.

Previous studies $^{[2, 3, 26]}$ have reported that RA may transform to martensite during the nanoindentation experiments. This transformation is manifested as a discontinuity or pop-in on the load-displacement curve. However, this phenomenon was not observed in the present investigations.

Taken together, the results shown in Figure VII-4 and Figure VII-5(b), indicate that LB is, in general, the softest microstructural constituent. The nanohardness may be arranged in descending order as 8.5 ± 0.9 GPa, 6.2 ± 0.3 GPa, and 5.8 ± 0.4 GPa, corresponding to FM, RA, and LB, respectively. Figure VII-3(b)) shows that TM obtained at $T_{iso} = 280 ^\circ C$ (i.e., below $M_s$) has a low-IQ, similar to that obtained for FM formed after isothermal holding of the steel above $M_s$. The carbon content and the lattice distortions in the initial martensitic structure usually decrease during tempering. However, this decrease did not occur in the current study, as evidenced by the absence of carbide precipitates in the blocky TM morphology.

Figure VII-6(a)–(b) show the nanohardness data, acquired in scanning mode from samples isothermally held below $M_s$ ($T_{iso} = 280 ^\circ C$), in combination with the corresponding microstructures. These results concur with those (Figure VII-3(a)–(b)) used to identify LB and TM regions on the basis of morphology and IQ.
Figure VII-6: $H_{Si,T_{iso}} = 280^\circ C$: (a)-(b) microstructure and nanohardness values of lower bainite (LB) and tempered martensite (TM), respectively. The numbers correspond to the nanohardness values in GPa.

Figure VII-7(a) shows the distribution of nanohardness values obtained above and below the $M_s$ temperature. The maxima of the distribution correspond to the LB, RA, and FM constituents resulting from the heat treatment at $T_{iso} = 325^\circ C$. Compared to those observed at this temperature, wider peaks occur at $T_{iso} = 280^\circ C$ for the LB and RA constituents. In addition, nanoindentation of RA was possible only in the case of coarse and blocky grains formed in the sample treated above $M_s$ (i.e., at $T_{iso} = 325^\circ C$), where the RA grains had a relatively large size and blocky morphology. The results in Chapter VI – Section VI.3.1 showed that microstructures consisting of interlath RA in bainite, are formed with decreasing isothermal temperature. The nanohardness determined at $T_{iso} = 280^\circ C$, constitutes a combination of the individual hardness values of LB and RA. Therefore, a broader peak (Figure VII-7(a)) is obtained at this temperature than at $T_{iso} = 325^\circ C$. Nanohardness values of 5.98 ± 0.6 GPa and 7.4 ± 0.3 GPa are obtained for LB and TM, respectively, below the $M_s$ temperature.

Furthermore, the radius of the plastic zone for individual indents was estimated in order to validate the results [3]. The contact radius ($a'$) was obtained using the equation $a' = \sqrt{\frac{A}{\pi}}$ where $A$ is the projected contact area of the indent.

For Berkovich tips, the ratio between the radius of the plastic zone ($c$) and the contact radius ($a'$) is determined as $\frac{c}{a'} = 3.4$. From this ratio, the radius of plastic zone was calculated for each microstructural constituent.

The radius of the plastic zone in LB formed above and below $M_s$, is approximately 1.1 µm. These values are smaller than the LB block size, which is 2.2 ± 0.7 µm for LB formed above
Chapter VII

$M_S$ and $2.3 \pm 1 \, \mu m$ below $M_S$, respectively. Hence, plastic deformation occurs predominantly in the interior of the blocks, validating the nanohardness values.

Nanohardness of RA was measured only on the sample that was heat treated at $T_{iso} = 325 \, ^\circ C$, on relatively large RA grains (0.4 - 0.8 \, \mu m). However, in this case, the radius of plastic zone in RA (~1.1 \, \mu m) exceeds the size of RA grains, extending into the surrounding microstructural constituents.

The radius of the plastic zone in the FM is ~1.0 \, \mu m. Although the blocks are small (0.15 - 0.5 \, \mu m), they are grouped in the bainitic matrix. This means that the indentation was normally performed in a single phase (FM). However, nanohardness data for this microstructural constituent contain the influence from the grain boundaries.

A similar observation was made for TM, where the small blocks of TM are 0.2 - 0.6 \, \mu m and the radius of the plastic zone in TM is ~1.0 \, \mu m. Nevertheless, as the nanohardness of the LB matrix is similar in the studied conditions, the elasto-plastic material properties obtained from the nanoindentation tests for the RA, FM and TM can be used for comparative purposes.

![Figure VII-7](image)

Figure VII-7: (a) Distribution of the nanohardness values corresponding to the microstructural constituents and (b) average nanohardness values.

As previously mentioned, the density of lattice defects influences the nanohardness as well as IQ of the diffraction pattern obtained from the EBSD measurement; these defects are attributed to various types of austenite decomposition products \[^4\]. Based on the correlation (Figure VII-8), between the experimentally determined nanohardness and the grain-average IQ, the microstructural constituents are classified as follows:

(i) FM: $500 < IQ < 700$ and $H = 8.5 \pm 0.9 \, GPa$,
(ii) TM: $450 < IQ < 800$ and $H = 7.4 \pm 0.3 \, GPa$,
(iii) RA (above $M_S$): $900 < IQ < 1100$ and $H = 7.3 \pm 0.4 \, GPa$,
(iv) LB:
   a. above $M_S$: $1100 < IQ < 1450$ and $H = 5.8 \pm 0.4$ GPa,
   b. below $M_S$: $900 < IQ < 1450$ and $H = 6.0 \pm 0.6$ GPa.

Figure VII-8: Correlation between the grain-average IQ and the corresponding nanohardness. An error bar was included in the average grain IQ determined for samples heat-treated at $T_{iso} = 280 \, ^\circ$C, since the nanoindenters were made in a similar region, rather than the exact pre-selected area.

VII.5.2. $L_Si$ Steel

The nanoindentation results obtained for the sample of $L_Si$ steel, isothermally transformed above $M_S$ ($T_{iso} = 450 \, ^\circ$C) and quenched to RT (Figure VII-2(c)-(d)), were similar to those of its $H_Si$ counterpart. As in the case of the $H_Si$ steel, LB and FM are the softest and hardness microstructural constituents with nanohardness values of $4.5 \pm 0.2$ GPa and $9.2 \pm 0.3$ GPa, respectively.

The nanohardness measurements performed on the microstructure obtained at $T_{iso} = 350 \, ^\circ$C (below $M_S$) are, however, more complex than those conducted on the sample treated at $T_{iso} = 450 \, ^\circ$C. As previously mentioned in Chapter VI, the microstructure consists of TM and LB, which are both decorated with carbide precipitates, cf. Figure VII-3(c)-(d). This results in minimal differences in the quality of the corresponding diffraction patterns and therefore the grain-average IQ criterion cannot be used to distinguish between these constituents. However, the nanohardness values can be classified into two groups (Figure VII-9(c)-(d) and Figure VII-10) by using the nanohardness of bainite above $M_S$ ($4.5 \pm 0.2$ GPa) as a reference.
Figure VII-9: $T_{iso} = 350 \, ^\circ C$: (a) Grain average IQ map corresponding to the selected area, (b) nanohardness indentations, (c) corresponding microstructure, and (d) load-displacement curves.

Figure VII-10: $T_{iso} = 350 \, ^\circ C$: Nanohardness obtained in scanning mode, corresponding microstructure, and nanohardness values of two zones from the same sample.
The radius of the plastic zone for individual indents was estimated \[^3\], as described in Section VII.5.2.1. Above \(M_s\), the radius of the plastic zone in LB is ~1.1 \(\mu\)m, which is well below the LB block size of 4.9 \(\pm\) 1.7 \(\mu\)m, validating the nanohardness values. Small blocks of FM of 0.5 \(\mu\)m size are grouped, and the radius of the plastic zone in FM is ~1.0 \(\mu\)m. This means that the indentation was performed in a single phase (FM) but its nanohardness includes the contribution of the grain boundaries. Below \(M_s\), the block size of the microstructural constituents (LB or TM) are averaged as 3.7 \(\pm\) 1.7 \(\mu\)m and the radius of the plastic zone is ~1.1 \(\mu\)m.

Figure VII-11(a) shows the distribution of nanohardness values obtained above and below \(M_s\). The peaks corresponding to LB (total of 230 indents) and FM (total of 13 indents) are indicated on the grey curve, which corresponds to samples treated at \(T_{iso} = 450^\circ C\). Initially, only one peak is obtained (black curve) for the samples treated at \(T_{iso} = 350^\circ C\). The corresponding microstructure consists of LB and TM and hence, it is assumed that the nanohardness data from both phases are represented by this peak. The fraction of LB formed below \(M_s\) was subtracted from the main peak, using the nanohardness of LB formed above \(M_s\) as a reference. The residual peak from this subtraction is assumed to result from TM, as indicated by the dashed curves.

Nanohardness values of 4.4 \(\pm\) 0.3 GPa and 4.9 \(\pm\) 0.5 GPa were obtained for the LB and TM, respectively. The microstructural constituents may be classified as follows, based on the correlation (Figure VII-12), between the nanohardness and the grain-average IQ:

(i) FM: 700 < IQ < 900 and \(H = 9.2 \pm 0.3\) GPa,
(ii) LB: 1100 < IQ < 1700 and \(H = 4.4 \pm 0.3\) GPa,
(iii) TM: 1100 < IQ < 1700 \(H = 4.9 \pm 0.5\) GPa.
VII.6. Discussion

AHSS with multiphase microstructures consisting of different fractions of LB, TM, FM and RA were characterized via EBSD and nanohardness.

In both steels, FM was formed during the final quench to RT from the remaining austenite and hence, has a high nanohardness. This resulted from the higher carbon concentration of the FM compared to the nominal concentration of the steel \[2\]. Moreover, FM in the H\textsubscript{Si} steel has a slightly lower hardness (8.5 ± 0.9 GPa vs. 9.2 ± 0.3 GPa) than its counterpart in the L\textsubscript{Si} steel. Variations in the grain average IQ of the H\textsubscript{Si} steel were also observed. These variations may have resulted from the carbon partitioning that occurred during isothermal holding. This partitioning resulted in some zones having a higher carbon concentration than others; the influence of the grain orientation, which differs among the different grains \[27\]; and the block boundaries may have also contributed to this variation.

In contrast to the L\textsubscript{Si} steel, similar relationships were obtained between the IQ and the nanohardness for TM and FM in the H\textsubscript{Si} steel. The differing trends observed for these steels result possibly from the softening that occurs during tempering. In other words, FM and TM are tempered at similar temperatures (325 and 280 °C) in the H\textsubscript{Si} steel but at significantly different ones in the L\textsubscript{Si} steel.

The aforementioned similar relationship between the IQ and nanohardness resulted from the occurrence of carbide precipitation in both constituents. As such, this relationship could not be used to distinguish between LB and TM.

Ambiguous results are sometimes obtained when RA is identified via nanohardness measurements and, in fact, various hardness values, ranging from 4.65 GPa to 10 GPa, have
been reported for RA. In this study, RA in the H_Si steel treated at temperatures above $M_S$ is stabilized with blocky morphology. Although it has been seen that the radius of plastic zone in RA exceeds its grain size, extending into the surrounding microstructural constituents, the corresponding nanohardness values are deemed adequate for comparative purposes. The resolution of nanoindentation measurements is insufficient, however, for obtaining reliable data from the fine interlath RA, which is formed at temperatures below $M_S$.

Although the proposed approach is limited in some respects, nanoindentation combined with EBSD can be used to differentiate among most of the microstructural constituents in the studied AHSS steels.

VII.7. Conclusions

The results obtained from the microstructural characterization of AHSS through a combination of EBSD and nanoindentation measurements, may be summarized as follows:

1. A combination of grain-average IQ and the nanohardness can be used to distinguish between martensite and LB.

2. Based on the inverse relation between the grain-average IQ and the nanohardness, the microstructural constituents can be identified as follows:

   - Isothermal transformation of both steels above and below $M_S$ gives rise to LB grains that have high IQ and low nanohardness.
   - Isothermal treatment above $M_S$ and subsequent quenching of both steels give rise to FM grains that have low-IQ and high nanohardness. In the case of the H_Si steel isothermally treated below $M_S$, these low-IQ high-nanohardness regions correspond to TM.

3. In the L_Si steel, LB and TM both had high IQ and low hardness and hence differentiation between these constituents was impossible.
References


http://dx.doi.org/10.106/j.msea.2015.07.096.
Chapter VIII: PHASE TRANSFORMATIONS IN ADVANCED HIGH STRENGTH STEELS DURING COILING

VIII.1. Introduction

In this chapter, the non-isothermal transformations that occur during cooling of a wound coil of two AHSS grades with differing chemical compositions are discussed. As shown in previous chapters, the composition has a direct influence on the transformation kinetics, microstructural evolution (including carbide precipitation and the stability of retained austenite), and hardenability of the steels.

VIII.2. Experimental Methods

VIII.2.1. Materials and Heat Treatments

The chemical composition of each of the steels was provided in Chapter III - Table III-1. Briefly, the Si, C and Mn concentration constitutes the main difference between the compositions, and the steels are referred to as L_Si and H_Si, corresponding to low- and high-silicon concentration, respectively.

The heat treatments (Figure VIII-1) of coiling simulations were performed in a dilatometer. Fully austenitic microstructures were obtained by reheating the steels to a temperature above $A_{c3}$. Subsequently, run-out table water cooling was simulated by rapidly cooling the steel with helium to selected temperatures (the same temperatures applied during the isothermal holding experiments, as described in Chapter V - Section V.5). The samples were then subjected to simulated coiling, i.e., slow cooling at 0.1 °C/s from various temperatures (referred to as coiling temperatures ($T_{coil}$)) to room temperature (RT). The coiling temperatures determine the initial fraction of martensite formed and austenite prior to coiling $^{[1,2]}$. The following temperatures were chosen for the steels.

- **L_Si steel:**
  - Coiling temperature above $M_S$ (420 °C) in the bainite temperature range: $T_{coil} = 450$ °C,
  - Coiling temperature below $M_S$: $T_{coil} = 350$ and 100 °C.
Phase Transformations in Advanced High Strength Steels during Coiling

- **$H_{\text{Si}}$ steel:**
  - Coiling temperature above $M_s$ (290 °C) in the bainite temperature range: $T_{\text{coil}} = 325$ °C,
  - Coiling temperature below $M_s$: $T_{\text{coil}} = 280, 250, 200$ and 100 °C.

These experiments did not include a deformation step, since other mechanisms, such as enhanced nucleation and recrystallization, would increase the complexity of the microstructural evolution.

As previously stated in Chapter III - Section III.4, the microstructures of the samples were characterized via conventional techniques such as scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and X-ray diffraction (XRD). Vickers hardness ($HV_3$) measurements were also performed.

**VIII.3. Results**

**VIII.3.1. $L_{\text{Si}}$ Steel**

**VIII.3.1.1. Dilatometry**

In Figure VIII-2(a)–(b), the phase transformations are depicted as temperature- and time-dependent changes in the length. The dilatation during the fast cooling from $T = 900$ °C to the coiling temperature and slow cooling after coiling to RT are shown. The dilatation signal
shown in Figure VIII-2(b) was obtained within the first few minutes of slow cooling, i.e., when the transformation occurs. The curves shown in Figure VIII-2(b) were shifted along the length axis in order to clearly visualize the transition between fast and slow cooling; \( t = 0 \) is considered the beginning of the fast cooling (\( T = 900 \, ^\circ C \)).

Figure VIII-2: Dilanometry curves of the L_Si steel as a function of the (a) temperature and (b) time, showing: (I) fast cooling to \( T_{\text{coil}} \) and (II) slow cooling to RT. The indicated temperatures are the coiling temperatures.

Figure VIII-2(a) shows that austenite decomposes to bainite shortly after coiling at \( T_{\text{coil}} = 450 \, ^\circ C \). As in the case of the isothermal experiments (discussed in Chapter V - Section V.3.1), transformations do not occur during first cooling. In fact, the bainitic transformation during slow cooling is manifested (in the curve) as an increase in the length of the sample \(^{[3]}\)(Figure VIII-2(a)). Most of the transformation occurs rapidly, i.e., within the first minute, as shown in Figure VIII-2(b).

The curves corresponding to \( T_{\text{coil}} = 350 \, ^\circ C \) and \( T_{\text{coil}} = 100 \, ^\circ C \) (below \( M_S \)) show the typical martensitic transformation during fast cooling, prior to reaching the coiling temperatures (Figure VIII-2(a)). These temperatures resulted in volume fractions of 0.69 ± 0.05 and 0.97 ± 0.03, respectively, of IM. Furthermore, the length increases initially during slow cooling at \( T_{\text{coil}} = 350 \, ^\circ C \), and the transformation progresses rapidly in the first minute of slow cooling. This increase in length is attributed mainly to the bainitic transformation, as in the case of previous studies\(^{[3]-[4]}\). The curve corresponding to the lowest cooling temperature (\( T_{\text{coil}} = 100 \, ^\circ C \)) does not show transformation effects during cooling, after the almost complete formation of martensite during quenching (cf. Figure VIII-2(a)–(c)).

VIII.3.1.2. Microstructural Evolution

The prior austenite grain size (PAGS) was determined from the EBSD data by considering only grain boundaries with misorientation angles between 21.1° and 47.1°, as suggested by Bernier et al.\(^{[5]}\). An alternative method, also based on grain boundary misorientations, was used for the
Phase Transformations in Advanced High Strength Steels during Coiling

130

parent phase reconstruction, as described in Chapter VI - Section VI.2.1. An average PAGS of 7.3 ± 1.8 µm was determined by using the linear intercept method. Figure VIII-3(a)–(b) show SEM micrographs of the microstructure formed after coiling at $T = 450$ °C. At this coiling temperature, the formation of lower bainite (LB), see Figure VIII-3(a), is accompanied by the precipitation of rod-like carbides. Besides bainite, fresh martensite (FM), and retained austenite (RA) are also observed, as indicated by the dashed line in Figure VIII-3(b). This suggests that a certain fraction of austenite transforms to FM during slow cooling. However, a small fraction of austenite remains (Figure VIII-3(b)), mainly locked within the FM. The FM is considered to be untempered martensite [6, 7], with a blocky phase morphology and exhibits a surface substructure [8].

Figure VIII-3: SEM micrographs of the microstructure formed after coiling at $T_{coil} = 450$ °C.

This was confirmed (Figure VIII-4(a)–(d)) via EBSD measurements. Figure VIII-4(a)–(b) show a SEM image of the studied area and the pixel-based image quality (IQ) map, respectively. The darker regions in this map have a lower IQ, and hence a higher density of lattice imperfections, than the light grey regions; these low-IQ regions are associated with FM. In the phase map (Figure VIII-4(c)) retained austenite is shown in green and the BCC transformation products (martensite and bainite) are shown in red. Figure VIII-4(d) provides a high-magnification view of the region enclosed in the white, dashed rectangle (Figure VIII-4(c)); in Figure VIII-4(d), only the phase boundaries (misorientations between 15 and 180°) between austenite and its transformation products are shown. The orientation relation between RA and bainite and martensite can be described by an axis/angle correspondence. The most referenced orientation relations are the Kurdjumov-Sachs (K-S) $<112>90°$, Nishiyama-Wasserman (N-W) $<362>95.3°$, and Bain (B) correspondences $<001>45°$ [9]. In Figure VIII-4(d), K-S, N-W, B, and general boundaries are shown in blue, orange, yellow, and black, respectively. A tolerance of 2.5° was used in order to prevent overlapping of these boundaries, and as the figure shows,

130
those exhibiting the N-W correspondence slightly outnumber their K-S counterparts; the boundaries in this region do not satisfy the Bain correspondence. In addition, the RA has an average diameter of $0.24 \pm 0.06 \, \mu m$.

Figure VIII-4: EBSD study of the microstructure formed in the experiment with $T_{\text{col}} = 450 \, ^{\circ}C$: (a) SEM image of the area studied, (b) pixel-based IQ map, (c) phase map with grain boundaries, and (d) high-magnification view of retained austenite with grain boundaries that satisfy the N-W and K-S correspondences (tolerance of $\pm 2.5^\circ$).

A relatively large fraction of fine carbides is formed after coiling at $T_{\text{col}} = 350 \, ^{\circ}C$ (Figure VIII-5(a)–(b)). As revealed by dilatometry, initial martensite (IM) and lower bainite are formed during cooling and after coiling, respectively. Carbide precipitation can therefore be attributed to the: (i) tempering of initial martensite during coiling $^{10, 11}$ and (ii) bainite formation, which is accompanied by the formation of rod-like carbides, after coiling above $M_S$. A blocky morphology is again observed (similar to that formed at $T_{\text{col}} = 450 \, ^{\circ}C$), indicated by
the dashed line in Figure VIII-5(a)–(b). The occurrence of carbide precipitates indicates that this morphology is not associated with FM.

Figure VIII-5: SEM micrographs of the microstructure formed after coiling at $T_{\text{coil}} = 350$ °C.

The EBSD results reveal that the microstructure contains only a relatively low fraction of FM, as indicated by the grain-average IQ map (Figure VIII-6(c)). In this map, the color of each grain corresponds to the average IQ of the entire grain [9]. Grains were usually defined as regions that contain at least four pixels and are misoriented by <5° from neighboring regions. Therefore, the grains with the lowest IQ (i.e., those shaded in blue) and the high-IQ grains correspond to FM and bainite, respectively. The phase map shows that austenite is not retained at this temperature (Figure VIII-6(b)). The aforementioned observations indicate that the microstructure formed at $T_{\text{coil}} = 350$ °C consists of tempered martensite, LB, and a relatively low fraction of FM.
Chapter VIII

Figure VIII-6: The microstructure formed after coiling at $T_{\text{coil}} = 350 \, ^{\circ}\text{C}$: (a) pixel-based IQ map, (b) phase map, and (c) grain-average IQ map.

Figure VIII-7(a) shows the lath martensite formed when the sample is cooled at $T_{\text{coil}} = 100 \, ^{\circ}\text{C}$. This microstructure bears a striking resemblance to the fully martensitic microstructure (Figure VIII-7(b)) obtained by quenching a sample to RT. The carbide precipitates present in both microstructures are attributed to the auto-tempering process that results from the low-carbon concentration and hence, high $M_s$ temperature \cite{12, 13}. Auto-tempering also leads to carbide precipitation at $T_{\text{coil}} = 350 \, ^{\circ}\text{C}$, i.e., a portion of the carbides has already precipitated during cooling. Carbide precipitates were not thoroughly examined during these experiments. However, these precipitates have the same morphology as those formed during the isothermal experiments (Chapter VI - Section VI.2.1), and are therefore assumed to also be iron carbide, cementite (Fe$_3$C).

Figure VIII-7: SEM micrographs of the microstructure formed (a) after coiling at $T_{\text{coil}} = 100 \, ^{\circ}\text{C}$ and (b) in the sample quenched to RT.
Figure VIII-8(b) shows that austenite is not retained after coiling at this temperature; the low-IQ grains correspond to FM.

X-ray diffraction analysis confirmed (Figure VIII-9) that the BCC phase is present at all three coiling temperatures. However, consistent with the EBSD results, the FCC phase (RA) occurs only at $T_{\text{coil}} = 450 \, ^\circ\text{C}$. The RA volume fraction of $4.7 \pm 0.7 \, \%$ was determined from the integrated intensity of the peaks.
Figure VIII-9: X-ray diffraction spectrum showing peaks corresponding to BCC and FCC phases.

Figure VIII-10 shows the hardness as a function of the coiling temperature. As expected, coiling at high temperatures leads to a relatively softer microstructure (since the microstructure is mainly bainitic) than those formed at low temperatures. On the other hand, owing to the higher IM fractions, lower coiling temperatures lead to higher hardness values, compared to those obtained at higher temperatures[^14]. Microstructures consisting of a mixture of bainite and martensite (which are formed for example, at 350 °C) have intermediate hardness values.

![Vickers hardness (HV₃) of the microstructures formed after coiling at the indicated temperatures.](image)

**VIII.3.2. H_Si Steel**

**VIII.3.2.1. Dilatometry**

In Figure VIII-11(a)–(c), the phase transformations are depicted as temperature- and time-dependent changes in the length. This dilatation occurs during fast cooling to the coiling temperature and slow cooling (after coiling) to RT. Figure VIII-11(c) provides a detailed view of the aforementioned dependencies after the coiling. The curves in Figure VIII-11(a)–(c) were shifted along the length axis in order to clearly visualize the transition at coiling.
As Figure VIII-11(b)–(c) show, the phase transformations at $T_{\text{coil}} = 325 \, ^\circ\text{C}$, are initiated after some incubation time. The decomposition of austenite to lower bainite (LB) begins immediately after this incubation (Figure VIII-11(a)–(b)). This decomposition is manifested as an expansion in volume, and the subsequent cooling-induced thermal contraction of the sample indicates that the transformation is finished. In addition, $M_S$ is reached during the slow coiling and athermal martensite may be formed immediately after or contemporary with the bainite formation.

On the other hand, the typical martensitic transformation occurs when the coiling is performed below $M_S$ ($T_{\text{coil}} = 280 \, ^\circ\text{C}, 250 \, ^\circ\text{C},$ and $200 \, ^\circ\text{C}$), as shown in Figure VIII-11(a). Coiling at these temperatures resulted in IM fractions of $0.27 \pm 0.06$, $0.6 \pm 0.1$, and $0.87 \pm 0.05$, respectively, as determined from the dilatometry data. During the slow cooling, the dilatation increases rapidly and continuously below $M_S$ for a certain period of time. This time-dependent dilatation decreases with increasing volume fraction of IM formed during cooling to $T_{\text{coil}}$ (cf. Figure VIII-11(b)–(c)).
VIII.3.2.2. Microstructural Evolution

Figure VIII-12(a)–(e) show the microstructural evolution of the H_Si steels after coiling. The microstructure formed at $T_{\text{coil}} = 325$ °C (above $M_S$) is shown in Figure VIII-12(a). This microstructure consists mainly of martensite, thereby confirming the formation of IM after coiling. Furthermore, IM undergoes tempering during slow cooling, and is referred to as tempered martensite (TM), thereafter. Lower bainite and rod-like carbides are also observed. Bainite is formed after the incubation time, as indicated by the dilatometry curve (Figure VIII-11(c)–(d)), and constitutes a small fraction of the predominantly martensitic microstructure. In addition to TM, fresh martensite may also form during slow cooling to RT, and a small fraction of austenite is retained (Figure VIII-13(b)). In Figure VIII-13(c)–(d), the K-S and N-W boundaries are shaded in blue and orange, respectively; the K-S type boundaries slightly outnumber the N-W and those satisfying the Bain correspondence do not occur. The average grain size (i.e., diameter) of RA, as determined from the EBSD data, and the prior austenite grain size (PAGS) $^{[5]}$ were 0.26 ± 0.02 µm and 5.8 ± 0.1 µm, respectively.
Phase Transformations in Advanced High Strength Steels during Coiling

Figure VIII-12: SEM micrographs of the microstructures formed at: (a) $T_{coil}$ 325 °C, (b)-(c) $T_{coil}$ 280 °C, (d) $T_{coil}$ 250 °C, (e) $T_{coil}$ 200 °C, and (f) quenched to RT.

Figure VIII-13: $H_{Si} (T_{coil} = 325 ^\circ C)$: (a) IQ map, (b) phase map, (c) misorientation of RA, martensite and bainite, (d) high-magnification view of the regions enclosed in the rectangles in (c).

The microstructures formed after coiling below $M_s$ are quite similar to those (Figure VIII-12(a)–(e)) formed above $M_s$. As previously mentioned, IM is tempered after coiling. Regions containing carbide precipitates, typical for TM, are also observed, for example, at $T_{coil} = 280 ^\circ C$ (Figure VIII-12(c)). However, the carbides formed at $T_{coil} = 200 ^\circ C$ are significantly finer than those formed at higher coiling temperatures (Figure VIII-12(d)). This microstructure is similar to the one (Figure VIII-12(e)) formed when the sample is quenched.
to RT. In all of the experiments, austenite was retained after coiling to RT (Figure VIII-14(a)–(d)). Figure VIII-15(b) shows, however, that the fraction of RA, as determined from XRD measurements, is relatively insensitive to the coiling temperature.

Figure VIII-14: Phase maps of samples coiled at (a) 325 °C, (b) 280 °C, (c) 250 °C, and (d) 200 °C; the retained austenite grains are highlighted in green.

Figure VIII-15: (a) X-ray diffraction spectrum showing the peaks corresponding to the BCC and FCC phases and (b) volume fraction of retained austenite, as determined from the spectrum.

Figure VIII-16(a)–(h) show that similar IQ maps and corresponding grain-average IQ maps, are obtained at all of the coiling temperatures. The SEM micrographs (Figure VIII-12(a)–(f)) revealed that the predominantly martensitic microstructures formed after coiling, consists of only a low fraction of bainite. Moreover, each microstructure consists of only a few very-low-IQ grains (i.e., grains shaded in blue), which are assumed to be FM. The high-IQ grains correspond mainly to TM, which is accompanied by carbide precipitates. However, as
previously stated, the carbides formed at $T_{\text{coil}} = 200^\circ\text{C}$ are significantly finer than those formed at other temperatures.

Figure VIII-16: IQ and grain-average IQ maps: (a)-(b) 325 °C, (c)-(d) 280 °C, (e)-(f) 250 °C, and (g)-(h) 200 °C.
Figure VIII-17 shows the hardness as a function of the coiling temperature. The hardness values decrease slightly with increasing the coiling temperatures, since the resulting microstructures consist mainly of tempered martensite.

![Figure VIII-17: Vickers hardness (HV) of the microstructures formed after coiling.](image)

### VIII.4. Modeling of the Kinetics of Martensite and Bainite Formation

As observed in this study, austenite decomposes mainly to bainite and martensite during slow cooling. As such, the corresponding transformation kinetics was investigated via dilatometry and by using models based on displacive growth. The model proposed by Van Bohemen et al.\(^{[15]}\) is used for the L\_Si steel. In the case of the H\_Si steel, the model is modified to account for the increase in carbon in the remaining austenite\(^{[16]}\). The formation of martensite is modeled by including Koistinen-Marburger (K-M) relation in the model.

In the model\(^{[15]}\) the volume fraction of bainite varies with time as follows:

$$\frac{df}{dt} = (1 - f)(1 + \lambda f)\kappa$$

(Equation VIII-1)

where \(f\), \(\lambda\), and \(\kappa\) are the volume fraction of bainite, autocatalytic nucleation parameter, and rate parameter, respectively. At temperatures lower than \(M_s\), the volume fraction of martensite \((f_M)\) is included in (Equation VIII-1).

The rate parameter can be described as:

$$\kappa = \frac{kT}{h} \alpha^b (T_h - T) \exp \left( -\frac{Q}{kT} \right)$$

(Equation VIII-2)
This equation shows that the temperature dependence of $\kappa$ is governed by $(T_h - T)$; $T_h$ is the highest temperature at which displacive transformation can take place, $Q^*$ is the activation energy and $\alpha_b$ is the effectiveness of austenite grain boundaries for the nucleation of bainite.

$T_h$ is determined from the equation below, i.e., as a function of the chemical composition. This dependence is given as follows:

$$T_h(°C) = 835 - 198x_C - 91x_{Mn} - 15x_{Si} - 73x_{Cr} - 36x_{Ni} - 87x_{Mo}$$

A $T_h$ of 567 °C was determined in this work for the L_Si steel. Figure VIII-18(a)–(c) compare the experimentally determined and fitted volume fraction curves corresponding to the different coiling temperatures used for the L_Si steel. The vertical axis of the figures represents the total volume fraction of the decomposed austenite, i.e., the sum of martensite and bainite. The progression of bainite formation during cooling depends strongly on the autocatalytic parameter and the grain size of the austenite. The same austenitization conditions were used for the isothermal and coiling experiments. Therefore, the austenite grain size prior to coiling was considered comparable to the one prior to isothermal holding. The fitting parameters ($\lambda$ and $\kappa$) were determined from the best fit to the kinetics of the experimental isothermal transformation (presented in Chapter V - Section V.4.1). The kinetics of bainite formation in this temperature range (100 – 450 °C) was well-described by $\lambda = 0$, indicating that autocatalytic nucleation was negligible at those temperatures.

Figure VIII-18: L_Si steel: transformation kinetics determined by the model and from experimental data obtained at $T_{coi}$: (a) 450 °C, (b) 350 °C, and (c) 100 °C.
The agreement between the simulations and the experimental data was satisfactory (Figure VIII-18(a)–(c)) and poor in the case of the L_Si and H_Si steels, respectively. As previously mentioned, the model was modified to account for the increase in carbon in the remaining austenite\textsuperscript{[16]} of the H_Si steel. The fitting parameters used in the isothermal experiments (Chapter V - Section V.4.2) were extracted and applied also to the coiling simulations. However, the model does not predict the continuous formation of martensite (in accordance with the mainly martensitic microstructures) that is observed experimentally (Figure VIII-19(a)–(d)).

\textbf{Figure VIII-19: H_Si steel: transformation kinetics determined by the model and from experimental data at } T_{coil} \text{ = (a) } 325 \, ^\circ\text{C}, \text{ (b) } 280 \, ^\circ\text{C}, \text{ (c) } 250 \, ^\circ\text{C}, \text{ and (d) } 200 \, ^\circ\text{C}.\textbf{

VIII.5. Discussion

Dilatometry and microscopy revealed that phase transformations in the L_Si steel exhibit the same trends under both non-isothermal and isothermal conditions. Austenite rapidly transforms to bainite within the first minute after coiling, above and below $M_s$. Owing to the increasing amount of martensite formed, the microstructure of the L_Si steel changes when the coiling temperature is lowered. This martensite is tempered after coiling and the resulting microstructure consists mainly of TM and LB, which are both accompanied by carbide precipitates. The influence of auto-tempering on the tempering of martensite is also taken into
account. In addition, the modeling performed provided an adequate description of the transformation kinetics of bainite and martensite.

On the other hand, when the coiling of the H_Si steel is simulated, the transformation kinetics under isothermal conditions differs from that under other conditions. A negligible amount of LB forms, if coiling takes place at temperatures above $M_s$. As such, similar microstructures (mainly martensitic) are formed at each coiling experiment, thereby resulting in only a small variation in the hardness; in other words, similar microstructures are formed irrespective of the coiling temperature. Carbide precipitation, occurs at each coiling experiment and austenite is retained in all of the microstructures (i.e., of the H_Si steel). Furthermore, austenite is stabilized when the sample is quenched to room temperature from each of the temperatures.

The kinetics of bainite and martensite of the L_Si steel was adequately described by the proposed model (which operated on the basis of a displacive mechanism), for transformations completed at the coiling temperatures. On the other hand, in the case of the H_Si steel, the volume fraction curves were not accurately predicted, owing possibly to the continuous formation of martensite during slow cooling.

VIII.6. Conclusions

AHSS with different Si contents were subjected to coiling simulations via dilatometry, and the corresponding phase transformations and microstructural evolution were evaluated. The main influence of the coiling temperature is summarized as follows:

✓ Carbide precipitation accompanies the formation of bainite at isothermal temperatures above and below $M_s$ of both steels.
✓ Significantly more carbide precipitation occurs in the L_Si steel than in its H_Si counterpart.
✓ The L_Si steel has a lower volume fraction of retained austenite than the H_Si steel.
✓ The microstructure of the H_Si steel changes only slightly with variations in the coiling temperature. These microstructures consist mainly of tempered martensite, bainite, and low fractions of retained austenite.
✓ The applied model provides an adequate description of the transformation kinetics of bainite and martensite in the L_Si steel, but not in the H_Si steel.
References


Chapter IX: GENERAL DISCUSSION, CONCLUSIONS AND SUGGESTION FOR FUTURE WORK

IX.1. General Discussion

This chapter compares the AHSS studied, isothermal and coiling experiments, summarizing the results, discussions and the conclusions of the dissertation.

Two AHSS grades have been studied in this thesis, the L_Si and H_Si steel with 0.16C-1.6Mn-0.4Si-0.8Cr-0.3Mo and 0.3C-3.0Mn-1.5Si (both in wt.%), respectively. Thermal treatments with different cooling rates yielded final microstructures consisting of ferrite, bainite, and martensite in the L_Si steel (Chapter IV). Low cooling rates resulted in microstructures formed via diffusional transformation (ferrite) at high temperatures, whereas microstructures formed via diffusionless transformation (bainite and martensite) resulted from cooling with high cooling rate. The critical cooling rate to avoid ferrite and bainite transformation, as experimentally determined, is 30 °C/s. In the H_Si steel, a fully martensitic microstructure is obtained for a wide range of cooling rates and the critical cooling rate for preventing bainite formation is 10 °C/s. Carbide precipitation is significantly more pronounced in the L_Si steel than in the H_Si steel. Moreover, the transformation in the latter occurs at is slower than those occurring in the former.

IX.1.1. Quenching to RT

The dilatometry results from direct quenching from the austenitic temperature to room temperature (RT) show the progression of the martensitic transformation in both steels, see Figure IX-1(a)–(b). The volume fraction of IM was also calculated by using the Koistinen-Marburger (KM) relationship \( f_m = 1 - \exp^{-\alpha(M_S-T_Q)} \). The H_Si steel has a higher concentration of C and alloying elements (Mn), than the L_Si steel. These elements are \( \gamma \) stabilizers. Therefore, the \( M_S \) temperature of the former is lower (\( M_S (5\%) = 290 °C \) vs. 420 °C) than that of the latter. This difference is somewhat larger than would be predicted on the basis of Andrews’ equation (± 100 °C).
General Discussion, Conclusions and Suggestion for Future Work

Figure IX-1: Martensitic transformation (a) dilatation showing $M_s$ temperatures, and (b) fraction of martensite formed during quenching to room temperature and fits with the Koistinen-Marburger equation.

The aforementioned observations reflect the influence of the chemical composition, mainly on the transformation kinetics and on the final microstructures. Si retards cementite precipitation in ferrite and therefore, the microstructures in the H_Si steel have a low fraction of carbides (cementite). A fully martensitic microstructure with typical lath morphology (Figure IX-2(a)-(b)) forms when both steels are directly quenched to RT. The martensitic microstructure is much coarser for the H_Si steel than for the L_Si steel. However, in the case of the L_Si steel, carbides, which precipitate during the quenching, are distributed within the quenched martensite, as shown in Figure IX-2(a). This precipitation is correlated with the auto-tempering process \cite{1,2} that results from the relatively high $M_s$ temperature of the steel. Carbide precipitation also occurs within the lower bainite (LB), owing to the low-silicon concentration in the L_Si steel.

Figure IX-2: SEM micrographs of the microstructures formed after quenching of the (a) L_Si steel and (b) H_Si steel to RT.

**IX.1.2. Isothermal Experiments**

The previous observations are complemented by the results of the isothermal transformation experiments (Chapter V). In the case of the highly alloyed H_Si steel, the bainitic
transformation is slower than in the L_Si steel. In fact, as Figure IX-3(a)–(b) show, bainite forms more rapidly in the later at isothermal holding temperatures above $M_S$ than in the H_Si steel. The transformation in the L_Si steel starts immediately after cooling and is almost finished within 60 seconds (Figure IX-3(b)). In contrast, in the case of the H_Si steel, bainite forms only after some incubation period of approximately 200 s in which ~ 5% bainite forms. In addition, as evidenced by the increase in length (Figure IX-3(a)), bainite formation is incomplete even after 1 h of isothermal holding.

The transformation kinetics below $M_S$ of the L_Si steel is shown in Figure IX-3(c)–(d). These figures indicate that bainite formation starts immediately after the initial martensite has formed (Figure IX-3(d)). The influence of initial martensite on bainite formation [3-5] is even clearly revealed in the case of the H_Si steel. The bainitic transformation occurs without an incubation period, which indicates that previously formed martensite accelerates the formation of bainite in adjacent regions of untransformed austenite (Figure IX-3(d)). The bainitic transformation is incomplete even after 1 h of isothermal holding, as evidenced by the increase in length (Figure IX-3(c)).

![Figure IX-3: Comparison of transformation kinetics for both steels during isothermal holding at temperatures: (a)-(b) above $M_S$ and (c)-(d) below $M_S$.](image)

For both steels, the transformation kinetics of isothermal austenite decomposition below $M_S$, after initial martensite formation, is similar to the kinetics of isothermal bainite formation.
above $M_S$. This observation is confirmed by modeling the transformation kinetics, based on the assumption that a displacive mechanism governs bainite formation in both steels \cite{6, 7}. The results of the model indicate that, under the employed experimental conditions, negligible and autocatalytic nucleation occurs in the case of the L_Si and the H_Si steel, respectively.

The microstructures formed during isothermal holding (Chapter VI) consisted mainly of LB and tempered martensite (TM). In the L_Si steel, the microstructures contain a high fraction of carbides (cementite). However, auto-tempering have also resulted in the precipitation of carbides during the initial cooling process. In addition, fresh martensite (FM) and retained austenite (RA) are always observed if the isothermal holding temperature is above $M_S$. Austenite stabilization is favored in the H_Si steel \cite{8-11}, where RA also occurs after isothermal treatments at temperatures below $M_S$. Furthermore, the orientation relationship between RA and martensite and bainite in both steels, is most closely described by the N-W orientation relationship.

As expected, the (mainly bainitic) microstructures formed at high temperatures are softer than the mainly martensitic microstructures formed at low temperatures. The individual microstructural constituents can be arranged in descending order of hardness as FM, TM and LB, as discussed in Chapter VII. Moreover, the grain-average IQ displays an inverse relation with the nanohardness \cite{12}. Grains with high-IQ and low nanohardness (i.e., LB grains), occur after isothermal transformation above and below $M_S$ of both steels. Grains with low-IQ and high nanohardness (i.e., FM grains), occur above $M_S$. The grain-average IQ is also inversely related to the nanohardness in the case of TM formed below $M_S$ of the H_Si steel. In addition, RA is an intermediate-hardness constituent of the H_Si steel, when stabilized in blocky morphology.

Similar grain-average IQ and nanohardness values of TM and LB were obtained in the L_Si steel, owing to carbide precipitation in both constituents. However, these constituents could not be distinguished only based on the above parameters.

**IX.1.3. Coiling vs. Isothermal Experiments**

The results on the decomposition of austenite during coiling (Chapter VIII) exhibited the same trends as those obtained from the isothermal experiments in the L_Si steel. Figure IX-4(a)–(d) show the transformations that occur during isothermal holding and coiling, above and below $M_S$, of the L_Si steel. The dilatation curves obtained at $T_{iso} = 450$ °C and after coiling at 450 °C (above $M_S$), are shown in Figure IX-4(a) and in greater detail in Figure IX-4(b). As the figures show, austenite decomposes to bainite at the beginning of both isothermal and slow cooling
stages. Most of the bainitic transformation occurs rapidly, i.e., within the first minute, as shown in Figure IX-4(b). Below $M_S$, Figure IX-4(c)–(d), the initial formation of martensite during rapid cooling is followed by bainite formation during isothermal holding and/or after coiling. The bainitic transformation progresses rapidly after coiling and austenite is completely decomposed within the first minute.

Figure IX-4: Transformations during isothermal holding and after coiling of the L$_{Si}$ steel holding/coiling: (a)-(b) above $M_S$ and (c)-(d) below $M_S$.

Figure IX-5(a)–(f) confirms these trends in the final microstructures formed after isothermal and coiling heat treatments of the L$_{Si}$ steel. Lower bainite (LB) and rod-like carbides are formed at $T_{iso} = 450 \, ^\circ C$ and after coiling at $450 \, ^\circ C$, i.e., above $M_S$. Fresh martensite (FM) and retained austenite (RA) also occur, as shown in Figure IX-5(a)-(b). As previously mentioned in Chapters V and VIII, during the quenching to RT (after isothermal holding) and slow cooling (after coiling), a certain fraction of austenite transforms to FM [8, 13, 14]. The dark regions in the EBSD micrographs in Figure IX-6(a)–(b) correspond to low-IQ and therefore a high density of lattice imperfections, which are associated with FM. However, a small fraction of austenite remains, surrounded primarily by FM. The fraction of RA resulting from coiling experiments is slightly higher than that resulting from isothermal treatments, as shown in the EBSD phase maps of Figure IX-7(a)–(b).
Figure IX-5: SEM micrographs of the microstructures formed in the L_Si steel after isothermal holding and coiling at (a) - (b) $T = 450 \, ^\circ C$, (c) - (d) $T = 350 \, ^\circ C$, and (e) - (f) $T = 100 \, ^\circ C$.

Isothermal holding or coiling at $T = 350 \, ^\circ C$ gives rise to microstructures (cf. Figure IX-5(c)–(d)), that have a relatively large fraction of fine carbides. As determined via dilatometry (Figure IX-4(c)–(d)), initial martensite is formed during the cooling stage of both heat treatments and LB forms during isothermal holding and after coiling. Therefore, the aforementioned carbide precipitation is attributed to: (i) auto-tempering \cite{1, 2}, (ii) the tempering of initial martensite during the isothermal experiments or after coiling \cite{17, 18}, and (iii) bainite formation, and the accompanying formation of rod-like carbides \cite{19, 20}. The phase maps in (Figure IX-7(a)–(f)), show that austenite is not retained at temperatures below $M_S$ in either the isothermal or coiling experiments.
Isothermal holding or coiling at $T = 100 \, ^\circ C$ results in the formation of lath martensite, which is similar to that formed in the experiment in which the steel was direct quenched to RT, cf. Figure IX-2(a) and Figure IX-5(e)–(f). Figure IX-5(e)–(f) and Figure IX-7(e)–(f) reveal that FM and RA are both absent in these microstructures.

The transformations in the H_Si steel proceed in a different manner from those in the L_Si steel. For example, during isothermal holding above $M_S$, bainite forms only after some
incubation period, as shown in Figure IX-8(a)–(b). This incubation period is shortened (Figure IX-8(b)), however, during slow cooling after coiling. Figure IX-8(c) shows the temperature dependence of bainite formation during the experiments. During bainite formation, $M_S$ is reached during slow cooling and the ensuing formation of martensite is governed by the kinetics shown in Figure IX-8(d).

During the initial fast cooling, athermal martensite forms when isothermal holding and coiling are performed at temperatures below $M_s$ ($T = 280 \, ^\circ C$). The change in length increases rapidly below $M_s$, owing to martensite formation, and continues to increase, Figure IX-9(a)–(b) even after martensite formation is complete. The dilatation that occurs during isothermal holding after the martensitic transformation is attributed to the formation of bainite; bainite formation continues for a certain period of time. As previously mentioned, the bainitic transformation in L$_{\text{Si}}$ steel occurs without an incubation period. This indicates that previously formed martensite can accelerate the formation of bainite in adjacent regions of untransformed austenite$^{[4, 5, 19, 20]}$. However, in the case of the coiling experiments, austenite undergoes continuous transformation to martensite during slow cooling, i.e., after first cooling and coiling. Therefore, carbon partitioning and martensite formation constitute competing effects during the slow cooling. The effect of bainite formation on the dilatation during slow cooling cannot, however, be excluded.
After dilatation, the change in length decreases, owing to the thermal contraction that occurs during slow cooling [3-5, 20].

The aforementioned observations are complemented by the SEM (Figure IX-10(a)–(b)) and EBSD micrographs (Figure IX-11(a)-(d)), where the final microstructures formed after cooling above $M_S$ ($T = 325 \, ^\circ\text{C}$) differ from those formed after isothermal holding at the same temperature.

Figure IX-10(a)–(b), show that the latter consists mainly of bainite and small fractions of FM and RA, whereas the former is mainly martensitic. These results concur with those obtained from dilatometry (Figure IX-8(a)–(c)), which show that after bainite forms, $M_s$ is crossed during slow cooling after the coiling and martensite is formed. Features corresponding to LB and rod-like carbides are also observed. This indicates that a small fraction of bainite is formed after coiling, thereby resulting in a predominantly martensitic microstructure.
Figure IX-10: SEM micrographs of the microstructures formed after isothermal holding and coiling of the H_Si steel at (a) - (b) $T = 325 \, ^\circ C$, (c) - (d) $T = 280 \, ^\circ C$, (e) - (f) $T = 250 \, ^\circ C$, and (g) - (h) $T = 200 \, ^\circ C$. 

$M_S$
Figure IX-10(a)–(f) show that the microstructures formed after coiling below $M_S$ are similar to the ones formed above $M_S$. The initial martensite is tempered after coiling, where carbide precipitates are observed. This occurs at all coiling temperatures, and at 200 °C, the carbides are significantly finer than at higher temperatures, as shown in Figure IX-10(g)–(h). The resulting microstructure, Figure IX-10(h), is comparable to that of the sample quenched to RT (Figure IX-2(b)), but with carbide precipitates.

![Image: Image Quality (IQ) maps from microstructures formed in isothermal and coiling in H_Si steel: (a)-(b) 325 °C and (c)-(d) 280 °C.](image)

The RA and BCC phases are shown in green and red, respectively, in the EBSD phase maps (Figure IX-12(a)–(h)) corresponding to samples of the H_Si steel subjected to isothermal holding and coiling. These maps indicate that, in addition to interlath lamellar austenite, blocky RA grains are also stabilized at high temperatures of isothermal holding. However, the fraction of RA after coiling is, in general, significantly lower than that after isothermal holding.
The fractions of RA, as determined via XRD, are shown in Figure IX-13(a)-(b). In the case of the H_Si steel (Figure IX-13(a)), two main trends are observed: (i) higher fractions of RA are stabilized during isothermal holding than after coiling and (ii) almost the same fractions of RA (~ 0.1 and 0.05, respectively) are obtained at all isothermal and coiling temperatures above and below $M_S$. This is attributed to the high fraction of martensite formed during rapid cooling and also after coiling. As previously mentioned, carbon partitioning and martensite formation constitute competing events during slow cooling. Therefore, lower levels of carbon-enrichment of the austenite occur during coiling experiments than during isothermal conditions.
In the case of the L\textunderscore Si steel, isothermal holding and coiling only above $M_S$ results in RA, which fractions are smaller than 0.04, as shown in Figure IX-13(b).

![Figure IX-13: Fraction of retained austenite, as determined via XRD, in (a) H\textunderscore Si and (b) L\textunderscore Si steel subjected to isothermal holding and coiling.](image)

Figure IX-14(a)–(b) show the hardness of both steels as a function of the temperature. The L\textunderscore Si samples subjected to isothermal and coiling experiments have similar hardness (Figure IX-14(a)), as resulting from the transformation kinetics and microstructural evolution. However, owing to the higher fraction of martensite in the final microstructure, the H\textunderscore Si steel has a higher hardness after coiling than after isothermal holding (Figure IX-14(b)). Furthermore, the hardness values are basically the same for all the coiling temperatures, in good agreement with the previous microstructure observations. The H\textunderscore Si steel has higher hardness than the L\textunderscore Si steel owing to the higher concentration of C and alloying elements such as Mn and Si. Furthermore, the hardness values of both steels decrease, in general, with increasing processing temperature, i.e., the microstructures are mainly formed by bainite above $M_S$. An exception to this trend occurs in the H\textunderscore Si steels after coiling experiments, in which the $M_S$ temperature does not influence the hardness.

![Figure IX-14: Hardness of (a) L\textunderscore Si steel and (b) H\textunderscore Si steel for different thermal conditions.](image)
IX.2. Conclusions

The decomposition of austenite, under various thermal conditions (isothermal and coiling experiments) above and below \( M_S \), mainly after the formation of varying fractions of initial martensite, was studied. Referring back to the scientific issues mentioned in Chapter I, the conclusions of this work are summarized as follows:

1) The nature of the transformation mechanisms during:

- **Isothermal treatment** is correlated with the formation of bainite, above and below \( M_S \), for both steels.

- **Non-isothermal treatment** is correlated with the formation of (i) bainite, above and below \( M_S \), for the L\(_{Si}\) steel, and (ii) martensite, above and below \( M_S \), for the H\(_{Si}\) steel.

2) The influence of the microstructure prior to isothermal holding and coiling, can be described based on:

- Cooling rates: moderate cooling rates are sufficient to prevent the formation of phases other than martensite during the first cooling, in both steels (30°C/s for the L\(_{Si}\) steel, whereas for the H\(_{Si}\) steel the cooling rate is even lower than its counterpart, i.e., 10°C/s).

- **The temperatures at which isothermal or coiling experiments were performed**: (i) isothermal treatments below the \( M_S \) temperature influence bainite formation: during isothermal holding, the presence of initial martensite accelerates bainite formation in both steels; (ii) coiling treatments below \( M_S \) do not influence the transformations during the slow cooling; similar final microstructures are obtained at all coiling temperatures in the case of the H\(_{Si}\) steel, and (iii) isothermal and coiling treatments: austenite in the H\(_{Si}\) steel is stabilized irrespective of the isothermal holding or coiling temperature.

3) The alloying elements influence on:

- Transformation mechanisms: owing to the high concentration of alloying elements (C, Mn and Si), the H\(_{Si}\) steels exhibits slower transformation kinetics and austenite transforms at lower temperatures than in the L\(_{Si}\) steel.
Microstructural evolution: carbide precipitation occurs even at high concentrations of Si, as in the case of the H_Si steel. Austenite stability is favored at high concentrations of C and Mn.

Mechanical properties: hard microstructural constituents are obtained at high concentrations of C and Mn. These constituents may be ranged in descending order of hardness as: fresh martensite, tempered martensite and lower bainite.

According to the aforementioned conclusions, an overview of the transformation mechanisms which take place in each step of the isothermal and coiling experiments is given in Figure IX-15 and Figure IX-16, for the L_Si and H_Si steel, respectively.

Figure IX-15: Overview of the microstructure development in the L_Si steel.

Figure IX-16: Overview of the microstructure development in the H_Si steel.
XI.3. Suggestions for Future Work

The current study attempts to provide understanding of several points, concerning the austenite decomposition above and below the $M_S$ temperature. However, several new questions that remain to be clarified originated from the results. As such, some suggestions for future work are:

- To differentiate the carbides resulting from both quenching and isothermal holding or slow cooling. In this way, it will be possible to understand the contribution of each cooling step to the final microstructures.
- The carbide precipitation occurring during the coiling in the H_Si steel could be investigated more in detail, considering that this precipitation during coiling is more pronounced than in the isothermal experiments.
- To design an accurate method to distinguish lower bainite and tempered martensite, when carbide precipitates are present. The useful tool in this clarification could be a combination of nanohardness and high resolution characterization techniques combining microstructure and orientation measurements.
- Martensite formation during the slow cooling in the coiling experiments has to be included in the modeling of transformation kinetics.
- The stabilization of austenite should be studied in more detail based on the temperatures selected for the experiments. Transmission Kikuchi Diffraction (TKD) in the Scanning Electron Microscope (SEM) could be an suitable technique for this purpose.
- Deformation could be included in dilatometer experiments, to get final products more similar to the ones obtained from the industry processing.
References


